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and

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ABSTRACTS

I. SYMPOSIUM ON ELECTROCHEMISTRY

DISTRIBUTION OF DIELECTRIC RELAXATION TIMES AND PROTONIC CONDUCTIVITY IN HYDRATED METHEMOGLOBIN

S. MARIČIĆ, G. PIFAT, and. **V. PRAVDIĆ**

Ruđer Bošković Institute and University Institute of Biology, Zagreb.

Investigations of the threshold hydration for the onset of protonic conduction in methemoglobin were supplemented by measurements of the dielectric constant and loss as a function of adsorbed water. The results indicate that the fundamental change of the conduction mechanism from electronic to protonic occurs within a relatively narrow region of hydration, 13 to 21 w%.

PROTONIC CONDUCTANCE AS A FUNCTION OF HYDRATION IN BIOLOGICAL MACROMOLECULES. MODEL SYSTEM: *Na-DNA*

G. PIFAT, V. MIKAC and V. PRAVDIĆ

Ruđer Bošković Institute, Zagreb, and Institute of Biology, University, Zagreb.

Electrical transport through *Na-DNA* was measured using the technique of solid state electrolysis. The experimental results for *Na-DNA* of different degrees of hydration show that the transport is entirely electronic up to 29—32.5 w.% of H_2O. At higher hydrations the mechanism switches over to protonic conductance with 100% faradaic efficiency. A hypothesis is advanced on the structure of the adsorption layer whereby this mode of transport operates.

A STUDY ON THE ELECTRICAL CONDUCTIVITY OF BOEHMITE AND "AMORPHOUS ALUMINUM OXIDE"

B. LOVREČEK and **D. ZOROVIĆ**

Faculty of Technology, Zagreb.

The temperature dependence of the electrical conductivity of boehmite and "amorphous aluminum oxide" indicates the possibility of semiconductivity as well as ionic conductivity. Proton conductivity in these systems may be due to their structural characteristics or to a layer of adsorbed water. It was also found that conductivity changes can indicate structural changes in the sample due to heating.

INVESTIGATIONS OF ANODIC BARRIER LAYERS ON ALUMINIUM

B. LOVREČEK and **O. KORELIĆ**

Faculty of Technology, Zagreb.

Anodic barrier layers on aluminium were investigated by impedance measurements in the frequency range 50 to 20,000 c/s. The influence of composition and *pH* of the electrolyte was studied. The results are analyzed in terms of the equivalent electrical circuit in order to get an idea about the structure of the oxide layer and hence of the possibility of explaining the charge transport mechanisms in such systems.

TRANSFERENCE NUMBER AS A FUNCTION OF PRESSURE (AQUEOUS HYDROCHLORIC ACID SOLUTIONS AT 25°C)

G. J. HILLS and **N. Đ. JAKOVLJEVIĆ-HALAI**

Chemistry Department University of Southampton, England.

The EMF's of concentration cells with transport *(Pt)* quinhydrone, HCl_{m1}/HCl_{m2}, quinhydrone *(Pt)* were measured to estimate the change in transference number of chlorine ion with pressure.

The experiments were carried out at 25°C and pressures up to 1500 atm. An exponential dependence of the transference number on pressure was derived. The constants of the equations, $t_{Cl}^{-} = f(p)$ and $t_{H}^{+} = f(p)$ were calculated. The constants do not depend on concentration or temperature in the temperature range 25—45°C.

OXYGEN REDUCTION KINETICS AT GOLD ELECTRODES IN ALKALINE MEDIA

A. DAMJANOVIĆ, D. B. ŠEPA and M. VOJNOVIĆ

Institute of Chemistry, Technology and Metallurgy, Beograd, and Faculty of Technology and Metallurgy, Beograd

The electrochemical oxygen reduction reaction at gold electrodes in alkaline media has been studied. The overpotential — log current density relationship in solutions of different *pH* and with different partial pressures of oxygen was determined. Kinetic parameters of the reaction are discussed.

OXYGEN REDUCTION AT SILVER ELECTRODES IN ALKALINE MEDIA

A. DAMJANOVIĆ, D. B. ŠEPA and M. VOJNOVIĆ

Institute of Chemistry, Technology and Metallurgy, Beograd, and Faculty of Technology and Metallurgy, Beograd

The reaction of oxygen reduction at silver electrodes in alkaline solutions of different *pH* and at various partial pressures of oxygen has been studied. From the overpotential — log current density relationship kinetic parameters were determined. The mechanism of the process is discussed.

ISOTOPE EFFECT OF D_2O ON ELECTRODE KINETICS OF OXYGEN REACTIONS

B. JOVANOVIĆ and A. DAMJANOVIĆ

Boris Kidrič Institute of Nuclear Sciences, Vinča.

Anodic and cathodic reactions of oxygen at smooth surfaces of noble metal electrodes in acid solutions, in H_2O and 95% enriched D_2O were examined. Results for oxygen reduction on oxide-free and bare electrodes in these solutions are compared and analyzed with regard to the mechanisms at these electrodes reaction.

USE O^{18} IN THE STUDY OF OXYGEN ADSORPTION AT ELECTRODES

B. JOVANOVIĆ and A. DAMJANOVIĆ

Boris Kidrič Institute of Nuclear Sciences, Vinča.

Adsorption of oxygen at smooth electrodes of noble metals in acid solution saturated with gaseous oxygen enriched with isotope O^{18} was examined. Equilibrated enriched oxygen was diluted with unenriched oxygen gas and equilibration of this mixture at the electrodes was followed by mass spectrometry. Conclusions are about the nature of adsorbed species and the kinetics of adsorption.

OXYGEN REDUCTION AT THE ELECTRODES MADE OF NICKEL AND SOME NOBLE METALS

D. M. DRAŽIĆ, **P. RAKIN**, D. B. ŠEPA and M. VOJNOVIĆ

Faculty of Technology and Metallurgy, Beograd, and Institute of Chemistry, Technology and Metallurgy, Beograd

The reduction of oxygen in alkaline media was investigated. Electrodes were prepared of nickel powder coated with a noble metal by immersion plating and then pressed under high pressure.

The overpotential — log current density relationship was determined for each electrode at various *pH* of the solution and partial pressure of oxygen. The influence of some parameters of the electrode preparation technique on their electrochemical behavior was investigated.

EVALUATION OF SOME KINETIC PARAMETERS OF THE ELECTROCHEMICAL REACTION $Cd^{2+}/Cd(Hg)$ USING AN ANALOGUE COMPUTER

A. R. DESPIĆ, **D. JOVANOVIĆ** and S. BINGULAC

Faculty of Technology and Metallurgy, Beograd, Boris Kidrič Institute of Nuclear Sciences, Vinča and Institute of Chemistry, Technology and Metallurgy, Beograd

Faradaic impedance of the system $Cd^{2+}/Cd(Hg)$ was measured at several concentrations of Cd^{2+} — ions and different *Cd* contents of the amalgam electrode. Measurements were performed using a bridge technique and at low potential (up to 5 *mV*).

Experimental values were processed on a PACE-231R analogue computer using a model of a probable reaction mechanism. The rates of the reaction steps, the concentrations of Cd^{+} — ions and the double-layer capacity were evaluated.

KINETIC STUDIES OF THE REACTION Sn^{2+}/Sn^{4+} ON MERCURY ELECTRODE BY THE FARADAIC IMPEDANCE METHOD

A. R. DESPIČ, **D. JOVANOVIĆ** and S. BINGULAC

Faculty of Technology and Metallurgy, Beograd, Boris Kidrič Institute of Nuclear Sciences, Vinča and Institute of Chemistry, Technology and Metallurgy, Beograd

In order to obtain some kinetic parameters for the reaction Sn^{2+}/Sn^{4+} on mercury electrode, faradaic impedance was measured at several concentratinos of Sn^{2+} and Sn^{4+} ions in concentrated acid solutions, using a bridge technique. The working electrode was polarized with sinusoidal potentials of 5 mV amplitude and a frequency in the range 20 to 10000 c/s.

Experimental data were processed on a PACE-231R analogue computer using a mathematical model of a probable reaction mechanism. The rates of some reaction steps and concentration of Sn^{3+} ions were thereby evaluated.

PROBLEM OF THE SO-CALLED LIMITING CURRENT IN THE ELECTROCHEMICAL OXIDATION OF ALCOHOLS ON PLATINUM

D. M. DRAŽIĆ, **V. J. DRAŽIĆ** and I. MILIN

Faculty of Technology and Metallurgy, Beograd, and Institute of Chemistry, Technology and Metallurgy, Beograd.

The rate of the electrochemical oxidation of ethanol on a rotating platinum disc was studied as a function of electrode potential and ethanol concentration in $1N$ H_2SO_4. Instead of the limiting current reported in the literature, characteristic current maxima at potentials $\approx +1$ V are obtained. By analysis of the experimental curves this effect was explained in terms of oxidation of the platinum surface in this range of potentials and the subsequent inhibition of the ethanol oxidation reaction, while the heights of the maxima are still proportional to the ethanol concentration.

CHARGE TRANSFER KINETICS OF THE As(III)/As(V) SYSTEM ON PLATINUM ELECTRODE

S. Đ. ĐORĐEVIĆ, **O. Ž. TATIĆ-JANJIĆ** and M. V. VOJNOVIĆ

Faculty of Technology and Metallurgy, Beograd, and Institute of Chemistry, Technology and Metallurgy, Beograd.

The overvoltage-log current density relationship for the electrochemical oxidation of trivalent arsenic in sulfuric acid solutions on platinum electrode was determined at various concentrations of the reduced and the oxidized form of arsenic. From the experimental results the kinetic parameters have been determined. The mechanism of the process of electrochemical oxidation of arsenic (III) is discussed.

KINETICS OF THE HYDROGEN EVOLUTION REACTION AT SODIUM TUNGSTEN BRONZES

M. VOJNOVIĆ and D. B. ŠEPA

Faculty of Technology and Metallurgy, Beograd, and Institute of Chemistry, Technology and Metallurgy, Beograd.

Kinetics of the hydrogen evolution reaction at sodium tungsten bronzes, Na_xWO_3, in acid media (H_2SO_4) have been studied. The overpotential — log current density relationship was determined in solutions of different *pH*.

Kinetic parameters have been determined and the mechanism of the reaction are discussed.

CHARGE TRANSFER KINETICS OF $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ AT SODIUM TUNGSTEN BRONZE ELECTRODES

D. B. ŠEPA and M. VOJNOVIĆ

Faculty of Technology and Metallurgy, Beograd, and Institute of Chemistry, Technology and Metallurgy, Beograd.

Charge transfer kinetics in the system $Fe(CN)_6^{3-}$ /$Fe(CN)_6^{4-}$ at sodium tungsten bronze (Na_xWO_3) electrodes of different composition have been investigated. Overpotential-current density and overpotential — log current density relationships were determined for various concentrations of $Fe(CN)_6^{3-}$ /$Fe(CN)_6^{4}$. Kinetic parameters obtained are discussed with regard to mechanism of the charge transfer process.

CORROSION RESISTANCE OF SODIUM TUNGSTEN BRONZES IN ACID MEDIA

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Corrosion resistance of sodium tungsten bronzes (Na_xWO_3) of various composition ($0.5 < x < 0.9$) has been investigated. These bronzes appear to be promising as catalysts for oxygen reduction in acid media. Powders of known texture were leached 1 *M* H_2SO_4 at 50°C for a prolonged period. The amount of tungsten in solution was determined at definite time intervals by a spectrophotometric method. Corrosion resistance was estimated from the results.

RADIO-FREQUENCY POLAROGRAPHY

J. RADEJ and M. BRANICA

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Using a commercial square-wave polarograph (Mervyn-Harwell, Type MK3) a radio-frequency polarography setup has been constructed at the Ruđer Bošković Institute. The RF polarographic method(1) makes it possible to study fast electrochemical processes in new way. The method uses the faradaic rectification effect caused by nonlinear behavior of the electrochemical system. In some cases RF polarography has been found to be more sensitive than conventional and/or impulse polarography.

RF polarographic curves obtained for some electrochemical systems are discussed and compared with the theoretically predicted curves.

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1) *G. C. Barker*, Anal. Chim. Acta **18**, 118 (1958).

APPLICATION OF OPERATIONAL AMPLIFIERS IN ELECTROCHEMICAL INSTRUMENTS

T. RABUZIN and V. PRAVDIĆ

Ruđer Bošković Institute, Zagreb.

Various complex systems for measuring and monitoring electrochemical processes can be made using operational amplifiers. In this article two original electrochemical instruments, consisting of operational amplifiers, are presented. One of them is a two channel potentiostat-galvanostat with the counter electrode common. The second is a fast commutator for cyclic chronopotentiometry employing only electronic switching.

ROTATING DISK AND ROTATING RING-DISK ELECTRODE TECHNIQUES IN THE STUDY OF COMPLEX ELECTROCHEMICAL REACTIONS IN THE SYSTEM URANIUM (VI) — SODIUM CARBONATE

Đ. ČUKMAN and V. PRAVDIĆ

Ruđer Bošković Institute, Zagreb.

Simple, small, rotating disk and ring-disk electrodes for rates up to 12,000 rpm. are described. A special galvanostat, combined into a single unit with the counter electrode grounded, is described. The unit uses tube-type operational amplifiers. The electrode was used to study the complex reduction mechanism of uranium (VI) in sodium carbonate solutions. The aim of the work was to establish the maximum rate of the electrochemical reaction still under diffusion control. Results indicate that the reduction of uranium (VI) to (V) proceeds with a heterogeneous rate coeficient in excess of 1.2×10^{-2} cm/sec.

APPLICATION OF CYCLIC CHRONOPOTENTIOMETRY TO THE STUDY OF COMPLEX ELECTROCHEMICAL-CHEMICAL REACTION MECHANISMS

M. VUKOVIĆ, J. ČAJA and V. PRAVDIĆ

Ruđer Bošković Institute, Zagreb.

Using an original electronic commutator for cyclic chronopotentiometry the kinetics of consecutive electrochemical, and first or second order chemical reactions was studied. The aim of the present investigations was to obtain precise information on the kinetics of the reaction from a single experiment using only the reduced relative transition time, thus avoiding the difficulty of exact determination of the current density. Experimental results are reported for the reduction and oxidation mechanism of uranium in carbonate media.

OXIDATION-REDUCTION REACTION IN THE SYSTEM URANIUM (VI) — URANIUM (V) — URANIUM (IV) IN AQUEOUS SODIUM CARBONATE AND BICARBONATE MEDIA, MEASURED USING CURRENT REVERSAL CHRONOPOTENTIOMETRY

J. ČAJA, D. ČUKMAN and **V. PRAVDIĆ**

Ruđer Bošković Institute, Zagreb.

Kinetic parameters for the electrochemical reduction of uranium (VI) into uranium (V) and (IV), and for the oxidation of uranium (IV) into uranium (V) and (VI) in sodium carbonate-bicarbonate media were determined by current reversal chronopotentiometry. The aim was to determine the elementary steps in a process used in pilot plant production of uranium dioxide nuclear fuel. The results indicate that the reactions investigated are all irreversible and diffusion controlled, and that no uranium species is specifically adsorbed at the mercury electrode.

STUDY OF THE ELECTROSORPTION OF BENZENE USING THE POTENTIAL SWEEP METHOD

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Electrosorption of benzene on platinized platinum at three temperatures (30, 50 and 70°C) has been studied. Results obtained by the potential sweep method were compared with those of the radiotracer method for the same system.

Both sets of results are in good agreement in a certain potential range and at some temperatures. At more positive potentials (within the range studied) the radiotracer method gave higher values of the coverage. The difference was due to partial oxydation of benzene at these potentials influencing the results of the electrochemical method, while the radiotracer method was insensitive to these changes.

The results suggest the use of both methods in similar studies of organic compounds.

MODEL OF THE ELECTRODE DOUBLE LAYER AT THE PIROLYTIC GRAPHITE-ELECTROLYTE SOLUTION INTERFACE

K. POPOV, D. M. DRAŽIĆ and A. R. DESPIĆ

Institute of Chemistry, Technology and Metallurgy, Beograd and Faculty of Technology and Metallurgy, Beograd.

From the theory of electrode double layer for a metal-electrolyte and semiconductor-electrolyte interface, a theoretical model of the electrode double layer for a pirolytic graphite-electrolyte interface has been derived, taking into account the anisotropy of the pirolytic graphite.

DOUBLE LAYER CAPACIY AT PIROLYTIC GRAPHITE

D. M. DRAŽIĆ, **R. ATANASOSKI** and G. SAVIĆ MAGLIĆ

Faculty of Technology and Metallurgy, Beograd, and Institute for Chemistry, Technology and Metallurgy, Beograd.

Differential capacity measurements of the electrode double layer at pirolytic graphite in a neutral electrolyte (KF, Na_2SO_4) are reported. The capacity is given as a function of the electrode potential and the anisotropy of the graphite. The high frequency bridge method with the potentiostatic monitoring of the electrode potential was applied. The results are compared with the known capacities at mercury and platinum, and with the capacity calculated for a model of the double layer at graphite of ideal structure.

DENDRITIC GROWTH IN ELECTRODEPOSITION OF METALS

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The dendrite growth appearing in the electrodeposition of zinc from the alkaline zincate solutions was studied. While in the case of silver a tendency for fast growth of separate dendrites is existing, zinc dendrites appear in much larger number and more developed forms, but growing much slower.

Based on the experimental results obtained in this work, as well as on the facts known before, a general model for the dendritic growth is postulated. It shows that the dendrite starts to grow only when the electrodeposition reaction at the rough electrode surface is completely diffusion controlled. Such a kinetics leads to the exponential increase of the electrode roughness with time, and to the appearence of the outgrowths. At these places the spherical diffusion conditions are controlling the process what increases the rate of deposition regarding to that at the plane surface.

In such a way it has been established that, contrary to the generally accepted belief, dendritic growth is not a specific characteristic of certain number of metals connected with their crystallographic structure, but more general phenomenon of metal deposition.

DYNAMIC POTENTIOSTATIC POLARIZATION OF *Pb* — *Sb* ALLOYS IN 5 M SULFURIC ACID

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Faculty of Technology, University of Zagreb, Sisak.

Alloys of various compositions (X_{sb} = 0.02 — 1) were polarized in the potential range — 1 *V* to + 3 *V* (and vice versa) and at a rate of polarization of 400 *mV/min*. The curves obtained allow of an explanation of the dissolution mechanism. The results are compared with thermodynamic data for assumed reactions and with the phase diagram. The microstructures of the alloys are given.

APPLICATION OF EMF MEASUREMENT FOR THE DETERMINATION OF THE THERMODYNAMIC PROPERTIES OF ALLOYS

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Boris Kidrič Institute of Nuclear Sciences, Beograd, and Faculty of Natural Sciences, Beograd.

The method of *EMF* measurement for determining the relative partial and integral molar thermodynamic functions of alloys is described. The cadmium-mercury system was investigated by this method using the following galvanic cell:

Cd/0,1 *M* CdJ_2, *2M* *KJ* in glycerine/*Cd-Hg*

whose *EMF* was measured as a function of alloy composition and temperature.

The cadmium-mercury system had been earlier investigated by this method, but results were contradictory. The reasons for the disagreement are most probably the use of different solvents for electrolyte and unsatisfactory preparation of alloys. The values obtained for the thermodynamic functions of the cadmium-mercury system are discussed from the point of view of the physical and chemical properties of cadmium and mercury and the interaction of their atoms in the solid solution.

THERMODYNAMIC KINETICS OF CURRENT-LESS COPPER PLATING

M. AHMEDBAŠIĆ and T. MARKOVIĆ

Faculty of Technology, Tuzla.

The mechanism of current-less copper plating is explained using thermodynamic and thermodynamic-kinetic data. The corresponding U_H — J diagrams have been constructed showing that chemical reduction of copper is possible with simultaneous evolution of hydrogen.

The state of the measuring potential $U_{H,\ b}$ for the double-electrode has been calculated and determined:

α) $8Cu + 6C_4H_4O_6^{2-} + 10\ OH^- \longrightarrow Cu_8(C_4H_4O_6)_6(OH)_{10}^{6-} + 16e$

ß) $R^n \longrightarrow R^{(n+z)+} + ze$

POROUS ELECTRODES OF NICKEL AND SOME NOBLE METALS FOR OXYGEN REDUCTION IN ALKALINE SOLUTIONS

D. DRAŽIĆ, V. VUJČIĆ, P. RAKIN, M. VOJNOVIĆ and D. ŠEPA

Faculty of Technology and Metallurgy, Beograd, and Institute of Chemistry, Technology and Metallurgy, Beograd.

Porous electrodes were prepared in two ways: (i) A noble metal by immersion plating was deposited on nickel powder and organic additive for increasing the porosity was mixed in with this powder, which was then pressed and sintered. (ii) A mixture of nickel powder and a powder organic additive for increasing of the porosity was pressed. Then a noble metal was immersion- electroplated into the porous matrix. Electrochemical characteristics of these two types of electrode were investigated and compared for oxygen reduction in alkaline solutions.

INFLUENCE OF TREATMENT OF ACTIVE CARBON ON ITS ACTIVITY IN POWDER HYDROGEN FUEL CELL ELECTRODE

D. M. DRAŽIĆ and **R. ADŽIĆ**

Institute of Chemistry, Technology and Metallurgy, Beograd

The influence of grain size, mode of catalyst impregnation, and different surface treatments of active carbon (*R-52* "Miloje Zakić") on its electrochemical activity for hydrogen fuel cell electrode was studied. The experiments were done with the carbon powder in a special powder electrode assembly without binder, in $5N$ H_2SO_4 and $6N$ KOH at 40°. The best results were obtained with 60—100 micron particles, washed with azeotropic HCl, heated at 950° in CO_2 and impregnated with $2\ mg$ Pt per cm^2 of the electrode. The polarization curves, after corection for ohmic voltage drop, had slopes less than $1\ ohm\ cm^2$. The effects of treatment are explained by a change of state of the carbon surface.

POLAROGRAPHIC BEHAVIOR OF TITANIUM, VANADIUM AND URANIUM IN PRESENCE OF DIETHYLENTRIAMINE-PENTAACETIC ACID *(DTPA)*

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Titanium gives a well defined cathodic wave, the diffusion current is a linear function of *Ti* concentration at constant *pH* and exceeding concentration of *DTPA*. The half-wave potential is dependent on the *pH*. Vanadium gives three cathodic waves. The first one, which is disturbed by the anodic current, cannot be used analytically. The second and third waves are well defined and diffusion current are proportional to the vanadium concentration at constant *pH*. The half-wave potentials depend on *pH* in different *pH* ranges. Uranium also gives well-defined wave which can be used for determination.

In all cases the metal-*DTPA* complexes are reduced at the dropping mercury electrode.

REDUCTION OF *As*(III) AT THE DROPPING MERCURY ELECTRODE IN ALKALINE MEDIUM

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The reduction of *As*(III) at the dropping mercury electrode in alkaline solution of citrate at *pH* ranging from 9.4 to 10.3 was studied. It was shown that *As*(III) gives a welldefined cathodic wave, the half-wave potential of which depends on the *pH*. From the change of half-wave potential it was proved that two hydrogen ions take part in the reduction of *As*(III). By comparison of the hight of this wave with that of a tri-electronic reduction of a chosen trivalent element in the same molar concentration as the *As*(III) solution it was found that the reduction of *As*(III) proceeds to the metallic state via an irreversible tri-electronic process.

A STUDY OF THE INTERACTION BETWEEN Cd AND EDTA IN SEA WATER

D. MALJKOVIĆ and M. BRANICA

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Square wave polarography was used to investigate the rate of formation and stability of the cadmium-ethylendiamintetraacetic acid *(EDTA)* complex in sea water. Using the same method a comparison was made between the formation of the complex in a sodium chloride solution and in sea water.

The results indicate that:

- at $pH = 8$ *Cd* and *EDTA* form an irreducible ionic complex of the type CdY^{2-},
- the complexing of cadmium with chloride schifts the concentraion ratio of the reactants,
- the calcium ion (a macroconstituent of sea water) has the predominant influence on the degree of complexing of *Cd* with *EDTA*,
- the rate of formation of the *Cd-EDTA* complex in sea water is lower than that in the corresponding solution of sodium and calcium chloride.

A POLAROGRAPHIC STUDY OF INDIUM (III) IN SEA WATER

A. BARIĆ and M. BRANICA

Ruđer Bošković Institute, Zagreb

The precipitation, hydrolysis and complexing of indium(III) in sea water and sodium chloride solutions were investigated using pulse polarography and anodic stripping on *HMDE*. Indium(III) cloride was added to sea water and sodium chloride solutions of different *pH* in concentrations ranging from 10^{-4} to 10^{-7} *M*. The concentration of ionic indium in equilibrium with the precipitate formed was found to vary from 10^{-4} to 10^{-9} *M*, this concentration being the limit of the method used.

From the dependence of the concentration of ionic indium and the half-wave potential on the *pH* and the concentration of chloride the composition of the precipitate and the ionic form of indium in the solution are proposed, viz: probable composition of the precipitate: $InCl_2OH$ or $In(OH)_3$, and that of the ionic species in equilibrium with the precipitate: $InCl_2^+$ and/or $In(OH)_2^+$. The solubility products were evaluated as $[InCl_2^+]\ [OH^-] = 10^{-13.9}$ and $[In(OH)_2^+]\ [OH^-] = 10^{-16.2}$.

The only reported value for the concentration of indium in sea water was 20 µg/1. From the solubility products and the limits of the analytical method used, it may be concluded that the concentration of indium in sea water is less than 0.2 µg/1.

POLAROGRAPHIC INVESTIGATION OF ZINC IN SEA WATER

M. PETEK and M. BRANICA

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The concentration and physico-chemical form of zinc present in sea water was determined by pulse polarography and anodic stripping on a hanging mercury drop electrode.

The sea water samples gave a composite pulse polarographic peak at about —1.0 *V*. vs. mercury pool anode. It was found that the peak was due to the reduction of zinc (E_p = —1.0 *V*). and of iodate (E_p = —1.14 *V*.) originally present in the sea water. By acidifying the samples to a *pH* below 4 the iodate peak shifted to more positive potentials (E_p = —0.3 *V.*) and at —1.0 *V.* there remained only the pronounced zinc peak.

By the anodic stripping technique the concentration of zinc was determined at the *pH* of sea water (*pH* ≈ 8). At *pH* 3 however the reduction of hydrogen ions overlapped the zinc peak.

It has been found that the concentration of zinc in sea water samples is considerably higher when measured at *pH* 3 than at the *pH* of sea water. This led us to assume that some of the zinc in normal sea water is bound in a complex form which does not undergo reduction in the measurable potential range.

POLAROGRAPHIC INVESTIGATION OF THE ELECTROCHEMICAL REDUCTION OF COBALT(II) IN AQUEOUS SOLUTIONS OF ACETYLACETONE

B. ĆOSOVIĆ and M. BRANICA

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The electrochemical reduction of cobalt (II) was studied by d.c. and a.c. polarographic methods. The composition of the solution (i.e. *pH,* concentration of acetylacetone and sodium perchlorate) influenced the polarographic characteristics of the cobalt(II) reduction.

The kinetic parameters of the irreversible electrode reduction of the hydrated cobalt(II) and the monoacetylacetonato complex were determined.

The rate constant of the dissociation of the electroinactive cobalt(II) diacetylacetonato complex to the reducible cobalt(II) monocetylacetonato ion was also calculated.

On the basis of the results a sheme of the mechanism of the electrochemical reduction of cobalt(II) in aqueous solutions of acetylacetone is proposed.

EFFECT OF THE SUPPORTING ELECTROLYTE ON THE POLAROGRAPHIC REDUCTION OF URANYL PEROXODICARBONATE

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The effect of the supporting electrolyte (alkali carbonates and perchlorates) on the polarographic reduction of uranyl peroxodicarbonate ion has been studied. In all cases a single irreversible wave corresponding to a three-electron reduction was observed, shifting to less negative potentials with increasing concentration and atomic number of the cation of the supporting electrolyte.

The Frumkin correction for the effect of the double layer was found to hold quite well when the double layer structure was varied by adding sodium perchlorate. From the corresponding variation of the apparent rate constant the charge of the depolarizing particle ($z = -2$), the transfer coefficient ($\alpha = 0.56$), and the rate constant of the electrode process ($k_0 = 2.5 \times 10^{-8}$) were evaluated. The difference between the formal charge of the complex ($z = -4$) and the calculated value ($z = -2$) indicates ion pair formation, probably $[UO_2(CO_3)_2(O_2)]Na_2^{2-}$.

ON THE ADSORPTION OF LEAD ON MERCURY ELECTRODES IN IODIDE SOLUTION

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The adsorption of lead in iodide solutions on the dropping mercury electrode and the hanging mercury drop electrode was investigated. The variation of the electrical double-layer capacity was followed by means of an apparaturs after Kowalski, Srzednicki, Valeriote and Barradas. An improved modification of the hanging mercury drop electrode was constructed. Measurements were made in solutions containing 0.1 to 1.2 *mM* of lead and 0.5 to 15 *mM* and 0.5 to 3 *M* of iodide.

All capacity-potential curves recorded showed two peaks at potentials characteristic of the post-wave due to adsorption. This is in accordance with published results for the same phenomenon of tensametric, chronopotentiometric and chronocoulometric methods. The capacity maximums correspond to desorption and reduction of the lead iodide species.

THE POLAGOGRAPHIC DETERMINATION OF THE *O/U* RATIO IN URANIUM OXIDES

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An analytical method for the polarographic determination of the *O/U* ratio of uranium oxides is proposed. The sample is dissolved in ortho-phosphoric acid, and after dilution with sulphuric acid hexavalent uranium is determined polarographically. Uranium present in the solution is oxidized with ceric ions to the hexavalent state. The oxidized sample is diluted with a mixture of ortho-phosphoric and sulphuric acid to the required concentration and than polarographed. The *O/U* ratio is calculated from the limiting current and dilution. It is not important to know the weight of the sample accurately but it should be between 0.1 *mg* and 50 *mg* if the *O/U* ratio of the sample is between 2.5 and 2.001. The coefficient of variation for the proposed method is about 0.6%.

POLAROGRAPHIC DETERMINATION OF ZINC IN PRESENCE OF NICKEL AND COBALT

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Polarographic determination of zinc in the presence of cobalt in a solution of ammonium hydroxide and amonium chloride is not possible because of the superposition of their polarographic waves.

If the amount of nickel exeeds the amount of zinc by a factor of ten the polarographic determination of zinc in the above solution is also not possible.

In a solution containing ammonium hydroxide, ammonium chloride and complexon I, zinc can be determined polarographically in the presence of cobalt and nickel.

BIAMPEROMETRIC NEUTRALIZATION TITRATION USING A BISMUTH-BISMUTH SYSTEM

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A bismuth-bismuth electrode pair was used as the indicator and reference electrode system for the neutralization titrations of strong and weak acids by a strong base and vice versa. The end-point was detected by minimum indicator current. The results are in an agreement with the potentiometric method. Also, mixtures of acids with sufficiently different pK_a values could be titrated. The method is simple and can replace the technique using easily breakable glass electrodes used in potentiometry.

CONDUCTOMETRIC TITRATION OF HYDRAZINUM FLUORIDES

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Conductometric titration of hydrazinum salts was applied to hydrazinum fluorides. An apparatus with two cells, for diluted and concentrated solutions, is described. By this method, quantitative determination of $N_2H_5^+$ ions in the presence of $N_2H_6^{++}$ ions is possible.

COULOMETRIC DETERMINATION OF PERMANGANATE, DICHROMATE, FERRIC AND CERIC IONS

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A coulometric method for determination of permanganate, dichromate, ferric and ceric ions has been developed.

Ferric ions are first reduced to ferrous ions by means of zinc amalgam, and then titrated with electrolytically generated permanganate.

After reduction of permanganate and ceric ions by means of hydrochloric acid, dichromate and ferric ions are titrated with electrolytically generated titanous inos.

Permanganate, dichromate and seric ions are titrated with electrolytically generated ferrous ions.

Permanganate, dichromate, ferric and ceric ions are titrated together with the electrolytically generated titanous ions.

Permanganate, dichromate and ceric ions are determined individually from the differences in the quantity of electricity used during the titrations.

COULOMETRIC TITRATION OF BASES IN ACETIC ACID AND ACETONITRILE

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The procedure described by Mather and Anson (Anal. Chim. Acta 21 : 468, 1959), for coulometric titration of tertiary amines and salts of organic acids in a mixture of acetic acid, acetic anhydride and sodium perchlorate, by generation of H^+ ions at the mercury anode, has been modified. The titration end-point is determined photometrically in the presence of crystal violet or malachite green as indicator. The main disadvantage of the original method, the necessity for frequent interruption of the current before the end-point, is avoided by adding hydroquinone to the analysis.

Better results can be obtained by coulometric titration of bases using the electrolyte mentioned as catholyte, retitrating the excess of added perchloric acid coulometrically on the platinum cathode. Amounts ranging from 1—5 *mg* were determined with an error of —0.3% and with an average deviation of ± 0.3%. Sixteen bases were investigated.

A new procedure for coulometric titration of bases in acetonitrile was also developed. Instead of $LiClO_4 \cdot 3H_2O$, by means of which water is introduced into the analysis (Streuli, Anal. Chem. 28 : 130, 1965), a mixture of $AgClO_4$ and hydroquinone was used as supporting electrolyte, and the titration end-point was determined photometrically in the presence of malachite green.

BLACK NICKEL COATINGS

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The color intensity and porosity of galvanic black nickel coatings depend on the concentration of components in the nickeling bath and on the operating conditions.

The corrosion resistence of steel under a black nickel coating depends on the previous treatment of the steel and the subsequent treatment of the black nickel deposit.

A certain dependence of color content and porosity was established.

PRODUCTION OF FLUORINE AND ITS PURIFICATION AND COMPRESSION INTO CYLINDERS

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A 120 amp electrolytic fluorine generator and a laboratory setup for purification and compression of fluorine into cylinders is described. The apparatus can fill six 10.5 liter cylinders with fluorine up to 30 atm pressure without an intermediate regeneration of the electrolyte in the cell.

CHEMICAL REMOVAL OF OXIDE FROM COPPER WIRES AND ELECTROLYTIC REGENERATION OF ETCHING SOLUTIONS

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The rate of oxide removal from copper wires in a solution of sulfuric acid and copper sulfate increases with decreasing copper sulfate concentration, and with increasing temperature and sulfuric acid concentration.

At the end of leaching the copper potential becomes constant.

The current efficiency for copper during the electrolytic regeneration of the solution for oxide removal depends on the concentration of copper sulfate and sulfuric acid, on current density and on the temperature of the electrolyte.

DEPOLARIZATION OF CATHODE HYDROGEN EVOLUTION IN BIPOLAR CHLORATE CELL PROCESS

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Recently developed bipolar cells for electrolytic chlorate production with graphite electrodes, due to high load and current density, exhibit appreciable cathode polarization. A method for depolarization of hydrogen evolution with suitably metallized graphite surfaces has been developed, giving an appreciable reduction of cell voltage.

POLARIZATION CHARACTERISTICS OF LEAD-PEROXIDE ELECTRODE IN ELECTROLYTIC PRODUCTION OF ALKALI CHLORATES AND PERCHLORATES

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A lead-peroxide electrode has been developed using electrolytic deposition on an indiferent graphite carrier and other, known, methods. Polarization characteristics of lead peroxide, platinum and graphite electrodes were determined in solutions for electrolytic production of alkali chlorates and perchlorates. The lead dioxide electrode exibits a very high oxygen overpotential and due to the known pseudo-stability at high oxidation potentials it represents a good and economical anode material to replace graphite or platinum in electrolytic production of chlorate or perchlorate, respectively.

ELECTRODEPOSITION OF NICKEL FROM SULPHAMATE SOLUTIONS

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The influence of i) concentration of nickel (at constant *pH)*, ii) *pH* (at constant nickel concentration) and iii) composition of the elecrolyte, on the mechanism and kinetics of the process was studied. Results are discussed with regard to the mechanism of the process.

II. GENERAL CHEMISTRY

SYNTHESIS AND INVESTIGATION OF HYDROLITIC STABILITY OF SOME ESTERS OF BORIC ACID — MODELS OF POLYMERIC ESTERS

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The synthesis of hydrolytically stable esters of boric acid by making use of the tendency of the boron atom to coordinate with nitrogen atom was studied. In view of our intention to use the results of this work, should it succeed, for the synthesis of polymeric esters, the monomeric esters are taken as models of them.

A mixed ester of boric acid and ortho-*N*, *N*-dimethylaminophenol and pyrocatechol was synthesized. It can be considered a model of the polymer which could be obtained by esterification of boric acid with the product of condensation of pyrocatechol, ortho-*N*, *N*-dimethylaminophenol and formaldehyde or acetone.

The possibility of testing the coordination between boron and nitrogen and the hydrolytic stability of ester bond by a potentiometric method, measurement of UV absorption and determination of molecular weight is discussed.

STEREOCHEMISTRY OF THE TRIGONAL COBALT(III) COMPLEXES WITH β-AMINO ACIDES

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The synthesis and the stereochemistry of the new trigonal tris-bidentate complexes of trivalent cobalt with β-amino acids — β-alanine (I) and β-amino-*n*-butyric acid (II) — are described. The violet (α) and red (β) isomers were synthesized by indirect methods from sodium-tricarbonatocobaltate (III) and hexamminecobalt (III)-chloride, respectively. The electronic absorption spectra show the violet isomer to be *meridial* or *trans* (C_1) and the red isomer to be *facial* or *cis*(C_3). The assignment of geometrical configurations to the *tris* (β-alaninato) cobalt(III) complexes was confirmed by *NMR* spectra. The geometry of six-membered chelate rings was studied.

SALTS OF TRIMETAPHOSPHIMIC ACID WITH DIVALENT CATIONS II

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Attempts to obtain the salts of trimetaphosphimic acid with magnesium, zinc, cadmium and barium from phosphornitrile chloride trimer and acetates of corresponding metals in water suspensions were made. Quantitative analysis and infra-red spectra of the compounds obtained were done. The results are discussed.

INFLUENCE OF THE THERMICAL HISTORY AND STRUCTURAL CHANGES ON THE REFRACTIVE INDEX OF WINDOW GLASS

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First the fundamental characteristics of Yugoslav window glass were determined by Fourcault's procedure. Then the samples were exposed to various temperatures (570, 600, 620 and 650°) tor 15, 30, 60 and 120 minutes. After treatment, different values for the refractive index were obtained, depending of the maximum temperature to which the glass had been exposed, the duration of exposure, and the rate of cooling (n_D = 1.5083 — 1.5162). The results are discussed and the conditions given under which a stable refractive index is obtained, i.e. under which a structural equilibrium is soon attained.

INVESTIGATION OF THE COMPLEXING OF VANADIUM WITH *N*-BENZOYL-*N*-PHENYLHYDROXYLAMINE

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Absorption spectra of vanadium -*N*-benzoyl-*N*-phenylhydroxylaminate complexes formed in different media with acids of different types — HCl, HBr, H_2SO_4 and $HClO_4$ — have been investigated.

The vanadium-*N*-benzoyl-*N* - phenylhydroxylamine-HCl-chloroform system has been studied. Using the spectrophotometric and extraction methods, the composition of the complexes was determined as a function of the pervanadul-ion ratio, the reagent and the acid. It has been proved that a molecule of HCl incorporates into a molecule of the complex. A composition $VO_2R(HR)_2$. HCl was found in an excess of the reagent and $VO_2R(HR)$. HCl in an excess of the metal.

THE POSSIBILITY OF USING CRYOSCOPY FOR DETERMINING HYDROGEN BOND IN SOME SILANOLS

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In view of certain properties of freshly formed hydrolysis products of methyl trichlorosilane, which differ depending on the kind of solvent present during hydrolysis, we hypothesized that the silanol groups make a hydrogen bond with ether or other substances possessing one markedly electronegative atom. With benzene solutions of a mixture of polysiloxanes with some silanol groups we have proved by the cryoscopic method that the addition of ether, CF_2Cl-$CFCl_2$ or $CFCl_3$ depresses the freezing-point less than calculated. The occurrence of this association was attributed to hydrogen bond formation between silanols and ether, $C_2F_3Cl_3$ or $CFCl_3$.

HYDROGEN GENERATOR FOR FUEL CELL BATTERY

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A pilot hydrogen generator with a capacity of 100 1/*h* was designed and built. The pyrolysis of liquid hydrocarbon is used. The thermodynamic calculation revealed that the pyrolytic reaction is practically complete even at 1000°. Therefore a temperature of 1200° was estimated as convenient for practical use. Experimental data concerning hydrogen conversion efficiency, hydrogen purity and heat are reported and discussed.

DETERMINITION OF THE CONFIGURATIONS OF DINITRO-BIS (*d*-VALINATO)-COBALTATES(III), DINITRO-BIS (*d*-LEUCINATO) COBALTATES(III) AND DINITRO-BIS (*d*-ISOLEUCINATO) COBALTATES(III)

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By the action of *L*-valine, *L*-leucine and *L*-isoleucine on sodium hexanitrocobaltate(III), in all cases two optical isomers of the corresponding dinitrobis (aminoacidato) cobaltates(III), $Na(CoAm_2(NO_2)_2)$ were obtained.

The position of the nitro-specific bands in the near *UV* of the dinitro-complexes shows that there is *cis*-coordination of the nitro groups in these optical isomers. The absorption curves are nearly identical with those of the optical isomers of the analogous dinitro-complexes with glycine and alanine prepared by us previously. From these facts we have tentatively concluded that all isomers have the same crystal field and structure.

On the basis of *IR* molecular spectra of the optical isomers, the nature of the coordinate bonds and the existence of hydrogen bonding are discussed.

SYNTHESES OF THE STEARATE COMPLEXES OF CHROMIUM AND THE INVESTIGATION OF THEIR POLYOLATION

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The ion of chromium (III) can be bonded by coordination bonds to the residues of various organic acids. On the other hand, the same ion is able to form the so-called olate polymers, known for their ability to fix themselves on the surface of many of organic and inorganic materials. In this way, it is possible to fix the residue of any organic acid to the surface of many materials.

However, the majority of the works in this field have dealt with the practical application of this possibility without studying the fundamental phenomena. The objective of this work was therefore the investigation of the composition of the initial complexes of stearic acid and chromium (III) ion, and the conditions under which they polyolate.

The initial complexes were fractionated by extraction with solvents, by precipitation from solutions and by gel chromatography. By analysis of the products, the formation of certain chemical species was established. Polyolation was carried out at different *pH* values and was followed by the evolution of hydrogen ion.

INFLUENCE OF ALCOHOLS ON ADSORPTION OF OXYGEN AND NITROGEN ON SYNTHETIC ZEOLITE

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The influence of alcohols (C_1 to C_5) on the adsorption of oxygen and nitrogen was investigated using gas chromatography. It was found that the vapors of the investigated alcohols had different influences on the adsorption characteristics of zeolite, especialy on the Linde 5 A type. This is due to the different penetration of vapors with different molecular diameters (normal and branched alcohols) trough the zeolite channels, hence more or less decreasing the adsorption of oxygen and nitrogen.

PREPARATION OF SODIUM FLUOROALUMINATES FROM A SOLUTION OF AlF_3

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In the reaction between water solutions of AlF_3 and $NaCl$, depending on the ratio of the reactants and the reaction conditions, sodium fluoroaluminates of different composition are obtained. The experimental results are used in an attempt to prove the presence of certain complex fluoroaluminates ions in the solution of AlF_3

SPECTROPHOTOMETRIC INVESTIGATION OF THE COMPOSITION AND STABILITY OF COPPER AND CHROMIUM COMPLEXES WITH *DL*-THREONINE

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Equilibrium in solutions of copper or chromium salts and *DL*-threonine were investigated spectrophotometrically. It was found that in the *pH* range 2 to 12.5 the Cu^{2+}-ion forms four and the Cr^{3+}-ion two complexes with *DL*-threonine. For some of the complexes the composition was determined by Job's method. In addition, the *tris*(threoninato) chromium(III) complex was isolated in a good yield. The stability constants of the 1 : 1 copper complex was determined by the methods of equimolar and unequimolar solutions

HYDRATION OF BIIONIC (*Ca, K*)-FORMS OF MONTMORILLONITE

III MECHANISM OF THE HYDRATION OF THE SYSTEM WITH LOW H_2O CONTENT

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According to some authors the hydration takes place primarly through formation of hydrogen-bonds between molecules of water and basal oxygen surfaces of montmorillonite. Some other authors consider hydration of the exchangeable cation as the predominant process in the hydration of montmorillonite. It is very difficult to obtain direct data in order to support any of the two mechanisms, by the common contemporary analytical methods. A new indirect

way for approaching the problem is study of hydration of the exactly specified biionic forms of montmorillonite. In this paper the results obtained by thermogravimetric analysis were quantitatively processed and compared with the results obtained by studying adsorption izotherms for H_2O in the system and results of DTA. The results are in favour to the opinion that in the system with low water content the hydration of the basal surfaces is the primary process. From the shape of the dehydration curves it is obvious that dehydration is a discontinuous process.

KINETICS OF THE PROCESS OF ALKALINE OXIDIZING HEATING OF PYROLUSITE

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Assuming diffusion kinetics of the process of preparation of potassium manganate by the alkaline oxidizing heating of the pyrolusite, an approximate relationship between conversion of manganese dioxide and reaction time was derived. Experimental and calculated results are in good agreement and the assumption of diffusion kinetics so confirmed.

III. PHYSICAL CHEMISTRY

THE EQUATION OF STATE OF SATURATED VAPORS OF MONOATOMIC ELEMENTS

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In this paper the authors treat some equations of state of saturated vapors and their application to monoatomic elements. It is first shown how F. A. Guggenheim, on the basis of experimental data, obtained graphically an equation of state of saturated vapor which also applies to some polyatomic elements. Dührings rule is then analyzed in more details, and finally it is shown graphycally that equation of J. Žvojinov (derived from statistical and quantum mechanical considerations and the equation of state of an ideal gas) has the same constants. This means that it is of the some form as Guggenheim's equation which had no theoretical basis. The only difference is that Živojinov's equation applies only to monoatomic elements.

ANALYSIS OF DIFFUSION LAYERS IN THE *Mn-Si* SYSTEM WITH THE ELECTRON PROBE MICROANALYSER

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The working principle of the electron probe microanalyser and its application to the study of solid state reactions are described. The diffusion layers in the system *Mn-Si* obtained by diffusion of manganese into silicon single crystals at high temperature were analysed. The intermetallic compounds Mn_5Si_3 and *MnSi* were detected.

REACTIONS OF HYDROGEN ATOMS AND SOLVATED ELECTRONS WITH MOLECULAR OXALIC ACID AND OXALATE IONS IN AQUEOUS SOLUTION

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Oxalic acid reacts with the short-lived water radiolysis products: *OH* radicals, *H* atoms and solvated electrons. Hydroxyl radical reactions with different forms of dissociation are known and the rate constants have been determined. However, there is no published data on reactions with *H* atoms and e^-_{aq}.

In order to get these data, molecular hydrogen yields were measured for different oxalate ion concentrations at different solution *pH* (0.5, 1.3, 2.8, 4.3 and 7). The irradiated solutions were oxygen-free. Ethanol and potassium ferricyanide were used as scavengers in some experiments. Rate constants of reactions of the different dissociation forms of oxalic acid with hydrogen atoms and solvated electrons were determined. The effect of ionic strength on these reactions was also studied. From the results, primary yields of solvated electrons in acid media were obtained.

SOME CONSEQUENCES OF THE USE OF THE QUANTITATIVE EQUATIONS IN THERMODYNAMICS

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Fundamental definitions of quantities, quantities relationships between them, equivalence relations, particle and mol are given. Possibilities of quantitative treatment of chemical reaction equations, equilibrium constants and the Nernst heat equation are considered.

THERMODYNAMICAL INTERPRETATION OF THE AMPHOTERIC BEHAVIOR OF *Pb*-HYDROXIDE

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A proposed mechanism of *Pb*(II)-hydrolysis, i.e. the formation of simple and polynuclear hydrolysis products, and the behavior of *Pb*(II)-hydroxide in alkaline media, were considred from the standpoint of electrochemical thermodynamics. For the theoretical considerations it was necessary to predict, or from known equilibrium constants calculate the values of ΔG°*(kcal/mol)* for those components which could not be found in the literature.

Using the predicted and calculated ΔG°-values it was possible to establish diagrams of homogeneous and heterogeneous equilibriums for the system. These diagrams show the distribution of concentrations of *Pb*-hydrolysis products as a function of solution *pH*. At the same time, they represent a critical survey of the probability of the predicted ΔG°-values.

MASS-SPECTROMETRIC STUDY OF CHEMICAL REACTIONS AT HIGH TEMPERATURES

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A mass spectrometer coupled with a Knudsen effusion cell was used to study chemical reactions at high temperatures. Equilibrium constants of reactions involving the difluorides of the *IV A* group elements were determined and used to calculate the dissociation energies of these molecules.

APPLICATION OF THERMODYNAMICS OF IRREVERSIBLE PROCESSES TO DIFFUSION IN TERNARY SYSTEMS

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The phenomenological method of irreversible thermodynamics provides a basis for analysis of different simultaneous processes in open systems. The application of this method to diffusion in a ternary system is shown.

Assuming local equilibrium and linear relation between thermodynamic forces and fluxes, Onsager's reciprocal relations are derived.

RADIOLYSIS OF ETHANOL AND FORMIC ACID AQUEOUS SOLUTIONS IN PRESENCE OF OXYGEN. INFLUENCE OF *pH* ON PRIMARY RADIOLYSIS PRODUCTION OF WATER

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Of all the systems studied so far, oxygenated aqueous solutions of carbon monoxide, oxalic acid, ethanol and formic acid have proved to be the most suitable for determining the primary radiolytic products of water. The radiolysis mechanisms of these systems are practically identical and rather simple. Furthermore, owing to their chemical behavior, all of them can be used to follow the radiation chemical changes with *pH* of the solution varying from about 1 to 13.

Comparison of the published data for primary yields determined in aqueous solutions of oxalic acid and carbon monoxide with the incomplete data for the ethanol-oxygen and formic acid-oxygen systems reveals disagreement. We therefore considered it useful to investigate in more detail the effect of solute concentration and the *pH* of the formic acid and ethanol solution on the yields of the radiolysis products of the above systems — CO_2, acetaldehyde, hydrogen peroxide and hydrogen.

In addition, in a series of experiments at $pH = 13$, the concentration ratios $(HCOOH)/(O_2)$ and $(C_2H_5OH)/(O_2)$ were varied, allowing study of the competition reaction between oxygen and the solute for O^- ion-radicals.

X-RAY DIFFERACTION ANALYSIS OF *AgI* SOLS

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From an X-ray diffraction analysis of differently prepared *AgI* it was concluded that electrolyte (KI, $AgNO_3$, HNO_3, KNO_3, K_2SO_4, K_3PO_4, *K*-*n*-myristinate, *n*-myristylaminnitrate, TRITION X-305 and Rhodamine 6G) concentration, the method of mixing, the age of the sol, and the quantity of sol, are very important for the dispersity and crystallographic modification of *AgI*.

ON THE INFRARED SPECTRUM OF LIQUID MIXTURES OF DIMETHYL ETHER AND SULFUR DIOXIDE

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Dimethyl ether and sulfur dioxide form an azeotropic mixture boiling at O°C with 42 mol percent of the ether. To obtain more information on a possible addition compound between dimethyl ether and sulfur dioxide, infrared spectra of liquid dimethyl ether and spectra of a series of liquid and solid mixtures were recorded at temperatures between — 30° and — 160°C. Frequency shifts of the absorption bands and changes in their intensities indicate bonding between the ether oxygen and the sulfur atom. The question of a compound in 1 : 1 ratio, could not be reliably answered from the data obtained.

DETERMINATION OF DISSOCIATION CONSTANT OF HYPOCHLORIC ACID

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The formal constant of dissociation of hypochloric acid has been determined using the straight line method. Measurements were made at temperatures of 20°, 40°, 50° and 60°C in a solution for the electrolytic preparation of $NaClO_3$.

STRUCTURAL ANALYSIS OF URANIUM OXIDE U_3O_8

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U_3O_8 exists at room temperature as an orthorhombic phase, but at higher temperatures (about 300°C) it transforms into a hexagonal modification. The crystal structure of the hexagonal modification was earlier deduced from the orthorhombic structure without a detailed analysis. It is shown by analysis of X-ray and neutron diffraction data that the hexagonal structure has to be modified, particulary with respect to the positions of oxygen atoms. New positions of atoms in the unit cell are proposed.

DIFFUSION COEFFICIENTS IN TERNARY SYSTEMS

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Diffusion coefficients of ternary systems describe the diffusion of each component and the influence of all constituents on this process.

The definition and the method of determining local diffusion coefficients are given.

Different methods for the determination of experimental diffusion coefficients are analyzed and their transformation into the local coefficients of Onsager's reciprocal relations is presented.

STUDY OF THE RADIOLYSIS OF SOLID MALONIC AND SUCCINIC ACID

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Results obtained so far with the radiolysis of solid oxalic acid prompted us to investigate the behavior of its higher homologues, malonic and succinic acid. The behavior in the reactor mixed-radiation field was of primary interest; a number of measurements in a ^{60}Co gamma field were performed for the sake of comparison. The absorbed dose range was 10^8—10^9 rads. As found by chemical analysis of the samples, both acids decomposed giving as the main products CO_2 and a corresponding stoichiometrically fatty acid (malonic acid gave acetic and succinic propionic acid). In addition, a number of other products were identified of which less was formed: CO, CH_4, C_2H_6, formic, butyric, valeric acids. Quantitative features of decomposition are discussed and the material balance is considered. The need to identify an as yet unidentified species the mass of which was determined is pointed out.

DISSOCIATIVE MECHANISM OF IMPURITY ATOM DIFFUSION IN GERMANIUM

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The electrical activity and diffusion of Na in Ge is examined. In germanium sodium atoms exist in interstitial and substitutional positions. In the temperature range examined, the solubility of the substitutional atoms is higher than that of the interstitial atoms *Na* diffuser in *Ge* by a dissociative mechanism. Experimental results for *Na* and literature data for *Cu*, which diffuses in *Ge* by the same mechanism, are used to determine some basic parameters for diffusion and to characterize the dissociative mechanism of diffusion in germanium.

DETERMINATION OF SOME CHARACTERISTICS OF FLUIDIZED BEDS OF SODIUM BICARBONATE, DISODIUM CARBONATE AND MIXTURES THEREOF

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Hydrodinamic characteristics of a fluidized bed of sodium bicarbonate, disodium carbonate and mixtures thereof with differing particle sizes were investigated in a glass column 60 *mm* in diametar and 800 *mm* high.

For several fractions and mixtures the pressure drop in the bed was determined as a function of air flow velocity and minimum rate of fluidization. A comparison with the hydrodynamic behavior of a bed of glass beads of known diameter was made.

In order to compare the results obtained with existing relationships, parameters characterizing the particles and beds were determined.

ISOTOPE EFFECTS IN THE DISTILLATION OF THE DIMETHYL ETHER—SULFUR DIOXIDE AZEOTROPE

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Elementary isotope separation factors for the $^{32}S/^{34}S$ and $^{16}O/^{18}O$ pairs in the distillation of pure sulfur dioxide, $^{16}O/^{18}O$ in the distillation of dimethyl ether, and the factors in the distillation of the $(CH_3)_2O$—SO_2 azeotrope at — 26°C were determined. The $^{16}O/^{18}O$ separation factor in the distillation of the ether was found to differ considerably from that in the distillation of the azeotrope. The isotope effect for sulfur is higher in the latter. The isotope effect for SO_2 oxygen is the same in both pure SO_2 and the azeotrope. The results are interpreted in terms of the molecular interaction of SO_2 and $(CH_3)_2O$ in the azeotrope.

REACTIONS OF *Br* ATOMS IN AQUEOUS *KBr* AND OXALIC ACID SOLUTIONS IN PRESENCE OF O_2

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Br atoms appear as secondary radicals in the gamma radiolysis of bromide aqueous solutions. They are formed by reactions of Br^- with *OH* radicals. The rate constant of this reaction is5.8 × 10^9 M^{-1} sec^{-1}. Since oxalic acid is also present in the solution, and it too reacts with *OH* radicals ($k_{OH + H_2C_2O_4} = 10^7 M^{-1} sec^{-1}$), the concentrations of the scavengers present were so adjusted that practically all *OH* radicals were converted to *Br* atoms.

Reactions of Br atoms with oxalic acid, H_2O_2 and *Br* ions were followed by measuring the stable radiolytic products CO_2, H_2 and H_2O_2. The radiation chemical yields of these products were measured for different absorbed doses, dose rates, and different concentration ratios of *KBr* to oxalic acid.

The proposed mechanism and the experimental results enabled us to calculate the rate constant of the reaction between *Br* atoms and oxalic acid. They indicate the existence of a reaction between H_2O_2 and Br_2^- ion radicals, most often completely neglected by other authors. This reaction and its products offers a new explanation for the cube dependence of the measured hydrogen peroxide yields in oxygenated *KBr* solutions on the cube root of the *KBr* concentration.

KINETICS OF HYDROGEN PEROXIDE DECOMPOSITION AT THE SURFACE OF A ROTATING DISK

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The rate of catalytic decomposition of hydrogen peroxide at the surface of rotating silver disk has been investigated. Rates were measured as a function of H_2O_2 concentration, solution temperature, surface temperature and angular velocity of the disk. As the catalytic decomposition of H_2O_2 is a very rapid reaction it becomes diffusional already at low temperature (about 20°C), and it is impossible to separate transport effects from kinetic phenomena. With a rotating disk it was possible to investigate the kinetics of the catalytic decomposition at much higher temperatures. The activation energy and order of the reaction have been determined.

MOLECULAR SPECTRUM OF COPPER IN THE REGION BETWEEN 5100 AND 5500 Å

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The emission molecular spectra of copper in the region 5100 to 5500 Å in oxy-acetylene, oxy-hydrogen and butane-air flame, and in vacuum arc have been investigated. The flame bands showed that the spectra are independent of the copper salt used. The spectrum obtained in a vacuum arc in a hevay water vapor atmosphere is a similar to that in ordinary water vapor, but the bands are shifted. The isotope shifts show the presence of hydrogen in the emitter molecule, consistent with James and Sugden's suggestion that *CuOH* is responsible for these bands.

DETERMINATION OF ACTIVITY COEFFICIENTS IN TERNARY SYSTEMS FOR TESTING ONSAGER'S RECIPROCAL RELATIONS

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A method of determining the analytical relationship between activity coefficients and concentration in ternary mixtures is presented. It is shown that the desired relationship can be derived from the known equilibrium data for a given ternary system as well as for all three binary combinations. The form of the expression allows the transformations necessary for using Onsager's reciprocal relations.

A SPECTROPHOTOMETRIC METHOD FOR DETERMINATION OF STABILITY CONSTANTS. AQUEOUS *Fe*(III) SOLUTIONS WITH ACETYLACETONE

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For determination of stability consants of complex compounds of *Fe*(III) with acetylacetone Jacimirsky's spectrophotometric method was chosen, as it seemed to be very convenient for complex systems with more than two complex compounds. It was found that for systems with two complex compounds Jacimirsky's equations can be applied. During the experiments with *Fe*(III) and acetylacetone, involving more than two complex compounds, errors in the function series were discovered. The series of equations for determining stability constants was corrected. The stability constants k_1, k_2 and k_3 for the *Fe*(III)-acetylacetone-water system have been determined.

MODERN CATALYSTS FOR AMMONIA SYNTHESIS

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The importance of catalysts in industrial ammonia synthesis is considered in the light of an analysis of reaction conditions. The technological development of this catalyst, and ways for further improvement in order to achieve a higher degree of synthesis efficiency, are presented.

INFLUENCE OF TEXTURAL PROPERTIES OF CATALYSTS ON THE KINETICS OF CATALYTIC REACTIONS. II. INVESTIGATION OF TEXTURAL AND SURFACE PROPERTIES OF ALUMINA

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Changes of the textural properties of alumina as a result of catalyst calcination in the temperature range 500—900°C and the addition of different organic additives during the precipitation of hydroxides were investigated.

Conclusions about the influence of textural properties on the catalytic activity are drawn from consideration of the nature and the number of active sites on the catalyst surface determined by the EPR method and of the kinetic parameters of the reaction of cyclohexene isomerization.

EFFECT OF ADDITIVES ON PROPERTIES OF LOW-TEMPERATURE WATER-GAS-SHIFT REACTION CATALYSTS

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As part of a study of the preparation conditions of three component water-gas-shift reaction catalysts, the influence of some metal oxides on activity, thermal stability and textural properties of catalysts was investigated.

The results show that the catalytic activity remains within the same range as before the addition of these components, but the resistance to temperature variations is remarkably improved, depending on the type of additive. The textural property changes depend on the nature and quantity of the additives.

IV. ORGANIC CHEMISTRY

OXIDATIVE DECOMPOSITION OF ALKALI CELLULOSE WITH OXYGEN (PART I)

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The rate of oxidative decomposition – depolymerization — of alkali cellulose was monitored by viscometric determination of changes in the degree of polymerization P_w with decomposition time.

In other experiments the amount of oxygen consumed during the depolymerization of alkali cellulose was measured.

For the whole P_w range investigated the ratio P_w/P_n was determined, so as to find out values of P_n necessary for the kinetic calculations.

OXIDATIVE DECOMPOSITION OF ALKALINE CELLULOSE WITH OXYGEN (PART II)

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A new model for alkaline cellulose depolymerization with oxygen has been set up and verified.

Kinetic equations for the rate of depolymerization and the rate of consumption of oxygen have been derived for alkaline cellulose.

Rate constants for some reaction steps have been determined.

DETERMINATION OF REFFRACTIVE INDEX INCREMENTS (*dn/dc*) OF STYRENE-DIALKYLITACONATE COPOLYMERS

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In connection with molecular weights determination of copolymers with light scattering techniques, refractive index increments of methylketone solutions at 20°C were determined for homopolymeric *di-n*-alkyl esters of itaconic acid from dimethyl- to the dioctyl-ester and for copolymers of dimethyl, diethyl, diamyl-, diisoamyl-, diheptyl- and dioctylitaconate with styrene. Determining *dn/dc* for the range of 0—100% by weight of dialkylitaconate in the copolymer, the additive character of this magnitude was demonstrated and expressions for the *dn/dc* dependence on weight and molar composition calculated.

SELECTIVE DEHYDRATATION OF *1-n*-ALCANOLS

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The process of selective dehidration of *1-n*-alcanols on aluminum oxide-chromium trioxide catalyst has been investigated. The *α*-olefine yields were 90—96%.

Alcohol conversion ranges from 40 to 60%, depending on reaction temperature.

SYNTHESIS OF SOME BISCHELATE COMPOUNDS — POTENTIAL LIGANDS IN COORDINATION POLYMERS

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The basic idea was to make relatively stable chain polymers by polycoordination of metal ions and ligands whose functional groups can simultaneously satisfy both the oxidation and coordination number of the central atom, but so distributed that every ligand molecule must be bonded with two central atoms and vice versa.

In view of the coordination polymers of zinc, the ligand would therefore have two ionic groups — residues of some acid — and two electrically groups — electron donors. All this suggests that it would be best to distribute these groups in the shape of the so-called bischelate compounds.

The synthesis of 2,2'-bis (3-acetyl-4-hydroxyphenyl) propane was investigated and performed by Fries's rearrangement on 2,2'-bis (4-acetoxyphenyl) propane. The elementary composition of the compound, its content of functional groups and molecular weight were determined and the *IR* and *NMR* spectra recorded.

The corresponding bisoxime and bisphenyldrazone were synthesized and studied. The possibility of synthesizing other derivates and homologues is dicussed.

THE SYNTHESIS OF α-NAPHTHYLACETIC ACID VIA MONOCHLORACETIC ACID AND ITS ETHYL ESTER IN THE PRESENCE OF ALUMINUMCHLORIDE

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The syntheses of α-napthylacetic acid starting from naphthalene, monochloracetic acid, and its ethyl ester have been studied. Without aluminum chloride catalyst the reaction takes very long and a very small yield is obtained. With aluminum chloride a considerable abbreviation of reaction time and an increase of yield are achieved.

EFFECT OF LITHIUM AND SODIUM OXIDE PROMOTORS ON THE SELECTIVITY OF CATALYTIC PROPANE DEHYDROGENATION

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The promoting effect of Na_2O and Li_2O on the selectivity of *Cr-Al*-oxide catalyst in the temperature range 525—590°C and at a space velocity od 400—1.000 h^{-1} has been investigated. It was established that at elevated temperatures (570—590°C) Na_2O gives high selectivity while at lower temperatures (525—545°) Li_2O gave better results, and the reaction product did not contain ethylene.

ON SOME PROBLEMS IN THE DETERMINATION OF NATURAL GAS AND NATURAL PROPANE-BUTANE MIXTURES BY GAS CHROMATOGRAPHY

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A routine method for natural gas determinations by gas chromatography has been used more then 10 years. The method has undergone a series of modifcations during the last few years. Some of these modifications are described. *FID* or a katharometer were used as detectors. All determinations were carried out on relatively short columns (1—2 *m*), whereas long columns are usually used for natural gas analysis.

A fast method for propane-butane mixture determinations is also described. Gas sampling and sample injection are briefly discussed for both methods.

THE INFRA-RED SPECTRA OF α, β-UNSATURATED AROMATIC ALDEHYDES AND THEIR BIS DERIVATIVES

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Infra-red spectra of cynnamaldehyde, *o*-, *m*- and *p*-methoxy-, *o*-, *m*- and *p*-chloro- and *o*-, *m*- and *p*-nitro-cynnamaldehydes, and their bisamides and bisurethanes were recorded.

Absorption of stretching vibrations of the ethylenic bond in the α, β-unsaturated aromatic aldehydes and their bis-derivatives in which the carbonyl group is blocked (bisamides and bisurethanes) was studied to find out the effect of the substituent (methoxy-, chloro- and nitro-) and its position in the benzene ring on these vibrations. It was found that the nature and position of the substituent influences the intensity of absorption.

It was alo established that in the bis derivatives in which there is no conjugation of the ethylenic bond with the carbonyl group, the absorption of the aromatic double bond, almost negligible in the free aldehydes, was intensifiied.

Intensities were expressed in terms of the molecular extinction coefficient.

SYNTHESIS OF α-N-SUBSTITUTED THIOLACTIC ACIDS AND THEIR ESTERS

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Pyruvic acid and its esters were condensed with various nitrogen and sulfur-containing compounds. As nitrogen-containing compounds were used acetamide, urethane, urea and thiourea, and as sulfur containing compounds thio-acetic acid, thiophenol and benzyl mercaptan.

As a result α-N-substituted thiolactic acids and their esters were obtained. In addition, some intermediary products with nitrogen or sulfur so far not described in the literature were isolated.

REACTIONS OF ETHYLCARBAMATE WITH α, β-UNSATURATED ALDEHYDES

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By reaction of ethylcarbamate with α, β-unsaturated aromatic aldehydes (cinnamaldehyde, *o*-, *m*- and *p*-methoxy-, *o*-, *m*- and *p*-chloro- and *o*-, *m*- and *p*-nitro-cinnamaldehydes) besides the expected bisurethanes in some cases we got 1,1,3-tris(carbethoxy-amino)-compounds. This means that besides the carbonyl group the ethylene linkage also takes part in the reaction, undergoing addition of ethylcarbamate.

Cinnamaldehyde yielded either bisurethane or (under slightly different reaction conditions anhydrourethane of β-car-bethoxy-amino-aldehyde instead of the tris(carbethoxy-amino)-compound.

Of the two aliphatic aldehydes used — crotonaldehyde and 2-ethylpenten-2-al, only crotonaldehyde yielded the tris(carb-ethoxy-amino)-compound.

ON THE POSSIBILITY OF FRACTIONATION OF CELLULOSE NITRATE USING THE GEL PERMEATION CHROMATOGRAPH

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Seven samples with dergrees of polymerization P_w in the range 250—1 1300 were prepared by partial decomposition of cotton cellulose. The distribution curve of molecular weights for each sample was determined after nitration by the method of precipitation fractionation and on the gel permeation chromatograph *(GPC)*.

The distribution curves obtained by the standard method of precipitation fractionation and by the GPC are compared. Only the sample with $P_w = 1900$ gave some agreement of the two methods. Elution of samples with $P_w > 8000$ through the *GPC* showed no fraction.

COMPOSITION INHOMOGENEITY OF STYRENE--DIMETHYLITACONATE COPOLYMERS

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Several synthetized copolymer samples with varying styrene and dimethylitaconate contents were fractionated in a column with a temperature and solvent-nonsolvent concentration gradient and the composition and intrinsic viscosities of the fractions determined. Contrary to the expected observed increase of intrinsic viscosities the composition analysis indicated the presence of fractions with high styrene contents at the beginning and end of the fractionation, and the existence of a broad constant composition plateau with weight average molecular weights ranging from about 50.000 to 200.000.

THE REACTIVITY OF PYRIDINE-DICARBOXYLIC ACIDS AND PYRIDINE-DICARBOXYLIC ACID *N*-OXIDES IN THE REACTION WITH DIPHENYLDIAZOMETHANE

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The dependence of the acidity of pyridine-dicarboxylic acids and pyridine-dicarboxylic acid *N*-oxides on the relative position of carboxyl groups and nitrogen viz *N*-oxide has been determined by taking the rate constants of the reaction with diphenyldiazomethane as a measure of the acidity, the reaction rates at an eqivalent ratio of reactants being measured by following spectrophotometrically the decrease of diphenyldiazomethane concentration. The constants of the second-order reaction k_2 *(lit. mole*$^{-1}$*min*$^{-1}$*)* for the following acids have been determined: quinolinic-acid-*N*-oxide (29.0), cinchomeronic-acid-*N*-oxide (38.6), isocinchomeronic-acid-*N*-oxide (29.2), lutidinic acid-*N*-oxide (12.7), dipicolinc acid- *N*-oxide (55.6), lutidinic (21.6), dipicolinic (20.4), dinicotinic (19.8) and isophthalic (5.2) acid;

the constants of the other corresponding pyridine-dicarboxylic and phthalic acids have already been determined.

The acidity of pyridine-dicarboxylic acids pyridine-dicarboxylic acid *N*-oxides and phthalic acids with the same relative position of carboxyl groups *(o-, m-, p-)* was compared a theoretical explanation on the basis of inductive, resonance and steric effects is offered.

THE REACTION OF 3-NITROPHTHALIC ACID ANHYDRIDE WITH ATOMATIC AMINES

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The reaction of 3-nitrophthalic acid anhydride with *N*-methylaniline yielded 2-carboxy-6-nitro-*N*-methylbenzanilide; the structure of this compound was proved by its conversion into 2-carbomethoxy-3-nitro-*N*-methylbenzanilide and by comparison of the latter compound with two isomeric carbomethoxy-nitro-*N*-methylbenzanilides, prepared synthetically from two known isomeric monomethyl esters of 3-nitrophthalic acid which were converted into the corresponding acyl chlorides and treated with *N*-methylaniline. Such a mode of the opening of 3-nitrophthalic anhydride ring by the nucleophilic attack of the aromatic amine confirms the greater activity of *α*-carboxyl with respect to *β*-carboxyl, due to the inductive effect of the nitro group.

Analogously it has been proved that in the reaction with diphenylamine, the direction of the opening of 3-nitrophthalic anhydride ring was opposite giving 2-carboxy-3-nitro-*N*, *N*-diphenylbenzamide; this can be ascribed to steric hidrance which in this case dominates over electric effects.

ELECTROPHORESIS AND ELECTRODEPOSITION OF WATER-SOLUBLE ALKIDE RESINS

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Recently a procedure has appeared of coating metal objects by dipping them as an electrode in a suspension of a pigment in a water solution of a polymeric binder. Depending on the given author's point of view this procedure is termed electrophoresis or electrodeposition.

The purpose of this work was to observe the basic phenomena occuring in this process and to examine their individual contribution under different experimental conditions.

The essential phenomena are electrophoretic migration and electrodeposition, the latter being due to a process on the electrode. The electro-migration is due to bonded ions which get carried by the polymer molecules. The electrophoretic migration supplies material to the electrode but is only important in the absence of stirring of the electrolyte.

The processes at the electrodes seem to be more complicated. Most probably the bonded ions are converted into undissociated ionic groups. This conclusion is confirmed by measuring the coulombic yield and comparing it with the equivalent calculated from the acid number of the polymer.

THE EFFECT OF 1-PHENYL-TETRAZOLTIOL-5 ON THE POLYMERIZATION OF SOME VINYL MONOMERS

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The assumption that 1-phenyl-tetrazol-tiol-5 *(FTT)* due to the presence of a mercaptane group should be a chaintransfer agent in free radical polymerization was investigated polymerising styrene, methylmethacrylate and vinylacetate in presence of *FTT*. Mass and solution polymerization was carried out at 70° C, using azobisisobutyronitrile as initiator. Chaintransfer constants determined from molecular weights calculated from intrinsic viscosities indicate that *FTT* is an active chaintransfer agent with styrene and vinylacetate but has no effect on methylmethacrylate. During polymerizations with benzoyl peroxide destruction of *FTT* was observed.

CHARACTERISTICS OF CRUDE OIL FROM "VELEBIT", VOJVODINA

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The fractional composition of Velebit crude oil was determined and a group analysis made. The *TBP* distillation curve and the base of the crude oil are given. The structural and quality indexes are shown in tables.

V. BIOCHEMISTRY

THE INVESTIGATION OF SOME FORMS OF PHOSPHORUS IN WHEAT GRAIN IN DEPENDENCE ON MINERAL NUTRITION

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The contents of some forms of phosphorus (lipids, soluble, fittin, nucleic) were investigated on the variety "Mara".

The plants were grown in water cultures using nutritive solution after Reid-York. After 15 or 30 days one of the following elements was eliminated: nitrogen, phosphorus, sulphur, calcium or magnesium.

The results show that the contents of the different forms of phosphorus were lower in grain from the field than in that from the water cultures. The deficiency of the individual elements during vegetation affected the kernel weight and the content of the investigated forms of phosphorus, which indicates a different effect of different mineral nutrients on the metabolism of phosphorus.

RHEOLOGICAL CHARACTERISTICS OF STARCH--AMYLOPECTIN GELS OF DIFFERENT AGE

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Gels of the corn starch and of mixtures of starch and amylopectin were prepared by heating an 8% suspension in water to 95°C. On a Couette electro-rotational viscometer the shear stress

τ [dyn/cm^2], i.e. the apparent viscosity η, was measured, as a function of the shearing rate D [sec^{-1}]. The following starch-amylopectin combinations were investigated: 8/0, 6/2, 4/4 2/6 and 0/8. The measurements have been repeated in known time intervals. Changes of the η— D curves, and of thixotropy, as a function of aging time are given graphically and numerically.

CONTRIBUTION ON THE PROTECTION OF LIVING ORGANISMS AFTER IRRADIATION

ACTION OF PLANT HORMONE *PMAA* ON THE R_1, R_2 AND R_3 GENERATION YIELD OF X-IRRADIATED SOYABEAN

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In earlier works it was established that some plant hormones under certain conditions and within certain limits suppress the harmful effects of X-rays on the yield of R_1 and R_2 generations of soyabean.

In the present experiments beans of the variety Szürkebàrat of the R_1 generation were irradiated with filtered X-rays in doses 0,2 and 20 *kr* before planting.

During growth the plants were watered with *PMAA* (phenylmercaptoacetic acid) solution in quantities of 0.1 and 0.01 µg per seed. The results were compared with a control.

The best result was obtained with the radiation dose of 2 *kr* in R_1 R_2 and R_3 and watering in all the three generations with 0.1 μg *PMAA* per seed.

These experiments also confirmed our earlier observations that by using some plant hormones a certain degree of protection against ionizing radiation can be obtained. In some cases an increased yield was even observed.

ANALYTICAL FILTRATION CHROMATOGRAPHY OF PLASMA PROTEINS

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The application of filtration chromatography in clinical chemistry is demonstrated. Examination of many serum samples taken from patients with chronic inflammation of the joints, liver cirrhosis and malignant diseases of the blood vessels by filtration chromatography on Sephadex *G*-200, immunophoresis and paper electrophoresis showed that filtration chromatography permits determination of the molecular weight of paraproteins. It therefore represents a very useful additional to diagnostic methods differential diagnosis of paraproteinemic haemoblastoses replacing the ultracentrifugation method.

MITOCHONDRIAL AND CYTOPLASMIC MALATE DEHYDROGENASES FROM PIG HEART

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It has been shown that lactate dehydrogenase is more strongly adsorbed on calcium-phosphate gel than malate dehydrogenase. Using this fact it was possible to isolate both lactate and malate dehydrogenase (*L*-malate:*NAD* oxydoreductase, *EC* 1.1.1. 37) from the same starting material. Using a combination of gel-filtration, on ion exchanger chromatography and fractionation with ammonium sulphate, cytoplasmic (supernatant) and mitochondrial malate dehydrogenase were purified. By starch gel electrophoresis cytoplasmic the enzyme was shown to consist of at least 3 isoenzymic components. Partial separation of cytoplasmic *MDH* isoenzymes was achieved by column chromatography on *DEAE-Sephadex*.

By titrating the enzymes with *DTNB* (5,5'-dithiobis-2-nitrobenzoic acid) in urea, the number of *SH*-groups in both enzymes has been determined; their reactivity was measured by *DTNB*-titration of the native enzymes.

SOLUBILITY OF ERGOSTEROL AND ERGOSTERYLBENZOATE IN MIXTURES OF SOME ORGANIC SOLVENTS

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The solubility of ergosterol and ergosterylbenzoate in mixtures of a polar solvent (ethyl- butyl- or *n*-octylacohol) and a hydrocarbon (either benzene or cyclohexane) and the solubility of ergosterol in a mixture of two polar solvents (butylalcohol : cyclohexanol) over the temperature range 15—75° C have been determined. The hydroxyl group of the ergosterol molecule makes it soluble in polar solvents, while the nonpolar part makes it dissolve in nonpolar solvents. Thus, in the examined solvent mixtures a solubility maximum is observed. It is hence possible to estimate the solubility parameter of ergosterol. The plot of ergosterol solubility against the dielectric constant of the solvents gives a complete Semechenko curve. Ergosterylbenzoate was found to have a greater solubility in nonpolar solvents than in polar, due to the sheltered position of the polar ester group of the molecule. The solubility of both ergosterol and ergosterylbenzoate in alcohols increases with the number of carbon atoms, the alcohols thus showing the same properties as the solvent mixture.

CHEMICAL ANALYSIS OF ANIMAL FODDER. IV. SOLUBLE PROTEINS IN ALFALFA

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Total protein was determined in the domestic variety K_1, and the soluble proteins important from the point of view of nutrition of domestic animals were isolated by succesive extraction at room temperature with water, 10% sodium chloride water solution, 0,2% sodium hydroxide water solution and 72% ethanol. After dialysis, proteins were hydrolysed with 6 *N HCl* or with saturated barium hydroxide water solution and the amino acids obtained were separated by two dimensional paper chromatography (I. *n*-butanol-

-water-acetic acid in ratio 4 : 1 : 1; II. saturated solution of phenol in water) and quantitatively determined by a modification of the Montreuil-Khouvine method.

CHEMICAL ANALYSIS OF LICHEN PROTEINS.I. ISOLATION AND ANALYSIS OF SOLUBLE PROTEINS FROM *Evernia prunastri* and *Cetraria islandica*

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Total protein in *Evernia prunastri* and *Cetraria islandica* was determined and the crude soluble proteins were isolated by successive extraction with water, 10% *NaCl*, 0.2% sodium hydroxide solution and 72% ethanol. The fractions obtained were hydrolysed with 6*N HCl*, the amino acids separated by two dimensional chromatography (I.*n*-butanol-water-acetic acid in ratio 4 : 1 : 1; II. saturated solution of phenol in water) and quantitatively determined by a modification of the Montreuil-Khouvine method.

ON OLEANOLIC ACID FROM *EUGENIA CARYOPHYLLATA*

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Oleanolic acid was ispolated in various ways. The maximum yield was 1.1%. The whole process of isolation was followed by thin-layer chromatography on silica gel *G (Stahl)*. The isolated preparation was identified by color reactions, thin-layer chromatography, by determining the melting point, optical rotation and *IR* spectroscopy.

Oleanolic acid from cloves was compared with sapogenin from sugar beet.

It was also established that oleanolic acid is a component of the lotion “Koren” (“Merima” — Kruševac).

REFINING OF SUN FLOWER OIL WITH UREA

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Crude sun flower oil was refined with urea. Water was used as a catalyst. The best water-urea ratio for the maximum reduction of acid is 1 : 2. Experiments proved that a better quality of oil is obtained if a 1% solution sodium chloride is added as well as urea and water.

With thist method of refing the acid value of the oil has been reduced from 4.3 do 1.19.

ACID-BASE EQUILIBRIUM. APPLICATION IN STUDYING ANAEROBIC DIGESTION

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Studies were made of the possibility of monitoring anaerobic digestion process by *pH* measurement and calculation of the amount of alkalinity required, using an equation derived from the acid-base equilibrium conditions. Total concentration of all acid components was expressed as moles of acetic acid per liter, since this is certainly the predominating factor in part of the process, and total concentration of all alkaline components as moles of ammonia per liter. The experimental titration curves were compared with the appropriate calculated titration curves for a solution of pure acetic acid, for raw sludge and for a series of samples with various concentrations of supernatant from both raw and digested sludge to which different amounts of pure acetic acid were added. The results definitely show that the appropriate form of the equilibrium equation can be used as a process model for interpreting *pH* values, and hence the acid-base equilibrium itself, at least over the range where the acetate equilibrium system predominates.

VI. ANALYTICAL CHEMISTRY

TITRIMETRIC DETERMINATION OF ZINC WITH *EDTA* IN PRESENCE OF PALLADIUM(II)

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Macro and micro titrimetric methods for determination of zinc with *EDTA* in the presence of palladium(II) have been developed. In these methods palladium(II) is masked with potassium cyanide and the zinc content determined by direct titration with *EDTA* using methylthymol blue as indicator either at *pH* 6 or after demasking of zinc with chloralhydrate at *pH* 10. Zinc determination was also carried out in the presence of a palladium(II)-copper(II)-cobalt(II)-nickel mixture.

SUCCESSIVE TITRIMETRIC DETERMINATION OF CALCIUM AND MAGNESIUM WITH *EDTA* IN ETHANOLIC SOLUTION

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A method for successive titrimetric macro and micro determination of calcium and magnesium in 60% ethanol as a solvent with *EDTA* has been developed. First the total content of both metals is determined by direct titration with *EDTA* in weak ammonical solution, at *pH* 8 using methylthymol blue as indicator. Afterwards, by adding potassium hydroxide to the same solution magnesium hydroxide is precipitated and the liberated *EDTA* titrated witih standard calcium solution using a calcein and methyltymol blue indicator mixture. In this way magnesium is determined. The calcium content is calculated from the dfference.

Ethanol increases the stability of chelates, decreases solubility of magnesium hydroxide, deblocks methylthymol blue, and prevents indicator adsorption on magnesium hydroxide. As *EDTA* is in excess during the magnesium determination no errors appear because of calcium ion adsorption on the precipitate or carbon dioxide absorption.

THE APPLICATION OF KINETIC METHODS IN THE DETERMINATION OF ULTRAMICRO QUANTITIES OF MANGANESE

T. J. JANJIĆ, G. **JURIŠIĆ-MILOVANOVIĆ** and **M. B. ĆELAP**

Faculty of Sciences, Beograd

The catalytic oxidation of alizarine *S* with hydrogen peroxide in the presence of ammonium carbonate and manganese ($pH = 9 \cdot 34$) was applied for the determination of ultramicro amounts of manganese. The determination was performed by a modification of the simultaneous comparison method, by the method of tangents, and by the differential method.

SUBMICRO TITRIMETRIC DETERMINATION OF ZINC AND CADMIUM WITH VARIOUS CHELATING AGENTS IN FORMAMIDE SOLVENT

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Semimicro and submicro titrimetric methods have been developed for determination of zinc and cadmium in formamide solution of zinc sulphate and cadmium nitrate using formamide solutions of *NTA*, Na_2-*EDTA*, *EDTA*, *DCTA* and *HEDTA*, with *PAN* as the metalochromic indicator.

SPECTROCHEMICAL EXCITATION OF SOLUTIONS BY STABILIZED ARC

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Some parameters of stabilized arc important for spectrochemical analysis were investigated. A satisfactory emission stability is obtained by means of combined gas and wall stabilization. The influence of arc current, hole size on the stabilizing discs and spectrochemical buffers on limits of detection for some elements are discussed.

SPECTROPHOTOMETRIC DETERMINATION OF COPPER IN RUBBER

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A very sensitive, simple and rapid method for the determination of very small amounts of copper in rubber is given, using oxalyl-dihydrazide acetaldehyde in ammoniacal solutions at the *pH* 9.

Measurements were made in the concentration range of 2—30 γ. In this range Beer's law is closely followed.

SPECTROPHOTOMETRIC DETERMINATION OF BORON WITH CURCUMIN IN URANIUM DIOXIDE

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A method of spectrophotometric determination of boron, from 0.5 μg to 2.5 μg, in uranium dioxide has been developed. Boron is separated from uranium dioxide by distillation in the form of trimethylborate and after hydrolysis in dilute sodium hydroxide the

color is developed with corcumin in the presence of trichloracetic acid. The mechanism of the reaction of boron with curcumin has been investigated in detail, e.g. the effect of trichloracetic acid on the structure of curcumin, the effect of the drying temperature and time on the formation of a complex of curcumin with boron, the effect of the *pH* of the medium on color intensity and the time on color stability. Since uranium dioxide dissolves in nitric acid and trimethylborate neutralizes with dilute sodium hydroxide, the effect of nitric adid and sodium salts on the formation of a colored complex of curcumin with boron was investigated.

THE SORPTION OF I^-, Cs^+, Co^{2+}, Mn^{2+}, Sr^{2+} and Cr^{3+} IONS ON PRECIPITATES OF IRON, ALUMINUM AND LANTANUM HYDROXIDE

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Sorption was investigated by labelling with radioctive nuclides. The concentrations of ion and solid carrier were systematically changed and the influence of the conditions of preparation and some properties of the system was studied.

THERMODYNAMIC CRITERION IN QUALITATIVE ANALYTICAL CHEMISTRY

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The qualitative analysis of cations of the IIa analytical group is interpreted thermodynamically, applying a new thermodynamic parameter called "the thermodynamic criterion π *(volt. kcal)*". All chemical reactions characteristic for qualitative analysis of the IIa group cations are considered using both the π-value and other termodynamical parameters already known.

The aim of this paper is to verify whether π really represents a measure of the priority of the reactions within the system. The results of theoretical considerations are in complete agreement with the experimental evidence.

CATALYTIC THERMOMETRIC TITRATION OF BASES IN NON-AQUEOUS SOLVENTS

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Novi Sad

The principles of catalytic thermometric titration of bases in acetic acid, nitromethane and acetic anhydride with discontinuous and continuous measurement of the temperature are described. Catalytic thermometric titrations were made by continuous addition of the standard solution and automatic temperature recording. The results are compared with those of potentiometric titration.

Catalytic thermometric titrations were performed by coulometric generation of acid for the determination of micro amounts of weak bases in a mixture of acetic anhydride and acetic acid (7 : 1) in $NaClO_4$ as supporting electrolyte. The results are compared with coulometric titration using colorimetric and potentiometric determination of the end point.

INTERFEROMETRIC DETERMINATIONS OF WATER AND ACETIC ANHYDRIDE IN ACETIC ACID

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Interferometric determinations of water and acetic anhydride in glacial acetic acid were carried out. It was found that these substances can be best determined by means of a calibration curve.

The method is quick, simple and accurate. By interferometric titration accurate and reproducible results can also be obtained when the system is protected from the influence of atmospheric moisture and when it is well thermostated. The results were compared with the results of thermometric titration and K. Fischer's method.

STUDY OF ION-EXCHANGE KINETICS BY A POTENTIOMETRIC METHOD

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A potentiometric method for studying ion-exchange kinetics has been developed. It can be applied to ion-exchange reactions which lead to a change in *pH* of the solution phase. The rate of exchange and the rate-determining step have been determined for various commercial cation and anion exchangers.

POLAROGRAPHIC DETERMINATION OF ALUMINUM

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The possibility of polarographic determination of aluminum-ion in the presence of oxalyl dihydrazide has been studied. When a small amount of aluminum-ion is added to a solution containing an excess of oxalyl dihydrazide and potassium chloride a double wave is obtained, the first part depending on the concentration of aluminum-ion, and the second corresponding to the reduction of oxalyl dihydrazide. The half-wave potential of the first wave is 1.2—1.3 *V* for a concentration of aluminum-ion of about $10^{-3}M$. The second wave is displaced by about 0.3 *V* from the first.

VII. METALLURGY

A METALLOGRAPHIC STUDY OF MICROSTRUCTURAL DAMAGE IN STEEL FATIGUED IN CYCLIC STRAIN

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The plot of change in strength against number of strain cycles for metal specimens fatigued in cyclic strain indicate the existance of three stages in the deformation process. Each stage is defined by a specific mechanism of microstructural change. The objective of this experiment was to investigate the application of the methods of optical microscopy in studying the kinetics of microstructural damage in the body of specimens of 0.04% carbon steel fatigued in low-frequency cyclic bending.

THE INFLUENCE OF ULTRASONIC VIBRATION ON THE STRUCTURE OF PURE ALUMINUM

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The influence of ultrasonic vibration on the microhardness and structure of 99.5% *Al* has been investigated. Some specimens were annealed at 600° and others quenched from the same temperature. After heat treatment all specimens were exposed to ultrasonic vibration. It was observed that the geometry of the wave guide has some effect on the microhardness. Electron micrographs show that the probable reason for the increase of microhardness during ultrasonic treatment is an increase of dislocation density.

CHANGE OF THE PHYSICAL AND THERMODYNAMIC PARAMETERS OF COPPER AND BRONZE POWDERS DURING SINTERING

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The sintering kinetics of loose and non-pressed compacted copper and bronze powders in the temperature and time regions of 500—900°C and 15—240 minutes, respectively, were investigated. Kinetic equations of sintering for both powders, were set up from the experimental results.

Using the experimental date, the change in the Gibbs' function, entropy and enthalpy in the given temperature region were also calculated.

INVESTIGATION OF THE TEMPERING OF CARBON STEEL BY A DILATOMETRIC METHOD

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The steel contained 0.2 to 1.2% carbon. Tempering was followed by a dilatometric method and by hardness measurement. All the specimens were quenched from the optimum austenitizing temperature except the specimen with 1.2%C for which the austenitization temperature was varied to find the influence of retarded austenite on the tempering process. Tempering was followed during continual heating of the specimen in a Leitz dilatometer furnace, with a heating rate of about 5°/*min.*

To study the influence of the rate of heating on the temperature of individual tempering stages, the steel with 1.2%C was tempered at different heating rates: 5, 10, 25 and 50° C/*min.*

All the results show unembiguously that the carbon content, the austenitization temperature and the rate of heating have an important effect on the transformation processes in each tempering stage.

THE COPPER DROP CALORIMETER AND HEAT CONTENT MEASUREMENTS

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The copper drop calorimeter of the Nernst-Magnus type, intended for the temperature range up to 500°C, is made of a cast copper billet. The design of the calorimeter and details of the experimental procedure are presented. The results of water equivalent determination and of preliminary measurements of heats of transformation are given.

CONCENTRATION OF INDIUM FROM SOLUTION

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The technology of getting indium from various byproducts of zinc and lead obtained from ores includes convertion of *In* in to solution. Because of the low *In* concentration in the byproducts, the *In* solutions are weak. To get metallic indium from them *In* must be concentrated.

Using solutions with about 200 *mg/l In* we have investigated the following methods of concentration:

— chemical precipitation
— ion exchange
— extraction

The results with regard to the best method and optimal conditions are described.

PYRO-METALLURGICAL TREATMENT OF RAW SPEISS BY SULPHIDIZATION

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The processing procedure of the raw speiss (composition: 40% *Cu*, 12% *Pb*, 26% *As*, 16% *Ni*, 0.8% *S*, 1400 *g/t Ag*, 4 *g/t Au)* which is produced in lead metallurgy by sulphidization with elementary sulphur has been studied.

Sulphidization with elementary sulphur gives a *Pb-Cu* matt (45—56% *Cu*, 13—18% *Pb*, 5—12% *Ni*, 2—3% *As*, 16—18% S, 800—2000 *g/t Ag*, 3—4 *g/t Au)* which is further treated by conventional methods, and also a speiss (10—15% *Cu*, 2—3% *Pb*, 29—38% *Ni*, 32%—38% *As*, 1% *S*, 200—700 *g/t Ag*, 2—4 *g/t* Au) from which nickel and copper can be separated by a hydro-metallurgical method — leaching with sulphuric acid or ammonia solution.

In sulphidization with pyrite the following are obtained: copper matt (25‰ *Cu*, 8% *Pb*, 7% *Ni*, 1.8 *As*, 6.8% *Fe*, 1060 *g/t Ag* and 5 *g/t Au)*, speiss) (6.5% *Cu*, 1% *Pb*, 33% *Ni*, 41% *As*, 7% *Fe*, 260 *g/t Ag*, 1 *g/t Au)* and slag (22% *Cu*, 7% *Pb*, 3.3% *Ni*, 1.8% *As*, 23.5% *Fe)*.

The distribution of the metals is as follows:

	With elementary sulphur				With pyrite			
	Cu%	*Pb%*	*Ni%*	*Ag%*	*Cu%*	*Pb%*	*Ni%*	*Ag%*
Copper matt	79	80	8	65	67	64	39	86
Speiss	19	5	90	20	5	2[illegible]	50	6
Slag	—	—	—	—	27	28	9	5
Gases and losses	2	15	2	15	1	5	2	3

The optimum temperature for sulphidization with elementary sulphur is 900°C, and with pyrite 1000°C.

METALLURGICAL CONCENTRATION OF GERMANIUM FROM RE-FLOTATED BOR COPPER CONCENTRATE

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By flotation of Bor copper ore a concentrate with 100 *g/t Ge* is obtained. With re-flotation the germanium can be increased to 400 *g/t*.

This germanium content justifies investigation to discover the optimal process for obtaining germanium.

In this work the influence of various factors on the sublimation of germanium from re-flotated copper concentrate are dealt with. The results show that it is possible to separate germanium from the re-flotated concentrate by sublimation, and to enrich the sublimate by 3—4 times.

COMPARISON OF METHODS FOR CALCULATING TEMPERATURE STATES OF THERMAL PROCESSES IN METALLURGY

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Time and rate of heating of some samples of iron and steel have been investigated. The geometrical form of the samples was: cube, cylinder and plate (edge length 50 *mm*). In order to change the emissivity of the material the surface of the samples was treated thermally and mechanically. The experiments were carried out in a laboratory resistance-heated furnace. The results are compared with theoretical data (Heiligenstaedt, Greber-Shack, Svenchanskiĭ). They do not agree. Some of the disagreements are in our opinion due to shortcomings of the theoretical methods, expertmental conditions and so on.

INFLUENCE OF DYNAMIC RECOVERY ON THE STRUCTURE OF OFHC COPPER IN THE REGION OF HIGH DEFORMATIONS

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The structure of *OFHC* copper has been investigated in the region of high deformations produced by defined cold rolling schedules. A partially recovered structure was observed in all specimens deformed above 75% deformation. The partially recovered structure is due to dynamic recovery, present in all specimens deformed under various rolling conditions.

THE INFLUENCE OF COLD WORKING AND HEAT TREATMENT ON ANISOTROPY OF THE MECHANICAL PROPERTIES OF COPPER SHEET

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We studied the influence of the degree of cold working, the temperature of annealing before deformation and the temperature of final annealing on anisotropy of the mechanical properties of sheet copper. These were studied in five directions, at the following angles: 0°, 20.5° 45°, 67.5° and 90°.

STATISTICAL ANALYISIS OF STEELMAKING IN THE OPEN-HEARTH FURNACE

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The output of the open-hearth furnace has been studied a number of times in the past two decades by the methods of simple and multiple correlation analysis. In this way some knowledge about the

influence of various parameters on the furnace output is obtained. The results so far achieved and the methods used are reviewed.

The data of a campaign of a fully oil-fired open-hearth furnace of 45 tons capacity were analized on an Elliott 803 digital computer. The influence of charging, melting and decarbonizing, ore charge and feed ore, lime addition, difference between melt and tap carbon and furnace age on the total time of heat are considered. The results of simple and multiple curvilinear correlation are presented.

EFFECTS OF HEAT TREATMENT ON THE SIZE AND DISTRIBUTION OF DISPERSED PHASES IN DILUTE URANIUM ALLOYS

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The effect of heat treatment on the size and distribution of precipitated dispersed phases in five uranium alloys with small additions of molybdenium, silicon, iron and aluminum was studied. Thin foil transmission electron metallographic techniques were used. In *U-Si-Fe-Al* and *U-Mo-Si-Fe-Al* alloys slowly cooled (3°C/*min)* from the gamma phase range, very fine particles (0.02 microns) precipitate in long parallel lines. Ageing gamma solutions treated and oil-quenched alloys at 550°C did not produce parallel lines of fine precipitates. Particles were large (0.3 microns) and formed on the grain boundaries. It was found that the mechanism of the beta--alpha transformation has a great influence on the distribution and density of precipitated particles.

VISCOSITY OF METALS

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The dependence of the viscosity of metals on temperature is given by a modified Arrhenius equation $\eta = A \exp B/T\text{-}T_0$. The applicability of the equation is based on a better fit to the existing experimental data for some metals than could be achieved by other equations previously used. The possibility of giving a physical interpretation to the correction parameter T_0 is discussed.

THE DECOMPOSITION OF CHROMITE IN SLAG-WASTE IN THE PRODUCTION OF FERRO-CHROME

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Wastes in the production of ferro-chrome were investigated and it was found that they contained 8—16$^{0}/_{0}$ of Cr_2O_3. These wastes are in the form of fine powder and their composition is as follows: Sio_2 17.28$^{0}/_{0}$, Fe_2O_3 6.97$^{0}/_{0}$, Al_2O_3 6.42$^{0}/_{0}$, CaO 42.26$^{0}/_{0}$, MgO 11.95$^{0}/_{0}$.

Decomposition of chromite with simultaneous oxidation to chromate was performed with the slag and with pure chromite with addition of a certain quantity of dolomite, with the following results:

In pure oxygen, with the addition of spinellized material the reaction of decomposition of the chromite lattice begins at 850°C. The oxidation is almost complete. The investigations were made with various ratios of the mixtures and at various temperatures. It was concluded that the slag can be further used. Furthermore it is possible to use the chromium contained in the slag, and at the same time the chromite is decomposed.

VIII. TEXTILE CHEMISTRY AND TECHNOLOGY

AN INSTRUMENT FOR MEASUREMENT OF ELECTROSTATIC POTENTIAL ON CHARGED TEXTILE MATERIALS

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The instrument can measure potentials of the smallest electrostatic charges without any disturbance, making it specially suitable for measurements on textile materials. It is very sensitive, permitting measurements of potential in the wide range 10—100.000 *V*. The charged body can be easily located, and its polarity determined.

Instruments of this type use a radioactive source ionizing the air in a special chamber. The instrument described has the advantage over similar ones produced abroad in using a pure alfa- source, harmless for personnel. The intensity of the source is much less than the permissible maximum. The life of the source is of the order of thousands of years.

The application of the instrument in textile manufacturing is various: in yarn making, weaving, fabrication and finishing of textiles, and in checking the quality of finished materials.

AN INSTRUMENT FOR MEASUREMENT OF SURFACE ELECTRICAL RESISTANCE OF TEXTILE MATERIALS

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The appearance of electrostatic charges on textile materials during fabrication and use is usually undesirable. One way to reduce them is by reducing the surface resistance with antistatics. In order to test the efficiency of treatment by antistatics a simple instrument has been designed for measuring the surface resistance of textiles both semi-finished and finished products. The apparatus measures resistance in the range 10^6—10^{13} ohms. The measuring contacts are specially designed for measurements on fabrics, fibers and films. The circuit diagram and principles of the instrument are given. Calibration data and a calibration chart are presented.

INFLUENCE OF ANTISTATICS ON SOILING OF TEXTILE MATERIALS

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A method and an apparatus for laboratory examination of the polarity and magnitude of electrostatic charges on textiles of various fibres are described. The influence of some antistatics and of relative humidity of the atmosphere on soiling was analyzed by measuring electrostatical potentials and surface resistance of materials. A parallel test was performed on samples soiled by contact and electrostatically. The results indicated that the degree of soiling depends on the method of soiling and on the antistatic.

INFLUENCE OF TEXTURING PROCESS ON STRUCTURE AND SOME PROPERTIES OF YUGOSLAV POLYAMIDE FIBER

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The influence of the texturing process, temperature, number of turns and the tension on the structure and some properties of the polyamide fiber Yulon, gauge Td 70/24, have been examined. Textured filaments were produced on an ARCT type FTF-1 machine.

The cristallinity and birefrigence were taken as a measure of the degree of structural transformation. The change in tensile strength, strain, elasticity and swelling were taken as measures of the quality of the textured filament.

From the results we have determined the optimum conditions for production of textured Yulon. The temperature of texturing has the biggest effect on the structure and properties of the filament.

DYEING OF CELLULOSE DI- AND TRIACETATES BY NEW SULPHUR DYES

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New sulphur derivatives of anthracene and acenaphthene are applied for dyeing of cellulose di- and triacetates. Dyeing can be achieved in solution using only small amounts of dyes. The dyeing procedure is simple, allowing a choice of different colours in a wide range of hues, fast to light and wash.

Crystal diffractions were examined by electron microscope, and also *IR*, visible and *UV* absorption of the dyed cellulose acetates were determined. The results of these investigations indicate that the chemical bond between cellulose acetate and sulphur dyes does not exist and that the dye is most probably attached by absorption. Thus, sulphur derivatives of anthracene and acenaphthene could be classified to the group of supstantive sulphur dyes.

POSSIBILITY OF OPTIMUM FIBER YIELD IN THE TEXTILE INDUSTRY

R. JOVANOVIĆ and **B. MILJKOVIĆ**

Faculty of Technology and Metallurgy, Beograd

Textile fibers account for 70% of the price of some woolen products. We investigated production samples of worsted and semi--worsted yarn of mixed wool of different quality or of mixed wool with viscose and polyacrilonitrile fibers. We examined using Simplex methods to obtain optimum fiber yield with regard to:

— material expenditure
— utilization of production capacity
— coordination of production and sale

The optimum criterion was taken to be profit, expressed in terms of minimum expenditure of fibers or maximum income.

SYNTHETIC FIBERS DAMAGE IN PROCESSING OF TEXTILE WASTES

R. JOVANOVIĆ and **M. JOVANOVIĆ**

Faculty of Technology and Metallurgy, Beograd

Wastes were processed on a machine for drawing synthetic wastes by the garnetting procedure, to test for the degree of fiber damage caused by garnetting as a function of feed rate and precutting length.

Tests were carried out on regenerated fibers from: yarn and hosiery made of malon *(PAN)* fiber; textured, untextured filament, filament and hosiery products made of polyamide; yarn made of woll-polyester and woll-malon *(PAN)* blends.

Damage was determined by microscopic examination and by determnation of physical and mechanical properties of fibers.

Izdavač:

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Original Scientific Paper

X-RAY INVESTIGATION OF THE SYSTEM U_3O_8—V_2O_5

by

RAJNA M. HERAK and LJUBICA M. MANOJLOVIĆ

The U_3O_8—V_2O_5 system has been studied by phase analysis of samples heated from 450 to 1100°C in air. It was found that two oxides interact forming the compounds $UVO_{5\cdot5}$, UV_2O_8 and $UV_3O_{10\cdot5}$. An orthorhombic cell with constants $a = 13\ 19$ Å, $b = 12\ 03$ Å and $c = 16.97$ Å was found, on which a powder pattern of the $UVO_{5\cdot5}$ phase was indexed. It is shown that UV_2O_8 (Bobo, 1963) has the same powder pattern as α-$(UO_2)_2V_6O_{17}$ (Kovba *et al.*, 1963).

INTRODUCTION

In the literature there are insufficient and contradictory data about reactions between U_3O_8 and V_2O_5. King and Suber (1955) made a brief investigation of the reaction of UO_2 with VO_2 at 840°C. Bobo (1963) studied the U_3O_8—V_2O_5 system at 650°C in an oxygen atmosphere and in vacuum and also examined the thermal stability of the compounds obtained. In one of their papers Kovba *et al.* (1963) mention the possibility of reactions between U_3O_8 and V_2O_5 forming ortho-, pyro- and hexavanadates, but do not give any details concerning the reaction conditions or the results.

Our paper represents an approach to systematic investigation of the U_3O_8—V_2O_5 system by phase analysis of mixtures of the two oxides heated in air from 450 to 1100°C.

EXPERIMENTAL

The starting materials were U_3O_8 prepared by calcination of ammonium diuranate, and V_2O_5 "Soyuzexport". Chemical analysis showed that both oxides were of a purity satisfactory for such experiments. The lattice constants of both oxides were in good agreement with the literature data.

U_3O_8 and V_2O_5 powders of a variable U : V ratio were carefully mixed using an agate mortar and pestle and pressed under a constant pressure of 4 *t/cm²*. The pellets were heated on platinum in an electric furnace at temperatures 450, 650, 850 and 1100°C in air for a period of 10 hours.

X-ray powder patterns were run on a Philips PW-1010 diffractometer with a GM counter.

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RESULTS AND DISCUSSION

Results of phase analysis of the U_3O_8—V_2O_5 system presented in Table 1 show that under our experimental conditions the two oxides interact forming three compounds: $UVO_{5\cdot5}$, UV_2O_8 and $UV_3O_{10\cdot5}$. We indentified the $UVO_{5\cdot5}$ and UV_2O_8 phases from the X-ray powder diffraction data of Bobo (1963) and the $UV_3O_{10\cdot5}$ phase from the values of $sin^2\,\theta$ calculated from the data of Kovba *et al.* (1963) for the unit cell of the β-$(UO_2)_2V_6O_{17}$ compound. We did not make a chemical analysis because we could not isolate any of the phases.

As can be seen from the Table 1, U_3O_8 and V_2O_5 react even at 450°C. The lines of the newly formed phases are weak, while the phase which appears in mixtures rich in uranium could certainly be identified as $UVO_{5\cdot5}$, and the phase appearing in mixtures with a higher content of vanadium could be identified as $UV_3O_{10\cdot5}$ Very weak lines of the UV_2O_8 phase were found at the ratios 3 : 1 and 2 : 1.

In the series of mixtures heated at 650°C the lines of the new phases are considerably stronger, but lines of the starting substances can still be detected in all specimens. As in the previous series, the $UVO_{5\cdot5}$ compound appears in mixtures with U : V ratios from 6 : 1 to 1 : 1, and $UV_3O_{10\cdot5}$ from 1 : 1 to 1 : 6. Lines of the UV_2O_8 phase also appear in a wide concentration range. In samples with a U : V ratio from 1 : 1 to 1 : 4 this phase is predominant.

Lines of UV_2O_8 disappear completely at 850°C. The $UVO_{5\cdot5}$ phase dominates in the mixtures rich in uranium and the $UV_3O_{10\cdot5}$ phase in those rich in vanadium. In samples in the middle of the range both phases appear together.

At 1100°C the $UV_3O_{10\cdot5}$ phase dominates over a wide range of concentration. In the region where $UVO_{5\cdot5}$ dominates its lines are weaker than at 850°C, and the V_2O_5 phase could also be identified. This may suggest decomposition of the $UVO_{5\cdot5}$ phase at 1100°C.

Bobo obtained the $UVO_{5\cdot5}$ phase by heating mixtures of U_3O_8 and V_2O_5 at 650°C in an oxygen atmosphere. According to his results, this compound decomposes at 750°C to V_2O_5 and U_3O_8 whose lattice constants are slightly changed. Under our experimental conditions this phase, which reacts at 450°C, was also stable at 850°C, and only at 1100°C were there indications of its decomposition.

From the X-ray powder data for $UVO_{5\cdot5}$ we found an orthorombic unit cell and hence it was possible to index the powder pattern. This cell has lattice constants a = 13.19 Å, b = 12.03 Å, c = 16.97 Å. The most probable space group is P222. Table 2 gives the X-ray powder data for the $UVO_{5\cdot5}$ phase.

Bobo obtained the compound UV_2O_8 as a pure phase stable at 850°C by heating U_3O_8 and 50 mole % V_2O_5 in an oxygen atmosphere. Under our experimental conditions this phase appeared over a wide range of concentrations; however at higher temperatures it was unstable while at 850°C it could not be detected. We could not obtain UV_2O_8 as a pure phase by heating mixtures with a U : V ratio = 1 : 2 for 100 hours at 650°C. The UV_2O_8 was identified according to the X-ray diffraction data of Bobo. We

TABLE 1

Phase Detected in Mixtures of $U_3O_8-V_2O_5$ *Heated in Air for 10 hours*

U:V ratio (mole % V_2O_5	450°C	650°C	850°C	1100°C
6 : 1 (20%)	U_3O_8 $UVO_{5\cdot5}$ V_2O_5	U_3O_8 $UVO_{5\cdot5}$ V_2O_5	U_3O_8 $UVO_{5\cdot5}$	U_3O_8 $UVO_{5\cdot5}$ V_2O_5
4 : 1 (27.3%)	U_3O_8 $UVO_{5\cdot5}$ V_2O_5	U_3O_8 $UVO_{5\cdot5}$ UV_2O_8 V_2O_5	U_3O_8 $UVO_{5\cdot5}$	U_3O_8 $UVO_{5\cdot5}$ V_2O_5
3 : 1 (33.3%)	U_3O_8 $UVO_{5\cdot5}$ V_2O_5 UV_2O_8	U_3O_8 $UVO_{5\cdot5}$ UV_2O_8 V_2O_5	U_3O_8 $UVO_{5\cdot5}$	U_3O_8 $UVO_{5\cdot5}$ V_2O_5
2 : 1 (42.9%)	U_3O_8 $UVO_{5\cdot5}$ UV_2O_8 V_2O_5	U_3O_8 $UVO_{5\cdot5}$ UV_2O_8 V_2O_5	$UVO_{5\cdot5}$ U_3O_8	U_3O_8 $UVO_{5\cdot5}$ $UV_3O_{10\cdot5}$ V_2O_5
1.5 : 1 (50%)	U_3O_8 $UVO_{5\cdot5}$ V_2O_5	U_3O_8 $UVO_{5\cdot5}$ V_2O_5	$UVO_{5\cdot5}$ U_3O_8	U_3O_8 $UVO_{5\cdot5}$ $UV_3O_{10\cdot5}$ V_2O_5
1 : 1 (60%)	U_3O_8 V_2O_5 $UVO_{5\cdot5}$ $UV_3O_{10\cdot5}$	UV_2O_8 U_3O_8 $UVO_{5\cdot5}$ $UV_3O_{10\cdot5}$	$UVO_{5\cdot5}$ $UV_3O_{10\cdot5}$ U_3O_8	$UV_3O_{10\cdot5}$ $UVO_{5\cdot5}$ V_2O_5
1 : 2 (75%)	U_3O_8 V_2O_5 $UV_3O_{10\cdot5}$	UV_2O_8 $UV_3O_{10\cdot5}$ V_2O_5 U_3O_8	$UV_3O_{10\cdot5}$ $UVO_{5\cdot5}$ V_2O_5	$UV_3O_{10\cdot5}$ $UVO_{5\cdot5}$ V_2O_5
1 : 3 (81.8%)	U_3O_8 V_2O_5 $UV_3O_{10\cdot5}$	UV_2O_8 V_2O_5 $UV_3O_{10\cdot5}$ U_3O_8	$UV_3O_{10\cdot5}$ V_2O_5	$UV_3O_{10\cdot5}$ V_2O_5
1 : 4 (85.7%)	U_3O_8 V_2O_5 $UV_3O_{10\cdot5}$	UV_2O_8 V_2O_5 $UV_3O_{10\cdot5}$ U_3O_8	$UV_3O_{10\cdot5}$ V_2O_5	$UV_3O_{10\cdot5}$ V_2O_5
1 : 6 (90%)	U_3O_8 V_2O_5 $UV_3O_{10\cdot5}$	V_2O_5 UV_2O_8 $UV_3O_{10\cdot5}$ U_3O_8	$UV_3O_{10\cdot5}$ V_2O_5	$UV_3O_{10\cdot5}$ V_2O_5

showed, however, that the powder pattern of this phase can also be indexed according to the lattice constants of α-$(UO_2)_2V_6O_{17}$ which Kovba *et al.* (1963) denotes as a modification stable above 550°C. The composition of this phase remains uncertain, though our work supports the results of Bobo

TABLE 2

X-ray Powder Diffraction Data for $UVO_{5.5}$ *Phase* (*CuKα radiation*)

1)		2)		3)	
sin² θ	I	*sin²* θ	I	*sin²* θ	I
		0.01364	m−	0.01360	020
0.01885	m			.01854	003
.02471	w++	.02465	s	.02464	202
.02841	s	.02806	vs	.02804	212
		.03042	vw	.03060	030
.03418	w	.03419	m−	.03470	130
.03822	vvw	.03835	w	.03824	222
				.03834	213
.04629	s	.04602	m	.04656	024
.05152	w+	.05148	w+	.05150	003
.05448	vvw	.05460	w	.05440	040
.05941	w+	.05943	w+	.05900	115
.06254	w + +	.06276	m—	.06264	042
.06911	m	.06938	m—	.06900	410
.07567	m	.07510	m—	.07574	332
		.07913	vw	.07920	420
.08577	w +	.08540	w+	.08604	333
.08913	w +	.08920	w+ +	.08910	150
		.09872	w+ +	.09850	235
				.09856	404
.10130	vvw	.10042	vw	10140	250
.10257	w	.10213	m	.10250	500
.10652	w	.10619	w +	.10590	510
.10975	vw	.10998	w	.10984	343
		.11235	vw	.11216	424
.11514	w	.11481	w	.11474	433
		.12186	vw	.12190	350
.12258	w	.12275	w	.12240	060
.12835	w			.12850	046,161
.13263	w	.13199	w	.13184	008
.13846	vvw	.13871	w	.13854	443
.14468	w	.14386	w.	.14316	416
.15057	vw	.14981	w	.15060	450
.15683	w	.15656	m	.15690	540
				.16120	620
.16178	w	.16085	w	.16184	228
.16434	w	.16414	w	.16514	542
.16876	w	.16877	w	.16874	308
		.17090	vw	.17096	109
.17242	w	.17275	w	.17276	171
.18413	w	.18384	w	.18396	614
.18937	w	.18902	w	.18924	173
.19373	w	.19293	w	.19226	364,347

1) Bobo's measured values (Bobo, 1963) for $UVO_{5.5}$

2) Our measured values

3) Calculated values assuming orthorhombic cell, with a = 12.03 *Å*, b = 1319 *Å*, c = 16.97*Å*

concerning the composition range in which it appears. Table 3 shows the X-ray powder data of the UV_2O_8 phase according to our measurements and to Bobo and Kovba.

TABLE 3

X-ray Powder Diffraction Data for the UV_2O_8 Phase (CuKα radiation)

1) sin² θ	I	2) sin² θ	I	3) sin² θ	hkl
0.00990	m	0.00951	m—	0.00963	110
.01665	m	.01671	m—	.01668	020
.02373	s	.02351	s	.02372	200
.02780	w+	.02771	w+	.02789	111
.03822	w	.03830	w+	.03852	220
		.03972	m+	.04010	201
.04024	s	.04020	m+	.04020	212
		.04296	s	.04299	130
.04405	s	.04387	ss	.04427	211
.05318	w+			.05331	310
.06095	w+	.06105	w+	.06125	131
.06726	w	.06696	w	.06672	040
.07732	s—	.07722	m	.07720	012
.08322	vvw			.08267	112
.08643	w	.08617	w+	.08667	330
.08982	w+	.08912	w	.08856	240
.11070	w+	.10991	w	.10971	150
.12226	w+	.12295	w++	.12251	051
.12835	w	.12801	w	.12797	151
.13846	w	.13801	w	.13650	500
.14540	w	.14459	w	.14435	251
.15210	w	.15291	w	.15318	520
.15523	w	.15582	w	.15558	160,440
.16010	vw			.16040	402
.16434	vw	.16429	w	.16434	003
.17149	w	.17072	w	.17196	260
.17524	w	.17543	w	.17403	530

1) Bobo's data (Bobo, 1963) for UV_2O_8

2) Our measured values

3) Calculated values based on the data for the orthorhombic cell of $\alpha\text{-}(UO_2)_2V_6O_{17}$ $a = 10.42\ A$, $b = 11.92\ A$, $c = 5.70\ A$ (Kovba *et al.*, 1963).

Bobo obtained the $UV_3O_{10\cdot5}$ phase by slow oxidation of the UV_3O_{10} compound. According to his data this phase, which has a powder pattern similar to that of the UV_3O_{10} compound, is thermally very unstable and at only 600°C decomposes into UV_2O_8 and V_2O_5. We identified the $UV_3O_{10\cdot5}$ phase from the data of Kovba *et al.* (1963) for the compound of the same composition β-$(UO_2)_2V_6O_{17}$, a modification of the hexavanadate stable up to 550°C. Under our experimental conditions the $UV_3O_{10\cdot5}$ phase was, however, thermally very stable and at 1100°C it gave no indication of decomposition. In Table 4 we compared our X-ray powder data with the corresponding data calculated from the results of Kovba for the orthorhombic cell of β-$(UO_2)_2V_6O_{17}$.

TABLE 4

X-ray Powder Diffraction Data for the $UV_3O_{10\cdot5}$ Phase (CuKα radiation)

1)		2)
hkl	*sin² θ*	*sin² θ*
111	0.01858	0.01857
202	.02496	.02481
004	.03392	.03392
113	.03554	
311	.05154	.05272
022	.05784	.05817
220	.06584	.06604
400	.06592	
313	.06850	.06840
224	09976	09976
404	.09984	
315	.10242	.10266
511	.11746	.11733
131	.11730	
422	.12376	.12384
026	.12586	.12510
513	.13422	.13471
133	.13246	
008	.13568	.13560
226	.14216	.14194
331	.15026	.15012
135	.16816	.16977
515	.16834	
040	.19744	.19787
620	.19768	
517	.21100	.20923
319	.22114	22096
2010	.22848	.22802

1) Calculated values based on the data for the orthorhombic cell of β-$(UO_2)_2V_6O_{17}$ a = 11.992 Å, b = 6.936 Å, c = 16.71 Å, (Kovba, 1963)

2) Our measured values

CONCLUSION

The U_3O_8—V_2O_5 system was investigated by heating pressed specimens of a wide concentration range in air at 450, 650, 850 and 1100°C for a period of 10 hours. Phase analysis of the heated samples was carried out by the X-ray powder method.

On heating U_3O_8 and V_2O_5 react to form, depending on temperature and composition, the compounds $UVO_{5\cdot5}$, UV_2O_8 and $UV_3O_{10\cdot5}$.

The $UVO_{5\cdot5}$ phase appeared in mixtures rich in uranium. Under our experimental conditions there were indications of its decomposition at 1100°C. An orthorhombic cell was found with constants a = 13.19 Å, b = 12.03 Å, c = 16.17 Å on which the powder pattern of the $UVO_{5\cdot5}$ phase could be indexed.

The UV_2O_8 phase appeared in a wide concentration range, and it was stable up to 650°C, when it is in equilibrium with $UVO_{5\cdot5}$ and $UV_3O_{10\cdot5}$. Considering the fact that the powder patterns of UV_2O_8 (Bobo, 1963) and α-hexavanadate (Kovba *et al.*, 1963) are the same, we may conclude that these two phases are identical.

The $UV_3O_{10\cdot5}$ phase, existing in mixtures rich in vanadium, was under our experimental conditions very stable and there were no indications of its decomposition.

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of Nuclear Sciences
Belgrade

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Original Scientific Paper

AN IMPROVED PREPARATION OF 11-OXYGENATED CORTICOSTEROID INTERMEDIATES VIA THE "MARKER-LAWSON" ACID ROUTE

by

MILUTIN STEFANOVIĆ, MIROSLAV GAŠIĆ, JOVAN HRANISAVLJEVIĆ
and MIODRAG ĐERMANOVIĆ

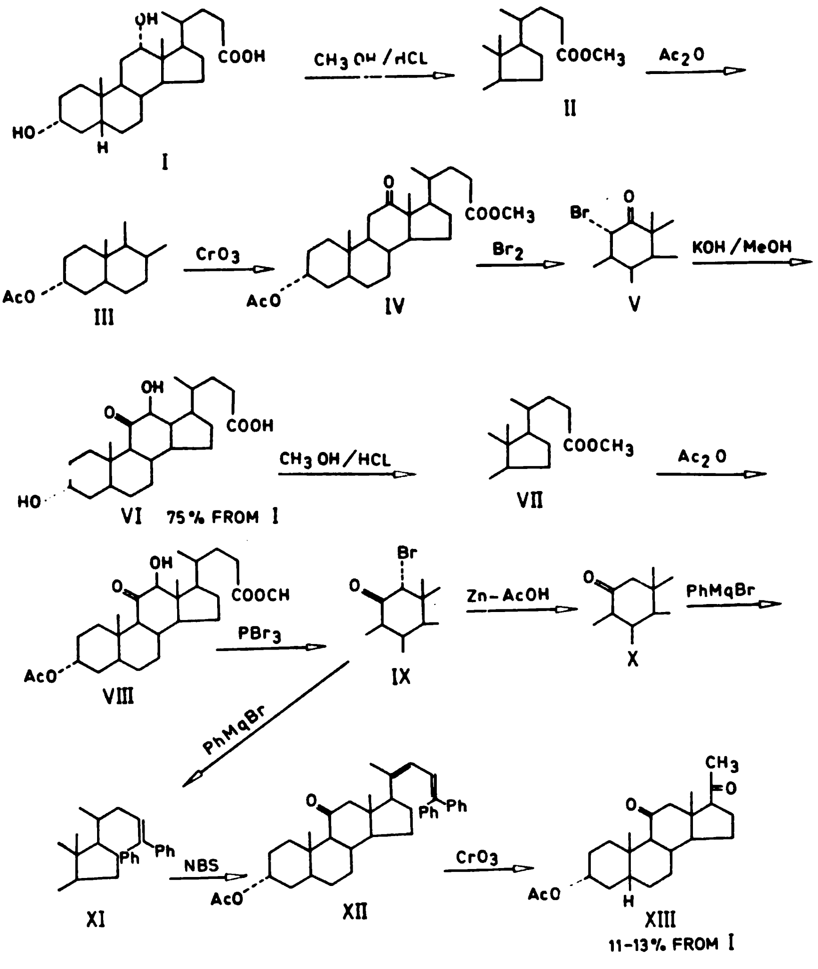
Microbiological oxidation and conversion of steroids by various microorganisms are rather effective and this method was also applied for the introduction of an oxygen function at C-11 of the steroid nucleus. Although this is a very attractive route to 11-oxygenated corticosteriods, the search for a purely synthetic method of converting desoxycholic acid or hecogenin to these derivatives was never abandoned.

Desoxycholic acid and hecogenin, both possesing an oxygen function at C-12 of the steroid molecule, represent a possible raw material for the production of cortisone and its analogues. As implied by this structural feature, the main problem represents the transposition of the oxygen function from C-11 to C-12. At present, there are numerous ways for effecting this transposition(1). However, none of the processes described in the scientific literature proved fully satisfactory in its original form.

It was previously stated that Gallagher's method of utilizing "Marker-Lawson" acid as an intermediate in the preparation of 11-oxygenated corticosteroids, starting with desoxycholic acid, did not reach the stage of large scale laboratory production due to low yields in several steps of the proposed sequence of reactions. We found that application of new methods to the proposed synthesis now provides "Marker-Lowson" acid (VI) and its monoacetate (VIII) in high yields, thus lending new utility to the method. By introducing suitable modifications, this sequence of reactions could be extended for the preparation of 3α-acetoxy-11,20-diketo-(5β)-pregnane (XIII), the key intermediate in the preparation of 11-oxygenated corticosteroids, according to the scheme I(2).

The preparation of acid (VI) by bromination and hydrolysis of ketone (IV) according to Marker and Lawson(3) represented a very important synthetic discovery although the structure which they assigned to the product was incorrect. This sequence of reactions was the subject of studies by Gallagher, Reichstein and Wintersteiner(4,5,6), and it was established that bromination of ketone (IV) at elevated temperatures affords a mixture of epimeric 11α- and 11β-bromo-12-ketones (V and XIV) in a 60—65%

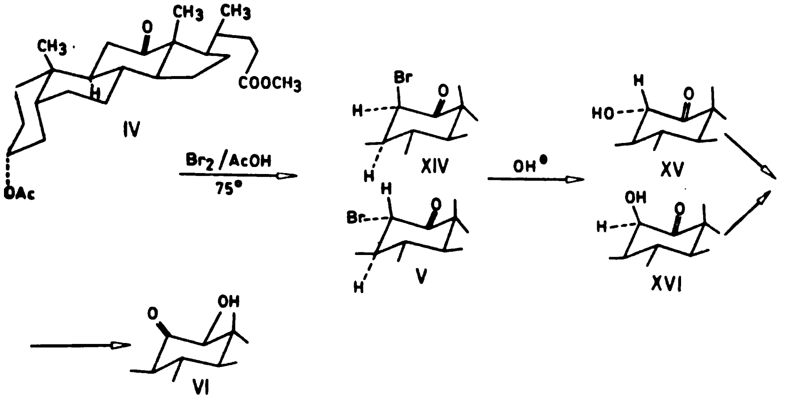
SCHEME I



yield. Mild alkaline hydrolysis proceeds with inversion of configuration and the corresponding 11α- and 11β-hydroxy-12-ketones (XV and XVI) are obtained. On alkaline hydrolysis of both bromo-ketones (V and XIV) under vigorous conditions, the intermediate epimeric 11-hydroxy-12-ketones (XV and XVI) isomerize and the most stable isomer, the 11-keto-12-hydroxy acid (VI) ("Marker-Lawson" acid) is obtained(7).

In this way, "Marker-Lawson" acid (VI) was obtained in a yield less than 50%, which was quite unsatisfactory considering the number of steps involved in the further degradation and conversion to the key intermediate 3α-acetoxy-11,20-diketo-(5β)-pregnane (XIII).

SCHEME II



The present investigation was undertaken to provide an improved method of preparation of this suitable intermediate, namely of the methyl ester of the monoacetate of "Marker-Lawson" acid (VIII).

A closer study of the reaction sequence in Scheme II indicates that the progress of each reaction must be dependent upon the keto-enol equilibrium in each of the intermediates. Both epimeric products obtained in each reaction of Scheme II (i.e. V, XIV and XV and XVI) cannot be equally suitable and during subsequent steps some of them may undergo side reactions, thus decreasing the yield of the final product significantly. Apparently, the main problem was to find out which of the epimeric bromo-derivatives would be more favourable for further conversion to "Marker-Lawson" acid and how to prepare it. Because of the accessibility of the α-side to rear attack in the S_N2' displácement with the hydroxide ion, the axial 11β-bromo-derivative (XIV) seemed to be the prefered isomer. On the other hand, the axial 11β-bromo-isomer (XIV) can easily react by a different pathway, namely transdiaxial elimination of hydrogen bromide, yielding the $\Delta^{9(11)}$--12-ketone and/or other rearrangement products. Furthermore, the two initially formed ketoalcohols (XV) and (XVI) isomerize under basic conditions to give the most stable isomer, — the "Marker-Lawson" acid (VI). In the ketoalcohol (XVI), which is formed from the equatorial 11-α-bromo-isomer, the relief of steric strain caused by two severe 1,3 interactions of the 11β-hydroxyl and the angular C-18 and C-19 methyl groups, provides a sufficient driving force for tetragonal to trigonal rehybridization, i.e. enolization and subsequent isomerization to "Marker-Lawson" acid without any elimination and/or rearrangement. These considerations provide sufficient evidence to conclude that the equatorial 11α-bromo-isomer (V) should be the more favourable derivative but the problem of its preparation still remained.

Methods for predicting the orientation of a bromine atom in an α-bromo-keto-steroid are available(8). It may be concluded that the 11β-bromo-isomer in which bromine is axial, should be the kinetically controled product of bromination of 12-keto-steroids, due to dipole-dipole interactions between the carbonyl group and the equatorial bromine atom. However, in this case steric 1,3 interactions of the axial supstituent and the angular methyl groups otuweigh the electronic effects, rendering the 11α-bromo-derivative (V) thermodynamically more stable. These arguments indicate that the vigorous reaction conditions applied by other authors for the introduction of bromine at C-11 were not correct in regard of yield and stereochemical purity of the desired product, since the short time of the reaction and the elevated temperature do not permit complete isomerization to the thermodynamically more stable 11α-bromo-derivative (V).*

We found that bromination of the methyl ester of 3α-acetoxy-12-keto-cholanic acid (IV) is carried out best in glacial acetic acid at 20°C, in presence of catalytic amounts of HBr, for an extended reaction time of 48—72 hours. Under such conditions, complete bromination and epimerization to the equatorial 11α-bromo-derivative (V) occurs and the crystalline product was isolated in a quantitative yield. The structure of this product was determined on the basis of published analytical data and by examination of NMR-spectra; the C-18 and C-19 methyl group signals appear exactly at calculated positions(9).

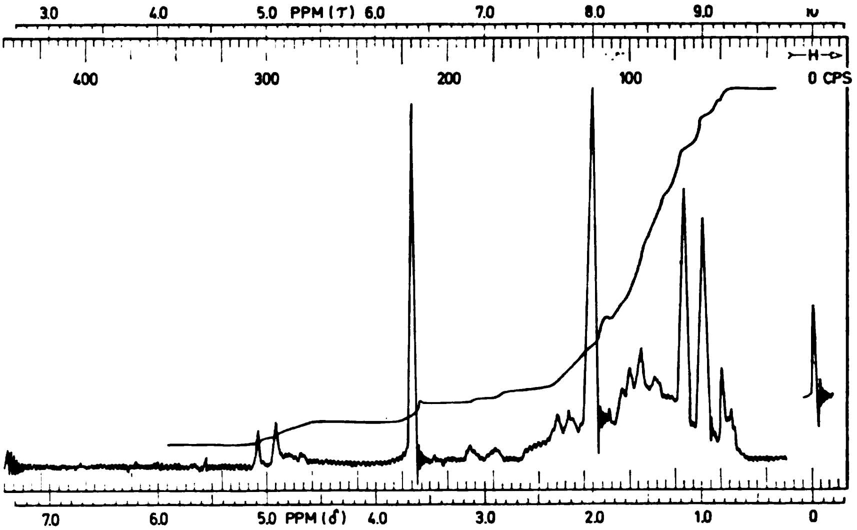


Fig. 1.

NMR-spectra of the methyl ester of 3α-acetoxy-11α-bromo-12-ketocholanic acid (V).

Upon alkaline treatment in an inert atmosphere, this derivative readily yields "Marker-Lawson" acid (VI), which was isolated by crystallization

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* It is possible that under such vigorous conditions of bromination side reactions also occur.

in a yield of over 60%. Mother liquors still contain the same acid (VI) as the major component but other isomers are also present; repeated treatment with alkali shifts the equilibrium of the four possible 11,12-ketol-isomers and additional amounts of the most stable isomer are easily obtained thus increasing the yield of the "Marker-Lawson" acid to over 75%, calculated on starting desoxycholic acid (I).

The remaining steps in this synthesis involve selective esterification of the 3α-hydroxy group, elimination of the oxygen function at C-12, and side chain degradation.

It was stated earlier(10) that selective acetylation of "Marker-Lawson" acid at C-3, under the standard conditions (acetic anhydride in pyridine), represents a great difficulty; the 3α-acetoxy-11-keto-12-hydroxy derivative (VIII) could be obtained only in a very low yield, while the major product is the corresponding 3.12-diacetoxy-derivative. A simple explanation for the decreased selectivity (as compared to desoxycholic acid), on the basis of configurational differences at C-12, was offered: in desoxycholic acid the 12-OH group is axial and therefore hindered by three OH : H interactions, while the equatorial 12β-hydroxy group in "Marker-Lawson" acid (VI) is quite accesible. By the examination of the acetylation procedure in pyridine, we have found that it is not only the formation of the diacetate that is responsible for the low yield of the monoacetate, but that also other isomeric acetates are present. It seems that pyridine is a sufficiently strong base to cause partial equilibration of the "Marker-Lawson" acid and the remaining three possible 11,12-ketol-isomers, so that this could be at least

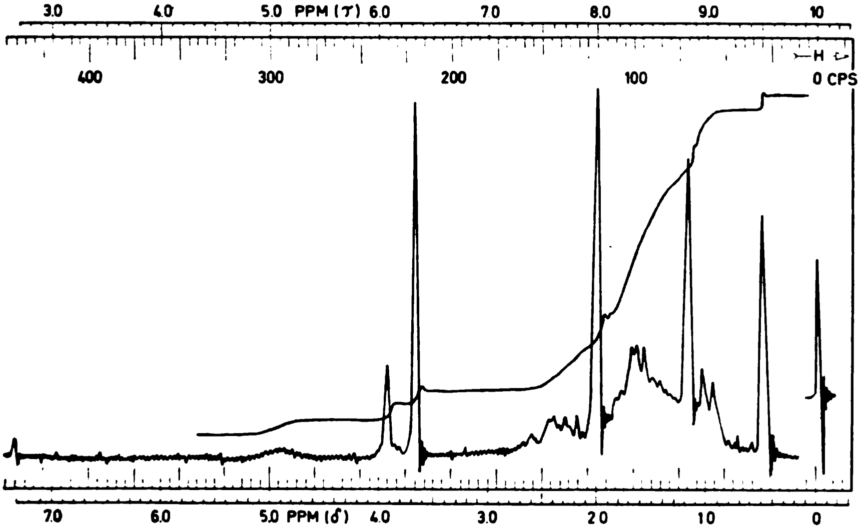


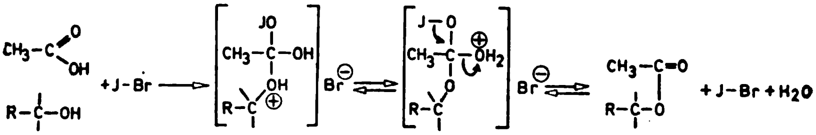
Fig. 2.
NMR-spectra of the methyl ester of 3α-acetoxy-11-keto-12β-hydroxycholanic acid (VIII)

an additional reason for the decrease in selectivity. Surprisingly enough, we found that selective acetylation may be easily effected by simply dissolving the ester (VII) in a threefold excess of acetic anhydride, without pyridine added, and by heating the reaction mixture on a water bath for 45 minutes. In this way, the pure crystalline monoacetate (VIII) was obtained in a yield averaging more than 80%, which makes this finding interesting from both the synthetic and the mechanistic point of view.

During these investigations we found that iodinemonobromide is a very efficient catalyst for various esterifications; in some cases of polyhydroxylic compounds great selectivity was also observed. Thus, the methyl ester of "Marker-Lawson" acid (VII) undergoes selective acetylation at position C-3 by means of glacial acetic acid in presence of catalytic amounts of iodinemonobromide, and the crystalline monoacetate (VIII) was obtained in a nearly quantitative yield. The structure of the monoacetate (VIII) obtained by both methods was established on the basis of analytical data and by analysis of NMR-spectra (Fig. 2).

This catalysis is being studied further and it appears that it may be an efficient procedure for esterification of various alcohols by means of a number of acids. Although at present only little evidence is available, a formal mechanism may be proposed for this reaction:

SCHEME III



It is worth mentioning that during investigations for possible methods of elimination of the oxygen function at C-12, selective esterification of the 3α-hydroxy group in the "Marker-Lawson" acid was accomplished by means of acids of different stereochemical features and requirements⁽¹¹⁾. However, this method is of little interest for practical purposes.

The elimination of the oxygen function can be accomplished according to the procedure developed by Gallagher⁽¹¹⁾. This method consists in the conversion of the ketol (VIII) to the corresponding 12α-bromo-derivative (IX) by means of phosphorus tribromide*, and treatment of this derivative with zinc in acetic acid to give the 11-keto-derivative (X). However, we found that Kendall's method of reductive elimination of bromine by means of phenylmagnesium bromide and the preparation of the 24,24'-diphenyl-derivative similar to (XI), applied as a one-step process in the transformation of the 3α, 9α-oxido-11-keto-12α-bromo-steroid of the same series may

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* In addition, we found that, depending on the reaction conditions, a very interesting rearrangement of the 12α-bromo-derivative (IX) may occur: when this reaction was carried out for a longer period of time (72 hours) and then worked up as usually (dilution with water, neutralization etc.), the methyl ester of 3α, 9α-oxido-11-ketocholanic acid is formed in a 5—15% yield. A detailed study of this rearrangement will be published later.

be utilized in our case also, affording the diphenyl-derivative (XI) in a 90% yield, directly from the 12α-bromo-derivative (IX)^(12)^.

Further degradation of the diphenyl-derivative (XI) into the key compound, 3α-acetoxy-11,20-diketo-(5β)- pregnane (XIII), was carried out by allylic bromination, dehydrobromination and subsequent oxidation of the diene (XII) by means of chromic acid, according to a somewhat modified Barbier-Wieland degradation procedure^(13)^.

We wish to point out that the reaction sequence (I—XIII) in Scheme I, according to which 3α-acetoxy-11,20-diketo-(5β)-pregnane (XIII) was obtained in a 11—13% yield calculated on starting desoxycholic acid (I), was actually performed as a seven-step process on a large laboratory scale; for the isolation of all the intermediates no special methods of purification, such as column chromatography or others, were necessary. The product (XIII) is the key intermediate for the synthesis of 11-oxygenated corticosteroids, such as dexamethasone, prednisone, etc., and this synthesis enabled us to prepare cortisone in only three additional steps.

EXPERIMENTAL

Melting points (uncorrected) were taken on a Kofler hot-stage apparatus. Infrared spectra were recorded (in KBr pellets) on a Perkin-Elmer spectrophotometer Model 337. NMR-spectra were determined on a Varian A-60-A spectrometer in carbon tetrachloride solution, using TMS as the internal reference standard. Thin-layer chromatography was performed on silica-gel G (Stahl) with cyclohexane-ethyl acetate in various ratios. Light petroleum used had a b.p. 40—60°C. The yields are given in weight percents.

Desoxycholic acid methyl ester (II).

Nine hundred grams (900 *g*) of desoxycholic acid (I) was dissolved in 3.6 *l* of 1% methanolic HCl and left for 24 hours at room temperature. The solution was cooled to 0°, carefully neutralized with a solution of sodium bicarbonate and left to crystallize at 0°C for 48 hours. The crystalline precipitate was colected and 750 *g* of ester (II) were obtained. By concentrating the mother liquor to 1/3 of the total volume, additional 140 *g* of pure ester (II) were obtained, m.p. 110—112°, $[\alpha]_D^{23^\circ} = +51^\circ$ (4).

Methyl ester of 3α-acetoxy-12α-hydroxy-cholanic acid (III).

a) Five hundred grams (500 *g*) of methyl ester (II) was dissolved in 900 *ml* of dry pyridine and 200 *ml* of acetic anhydride was added. The reaction mixture was left at room temperature for 36 hours and poured in an ice-cold 10% water solution of HCl. The reaction mixture was stirred for several hours and the separated solid collected by filtration, washed with water and dried. The crude monoacetate (III) thus obtained in a quantitative yield is 90% pure and can be used for the next oxidation step without purification. After crystallization from methanol, the product melts at 127—129°C, $[\alpha]_D^{23^\circ} = +64^\circ$ (4).

b) One hundred grams (100 *g*) of methyl ester (II) was dissolved in 400 *ml* of a 0.1 M solution of iodinemonobromide in glacial acetic acid and left at room temperature for 24 hours. An ice-cold saturated solution of sodium thiosulfate was added dropwise at 0°C until the solution becomes colourless; the solution was diluted with ice and then left at 0°C for several hours. The solution was filtered and the crystalline precipitate washed thoroughly with water and dried. The crude monoacetate (III), thus obtained in a quantitative yield, equals in quality the product obtained by standard procedure described under a).

The crude products obtained by both methods melt over a wide range (105—115°C); however, from the crude products, the corresponding 12-ketone (IV) was obtained in an excellent yield.

Methyl ester of 3α-acetoxy-12-keto-cholanic acid (IV).

To a solution of 617 *g* of crude monoacetate (III) in 2 *l.* of glacial acetic acid, a solution of 266 *g* of chromic oxide in 1 *l.* of water was added dropwise while stirring; the reaction is exothermic and the temperature should be maintained at 30—35°C. After all the reagent was added, the reaction mixture was stirred at room temperature and the progress of the reaction was followed by TLC; it was found that 2—3 hours is required for completion. The reaction mixture was diluted with 4 *kg* of crushed ice and stirred for 1 hour. The precipitated crystalline 12-keto-derivative (IV) was separated by suction, thoroughly washed with water and finally leached with methanol. In tihs way, 514 *g* (83%) of pure 12-keto-derivative (IV) was obtained, m.p. 151°C; $[\alpha]_D^{23°} = +108°^{(4)}$. Additional amounts of ketone (IV) can be obtained by purification of the mother liquor. However, the mother liquor, which containes mainly the ketone (IV) and the 3α,12α-diacetoxy-ester, can be saponified and the obtained mixture of acids suitably recycled.

Methyl 3α-acetoxy-11α-bromo-12-keto-cholanate (V).

Five hundred grams (500 *g*) of the 12-keto-ester (IV) was dissolved in 5 *l.* of glacial acetic acid and 20 *ml* of a 30% HBr/AcOH solution was added. A solution of 200 *g* of bromine in 2 *l* of glacial acetic acid was added dropwise while stirring over an 18 hours period; during the addition of the first 500 *ml* of the bromine solution, the temperature should be maintained close to 30°C. After the bromine solution was added, the reaction mixture was stirred for 42 hours more at room temperature. The solution was cooled and slowly diluted with 3 *l* of icewater while stirring. After 2 hours, the crystalline precipitate was collected, washed thoroughly with water and dried. The yield of more then 95% pure 11α-bromoderivative (V) is 575 *g*, m.p. 158—161°C, $(\alpha)_D^{23°} = +41°^{(5)}$. IR$\nu_{max}$ 1735 (broad), 1250 cm^{-1}.

NMR 3 H singlet (C-18) 1.05, 3 H singlet (C-19) 1.21,
3 H singlet (CH_3COO—) 2.0, 3 H singlet (—OCH_3) 3.66
and 1 H doublet centered at 5.0 $J_{H_{11}H_9}$ 10 cps.

Calculated for $C_{27}H_{41}O_5Br$	C 61.71,	H 7.86%
Found	C 61.90,	H 7.77%

3α,12β-dihydroxy-11-keto-cholanic acid ("Marker-Lawson" acid) (VI)

Six hundred grams (600 *g*) of 11α-bromo-derivative (V) was dissolved in 6 *l* of a 30% solution of potassium hydroxide in methanol and heated to a gentle reflux for 30 minutes in an inert atmosphere (N_2); separation of a white precipitate commences after several minutes of heating. The solution was cooled, poured on 3 *kg* of crushed ice and acidified by means of a 20% HCl solution while stirring. The amorphous solid was filtered off, washed thoroughly with water and dried. Crystallization from acetone affords 290 *g* of pure "Marker-Lawson" acid (VI), m.p. 201—203°C, $[\alpha]_D^{23°} = +64°$(6). Mother liquor was evaporated to dryness and the oily residue treated again with methanolic potassium hydroxide as described, and additional 80—120 *g* of acid (VI) were obtained.

Methyl ester of 3α,12β-dihydroxy-11-keto-cholanic acid (VII).

Methyl ester of acid (VI) was prepared by mixing the acid (VI) with a fourfold (w/v) amount of 1% methanolic HCl and by heating the reaction mixture until completely dissolved. The solution was left at room temperature for 24 hours, during which time most of the ester crystallizes, and for 24 hours at 0°C. Collection of two crops of crystalline material affords the methyl ester of "Marker-Lawson" acid (VII) in 96—98% yield, m.p. 156°C; $(\alpha)_D^{23°} = +67°$(13).

Methyl ester of 3α-acetoxy-11-keto-12β-hydroxy-cholanic acid (VIII).

a) The methyl ester (VII) was dissolved in a 2.5 fold amount of acetic anhydride by warming the reaction mixture at 90°C, the acetylation was carried on at 90° C for a total time of one hour. The reaction mixture was cooled, poured on crushed ice while stirring and left at 0°C for 16 hours. The crystalline precipitate was filterd, washed thoroughly with water, dried and finally leached with methanol affording the pure monoacetate (VIII) in an 80—83% yield, m.p. 112—114°C; $(\alpha)_D^{23°} = +70°$.

Calculated for $C_{27}H_{42}O_6$	C 70.10	H 9.15%
Found	C 70.17	H 9.35%

NMR One (CH_3COO—) singlet integrating for 3 H at 1.92.

b) Methyl ester of "Marker-Lawson" acid (VII) was treated with glacial acetic acid in presence of iodinemonobromide, under the same conditions as described for the preparation of methyl 3α-acetoxy-desoxycholate (III), affording the pure monoacetate (VIII) in an 85% yield.

Methyl ester of 3-α-acetoxy-11-keto-12α-bromo-cholanic acid (IX).

One hundred grams (100 *g*) of acetoxy-ester (VIII) was dissolved in 1 *l* of chloroform, the solution cooled to —5°C and treated with 50 *ml* of freshly prepared phosphorous tribromide. The solution was left at room temperature for 48 hours, poured on ice and the chloroform layer separated and freed of acidic material in the usual way. The solvent was removed and the semi-solid residue leached with methanol. In tihs way, 65—75 *g* of the 12α-bromo-derivative (IX) was obtained, m.p. 180—181°C; $[\alpha]_D^{22^\circ} = +11^\circ$(16).

The mother liquor was evaporated to dryness and chromatographed on a silica-gel column. Elution with petroleum ether afforded 2.8 *g* of a compound with the following characteristics:

m.p. 78—80°; $(\alpha)_D^{23^\circ} = +88^\circ$

IR 1740, 1712 cm^{-1} (no acetate band present).

Calculated for $C_{25}H_{38}O_4$	C 74.59	H 9.52
Found	C 74.81,	H 9.51

These data are in full agreement with those published by Kendall(16) for 3α,9α-oxido-11-keto-cholanic acid methyl ester; the NMR and mass spectra also confirm the proposed structure.

Further elution with benzene and benzene-ether afforded additional amounts of the 12α-bromo-derivative (IX) and of methyl 3α-hydroxy-11-keto-12α-bromo-cholanate, which is the possible intermediate in the formation of the 3α, 9α-oxido-derivative.

3α-Acetoxy-11-keto-24,24'-diphenyl-Δ^{23}-cholene (XI)

a) A solution of PhMgBr was prepared by treating 50 *g* of magnesium in 1.5 *l* of dry ether with 290 *g* of bromobenzene under the usual conditions. To this solution, 100 *g* of the 12-α-bromo-derivative (IX) dissolved in 2 *l* of dry benzene was added dropwise with stirring while the temperature was maintained below 10°C. After 10 hours of stirring at 10°C, the reaction mixture was poured on crushed ice and 200 *g* of ammonium chloride. The organic layer was separated, washed with a 10% HCl solution, dilute sodim carbonate solution and water and dried. The solvents were evaporated, the oily residue dissolved in 1 *l* of an 1 : 4 solution of acetic anhydride in glacial acetic acid and kept under reflux for 5 hours. The solution was cooled to 0°, gradually diluted with ice untill crystallization commences and left at 0° for 12 hours. The crystalline precipitate was filtered, washed well with water and dried. Trituration of the product with petroleum ether afforded 75—80 *g* of the pure diphenyl-derivative (XI), m.p. 166—168°C; $(\alpha)_D^{23^\circ} = +84^\circ$(14).

Mother liquors obtained by trituration of the crude product were evaporated to dryness, dissolved in 250 *ml* of a 5% methanolic potassium hydroxide solution, refluxed for 1/2 hour and then a rapid flow of steam was passed to remove diphenyl and other impurities. The mixture was cooled, the water layer decanted and the semisolid residue dissolved in ether, washed with water and dried. The ether was removed, the residue dissolved in 100 *ml* of acetic anhydride and refluxed for one hour. The solution was cooled and the crystalline product isolated as above, yielding 10—18 *g* of diphenyl-derivative (XI).

b) Twenty grams (20 *g*) of methyl ester of 3α-acetoxy-11-keto-cholanic acid (X), obtained in only 60% yield by treatment of the 12α-bromo-derivative with zinc and acetic acid(14), was treated with PhMgBr under the same conditions as described under a), yielding 16 *g* of the diphenyl-derivative (XI).

3α-*Acetoxy-11-keto-*$\Delta^{20,23}$*-24,24'-diphenyl-choladien (XII)*

One hundred grams (100 *g*) of diphenyl-derivative (XI) was dissolved at 50° in 5 *l* of carbon tetrachloride, 32 *g* of N-bromsuccinimide was added and the mixture vigourously stirred and heated by means of a 500 W lamp. The solution was cooled, the principitated succinimide filtered and the resulting solution evaporated to dryness. The oily residue was taken up in 200 *ml* of pyridine and heated at 100°C for 45 minutes in an inert atmosphere (N_2). Most of the pyridine was evaporated under reduced pressure, the residue dissolved in ether, washed with dilute HCl, sodium bicarbonate and water, and dried. The ether was evaporated and the residue crystallized from methanol yielding 70—75 *g* of the diene (XII), m.p. 170°C; $(\alpha)_D^{23°} = +55°$.

3α-*Acetoxy-11,20-diketo-(5β)-pregnane (XIII)*

One hundred grams (100 *g*) of the diene (XII) was dissolved in 1300 *ml* of 80% acetic acid and 1200 *ml* of chloroform, cooled to 0° and a solution of 75 *g* of chromic oxide in 1200 *ml* of 80% acetic acid was added dropwise over a 2 hours period while stirring. The temperature was maintained at 0° and the solution stirred for 6 more hours. A solution of sodium bisulfite was added and the mixture concentrated under reduced pressure. The residue was dissolved in ether, washed till neutral, dried and the solvent evaporated. The oily residue crystallizes from isopropyl ether affording 40—42 *g* of pure diketone (XIII), m.p. 133—135°C; $(\alpha)_D^{23°} = +128°C$(15). Mother liquors were evaporated to dryness and the residue chromatographed on a short column of silica-gel; the main impurity, diphenylacrolein, is easily eluted with petroleum ether while practically pure diketone (XIII) (15—20 *g*) is obtained by eluting the column with a 10 : 1 benzene-ether mixture.

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SUMMARY

A novel method for the preparation of 11-oxygenated corticosteroid intermediates is described. This preparation represents an improved and simplified procedure for the transposition of the oxygen function in desoxycholic acid from C-12 to C-11 via the "Marker-Lawson" acid route, by which 3α-acetoxy-11,20-diketo-(5β)-pregnane was obtained in a 11—13% yield, calculated on starting desoxycholic acid.

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Original Scientific Paper

MICROBIOLOGICAL TRANSFORMATION OF 5,10-SECO-STEROIDS. I.

THE ACTION OF *RHIZOPUS NIGRICANS* ON *CIS*-3β,17β-DIACETOXY-5,10-SECO-$\Delta^{1(10)}$-ANDROSTENE-5-ONE*

by

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IVANKA PEJKOVIĆ-TADIĆ and MIODRAG MARIĆ

Microbiological hydroxylation of sterodis is well known to take place at different positions of the steroid molecule, depending on the microorganisms⁽¹⁾. However, transformations of this kind with 5,10-seco-steroids, a relatively new type of steroidal derivative⁽²⁾, have not been reported so far. The aim of this work was to attempt the synthesis of hydroxy derivatives of 5,10-seco-steroids by the action of microorganisms.

The seco-steroid used was *cis*-3β,17β-diacetoxy-5,10-seco-$\Delta^{1(10)}$-androsten-5-one (I)**. On the basis of preliminary experiments with various species of microorganisms, *Rhizopus nigricans* (Ehr, C.S.B. Netherland) was chosen since it displayed the most specific action giving only a few transformation products, which could be isolated and separated. Hydroxylation was performed in a phosphate buffer (pH = 7) containing 1% of glucose, at 27°C, incubation time being 48 hours. The reaction products were isolated by continuous extraction with ether, mycelia being previously removed by centrifugation. The reaction course was followed by TLC. Reaction products were separated by silica gel column chromatography using benzene-methylene chloride mixtures of various composition for elution. All components were purified by additional column chromatography when necessary and by repeated crystallizations.

Incubation of I with *Rhizopus nigricans* yielded five crystalline products (II, III, IVa, IVb and IVc) (Scheme I):

The substrate was removed from the column by benzene-methylene chloride mixture (9 : 1). The first transformation product eluted from the column with benzene-methylene chloride mixture (1 : 1) was a crystalline material of melting point 180°C, whose R_f-value on a thin-layer chroma-

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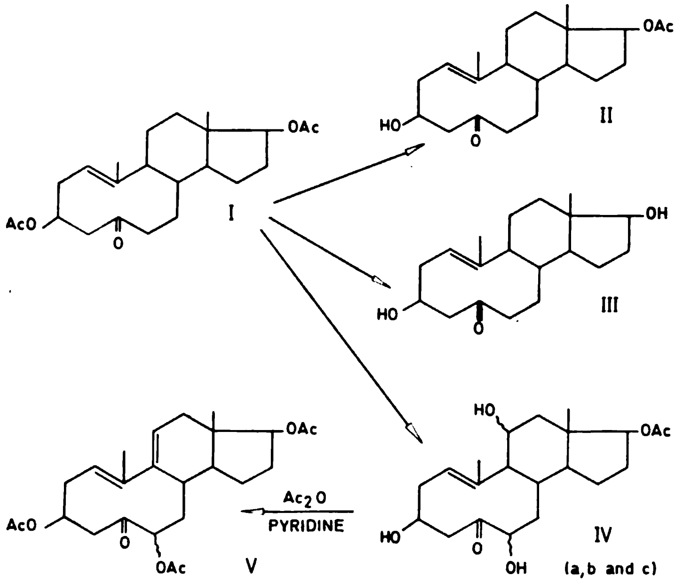
* Part of this work was communicated at the 4th International Symposium on The Chemistry of Natural Products (1966, Stockholm, Sweden).

** Obtained by the courtesy of prof. M. Lj. Mihailović, School of Sciences, Belgrade Univ.

SCHEME I



Microbiological Transformation of 5,10-Seco-Steroids. I. The action of ***Rhizopus nigricans*** on *cis* 3β,17β-diacetoxy-5,10-seco-$\Delta^{1(10)}$-androstene-5-one.

togram corresponded to *cis*-3β-hydroxy-17β-acetoxy-5,10-seco$\Delta^{1(10)}$-androsten-5-one (II). After treatment with petroleum ether and recrystalization from ethanol a product melting at 197°C was obtained. It was identified as *cis*-3β-hydroxy-17-β-acetoxy-5,10-seco$\Delta^{1(10)}$-androsten-5-one (II) by elemental analysis, spectral data and mixed melting point with an authentic specimen obtained by partial hydrolysis of I. The next transformation product, III (m.p. 210°C), eluted with the same solvent mixture was identified as *cis*-3β,17β-dihydroxy-5,10-seco-$\Delta^{1(10)}$-androsten-5-one by comparison of its constants with those of an authentic sample obtained by total hydrolysis of the starting material I.

Further elution with the same eluent gave predominantly a mixture of IV which was resolved into three new products (IVa, IVb and IVc) by rechromatographing on a silica gel column and gradient elution with benzene-ethylacetate.

The isolation of II and III, which represent hydrolytic products of the starting material I, indicated a possible hydrolysis in the course of the microbial transformation. Since blank experiments gave none of these products it could be concluded that the microbial transformation involved hydrolysis as a side reaction.

Rechromatography of the mixture IV resulted in the isolation of three isomeric compounds of molecular formula $C_{21}H_{36}O_6$ which indicated the presence of three hydroxyl groups in the molecule. They were designated as IVa, m.p. 262°C, $[\alpha]_D^{30}+$ 15,4° (±4°); IVb, m.p. 181—184°C, $[\alpha]_D^{30}+$

$+ 46{,}1^\circ$ ($\pm 1^\circ$), and IV*c*, m.p. 118—120°C, $[\alpha]_D^{30} + 22{,}6^\circ$C ($\pm 1^\circ$) in order of elution. Compounds IVa and IVb easily crystallized from 60% ethanol whereas compound IVc, which was eluted as an oily material, crystallized very slowly. The infra-red spectra of all three compounds showed characteristics absorption maxima for hydroxyl (about 3400 cm^{-1}), acetate (1740 cm^{-1}) and carbonyl (about 1700 cm^{-1}) and exhibited changes in the relative intensity of the C—H band in the region of 1420—1430 cm^{-1} which almost disappeared. As regards the position of the carbonyl of the ten-membered ring in the spectra of IVc its frequency was slightly shifted to longer wavelengths. The mixture of IVa and IVb was submitted to acetylation with acetic anhydride in pyridine at 0°C and only one acetylated product (V) was isolated (lack of material prevented us doing acetylation of individual components). After crystalization from 70% ethanol a product with two molecules of crystalline water (their presence being proved by IR spectrum) was obtained, melting at 66°C. Elemental analysis of V indicated that a dehydration reaction had taken place in the course of acetylation, since a triacetoxy instead of a tetraacetoxy derivative was derived. This indication was confirmed by UV spectral analysis which showed conjugation with the ethylene double bond ($\lambda_{max}^{ether} = 235\ m\mu$, $\varepsilon = 2000$). In agreement with these data the NMR spectrum of V showed a shift of the 19-CH_3 signal (0.36 ppm) with respect to the 19-CH_3 signal of compound I, and the presence of two vinyl protons at 4.65δ. These results would be consistent with a structure of *cis*-3β, 6,11-trihydroxy-17β-acetoxy-5,10-seco-$\Delta^{1(10)}$-androsten-5-one. On the basis of the acetylation product it might be concluded that the difference between IVa and IVb is due to different orientation of the 11-hydroxyl group. On the other hand from IR spectral data it seems most probable that the isomer IVc differs from IVa and IVb in the orientation of the 6-hydroxyl group. Since the data obtained so far give no direct proof for the stereochemical arrangement of microbially introduced hydroxyl groups in the seco-steroid molecule, the subject of our further investigation will be the stereochemical study of these isomeric compounds.

EXPERIMENTAL

All melting points (uncorrected) were taken on a micro-Kofler hot stage apparatus. Optical rotations were measured in 80% ethanol. TLC was performed on silica gel H (Merck) plates in: *a* — benzene-ethylacetate (1 : 1) and benzene-ethylacetate (1 : 4). The detection was effected with 50% H_2SO_4. Silica gel BDH for adsorption chromatography was used.

General procedure for the microbiological transformation

To a mixture containing 10 *g* peptone-1 ("Torlak"), 50 *g* glucose, 3 *g* cornsteep extract and 1 *g* NH_4NO_3 in 1 *lit* of distilled water, the spores were added from an agar slant prepared by growing a culture of *Rhizopus nigricans* (Ehr. CBS, 6226 b, Netherland) on potato dextrose agar. After distribution between ten Erlenmeyer flasks the mixture was incubated 24 hours at 27°C on a shaking machine. After filtration, mycelia were carried over into ten 500 *ml* Erlenmeyer flasks each containing 100 *ml* phosphate buffer (pH = 7) with 1% of glucose and then 20 *mg* of 3β,17β-diacetoxy-5,10-seco-$\Delta^{1(10)}$-androsten-5-one in acetone solution was added. Incubation lasted 48 hours at 27°C and reaction was followed by TLC. When transformation was complete, mycelia were removed by centrifugation, water solutions were combined and continuously extracted with ether. The ether extract, after being washed with water, was dried over anhydrous sodium sulphate and taken to dryness *in vacuo*. Adsorption chromatography was carried out on a silica gel column by elution with benzene-methylene chloride mixtures of various composition.

Cis-3β-hydroxy-17β-acetoxy-5,10-seco-$\Delta^{1(10)}$*-androstene-5-one (II)*

By the general procedure described above 1,8 *g* of I was incubated with *R. nigricans* to give 1.5 *g* of transformed products. TLC in solvent *b* revealed the presence of five main components (R_f = 0.47, 0.33, 0.21, 0.15, 0.09). The crude mixture (1.5 *g*) was dissolved in 2 *ml* of methylene chloride and run on the silica gel column (75 *g*). Elution was carried out with benzene-methylene chloride. Fractions of 10 *ml* were collected and after homogeneity was confirmed by TLC (solvents *a* and *b*) they were combined and evaporated under reduced pressure.

Substrate I was eluted first with benzene-methylene chloride (9 : 1) and identified by melting point 156—158°C, R_f-value (0.66) and microanalysis (Found: C, 70.70, H, 8.69, Calc. for $C_{23}H_{34}O_5$: C, 70.74, H, 8.78%).

II was eluted with benzene-methylene chloride (1 : 1). Since the R_f-value (0.47) corresponded to *cis*-3β-hydroxy-17β-acetoxy-5,10-seco-$\Delta^{1(10)}$-androsten-5-one, crystalization from ethanol was tried. Since the melting point did not sharpen, the product was treated with different organic solvents. It was found that part of the product was soluble in hot petroleum ether*. The insoluble fraction after crystalization melted at 197°C, the melting point was not depressed upon addition of an authentic sample obtained by partial hydrolysis of I, and possesed all other characteristic features of *cis*-3β-hydroxy-17β-acetoxy-5,10-seco-$\Delta^{1(10)}$ -androsten-5-one R_f = 0.47, ν_{max} (KBr) 3500, 1740, 1705, 1427, 1250 and 1018 *cm*$^{-1}$ (Found: C, 72.37, H, 9.00, Calc. for $C_{31}H_{32}O_4$; C, 72.38, H. 9.20%).

Cis-3β,17β-dixydroxy-5,10-seco-$\Delta^{1(10)}$*-androstene-5-one (III)*

III was eluted with benzene methylene chloride (1 : 1). This component showed the same physical constants as authentic *cis*-3,17-*dixydroxy*-5,10-seco-$^1(^{10})$-androsten-5-one (product of total hydrolysis of I: R_f = = 0.33, m.p. 210°C, v_{max} (KBr) 3500, 1706 *cm*$^{-1}$ (Found: C, 74.42, H, 9.81. Calc. for $C_{19}H_{20}O_3$: C, 74.47, H, 9.87%).

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* The nature of the product soluble in petroleum ether is the subject of further investigation.

Cis-3β,6,11-*trihydroxy*-17β-*acetoxy*-5,10-*seco*-$\Delta^{1(10)}$-*androstene*-5-*one* (*IVa, IVb and IVc)*

Elution of III was followed by a mixture of IVa and IVb, then pure IVb, a mixture of IVb and IVc and last pure IVc. (Total yield 37% calculated relative to the crude mixture). Fractions containing mixtures were rechromatographed on silica gel with benzene-ethyl-acetate and separated into components, which after crystalization from 60—70% ethanol showed the following physical constants: IVa, m.p. 262°, $[\alpha]_D^{30}$ + 15.4 (±4°), R_f = = 0.21, v_{max} (KBr) 3450, 1740, 1705 and 1430 *cm*$^{-1}$. (Found: C, 66.18, H, 8.35. Calculated for $C_{21}H_{32}O_6$: C, 66.30; H, 8.48%); IVb, m.p. 181—184°C $[\alpha]_D^{30}$ + 46.1° (± 1°), R_f = 0.15, v_{max} (KBr) 3410, 1740, 1705 and 1250 *cm*$^{-1}$ (Found: C, 66.15, H, 8.70; Calculated for $C_{21}H_{32}\ O_6$: C, 66.30, H, 8.48%); IVc, m.p. 118—120°C, $[\alpha]_D^{30}$ + 22.6° (± 1°), R_f = 0.09, v_{max} 3360, 1470, 1695, 1250 *cm*$^{-1}$. (Found: C, 66,20, H, 8.86; Calculated for: $C_{21}H_{32}O_6$: C, 66.30, H, 8.48%).

Cis-3β,6,17-triacetoxy-5,10-seco-$\Delta^{1(10)\,9(11)}$*-androsten-5-one* (*V*)

A solution of 50 *mg* of the mixture (IVa and IVb) in 2 *ml* of pyridine and 1 *ml* Ac_2O was allowed to stand at 0°C for 24 *hrs*. Usual treatment of the mixture yielded 42 *mg* of V, m.p. 66°C, $[\alpha]_D^{30}$ + 28.3° (±1°), v_{max} (KBr) 1740, 1705, 1600, 1580 and 1250 *cm*$^{-1}$, R_f = 0.59 (solvent b); λ_{max}^{ether} = 235 *m*μ, ε = 2000: NMR spectrum (run in $CDCl_3$ at 60 Mc/s with a Varian A-60-A spectrometer and TMS as reference): δ = 0.88 (CH_3—18, singlet), δ = 2.11 (CH_3—19, singlet),* δ = 2.03 (OAc, singlet), δ = 4.65 (C 1 and C 11 protons). (Found: C, 62,23, H, 7.89. Calculated for: $C_{25}H_{34}O_7.2H_2O$: C, 62.22, H, 7.94%).

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* δ = 1.75, CH_3 — 19 signal of compound I

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COULOMETRIC METALLOMETRY

COULOMETRIC-METALLOMETRIC DETERMINATION OF ANIONS

by

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Considering that it is in principle possible to bring metal ions into solution, and in the light of the theoretical postulates and studies of Tutundžić(1), after coulometric argentometry(2,3) and coulometric plumbometry(3,5), we proceeded to study the anodic dissolution of mercury and the conditions for the quantitative use of mercurous ions(3—11) almost at the same time as other authors(18—19).

Mercurous ion appeared to be a very interesting reagent for the determination of a number of other anions. There are several publications dealing with the routine volumetric determinations in the presence of indicators with potentiometric and amperometric determination of the end-point.

In order to develop the method of coulometric mercurometry we have studied the anodic dissolution of mercury, which did not show any overvoltage in an indifferent electrolyte of KNO_3, this finding being in full aggreement with the studies of LeBlanc(12). The anodic behavior of mercury was used as the basis for the quantitative application of the mercurous ions for the determination of those anions which in aqueous solutions form hardly soluble compounds with mercurous ions.

The anodic potential was recorded in a system of the following composition:

$$(+)\ \mathrm{Hg}\ \left|\ \begin{array}{c} 0.2\ \mathrm{M\ KNO_3,\ H_2O} \\ 10^{-2}-10^{-3}\ \mathrm{HNO_3} \end{array}\ \right\|\ \begin{array}{c} \mathrm{KNO_3,\ H_2O} \\ \text{in agar agar} \end{array}\ \left\|\ 0.2\ \mathrm{M\ KNO_3,\ H_2O}\ \right|\ \mathrm{Pt}\ (-)$$

A theoretical consideration of the possible chemical or electrochemical reactions showed that at a mercury anode reactions can take place whose potentials range from +0.10 to +1.80 V depending on the pH of the solution(13). From the possible reactions and on the polarization curve, obtained in our case at pH values between 2 and 3, we concluded that in a solution of potassium-nitrate mercury changes into mercurous ion, which we used in further study for the quantitative determination of anions.

The application of coulometric mercurometry based on anodic oxidation of mercury has revealed the universal application of mercury in electrolysis, considering that mercury as a cathodic material was introduced into laboratory practice as long as six decades ago.

EXPERIMENTAL

Chemicals. — The chemicals used were "Merck" p.a. Before use they were dried at 110°C. Solutions of desired molality were made and from these aliquots were taken by means of a calibrated burette. The indifferent electrolyte both for the anolyte and the catholyte was KNO_3 solution, in the anolyte from 10^{-2} to 10^{-3} M relative to HNO_3. Potassium nitrate had a favorable influence on the electrolysis not only as the conducting salt, supressing migration current, but also enabling the mercurous ions in solution to establish an equilibrium first with nitrate ions and only then, in a secondary reaction, to react with the anions which were to be determined, forming hardly soluble compounds.

The electrical circuit. — The apparatus for coulometric mercurometry has two circuits, the same as in coulometric plumbometry(4) and bismuthometry(14), viz: the coulometric circuit of electrolysis, and the indicator amperometric circuit. Both circuits consist of the usual parts(4,14).

In the coulometric formation of mercurous ions the form of the anodic mercury was the source of certain difficulties. It was possible to use three forms of mercury: electrode in the shape of the bottom of a container with a suitable connection via a Pt wire, electrode in the shape of the letter J, or a solid mercury electrode obtained by amalgamation with a noble metal.

The J-shaped was not satisfactory because of the small area of mercury, which impeded mixing of the anolyte and the regeneration of the electrode surface, for which reason we decided to use an anode with a larger area, in the form of a beaker bottom covered by 3 mm of mercury and with a suitable connection via a Pt wire.

We chose amperometric determination of the end-point because it enables the determination of micro and semi-micro quantities with great accuracy, and is very rapid. Before starting the work it was necessary to record polarograms of the two components of the system in the indifferent electrolyte KNO_3 at pH 2—3 separately, in order to chose the right potential.

The mixing of the electrolyte, which was necessary during the action of the coulometric circuit in order to accelerate the reaction and reduce the adsorption of ions on the precipitate, was interupted at predetermined intervals, in order to switch on the amperometric indicator circuit. The interuptions were repeated 3—5 times before and the same number of times after the end-point in order to obtain the necessary parameters for the amperometric curve $I_d = f(t)$. Kolthof and co-workers(15,16) carried out amperometric determinations mainly in the absence of oxygen, while we did coulometric-mercurometric-amperometric determinations in the presence of the oxygen remaining after boiling the distilled water twice in the cell, which was not hermetically sealed. Chovnyk(17) has also done amperometric determinations in the presence of oxygen. Amperometric end-point determination in coulometric metallometry has the advantage over simple amperometric titration in that the titrant is in fact the electrochemically generated reagent, i.e. quantity of electrolity, so that it is not necessary either to prepare previously a solution of known titer or to maintain and continuously monitor the titer. Since the titrant is added to the solution at the time of its formation, there is no dilution whatsoever, and there is no need for the calculation of the correction which is absolutely necessary with the simple amperometric titrations.

With regard to the choice of the working potential in the amperometric circuit, in order to avoid the possibility of anodic reaction of the dropping Hg electrode in the presence of halogen ion we chose a potential at which reduction of the mercurous ion occurs after the end-point and registered the change $Id_{Hg_2}+ = f(t)$.

Mercurometric determination of chloride ion

Chloride-ion coulometry was done under the conditions described in the experimental part. The results are shown in Table 1.

TABLE 1.

Mercurometric determination of chloride ion

Indifferent electrolyte: 0.3 M KNO_3
Volume of anolyte 50 *ml*, volume of catholyte 50 *ml*.
Generator current: I = 40.0, 30.0, 20.0, and 15.0 *mA*. Voltage 14.0 *V*.
Amperometric indicator circuit with polarized dropping mercury electrode and saturated calomel electrode. Potential of the amperometric circuit −0.6 *V/sce*.

Approximate molality KCl	Taken Cl^-	Found Cl^-	Error		Current	Theoretical time
mol/l	*mg*	*mg*	*mg*	%	*mA*	*sec*
$3.9 \cdot 10^{-3}$	7.09	7.11	0.02	0.31	40.0	482.5
$1.9 \cdot 10^{-3}$	3.55	3.57	0.02	0.56	30.0	321.6
$1.9 \cdot 10^{-3}$	3.55	3.54	−0.01	−0.28	15.0	643.2
$5 \cdot 10^{-4}$	1.77	1.79	0.02	1.13	30.0	160.0
$5 \cdot 10^{-4}$	1.77	1.79	0.01	1.17	20.0	241.3

It may be seen from Table 1 that Cl^- ion was determined in concentrations form $3.9 . 10^{-3}$ to $5 . 10^{-4}$ M with a mean error 0.48%. The smallest quantity determined was 1.77 *mg*, for the determination of which 4.82 coulombs was used, which corresponds to a rate of anodic oxidation of mercury of $2.04 . 10^{-7}$ *geq*. of mercury ions per second. The voltage in the amperometric circuit corresponded to the reduction of mercurous ion, so that a curve in the shape of an upturned L was obtained.

Mercurometric determination of the bromide ion

The conditions under which bromide ion was determined were the same as for chloride ion, except that the accuracy was better because of the lower product of solubility of bromide ion.

It may be seen from Table 2 that bromide ion was determined in concentrations of $5 . 10^{-4}$ to $1.0 . 10^{-3}$ M KBr. The relative errors in these determinations ranged from 0.10 to 1.0%. The smallest quantity of bromide ion determined was 1.99 *mg*, for the determination of which 2.41 coulombs was used, which corresponds to a rate of mercurous ion formation of $2.04 . 10^{-7}$ *geq* per second. The curve of the amperometric determination has the shape

TABLE 2.

Mercurometric determination of bromide ion

Indifferent electrolyte 0.3 M KNO_3.
Volume of anolyte 50 *ml*, volume of catholyte 50 *ml*.
Generator current: I = 40.0, 30.0 and 20.0 *mA*. Voltage 15.0 *V*.
Amperometric indicator circuit with polarized dropping mercury electrode and saturated calomel electrode. Potential in the amperometric circuit −0.6 V/*sce*.

Approximate molality KBr	Taken Br^-	Found Br^-	Error		Current	Theoretical time
mol/l	*mg*	*mg*	*mg*	%	*mA*	*sec*
$2.4 \cdot 10^{-3}$	9.56	9.57	0.01	0.10	40.0	289.5
$2 \cdot 10^{-3}$	7.99	8.00	0.01	0.13	30.0	321.6
$1.6 \cdot 10^{-3}$	6.39	6.39	—	—	30.0	258.1
$1 \cdot 10^{-3}$	3.99	4.00	0.01	0.28	20.0	241.3
$2.3 \cdot 10^{-3}$	3.19	3.21	0.02	0.62	20.0	192.7
$5 \cdot 10^{-4}$	1.99	2.01	0.02	1.0	20.0	120.6

of an upturned L, whose ascending part corresponds to the indicator reaction, the same as in the determination of chloride ion, that is to the corresponding diffusion current which was specific and proportional to the quantity of mercurous ion produced in the given time.

The results shown in Tables 1 and 2 indicate that the chloride and bromide ions can be determined in semi-micro and micro quantities with satisfactory accuracy.

Mercurometric determination of oxalate-ion

Further widening the possibilities of the mercurometric determination of anions, we undertook to determine oxalate ion, which with mercurous ion forms a poorly soluble compound whose product of solubility is slightly greater than that of mercurous halogenides. As in the previous determinations, we maintained the pH between 2 and 3, when starting from oxalate ion from sodium oxalate; in the case of oxalic acid there is no need for subsequent adjustment of pH. In both cases good results were obtained. They are shown in Table 3.

Table 3 shows that the quantities of oxalate ion ranged from 3.3 to 11.0 *mg* and were determined with a relative error from. 0.18 to —1.20%. The determination of the smallest quantity of 3.3 *mg* used 7.23 coulombs which corresponds to a rate of mercurous ion formation of 2.2 . 10^{-7} geq per second. The curve of the amperometric determination had an upturned L shape, the ascending part corresponding to the reduction of mercurous ion as in the previous two cases.

In comparison with simple volumetric amperometric determination the coulometric mercurometric determination of the oxalate ion has the advantage that the oxalate ion, like the majority of anions, is determined

TABLE 3.

Mercurometric determination of oxalate ion

Indifferent electrolyte: 0.2 M KNO_3
Volume of anolyte: 50 *ml*; volume of catholyte: 50 *ml.*
Generator current: I = 40.0, 32.0, and 20.0 *mA*. Voltage 15.0 V.
Amperometric indicator circuit: polarized dropping mercury electrode and saturated calomel electrode. Potential of the amperometric circuit −0.5 V/*sce.*

Approximate concentration $Na_2C_2O_4$	Taken $C_2O_4^{2-}$	Found $C_2O_4^{2-}$	Error		Current	Theoretical time
mol/l	*mg*	*mg*	*mg*	%	*mA*	*sec*
$2.5 \cdot 10^{-3}$	11.00	11.03	0.03	0.27	40.0	603.1
$1.8 \cdot 10^{-3}$	8.25	8.22	—0.03	—0.36	32.0	565.3
$1.25 \cdot 10^{-3}$	5.50	5.51	0.01	0.18	40.0	301.5
$7.5 \cdot 10^{-4}$	3.30	3.26	—0.04	—1.20	20.0	361.8

by means of electrochemically generated mercurous ions so that it is not necessary to prepare and store a solution of the mercurous salt, which requires a special procedure in view of the solubility of mercurous salts and hydrolytic decomposition.

Mercurometric determination of molybdate ion

The determination was done under similar experimental conditions as for oxalate ion, except that in the amperometric circuit a voltage of —0.8 V

TABLE 4.

Mercurometric determination of molybdate ion

Indifferent electrolyte: 0.1 to 0.3 M KNO_3.
Volume of anolyte: 50 *ml*, volume of catholyte: 50 *ml.*
Generator current: I = 40.0 and 15.0 *mA*. Voltage 17.0 *V*.
Amperometric indicator circuit: polarized dropping mercury electrode and saturated calomel electrode. Potential in the amperometric circuit −8.0 V/*sce.*

Approximate concentration $Na_2MoO_4 \cdot 2H_2O$	Taken MoO_4^{2-}	Found MoO_4^{2-}	Error		Current	Theoretical time
mol/l	*mg*	*mg*	*mg*	%	*mA*	*sec*
$1.8 \cdot 10^{-3}$	15.00	14.94	—0.06	—0.40	40.0	450.2
$1.25 \cdot 10^{-3}$	10.00	9.98	—0.02	—0.20	40.0	301.6
$7.2 \cdot 10^{-4}$	6.00	5.99	—0.01	—0.16	40.0	180.9
$4.2 \cdot 10^{-4}$	3.40	3.33	—0.07	—2.06	15.0	373.4

was used. The curves have the shape of a drawn-out letter V whose descending part corresponds to the reduction of Mo^{6+}, and ascending part to the reduction of mercurous ion. The results of the determination are shown in Table 4.

The smallest quantity of molybdate ion determined was 3.4 *mg*, and the greatest 15 *mg*. The determination of 3.4 *mg* used 5.59 coulombs, which corresponds to a rate of mercurous ion formation of $1.5 \,.\, 10^{-7}$ geq per second.

Mercurometric determination of iodate ion

A prerequisite for the coulometric mercurometric determination of iodide ion, as for the other anions, is maintenance of the pH in the anolyte between 2 and 3 relative to HNO_3, and the pH of the catholyte from 3 to 4 relative to sulfuric acid. The potential in the amperometric circuit was —0.6 V. The curve had the shape of the letter V. The results are shown in Table 5.

TABLE 5.

Mercurometric determination of iodate ion

Indifferent electrolyte: 0.2 to 0.3 M KNO_3.

Volume of anolyte: 50 *ml*; volume of catholyte: 50 *ml*.

Generator current: I = 30.0, 20.0, 15.0 and 10 *mA*. Voltage 14.0 *V*.

Amperometric indicator circuit: polarized dropping mercury electrode and saturated calomel electrode. Potential in the amperometric circuit -0.6 V/*sce*.

Approximate concentration KIO_3	Taken IO_3^-	Found IO_3^-	Error		Current	Theoretical time
mol/l	*mg*	*mg*	*mg*	%	*mA*	*sec*
$1.5 \cdot 10^{-3}$	13.11	13.07	—0.04	—0.31	30.0	241.3
$1.0 \cdot 10^{-3}$	8.71	8.67	—0.04	—0.47	20.0	241.3
$5.5 \cdot 10^{-4}$	4.37	4.35	—0.02	—0.45	13.0	160.8
$3.6 \cdot 10^{-4}$	2.19	2.16	—0.03	—0.38	10.0	120.6

Table 5 shows that the concentration of KIO_3 was between $1.5 \,.\, 10^{-3}$ and $5.5 \,.\, 10^{-4}$ M. The relative error in these determinations ranged between 0.31 and 1.38%, depending on the concentration determined. For the smallest quantity of iodate ion of 2.19 *mg* the determination used 1.2 coulombs, which corresponds to a rate of generation of mercurous ion of $1.03 \,.\, 10^{-7}$ geq in one second.

The results shown in Tables 1—5 represent the mean values of at least 4 determinations.

The results show that the coulometric mercurometry by means of electrolytically generated mercurous ions, at constant current and with amperometric determination of the end-point, is a convenient, simple and rapid method for the micro and semimicro determination of anions.

Electrolytic oxidation of mercury to mercurous or mercuric ion, depending on the operating conditions, permits the determination of other anions which form hardly soluble compounds. The amperometric end-point determination also makes it possible to determine anions which form hardly soluble compounds with a higher solubility product, since the equivalence point is the intersection of the characteristic branches of the diagram, so that the influence of solubility, which is manifested on the graph as a rounding near the end-point, does not faffect the result.

Owing to the much smaller solubility of a great number of mercurous compounds it is possible to determine mercurometrically even those anions which are determined with less accuracy by argentometry and plumbometry. Mercury as the anodic material makes it possible to obtain metallo-organic compounds, i.e. to determine those molecular groups or the corresponding ions which make up these compounds.

Coulometric mercurometry, verified on these examples, obviates the preparation of solutions of mercurous salts, makes it unnecessary to determine and check the variable titer, and introduces the coulomb, or the electron, into this field of analytical determination as well, instead of various chemical compounds which are often inadequately defined.

This coulometric method also justifies the suggestion of Tutundžić (1,10,20–22) that the coulomb or the electron, should be adopted as the primary substance in all analytical chemistry.

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Original Scientific Paper

COULOMETRIC-MERCUROMETRIC-POTENTIOMETRIC DETERMINATION OF ANIONS

by

DARINKA J. STOJKOVIĆ

On the basis of detailed studies of the polarization curves of solution anodes of silver, lead, mercury and copper, using a separate cathode and anode space, by means of coulometric quantitative electrolytic dissolution at constant current, coulometric argentometry(1—5), plumbometry(2,6,7), mercurometry(2,8,9) and cuprimetry(10) have been developed as specific methods, based on the general principle of coulometric metallometry, and have applied with success in micro and semi-micro determinations.

The coulometric-metallometric methods have considerable advantages over the classical volumetric methods, as there is no need for the preparation, adjustment and conservation of solutions of the corresponding metal salts, the metal ions generated during anodic electrolytic dissolution being sent whenever necessary into the solution for the quantitative sedimentation of hardly soluble metal salts, and it is also possible to determine the end-point by different chemical and, in particular, physico-chemical methods.

Tutundžić and Stojković(8,9) have described the possibilities and conditions for coulometric-mercurometric-amperometric determination of halogenide, molybdate, oxalate and iodide ions.

In view of the fact that mercurous ion has proved to be an interesting reagent, as it gives a number of hardly soluble compounds with a much lower product of solubility than the corresponding silver or other heavy metal compounds which give hardly soluble compounds, it is possible to determine anions by means of mercurous ion with greater accuracy, and even submicro quantities can be determined.

The aim of this study was to apply potentiometric end-point determination with single indicator electrode at $I = 0$ for the coulometric-mercurometric determination of micro and submicro quantities of a number of anions, under the same operating conditions as before and in an indifferent electrolyte of 0.2 M KNO_3 at $pH = 2—3$.

The end-point was determined not only by the drop on the $a = f(t)$ curve but also from the curve of the first derivative $\Delta a/\Delta t = f(t)$, where *a* represents the segment on the bridge proportional to EMF, and *t* the time in seconds. Recording the first derivative is particularly useful in the determination of micro and submicro quantities.

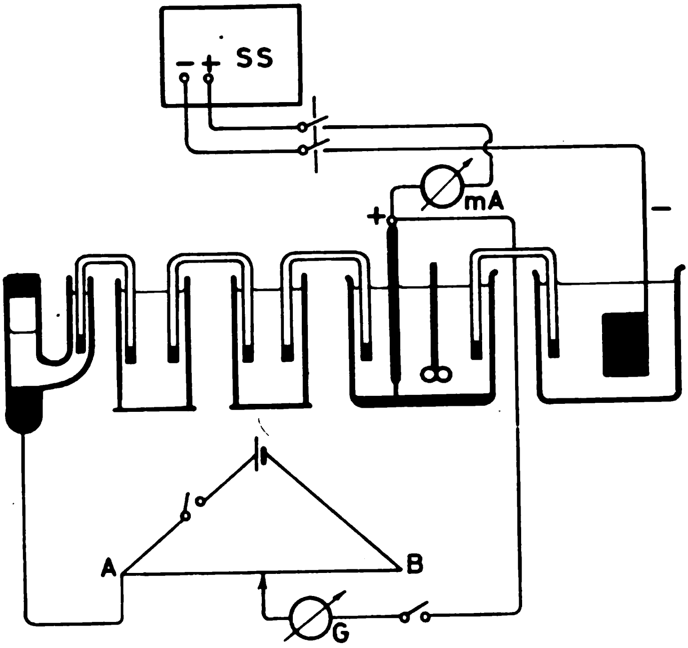

Fig. 1.

Sheme of the apparatus for the coulometric-mercurometric-potentiometric determination of anions.

The apparatus for the coulometric-mercurometric-potentiometric determinations, shown in Fig. 1, consists of the coulometric circuit, i.e. the electrolytic circuit, and the potentiometric indicator circuit. The coulometric circuit has already been described(9). The potentiometric indicator circuit represents the usual scheme for the measurement of EMF by compensation, in which the cell is composed of the anodic part of the coulometric circuit with a mercury electrode and a saturated calomel electrode. Instead of this improvised potentiometric circuit one could well use pH-meter which would record the changes of EMF with time.

In the determination of the chloride, bromide and oxalate ions the generator electrode, the anode of the coulometric circuit, in the shape of a vessel bottom, was used as the indicator electrode in the potentiometric circuit. This is possible because during the registration of the data given by the potentiometric circuit at predetermined time intervals the coulometric circuit is switched off. In the determination of iodide ion, as electrode we used an indicator electrode in the shape of the letter J which contained only a drop of mercury.

The chemicals were “Merck”, p.a.

All the determinations were done in a solution of 0.2 KNO_3 as the indifferent electrolyte, both in the anolyte and the catholyte, the only difference being that the anolyte was maintained at a pH between 2 and 3 in order to avoid the formation of base salts and ensure the existence of mercurous ions, while the catholyte was maintained at a pH between 2 and 4 in order to supress the influence of OH^+ ions which in the electric field could move towards the anode.

Determination of chloride ion

The results of the determination of the chloride ion are shown in Table I.

TABLE I

Approximate concentration KCl	Taken Cl^-	Found Cl^-	Error		Current	Theoretical time
mol/l	mg	mg	mg	%	mA	sec.
$2.9 \cdot 10^{-3}$	5.32	5.34	0.020	0.38	50	289.5
		5.35	0.030	0.55		
		5.29	−0.030	−0.55		
		5.30	−0.020	−0.38		
$1.25 \cdot 10^{-3}$	3.55	3.560	0.010	0.28	30	321.6
		3.560	0.010	0.28		
		3.530	−0.020	−0.56		
		3.580	0.030	0.84	10	965
		3.530	−0.020	−0.56		
$1.35 \cdot 10^{-3}$	2.66	2.640	−0.020	−0.74	50	144.7
		2.650	−0.010	−0.38		
		2.650	−0.010	−0.38		
		2.650	−0.010	−0.38	30	241.3
		2.650	−0.010	−0.38		
		2.660	0.000	0.00		
		2.680	0.020	0.75	10	723.3
		2.640	−0.020	0.75		
$6.25 \cdot 10^{-4}$	1.775	1.776	0.011	0.62	10	482.5
		1.784	0.009	0.50		
		1.773	−0.002	−0.11		
$3.12 \cdot 10^{-4}$	0.887	0.890	0.003	0.34	10	241.3
		0.880	−0.007	−0.79	10	
		0.891	0.004	0.45		
$4.01 \cdot 10^{-4}$	0.709	0.711	0.002	0.28	20	96.5
		0.713	0.004	0.56		
		0.707	−0.002	−0.28		
		0.704	−0.005	−0.70		
$1.25 \cdot 10^{-4}$	0.355	0.358	0.003	0.84	5	193
		0.353	−0.002	−0.56		
		0.358	0.003	0.84		
		0.359	0.004	1.13	2	482.5
		0.358	0.003	0.84		
		0.360	0.005	1.41		
$0.9 \cdot 10^{-4}$	0.177	0.176	−0.001	−0.56	10	48.3
		0.179	0.002	1.13		
		0.174	−0.003	−1.69		
		0.179	0.002	0.55		
$0.62 \cdot 10^{-4}$		0.178	0.001	0.56	2	241.3
		0.175	−0.002	−1.13		
		0.180	0.003	1.68		
$2.5 \cdot 10^{-5}$	0.071	0.073	0.002	2.82	0.5	386
		0.072	0.001	1.41		
		0.074	0.003	4.23		

As may be seen from Table I, chloride ion was determined in quantities from 0.071 *mg* to 5.32 *mg*. In fact the range of KCl concentration within which Cl^- ion was determined was $2.9 . 10^{-3}$ to $2.5 . 10^{-5}$ *mol/l*. Quantities from 0.709 to 5.32 *mg* were determined with a mean relative error of 1%, quantities from 0.355 *mg* to 0.177 *mg* with a mean relative error of about 1%, quantities of 0.071 *mg* with a relative error of 2.8%, and 0.035 *mg* with a mean relative error of 5—6%.

Determination of the bromide ion

The results of the determinations of bromide ion are shown in Table II.

It may be seen from Table II that Br^- ion was determined in quantities from 0.339 to 7.99 *mg*. quantities between 1.99 *mg* and 7.99 *mg* were determined with a mean relative error of 1.1%, while the quantity of 0.339 *mg* was determined with a mean relative error of 0.9%. The concentration of KBr in which bromide ion was ranged from $2 . 10^{-3}$ to $1 . 10^{-4}$ *mol/l*.

TABLE II

Approimxate concentration KBr	Taken Br^-	Found Br^-	Error		Current	Theoretical time
mol/l	mg	mg	mg	%	mA	sec.
$2 \cdot 10^{-3}$	7.990	7.970	−0.200	−0.25	50	193.0
		8.010	0.020	0.25		
		7.990	0.000	0.00		
		8.000	0.010	0.12		
$1 \cdot 10^{-3}$	3.994	4.014	0.020	0.50	50	96.5
		3.994	0.000	0.00		
		3.974	−0.020	−0.50		
		4.002	0.008	0.20		
		3.974	−0.020	−0.50	30	160.8
		3.999	0.005	0.13		
		4.010	0.016	0.40		
		3.986	−0.008	−0.21		
		3.998	0.004	0.10	10	482.5
		3.973	−0.020	−0.50		
		4.270	0.033	0.83		
$5 \cdot 10^{-4}$	1.997	2.004	0.007	0.35	40	60.3
		1.987	−0.010	−0.50		
		2.020	0.023	1.15		
		2.009	0.012	0.60		
		2.007	0.010	0.50		
$1 \cdot 10^{-4}$	0.399	0.402	0.003	0.78	10	48.2
		0.403	0.004	1.00		
		0.396	−0.003	−0.78		
		0.404	0.005	1.25		

Determination of iodide ion

The results of the determination of the iodide ion are shown in Table III. Iodide ion was determined in concentrations of KI solution from $1 . 10^{-3}$ to $5 . 10^{-5}$ *mol/l*. The quantities determined ranged from 0.317 to 6.35 *mg*. The quantity of 0.317 *mg* was determined with a relative error 1.3%, and 1.369 *mg* with an error of 1.25%. Iodides were determined with currents in the coulometric circuit of 10, 20, 40 and 50 *mA*.

Figures 2, 3 and 4 show sample curves of the determinations of halogenides, and Fig. 5 the determination of oxalate ion. It may be seen that the maximum was most prominent with iodide, which is in complete agreement with the solubility products which are: for $Hg_2Cl_2 = 2 . 10^{-18}$, for $Hg_2Br_2 = 4.6 . 10^{-23}$, and for $Hg_2I_2 = 3.7 . 0^{-29}$ (25°).

TABLE III

Approximate concentration KI	Taken I^-	Eound I^-	Error		Current	Theoretical time
mol/l	mg	mg	mg	%	mA	sec.
$1 \cdot 10^{-3}$	6.350	6.380	0.030	0.47	50	96.5
		6.410	0.060	0.94		
		6.360	0.010	0.16		
		6.350	0.000	0.00		
$5 \cdot 10^{-4}$	3.170	3.180	0.010	0.31	40	60.3
		3.160	0.010	0.31		
		3.200	0.030	0.95		
		3.210	0.040	1.26		
$2 \cdot 10^{-4}$	1.269	1.280	0.011	0.78	20	48.25
		1.290	0.021	1.65		
		1.300	0.031	2.45		
		1.270	0.001	0 10		
$5 \cdot 10^{-5}$	0.317	0.322	0.005	1.60	10	24.1
		0.319	0.002	0.63		
		0.322	0.005	1.60		

The coulometric-metalometric determination of the halogenides in perchloric acid has been studied by deFord and Horn⁽¹¹⁾, while Przybylowicz and Rogers⁽¹²⁾ used a mixture of sodium perchlorate and perchloric acid as the indifferent electrolyte. By using potassium nitrate we avoided any undesired oxidation at the anode. By using pure mercury with a large surface area as the anode we avoided the preparation of amalgam electrodes⁽¹²⁾ which requires skill and experiance, and the possibility of oxidation of a basic metal, e.g. silver, whose potential is close to that of mercury.

By recording the $\Delta a/\Delta t = f(t)$ curve we succeeded in determining micro and submicro quantities with considerable accuracy, in view of the fact that the diagrams $a = f(t)$ are too broad.

By rapid mixing of the anolyte, either with a magnetic stirrer or with an electric propeller mixer, we have achieved a rapid reaction and equilibrium between the ions generated and the corresponding anions. Since only small quantities of anions were determined, thick layers of poorly soluble salts were not formed. The big surface area of mercury in the form of the vessel bottom permitted the use of heavier currents.

In the determination of iodide ion a slower establishment of the potential was observed, which we ascribe to the smaller product of solubility and to the formation of the complex $(HgI)_4^{2-}$, which was also reason why the relative error was somewhat greater than with bromide and chloride. As regards the errors, we think that they would be much smaller with all the halogenides if alcohol were introduced into the indifferent electrolyte in order to decrease the solubility of the compounds produced.

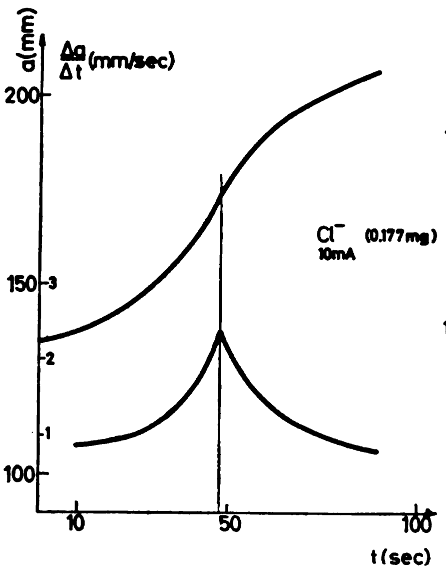

Fig. 2

Mercurometric-potentiometric curve of the titration of chloride ion

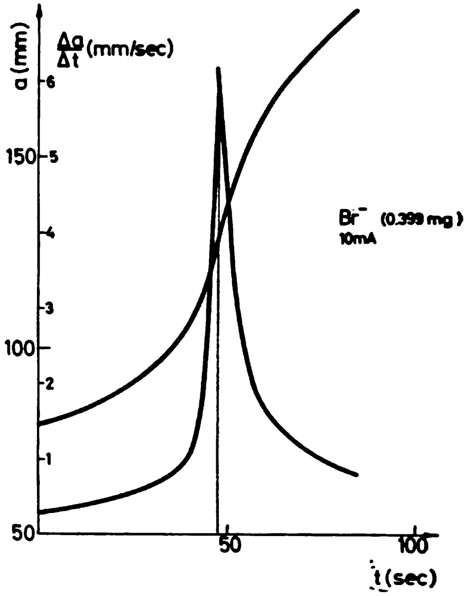

Fig. 3

Mercurometric-potentiometric curve of the titration of bromide ion

Determination of oxalate ion

The experimental conditions under which oxalate ion was determined were similar to those for chloride and bromide ion, only a mercury generator electrode was used as the indicator electrode. The results are shown in Table IV.

TABLE IV.

Approximate concentration $H_2C_2O_4 \cdot HO_2$	Taken $C_2O_4^{2-}$	Found $C_2O_4^{2-}$	Error		Current	Theoretical time
mol/l	mg	mg	mg	%	mA	sec.
$1.5 \cdot 10^{-3}$	6.60	6.590	−0.010	−0.15	50	289.5
		6.640	0.040	0.60		
		6.650	0.050	0.76		
		6.600	0.000	0.00		
$7.5 \cdot 10^{-4}$	3.30	3.300	0.000	0.00	50	144.7
		3.270	−0.030	0.91		
		3.330	0.030	0.91		
		3.320	0.020	0.60		
$2.5 \cdot 10^{-4}$	1.100	1.104	0.004	0.36	40	60.3
		1.090	−0.010	−0.90		
		1.109	0.009	0.82		
		1.113	0.013	1.18		
$7.5 \cdot 10^{-4}$	3.300	3.284	0.016	−0.50	30	241.3
		3.311	0.011	0.33		
		3.297	−0.003	−0.10		
		3.325	0.025	0.75		
		3.284	−0.016	−0.52	10	723.7
		3.311	0.011	0.33		
		3.320	0.002	0.6		
$1 \cdot 10^{-4}$	0.440	0.447	0.007	1.60	20	48.3
		0.444	0.004	0.91		
		0.438	−0.002	−0.45		
$1.66 \cdot 10^{-4}$	0.780	0.781	0.001	0.13	4	482.2
		0.783	0.003	0.39		
		0.770	−0.010	−1.30		
$0.83 \cdot 10^{-4}$	0.390	0.392	0.002	0.51	2	482.2
		0.397	0.007	1.80		
		0.389	−0.001	−0.25		
$0.41 \cdot 10^{-4}$	0.195	0.196	0.001	0.51	2	241.3
		0.197	0.002	1.20		
		0.192	−0.003	−1.53		

It may be seen from Table IV that the quantities of oxalate ion determined ranged from 6.60 *mg* to 0.195 *mg*. The quantity of 0.44 *mg* was determined with a relative error of 1%, while the quantities from 0.44 to 0.195 *mg* were determined with a relative error of about 1% or slightly greater.

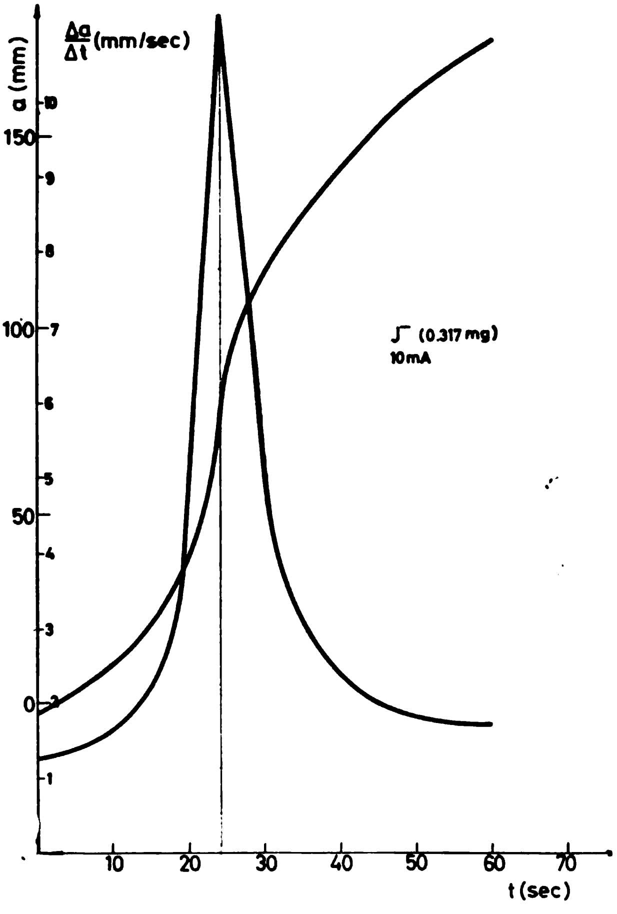

Fig. 4

Mercurometric-potentiometric curve of the titration of iodide ion

The results show that the coulometric-mercurometry with electrolytically generated mercuro-ions at constant current and with potentiometric end-point determination is suitable method for micro and submicro determinations of anions, It obviates the preparation of solutions of mercurous salts and the determination and checking of the changing titer, and at the same time makes it possible to express results, in this field of analytical determinations too, in coulombs, or electrons, and not in terms of various compounds which are often inadequately defined.

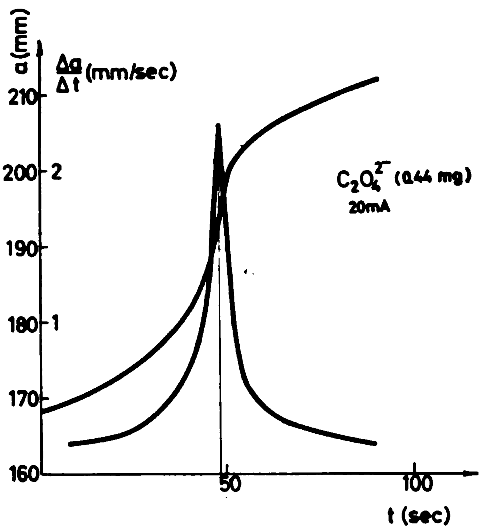

Fig. 5
Mercurometric-potentiometric curve of the titration of oxalate ion

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Original Scientific Paper

THE CONTENT OF RADIOACTIVE HYDROGEN AND OXYGEN IN SOME NATURAL LOCALITIES IN YUGOSLAVIA*

by

ZORKA B. VUKMIROVIĆ and MIRJANA D. MATIĆ

1. INTRODUCTION

The content of radioactive hydrogen and oxygen in natural waters depends on their origin. Of the surface waters the most constant content is found in oceanic waters(1): 0.0154 ± 0.0002 at% D and 0.1991 ± 0.0003 at% $^{18}0$, and of running waters in the rivers of the moderate climatic regions(1): 0.0149 ± 0.0002 at% D and 0.1970 ± 0.0003 at% $^{18}0$. Because of easier accessibility river waters are usually used as standars for comparative densimetric analysis.

In warmer climates the evaporation is increased, and in lakes there is no regeneration from running water, so that the concentration of the heavier isotopes may be increased. However, as these changes do not depend only on evaporation, this enrichment varies from case to case.

In Yugoslavia these differences have been determined for Lake Ohrid(2), the Adriatic Sea and Niška Banja(3). These changes were expressed as the differences between total density of the sample and of a standard. Considering that besides deuterium the content of heavy isotopes of oxygen is also changed, these data only give the enrichment with heavy isotopes in general. In the first case(2) inadequate accuracy of the analysis limited this possibility too.

The aim of the present study was to investigate the differences in isotope content of different rivers and natural waters in which there was reason to expect an increased content of the heavy isotopes of hydrogen. The study was widened to include the determination of deuterium in three samples of oil.

2. EXPERIMENTAL

Isotopic analysis was done by high-accuracy densimetry using the automated "falling drop" method(4,5). The tap-water in the town of Cluj was used as the standard. The precision of density difference determination was ±0.2 γd (γd = 10^{-6} *g/ml*).

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* This study was done in the Institute of Atomic Physics in Cluj, Rumania.

The content of deuterium was calculated from the difference in density between the sample and the standard in which the content of oxygen isotopes had been normalized by an exchange reaction with sulphur dioxide(6). The water was prepared for densimetric analysis by the following procedure(7): from an alkaline solution of potassium permanganate the water was recirculated over red-hot cupric oxide until the conductivity became less than $10^{-6}\Omega^{-1}cm^{-1}$, after which it was equilibrated with sulphurdioxide, again recirculated, and finally purified by double destillation in a stream of nitrogen. The terminal conductivity was of the order of $10^{-7}\,\Omega^{-1}\,cm^{-1}$.

The water formed by burning the samples of oil in a current of oxygen(8) was prepared for the densimetric analysis of deuterium in the same way.

A density difference of 1 γd corresponds to a change in the atomic fraction of deuterium, n of 0.000927 at% D. By means of this coefficient it is possible to express the relative change for deuterium α_D as:

$$\alpha_D = \frac{n_0 + 9.27 \cdot 10^{-4}\,\Delta d_D}{n_0} = 1 + C_D\,\Delta d_D$$

where n_0 is the atomic percent of deuterium in the standard, and Δd_D the difference in density between the normalized samples and the standard expressed in γd units.

This mode of presentation has been used in order to eliminate error in the knowledge of the absolute concentration of deuterium in the standard. The tap-water in Cluj comes from the river, and the corresponding value for deuterium was taken. In this case the constant C_D is $6.2\,.\,10^{-2}\,(\gamma d)$. The results for deuterium in Tables I and II are calculated with this value.

In order to determine the heavy isotopes of oxygen the density difference between non-normalized samples and the standard, $\Delta\,d_{tot}$, was measured. The relative change for oxygen, α_0, was by analogy with deuterium expressed as

$$\alpha_0 = \frac{m_0 + 9.9 \times 10^{-4}\,(\Delta\,d_{tot} - \Delta\,d_D)}{m_0} = 1 + C_0(\Delta\,d_{tot} - \Delta\,d_D)$$

where m_0 is the content of $^{18}0$ in the standard expressed as an atomic percent. The value of the constant C_0 is $5.0\,.\,10^{-3}.\,(\gamma d)^{-1}$. The results in Table I are presented in this way.

All the samples of water were taken during the period April—May 1967. Their global purity can be seen from the data on solid residue and conductivity (Table I).

3. DISCUSSION

The results obtained for the natural waters have mostly confirmed our hypotheses. The river waters showed almost no difference from the standard. The content of oxygen isotopes in them was determined as the differences for deuterium were within the limits of experimental error. This was important to determine as some research centers use these waters as standards.

Of the lake waters the greatest enrichment in heavy isotopes was found in Vransko jezero. This lake is a cryptodepression in the immediate neigh-

TABLE I

Differences in the Isotopic Composition of Naturel Waters

No.	Sample from	Locality of origin	Dry residue (g/l)	Burnt residue (g/l)	Conductivity ($\Omega^{-1}\,cm^{-1}$)	$\Delta\, d_D$ (γ d)	$\Delta\, d_{tot}$ (γ d)	(α — 1)	
								D	18_0
1.	River Danube	Aqueduct Vinča	—	—	—	+0.2	—	$+(0.01 \pm 0.01)$	—
2.	River Sava	Beograd	0.170	0.125	3.4×10^{-4}	+0.2	—	$+(0.01 \pm 0.01)$	—
3.	River Drina	Banja Koviljača	0.180	0.111	2.8×10^{-4}	+0.2	—	$+(0.01 \pm 0.01)$	—
4.	Lake Bled	The Island	0.190	0.105	3.4×10^{-4}	+0.4	+0.2	$+(0.02 \pm 0.01)$	$+(0.001 \pm 0.002)$
5.	Lake Palić	Subotica	1.45	1.16	2.2×10^{-3}	+0.8	+1.6	$+(0.05 \pm 0.01)$	$+(0.004 \pm 0.002)$
6.	Lake Skadar	Virpazar	0.180	0.104	3.2×10^{-4}	+0.8	+1.7	$+(0.05 \pm 0.01)$	$+(0.004 \pm 0.002)$
7.	Vransko jezero	Pakoštane	0.516	0.384	8.9×10^{-4}	+1.4	+2.5	$+(0.09 \pm 0.01)$	$+(0.005 \pm 0.005)$
8.	Seawater	Vis-Stončica 0 m	43.65	—	6.6×10^{-2}	+1.2	+2.8	$+(0.07 \pm 0.01)$	$+(0.008 \pm 0.008)$
9.	Seawater	Vis-Stončica 100 m	45.13	—	6.6×10^{-2}	+1.5	+3.1	$+(0.09 \pm 0.01)$	$+(0.008 \pm 0.002)$
10.	Seawater	Kaštelan Bay 0 m	40.35	—	6.1×10^{-2}	+1.2	—	$+(0.07 \pm 0.01)$	—
11.	Seawater	Kaštelan Bay 100 m	42.20	—	6.4×10^{-2}	+1.2	+2.8	$+(0.07 \pm 0.01)$	$+(0.008 \pm 0.002)$

borhood of the sea, being at the same time also closed. The similarity of the isotope content to that of the seawater is noticeable.

These findings could be of interest for the production of heavy water. With some approximations it is possible to demonstrate(9) that the work of separation per unit product is approximatively as many times smaller as is the relative enrichment (α_D) if the apparatus uses water rich in deuterium. From this aspect the data on Vransko jezero and seawater are the most interesting. However, the water from Vransko jezero is even more suitable for exploitation as the dry residue is much less than with seawater. In any case the final decision depends on the choice of the separation process.

TABLE II

Content of Deuterium in Oil

Sample No.	Sample	Nature	Δd_0	$(\alpha_D - 1)$
1.	Oil from Kikinda	Paraffin	—0.8	—(0.05±0.01)
2.	Oil from Elemir	Paraffin	—1.0	—(0.06±0.01)
3.	Oil from Velebit	Petroleum	—0.7	—(0.04±0.01)

From a comparison of the data for the samples of seawater* it may be noticed that the content of deuterium is greater at a depth of 100 *m*, while for oxygen isotopic effects with the change of depth are not evident. The difference for deuterium was also confirmed by direct measurement of the density difference between samples 8 and 9 (Table I) prepared for densimetry by the method of Shatenshtein and co-workers(1). These difference might be primarily ascribed to the influence of the gravitational field. The influence of gravity at this depth was calculated, but was found to be lower than the observed isotopic effect by an order of magnitude. The existing experimental data are inadequate for a discussion of the causes of this phenomenon.

In the context of this study we also investigated the content of deuterium in oil. Systematic studies in Rumania(10) have shown that oil and the accompanying gaseous hydrocarbons are depleted in deuterium, the gasses more so than the oil. In contrast to this, Grinberg and Petrikovskaia(11) found a significant enrichment both in methane accompanying oil, and the mine and marsh gas. It has also been observed(11) that oil from the Carpathians is markedly enriched in deuterium, even to 100%, in comparison with river water. Our data on oil from Yugoslavia** are in accordance with the results of Rumanian authors(8,10).

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* The samples of seawater were obtained from the Institute of Oceanography and Fisheries in Split.

** The oil samples were obtained from the Institute of Petrochemistry of the Beograd University School of Technology.

4. CONCLUSION

From the results it is possible to draw the following conclusions:

1. The lowest reaches of Yugoslavia's largest rivers have the same content of deuterium within the limits of measurement error.

2. Of the investigated lake waters the greatest enrichment with heavy isotopes was found in Vransko jezero. The water from this lake was similar to seawaters as regards the isotope content.

3. Seawater from a depth of 100 *m* had a higher content of deuterium, with an enrichment factor of 1.02 ± 0.01 in comparison with the surface.

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OXIDATION OF ARSENIC IN THE ELECTROLYTE FOR COPPER REFINING

by

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In electrolytic copper refining anodic and floating sludge are formed. In this an essential role is played by the so far inadequately studied conditions under which different constituents of the electrolyte precipitate, among which arsenic is quantitatively predominant. Arsenic in the anodic copper dissolves out under the influence of the direct current in the trivalent state, to be oxidized later into the pentavalent state and partly accumulated in the electrolyte in the form of arsenic acid(1). On the anode and in the electrolyte a precipitate is formed which contains arsenic bound to antimony, bismuth and tin, its formation being dependent, among other things, on the valency of the arsenic. Thus for example trivalent antimony or trivalent bismuth in the electrolyte only form a precipitate with pentavalent and not with trivalent arsenic(2,3).

There are divergent opinions in the literature concerning the way in which trivalent arsenic is oxidized into pentavalent in the electrolyte for copper refining. Livshits and Pazukhin(2) ascribe oxidation to the effect of atmospheric oxygen in the presence of cuprous ions as catalyst. Drozdov(4) has shown trivalent arsenic is also transformed into pentavalent by anodic oxidation at copper anodes. Graf and Lange(5) have found that oxidation can occur in both these ways.

If 0.56 V is accepted as the normal oxidation potential of trivalent arsenic in acid medium, than it is unlikely that under the conditions in electrolytic copper refining any significant anodic oxidation of trivalent arsenic could occur at the copper anodes, whose working potential lies within the range 0.3 to 0.4 V at the outside.

According to MacNewin(6) trivalent arsenic undergoes anodic oxidation with complete current efficiency in a solution 1 N sulphuric acid at platinum electrodes at a current density not exceeding 0.2 A/dm^2. Coursier(7) reports that in this oxidation there is also a high electrochemical as well as a diffusional overvoltage, i.e. that oxidation is only possible at a potential much more positive than the equilibrium potential.

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In our opinion the place in electrolytic copper refining plants where oxidation of trivalent into pentavalent arsenic could occur is the liberator tanks, where cuprous ion in excess of the permissible limits is eliminated from the electrolyte, for which reason the entire electrolyte circulates through these tanks. We have found no mention in the literature of these cells as the site where trivalent arsenic is oxidized into pentavalent, for which reason the aim of the present study was an investigation of this oxidation with particular reference to oxidation at lead anodes.

EXPERIMENTAL

The experimental were done with a specially prepared electrolyte made of pure chemicals in distilled water. The initial composition was as follows:

Copper (as $CuSO_4 \cdot 5H_2O$)	40 *g/l*
Arsenic (as As_2O_3)	5.0 *g/l*
Sulphuric acid	200 *g/l*

The electrolytic cell was a 250 *ml* beaker with the corresponding pair of electrodes. The cathodes were made of copper, and the anodes of copper, platinum or lead. In the experiments with platinum and lead anodes, the concentration of cuprous ions in the electrolyte decreased and the loss was compensated by the occasional addition of copper sulphate. Constant temperature was maintained by having the electrolytic cell in a thermostat. The experiments were done at 50 or 60°C, as these temperatures correspond to those used in practice. The duration of the experiment was in some cases 10 hours and in others up to 2 hours. The anodic current density ranged within the limits used in practice, from 100 to 300 A/m^2. The content of trivalent arsenic in the electrolyte was determined by bromatometric titration.

RESULTS AND DISCUSSION

The results are shown in Figs. 1, 2 and 3.

Curve 1 in Fig. 1 represents the oxidation rate of trivalent arsenic with aeration in the absence of metallic copper. Curve 2 in Fig. 1 represents the oxidation in the presence of air and metallic copper, which ensures the presence of cuprous ions in the electrolyte. It may be concluded from curve 1 that simple aeration of the electrolyte with the air did not produce any noticeable oxidation of the arsenic even when air was bubbled through for 10 hours. However, the presence of copper filings in the electrolyte, ensuring the equilibrium cuprous ion concentration, promoted the oxidation of arsenic by atmospheric oxygen, though the oxidation was not great. This is in accordance with the results of Livshits and Pazukhin(2).

Curve 3 in Fig. 1 shows the oxidation of trivalent arsenic during electrolysis with both cathode and anode made of copper. The electrolysis current was 0.025 A/cm^2. In this case the catalytic action of cuprous ions was supplemented by the oxidative power of the anode, for which reason it was logical to expect more oxidation, as the curve in fact shows, and as was also observed by Drozdov(4).

Bubbling pure oxygen through the electrolyte during electrolysis with all the other conditions the same produced the highest rate of oxidation, as shown by curve 4 in Fig. 1.

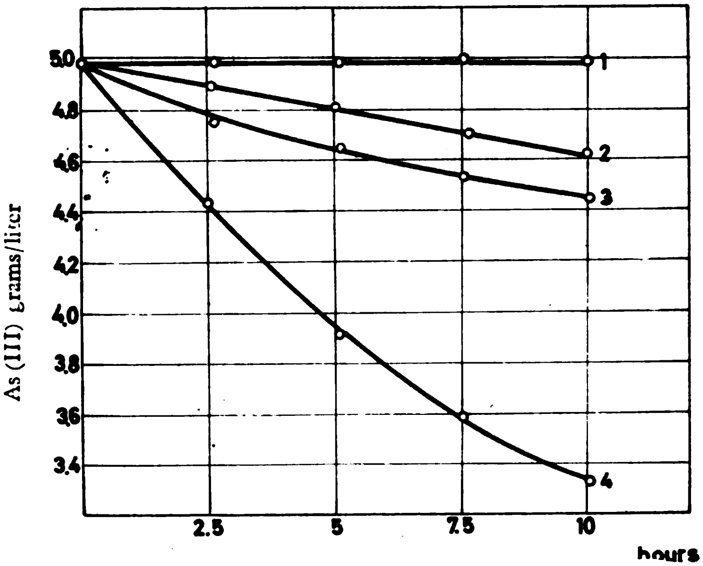

Fig. 1

Oxidation rate of arsenic (III) in a solution containing 200 *g/l* of H_2SO_4, 40 *g/l* of Cu and 5.0 *g/l* of As (III) at 60°C

1. Aeration
2. Aeration in the presence of metallic copper
3. Electrolysis at copper anodes
4. Electrolysis at copper anodes with bubbling through of oxygen

Figure 2 shows the rate of electrolytic oxidation of trivalent arsenic at a platinum anode, for current densities of 0.010 and 0.030 A/cm^2. Line 3 in Fig. 2 represents the rate of oxidation of trivalent arsenic which would have be obtained in the case of a quantitative reaction according to Faraday's law. It may be seen that at the beginning, when the concentration of trivalent arsenic was the greatest, the oxidation proceeded quantitatively, until its concentration had fallen to about half of the initial value; the oxidation still went on after that, and after two hours almost all the arsenic was oxidized.

Electrolysis at lead anodes was done at current densities from 0.0125 to 0.0300 A/cm^2. The results are shown by curves 1 to 5 in Fig. 3. Line 6 represents the theoretical value according to Faraday's law. It may be seen from Fig. 3 that the theoretical and experimental lines do not coincide even at the beginning of electrolysis, as was the case with the oxidation at platinum anode, Fig. 2. The oxidation was higher at lower current densities, as may be seen from curve 5 in Fig. 3. Depending on the current density the rate of oxidation ranged from 1 to 3 grams of arcsenic per liter of electrolyte per hour. This is 30 to 90 times greater than that with copper anodes. While with copper anodes the concentration of trivalent arsenic decreased from 5.0 to 4.7 *g/l* in 10 hours of electrolysis with lead anodes it decreased from 5.0 to 2.0 or even to 0.5 *g/l* in 2 hours.

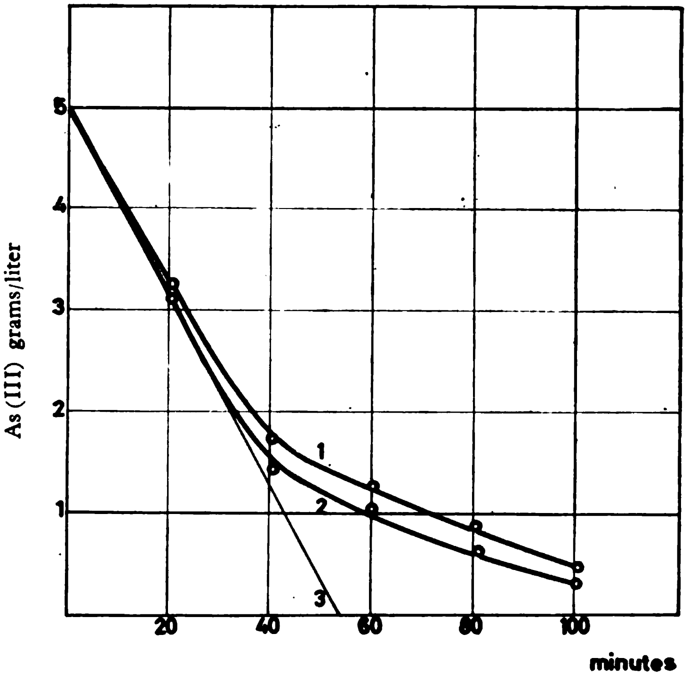

Fig. 2

Electrolytic oxidation of arsenic (III) at platinum anode in a solution containing 200 *g/l* of H_2SO_4, 40 *g/l* of Cu and 5.0 *g/l* As (III) at 50°C

1. Current density 0.03 A/cm^2
2. Current density 0.01 A/cm^2
3. Theoretical oxidation rate according to Faraday's law

CONCLUSION

Our earlier opinion that the oxidation of trivalent arsenic at lead anodes under the conditions in industrial copper refining cells can occur quite easily and that most of the trivalent arsenic gets oxidized in the liberator tanks has been confirmed. The rate of oxidation at copper anodes, in the presence of both air and cuprous ion, is very low in comparison with the oxidation at lead or platinum anodes.

It remains to clarify the mechanism of oxidation at lead anodes; a study of this problem is under way.

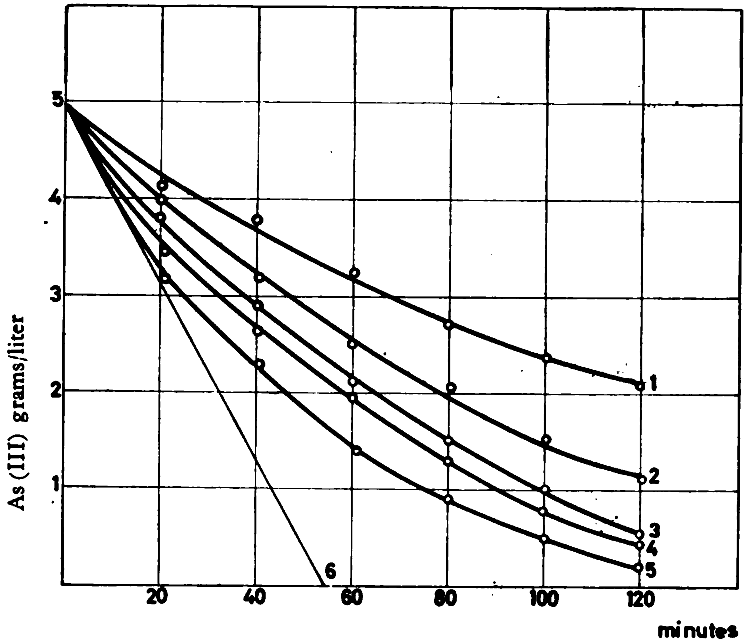

Fig. 3

Electrolytic oxidation of arsenic (III) at lead anode in a solution containing 200 *g/l* of H_2SO_4, 40 *g/l* of Cu and 5.0 *g/l* of As (III) at 50°C

1. Current density 0.0300 *A/cm²*
2. Current density 0.0250 *A/cm²*
3. Current density 0.0200 *A/cm²*
4. Current density 0.0150 *A/cm²*
5. Current density 0.0125 *A/cm²*
6. Theoretical oxidation rate according to Faraday's law

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THE EFFECT OF ARSENIC ON THE SOLUBILITY OF ANTIMONY, BISMUTH AND TIN IN ELECTROLYTIC REFINEMENT OF COPPER

by

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INTRODUCTION

In the electrolyte for copper refining impurities which pass into solution from the anode accumulate. Among these arsenic, antimony, bismuth and tin are of particular interest, as they can react among themselves to form undesirable sediments, known under the name of "floating sludge". In recent years the problem of "floating sludge" has been solved in several ways. Livshits and Pazukhin(1) have studied the influence of arsenic and antimony and their work has been continued by Drozdov(2). Hemming and Pawlek(3) have investigated the structure of sludges from copper refining by X-rays. More recently Graf and Lange(4) have studied the mechanism of formation of "floating sludge", determined the solubility of the sediment of arsenic and antimony and suggested that the probability of floating sludge appearing should be determined by means of a nomogram. At the same time S. Djordjević and co-workers undertook a study of the behavior of arsenic, antimony, bismuth and tin(5,6) in order to determine the conditions under which the insoluble compounds which constitute floating sludge form.

EXPERIMENTAL

Of all the constituents mentioned arsenic is present in the greatest quantity. Because of this in all the experiments, unless otherwise stated, an artificial electrolyte consisting of 200 *g/l* sulphuric acid, 157 *g/l* (40.0 *g/l* Cu^{2+}) crystalline copper sulphate and a known quantity of arsenic was prepared from pure chemicals. To this electrolyte antimony, bismuth and tin were added and the formation of sediment was studied. Some experiments were done in a solution of sulphuric acid without copper sulphate, if the presence of copper would constitute a problem in the analytical determinations and was not indispensable for drawing conclusions.

Arsenic was added in the form of As_2O_5 or As_2O_3. Trivalent antimony was introduced dissolved in concentrated sulphuric acid (1 : 1) Sb_2O_3, taking care that the quantity of sulphuric acid thereby added was such that the final acidity of the solution was always the same. Pentavalent antimony was added in the form of $K_2Sb_2O_7$. Bismuth-sulphate was prepared by dissolving metalic bismuth in hot concentrated sulphuric acid. The solution of bivalent tin was prepared by anodic dissolution of metallic tin in a water solution of sulphuric acid. A solution of tetravalent tin was prepared by dissolving metallic tin in hot concentrated sulphuric acid, with subsequent dilution to the desired concentration.

The supersaturated solutions of the desired initial composition were poured into Erlenmeyer flasks with ground glass stoppers. The flasks were left in an air thermostat immersed in water at the desired temperature. The experiments were done in the temperature range 50 to 60°C, wich corresponds to the conditions in practice. It was possible to maintain the temperature with an accuracy of ± 1°C. In the course of time the samples became turbid and insoluble compounds precipitated.

The experiments with solutions of known initial concentrations of different components were done in one of the following ways:

1. The time for turbidity to appear, i.e. to the beginning of sedimentation was recorded. Thereby it was possible, by changing the initial concentration, to determine approximately the limit of solubility of the different components and to test the stability of the supersaturated solutions.
2. The precipitation rate and the quantity of the given component which remained in solution after a certain time was determined.
3. The precipitates obtained under certain conditions after a long time were filtered, washed and dried, and the stoichiometric ratio of the components in them was determined.
4. With the thus defined sediments solutions of sulphuric acid of known concentrations were saturated for 2—3 days and the quantity of the component which passed into solution was determined, in order to determine the dependence of the solubility of the constituents of floating sludge on the temperature and concentration of sulphuric acid.

For certain initial combinations of the solutions not all of these experiments were done.

Analysis was done by volumetric and polarographic methods(7,8,9).

RESULTS AND DISCUSSION

a) *Experiments with antimony*

It was established that trivalent arsenic did not form any insoluble compounds with trivalent antimony, i.e. both elements can be kept in solution up to the limit of solubility of their trivalent oxides. Also, pentavalent arsenic does not form any insoluble compounds with pentavalent antimony, and they can be present together in the electrolyte.

The presence of pentavalent arsenic had a significant influence on the solubility of trivalent antimony in the electrolyte. Figure 1 shows (Sb (III) concentration in solution against log t for different concentrations of As (V) and H_2SO_4 in the electrolyte. At the beginning there was Sb (III) 0.86 g/l in solution. The initial concentrations of As (V) were 5.0 g/l and 10.0 g/l. The experiments were done at 53°C, at a sulphuric acid concentration of 200 or 150 g/l.

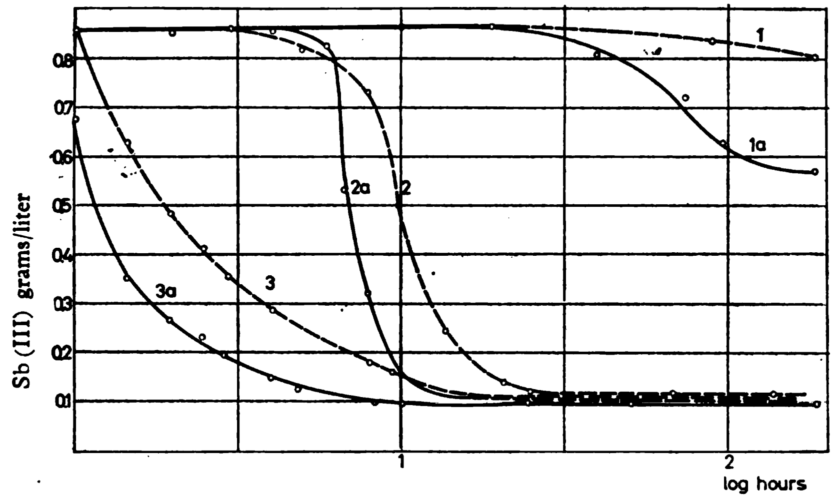


Fig. 1

Precipitation rate of Sb (III) in solutions containing 40.0 of *g/l* Cu^{2+} and various concentrations of As (V) and H_2SO_4 at 53°C

1. 200 *g/l* H_2SO_4
1a. 150 *g/l* H_2SO_4
2. 5·0 *g/l* As(V), 200 *g/l* H_2SO_4
2a. 5.0 *g/l* As(V), 150 *g/l* H_2SO_4
3. 10.0 *g/l* As(V), 200 *g/l* H_2SO_4
3a. 10.0 *g/l* As(V), 150 *g/l* H_2SO_4

Curve 1 in Fig. 1 represents the concentration of antimony in a solution which contained no arsenic, at a sulphuric acid concentration of 200 *g/l*, and curve la at a sulphuric acid concentration of 150 *g/l*. Curves 2 and 2a represent solutions with 5.0 *g/l* As (V), and the curves 3 and 3a solutions with 10.0 *g/l* As (V). It may be seen from the graph that Sb (III) precipitated very slowly from the supersaturated solutions, but that the precipitation was much faster if As (V) was also present: with increasing concentration of arsenic the precipitation rate of antimony increased. The sedimentation was more rapid in solutions which contained less sulphuric acid.

It was found that trivalent antimony and pentavalent arsenic behaved in the same way in solutions which did not contain copper sulphate. Copper sulphate did not influence the composition of the precipitate either.

There are statements in the literature that the ratio of antimony and arsenic in sludge from copper refining is not stoichiometric. However, it was found in the present study that in the experiments with artificial electrolytes, in which the only additions were pentavalent arsenic and trivalent antimony, the composition of the precipitate approximately corresponded to the formula $Sb_2O_3 \cdot As_2O_5$, as may be seen from Table 1. These ratios refer to a sulphuric acid concentration of 200 *g/l*, at a temperature of 60°C, with different initial concentrations of Sb (III) and As (V). Concentrations of sulphuric acid within the interval from 150 to 220 *g/l* gave precipitates

TABLE 1

Analysis of $Sb_2O_3.As_2O_5$ *precipitates formed in a solution of sulphuric acid, concentration 200 g/l, at 60°C, from different initial concentrations of* Sb (III) *and* As (V)

Sediment $Sb_2O_3 \cdot As_2O_5$ taken	Found			
	Sb(III)		As(V)	
mg	*mg*	%	*mg*	%
280.8	129.0	46.0	77.7	27.6
278.0	130.8	46.8	78.6	28.1
246.1	117.5	47.7	68.3	27.8

Note: The compound with the formula $Sb_2O_3 \cdot As_2O_5$ contains 46.7% Sb, and 28.7% As.

of the same stoichiometric composition were obtained. Determinations of solubility of the $Sb_2O_3 \cdot As_2O_5$ precipitate, whose composition corresponds to the formula of antimony arsenate $SbAsO_4$, are shown in Fig. 2. Curve 1 in Fig. 2 represents the solubility of antimony arsenate in a solution with a sulphuric acid concentration of 200 *g/l*, and curve 2 that in a sulphuric acid concentration of 150 *g/l*, within the temperature range from 25 to 65°C. It may be seen from the graph that the temperature coefficient of solubility is high, and that the solubility also depends on the concentration of sulphuric acid. From these results the conclusion may be drawn that if the temperature of the electrolyte drops one may expect precipitation of insoluble compounds of this type, i.e. the appearance of "floating sludge".

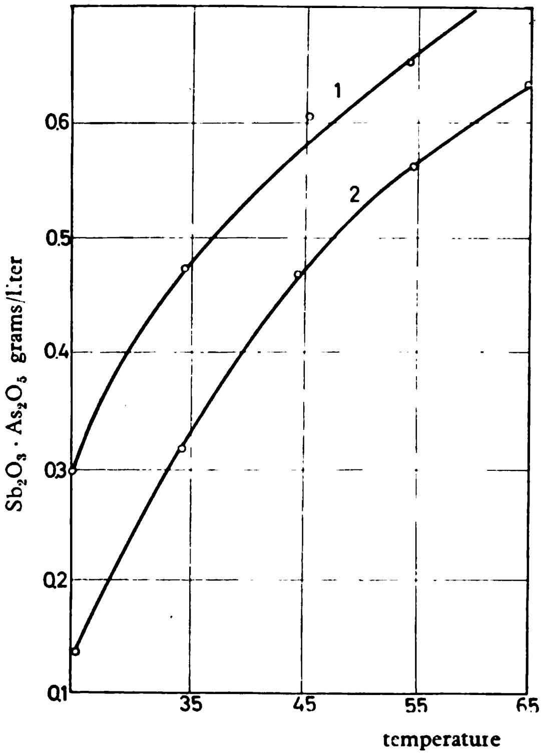


Fig. 2

Effect of temperature on the solubility of $Sb_2O_3 \cdot As_2O_5$ in aqueous sulfuric acid solutions

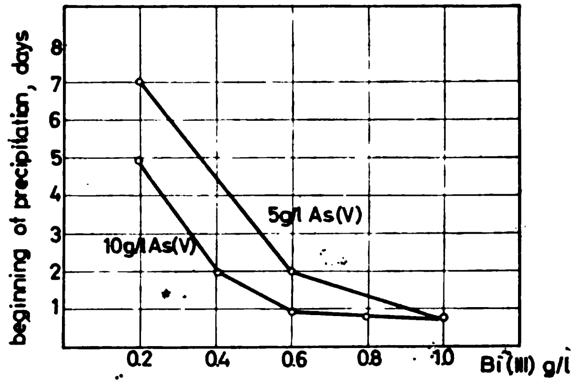
1. 200 *g/l* H_2SO_4
2. 150 *g/l* H_2SO_4

b) *Experiments with bismuth*

With pentavalent arsenic trivalent bismuth forms hardly soluble bismuth arsenate $BiAsO_4$. However, in the electrolyte for copper refining bismuth has a tendency to remain dissolved for a long time in a supersaturated solution.

Fig. 3

Beginning of the precipitation from supersaturated solutions containing 40.0 *g/l* of Cu^{2+}, 200 *g/l* of H_2SO_4 and various concentrations of As (V) and Bi (III) at 53°C



Figures 3 and 4 show the time at which turbidity occurred in supersaturated solutions. The experiments were done in a solution of copper sulphate and sulphuric acid, and those in Fig. 4 without copper sulphate. It may be seen from the graph that the presence of copper sulphate had no influence on the behavior of bismuth and arsenic in the electrolyte. It may be seen from Fig. 3 that both the content of arsenic and the content of bismuth had a great influence on the initiation of precipitation. While 1 or 2 *g* of bismuth per liter of electrolyte can be kept in solution in the absence of arsenic for a long time, any great quantity of arsenic accelerates its precipitation. Small quantities of arsenic (V) stabilize the bismuth solutions, and then the period of induction lasts several days.

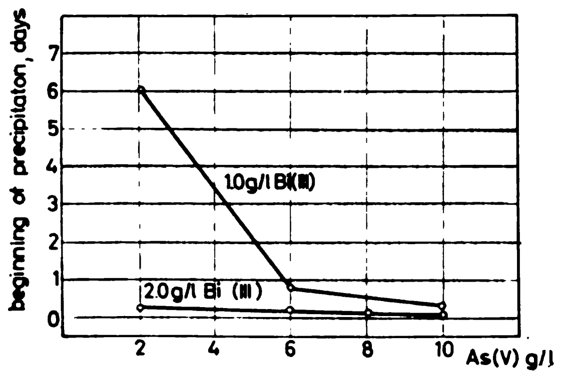


Fig. 4

Beginning of the precipitation from supersaturated solutions containing 200 *g/l* of H_2SO_4 and various amounts of As (V) and Bi (III) at 53°C

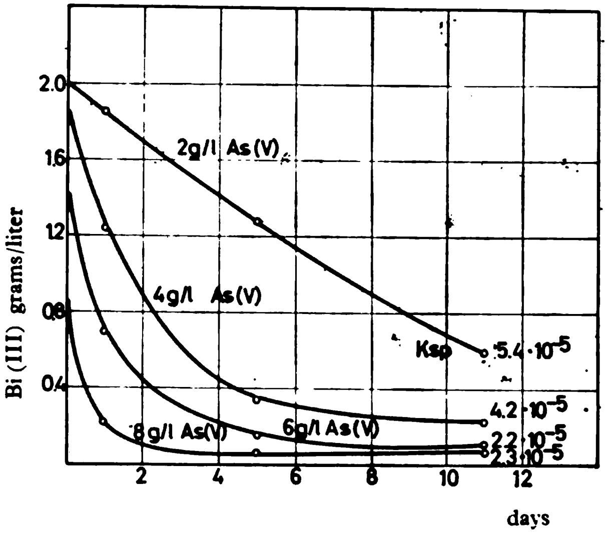


Fig. 5

Precipitation rate of Bi (III) in solutions containing 200 *g/l* of H_2SO_4 and various concentrations of As (V) at 53°C

Figures 5 and 6 show determinations of the precipitation rate of bismuth from a solution of sulphuric acid with different concentrations of As (V).

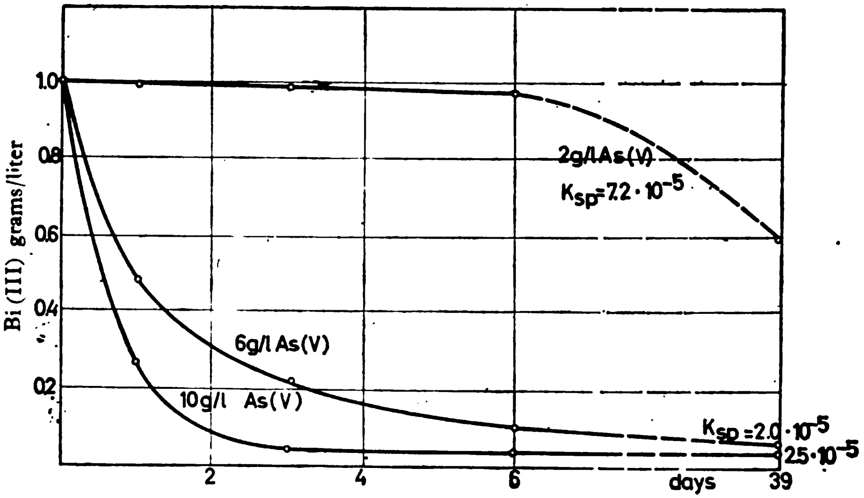


Fig. 6

Precipitation rate of Bi (III) in solutions containing 200 *g/l* of H_2SO_4 and various concentrations of As (V) at 53°C

The experiments shown in Fig. 5 lasted 11 days. Because of the marked supersaturation of the initial solutions with bismuth (2 *g* Bi/*l*) in all the cases there was immediate precipitation and no induction period was observed.

In the second series of experiments (Fig. 6) which lasted 39 days, bismuth precipitated much more slowly. The initial solutions contained 1.0 *g*/*l* of trivalent bismuth. At the lowest initial concentration of arsenic the induction period was very long, and it corresponded to that in a stable supersaturated solution.

From these experiments it may be concluded that in solutions which are sufficiently rich in pentavalent arsenic there is no danger of any great accumulation of bismuth in the electrolyte, but this possibility exists in solutions with less pentavalent arsenic.

The situation is different if arsenic is mainly in the trivalent state. In this case there could be a considerable accumulation of dissolved bismuth, as trivalent bismuth in solutions of sulphuric acid does not form insoluble compounds with trivalent arsenic. Therefore the accumulation of bismuth in the electrolyte for copper refining is not due to the fact that arsenic is mainly present in the form of arsenic acid.

It was found to be very difficult to determine the solubility of bismuth arsenate in a solution of sulphuric acid, as its dissolution resulted in supersaturated and a final equlibrium was hard to establish. For that reason the measurements were not quite reproducible, but they showed, as in the case of antimony arsenate dissolution (Fig. 2), that bismuth arsenate dissolves better at higher temperature and in more concentrated solutions of sulphuric acid. With a lowering of temperature the precipitation of bismuth arsenate in the form of the floating sludge is likely.

c) *Experiments with tin*

Metallic tin which is present as an impurity in the anodic copper passes into solution from the anode in the form of readily soluble stannous sulphate, and is immediately oxidized to tetravalent tin, because of the rather negative redox potential of Sn^{2+}, Sn^{4+}. It is known that tin precipitates from the electrolyte for copper refining in the form of a bulk precipitation together with arsenic(10).

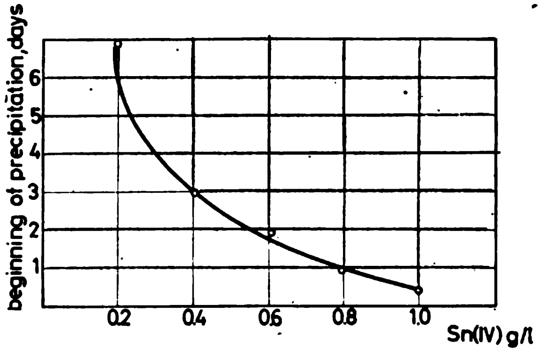


Fig. 7

Beginning of the precipitation from supersaturated solutions containing 200 *g*/*l* of H_2SO_4 and various amounts of Sn (IV) at 55°C.

The solutions of tetravalent tin in sulphuric acid were quite rapidly hydrolized, and a bulk precipitate of tin was obtained. The time to turbidity in such solutions, at different initial concentrations of tin, at a temperature of 55°C, is shown in Fig. 7. Under these conditions it was found that solutions which contained more than 0.4 *g* Sn (IV) per liter were hydrolized at this temperature within one day. However, in the presence of arsenic even much smaller quantities of tin could not stay in solution. Figure 8 shows the influence of pentavalent arsenic on the initiation of precipitation. Turbidity appeared only after a few hours even in solutions with only 0.1 *g* Sn (IV) per liter.

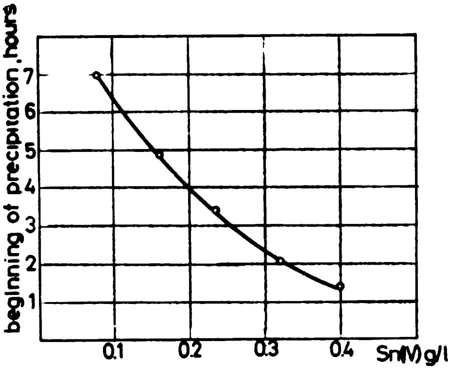


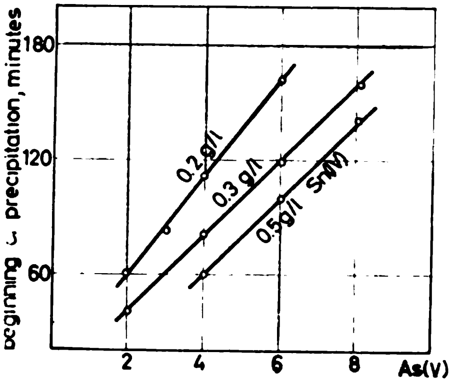
Fig. 8

Beginning of the precipitation from supersaturated solutions containing 200 *g/l* of H_2SO_4, 6 *g/l* of As (V) and various amounts of Sn (IV) at 55°C

The bulk precipitate from solutions containing arsenic and tin contained both these elements. An analysis of the solution and of the sediment showed that the tin binds about 10% more arsenic than would correspond to the formula of stannic arsenate. In this case this is due to the adsorption of arsenic acid.

Fig. 9

Beginning of the precipitation from supersaturated solutions containing 200 *g/l* of H_2SO_4 and various amounts of Sn (IV) and of As (V) at 55°C



Solutions from which after prolonged standing almost all the tin had precipitated together with the corresponding quantity of arsenic finally contained less than 0.01 *g/l* of tin, as determined by polarographic analysis. Trivalent arsenic also influences the precipitation of tetravalent tin, but it does not coprecipitate with tin to the same degree as pentavalent arsenic.

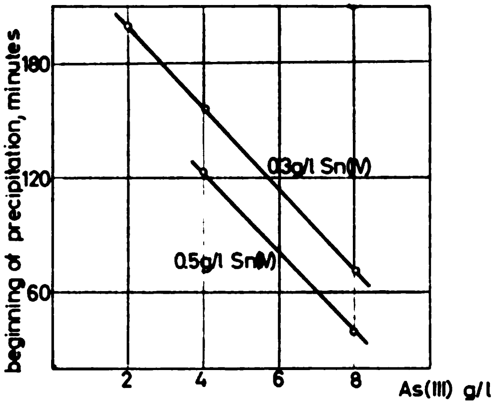


Fig. 10

Beginning of the precipitation from supersaturated solutions containing 200 *g/l* of H_2SO_4 and various amounts of Sn (IV) and of As (III) at 55°C

Figure 9 shows the time to the appearance of turbidity due to the precipitation of tetravalent tin for different concentrations of pentavalent and Fig. 10 trivalent arsenic. It may be seen that the curves in the first graph show a decrease, and in the second an increase. In other words, a surplus of pentavalent arsenic temporarily stabilized the dissolved tin and slowed down its precipitation. Because of this at lower concentrations of As (V) tin precipitated faster. Evidently these stabilizing and flocculation effects, which manifest the interaction of arsenic and tin, complicate the prediction of conditions under which the floating sludge will be formed.

CONCLUSION

The solubility of the ions of antimony, bismuth and tin in the electrolyte for copper refining depends to a large extent on the concentration and valency of the arsenic present. Pentavalent arsenic precipitates Sb (III), Bi (III) and Sn (III) in the form of poorly soluble arsenates. Precipitation of these compounds from supersaturated solutions proceeded very slowly and depended on the concentrations of sulphuric acid, arsenic and the corresponding ion. The solubility of the resulting compounds was increased with increased temperature. The experimental data obtained could be usefully applied in electrolytic copper refining.

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Original Scientific Paper

SEPARATION OF ALKALI METALS ON STARCH THIN LAYER

by

VELIMIR D. CANIĆ, SLOBODAN M. PETROVIĆ and SUZANA E. PETROVIĆ

Maize starch has been successfully applied in the separation of cations of analytical groups(1–3) I, II, III and IV. Good separation of groups I, II and IV was achieved by using an acetone-dilute HCl or acetone-diluted HNO_3 system solvent. Cations of group III could not be separated by means of these solvents, which necessitated the use of other solvents and of the two-dimensional technique(3). In the present study we attempted to separate the ions of alkali metals on starch as the adsorbent using the solvent acetone-HCl, observing the influence of changing the concentration of the acid and the ratio of aqueous to organic component in the solvent on the separation.

EXPERIMENTAL

For the preparation of the thin layer we used commercial maize starch ("Servo Mihalj", Zrenjanin) with the addition of gypsum. The purification of starch(4) and the preparation of thin layers(5) have already been described. On the thin layer 2 *μl* 1 M aqueous solutions of KCl, NaCl, NH_4Cl and LiCl was applied by means of a micropipette. Developing was done in a glass chamber containing 50 *ml* of solvent, without previous saturation of the chamber and at room temperature.

An acetone-dilute HCl mixture was used as the solvent for development. In studying the influence of acid concentration on the separation of the ions, the concentration of the acid in the aqueous component of the solvent was varied from 0.5—5 M, while the proportion of aqueous component was maintained at 40% (v/v). To the study the influence of the ratio of aqueous to organic component in the solvent on the separation the proportion of aqueous component was varied from 20 to 80% (v/v), while the concentration of the acid in the aqueous component was kept at 2 M. After development the dry chromograms were warmed in a drying chamber for about 10 minutes at 105°C, the white spots of the cations appearing on the brown background. If before warming the chromatograms were left exposed to air at room temperature for several hours, or overnight, the sensitivity of development was increased. When violuric acid was used for the development no color reaction was obtained, probably because of the presence of a strong acid in the thin layer.

RESULTS AND DISCUSSION

By means of the acetone-dilute HCl solvent (from 0.5 M to 3 M) Li^+, NH_4^+, and Na^+ were separated. The ions Na^+ and K^+ have similar R_f values, and their detection was possible only on special chromatograms by using zinc uranyl acetate for Na^+ and sodium cobalt nitrate for K^+. An increase of the concentration of the acid in the aqueous componet of the solvent to 2.5 M (Fig. 1) decreased the R_f values of all the cations. A further

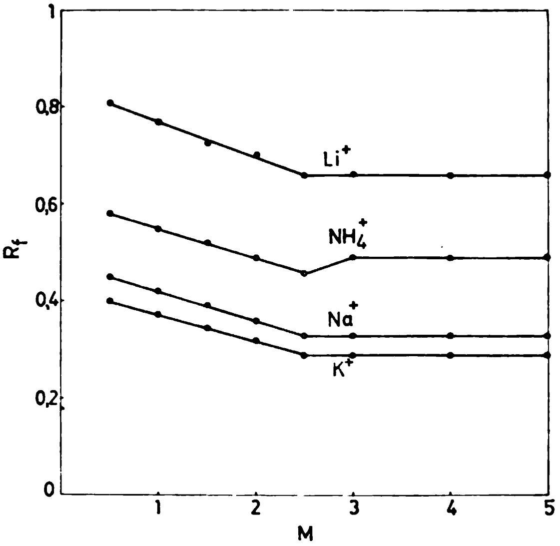

Fig. 1

Relationship between the R_f--values and molar concentration (M) of HCl in developing solvent

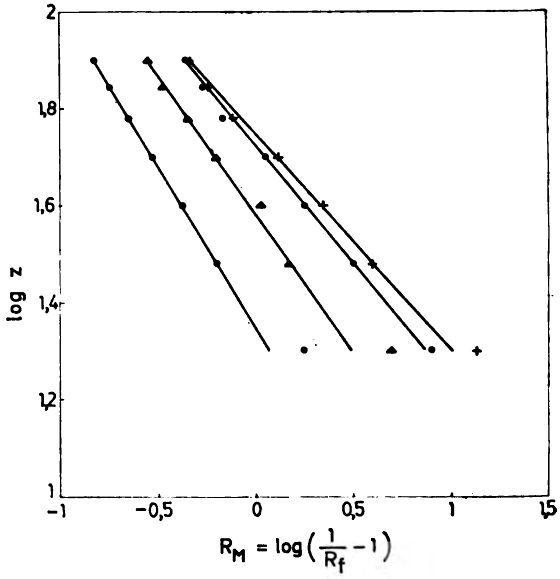

Fig. 2

Relationship between R_M-values and percentage of aqueous component (z) in developing solvent increase did not change the R_f values except for NH_4^+ ion, which increased from the concentration of 2.5 up to 3 M, after which it remained constant. Changing the concentration of the acid in the aqueous component had no effect on the separation of the ions under study. Concentrations above 3 M were not suitable, as hydrolysis of the starch occurred during development.

The change of the R_f values with the proportion of aqueous component in the solvent system is shown in terms of the R_M value (Fig. 2). There is a linear relationship between R_M and the logarithm of the proportion of aqueous component z:

$$R_M = \log z + \text{const.}$$

When the solvent contained only 20% of aqueous component low R_f values obtained for some cations, so that the R_M values calculated from them did not lie on the corresponding straight line. The best separation of ions was achieved when the proportion of aqueous component was 40%, that is when the acetone-dilute HCl ratio was 3 : 2.

Between the R_f values and atomic weights of Li and Na and the ionic weight of NH_4^+ ion there was a linear correlation within the range of concentration of the acid from 0.5 to 2.5 M.

The development procedure described here is not possible if a different carrier or adsorbant is used for the thin layer. The maize starch, used in the present study contained after purification 0.052% organic nitrogen, which came from uneluted proteins and free amino acids. During warming of the chromatogram there was obviously a reaction between the starch and the amino acids with the formation of melanoidin under the catalytic effect of HCl, so that the starch became darker except where there were cations. It is possible that the cation spots had a lower pH than the rest of the surface so that in these places the browning reaction would have occurred later. This is confirmed by the fact that after the chromatograms were left exposed to air for several hours, during which time some of the HCl evaporated from the thin layer, melanoidin was formed and the sensitivity of development was increased. After exposure of a chromatogram for 12 hours the sensitivity was 5×10^{-7} *g*-ion for Li^+, 10^{-6} for Na^+, 2×10^{-6} for NH_4^+ and 7×10^{-6} for K^+. Just after development the sensitivity was about hundred times smaller. The development sensitivity increased with decreasing electropositivity of the metal.

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Original Scientific Paper

INTERFEROMETRIC DETERMINATION OF WATER AND ACETIC ACID ANHYDRIDE IN ACETIC ACID

by

VILIM J. VAJGAND, TODOR J. TODOROVSKI and FERENC F. GAÀL

In an earlier study⁽¹⁾ we described the interferometric titration of bases in acetic acid. In that study the problem was raised of rapid and accurate determination of water or acetic acid anhydride in glacial acetic acid.

In practice the determination of water in glacial acetic acid is done by the method of K. Fisher⁽²⁾ or by thermometric titration⁽³⁾. Acetic acid anhydride is also usually determined in this solvent by the same methods, after the addition of excess water.

In the present paper we describe the determination of water and acetic acid anhdride in glacialy acetic acid by an interferometric method which permits the determination of very small changes of the refractive index. The determination is done with the aid of a calibration curve or by means of titration.

The principle of interferometric determinations using a calibration curve is derived from an analysis of curves of change of refractive index (Δn) against percentage of water or acetic acid anhydride in the acetic acid (Fig. 1). There is an almost linear relation up to 5% water, after which the curve begins to bend and the errors in the determination also become greater (curve I on the right).

The dependence of Δn on the content of acetic acid anhydride is represented by curve I on the left side of the same figure; it is linear up to 100% of anhydride, so that the concentration (percent) of acetic acid anhydride in acetic acid can be determined with high accuracy over a wide range.

The principle of the determination of water by interferometric titration is the reaction of water with acetic acid anhydride in the presence of perchloric acid catalyst. The acetic acid anhydride can also be determined on the same principle by means of a standard water solution. As the product of this reaction is acetic acid, which has the lowest refractive index in the titrated solution, a minimum is obtained at the equivalence point, as expected. With gradual addition of water or acetic acid anhydride to the acetic acid the refractive index increases linearly, so that a titration curve is obtained whose equvalence point lies at the intersection of two lines wich make an acute angle. This type of curve is very suitable for analysis as it allows high accuracy. The perchloric acid is not changed during titration, so that it causes only an increase of the refractive index without changing the shape of the titration curve (Fig. 1, curves II and III).

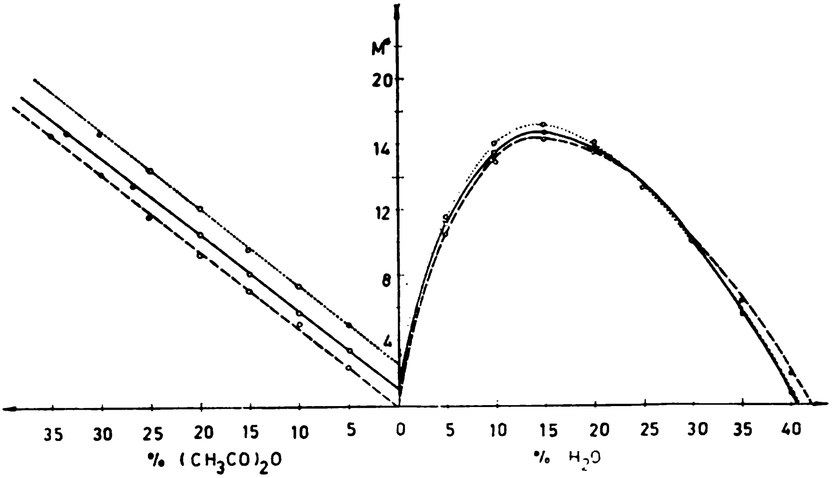

Fig. 1

Change of the refractive index Δn of acetic acid in the presence of water or acetic acid anhydride

------------- I — without perchloric acid.
— — — — — II — after addition of 1 *ml* 0.5 M $HClO_4$ per 25 *ml* of the solution.
.... III — After addition of 2 *ml* 0.5 M $HClO_4$ per 25 *ml* of the solution
* *M* represents corrected reading of the micrometer screw × 10^{-3}.

EXPERIMENTAL

Anhydrous acetic acid was prepared from commercial glacial acetic acid by a method constituting a combination of the method for obtaining pure acetic acid according to Greathouse(3) and the method of Novikov(4). The water or acetic acid anhydride in the initial acid were determined by means of thermometric titration. In the case when the glacial acetic acid contained water precisely the quantity of acetic acid anhydride necessary to bind the water was added. When the initial acid contained acetic acid anhydride, a calculated quantity of water was added. The acid thus prepared was worked up for 5 hours with a reflux condensor in the presence of 2 *ml/l* of conc. sulphuric acid catalyst, and then distilled at 118.1°C (1 atm). In both cases all the openings on the apparatus were protected from the ingress of atmospheric moisture with phosphorous pentoxide. The purity of the distillate was checked by qualitative and qunatitative analysis for water and acetic acid anhydride by the thermometric method according to Greathouse(3). Standard water solutions (0.3—2 M) were prepared by accurate weighig out of water and dissolution in the specially purified acetic acid (with a water content less than 0.03%). Standard solutions of acetic acid anhydride (2—6 M) in acetic acid were prepared from the acetic acid anhydride of C. Erb (min. 97%) and acetic acid which contained a small excess of acetic acid anhydride; the normality of the solution was determined by thermometric titration with a water solution of known concentration. A solution of 0.5 M $HClO_4$ in acetic acid was prepared from concentrated perchloric acid, spec. gravity 1.70, according to Greathouse(3). Finally water or acetic acid anhydride was added to the resulting acid until the temperature did not increase on adding water or acetic acid anhydride, which was a sign that the solution did not contain either of these components. If the solution was not sufficiently cooled during the preparation, the acid turned yellow, which interfered with the interferometry.

All the measurements were done on Zeiss and an ITR-1 (USSR) interferometers. The length of the most frequently used cuvette was 20.05 *mm*. The original cover of the cuvette was replaced by a metal plate with an opening in the middle covered by soft rubber, cork and a PVC sheat and held tight by springs. The standard solution was added through a capillary which passed through the opening in the middle and through the cover. The upper part of the cuvette was covered on the inside with silicon grease in order to prevent the solution ascending. All the measurements were done at 22°C; constant temperature was maintained by means of the water-bath of the interferometer. Pure acetic acid or 3.98 M water solution of NaCl were used as the reference solution. The measurements were always done at equal time intervals from 1 to 3 minutes after the addition of the standard solution.

Thermometric titrations were done in a closed Dewar vessel with tight fits to prevent the absorption of moisture. Temperature was measured with a thermometer graduated to 1/10°C or with a thermistor conncected to an apparatus for automatic registration.

The determination of water by the method of K. Fisher (reagent produced by "Merck") was done by direct titration of the sample to which 1 *ml* of pyridine per 25 *ml* had been previously added.

During all measurements the access of atmospheric moisture was prevented by tubes filled with phosphorus pentoxide.

Interferometric determination of water and acetic acid anhydride by means of a calibration curve

Twenty samples of water in acetic acid in which the water content ranged from 1.0 to 40 *mg/ml* were used as the standards for plotting the calibration curve (Fig. 2). A number of commercial products and some prepared artificially were analyzed. The results are shown in Table 1. The deviation of the interferometric determinations from the results obtained by Fischer's method are small, particularly when small quantities of water were determined. Considering that the same calibration curve can be used for all the interferometric measurements (when using the same apparatus and the same cuvette), this method is very suitable for serial analysis as it is rapid, economical and accurate.

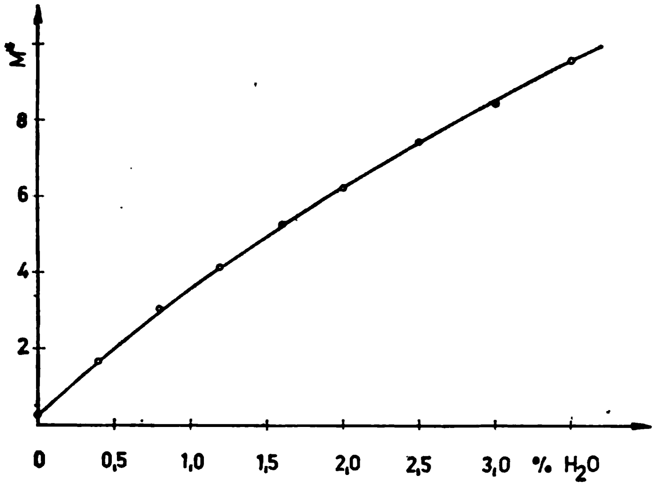

Fig. 2

Calibration curve for the determination of water in acetic acid (22°C, length of the cuvette 5.00 *mm*)

* *M* represents corrected reading of the micrometer screw × 10^{-2}

TABLE 1

Comparative results of the determination of water by the method of K. Fischer and the interferometric method using a calibration curve

No. of sample	Taken % H_2O	By Fischer's method % H_2O	Interferometric method % H_2O	Deviation in %	Remark
1	—	0.09	0.10	—	Glac. acet. acid C. Erb
2	—	0.12	0.12	—	Glac. acet. acid Osw. zakl. chem.
3	0.40	0.42	0.40	±0.00	
4	—	0.60	0.55	—	Glac. acet. acid C. Erb, used for some time
5	—	0.62	0.60		Osw. zakl. chem. Glac. acet. acid used for a some time
6	0.94	0.95	0.92	—0.02	
7	1.52	1.53	1.48	—0.04	
8	1.93	1.90	2.03	+0.10	
9	2.41	2.40	2.48	+0.07	
10	4.01	4.00	4.02	+0.01	

For the interferometric determination of acetic acid anhydride in glacial acetic acid a calibration curve was plotted with a series of 15 prepared samples. The content of acetic acid anhydride was determined by thermometric titration. As acetic acid anhydride absorbs moisture from the air much more than does pure acetic acid, care had to be taken that the system was well sealed. The following example illustrates the amount of moisture absorbed when the cuvette is opened to change the sample: In ten consecutive determinations on the same sample opened as if to change the sample the mean deviation of the measurements was ±0.12%; when the same analysis was done in the apparatus shown in Fig. 3, without opening the cuvette, the mean deviation was reduced to ±0.01%.

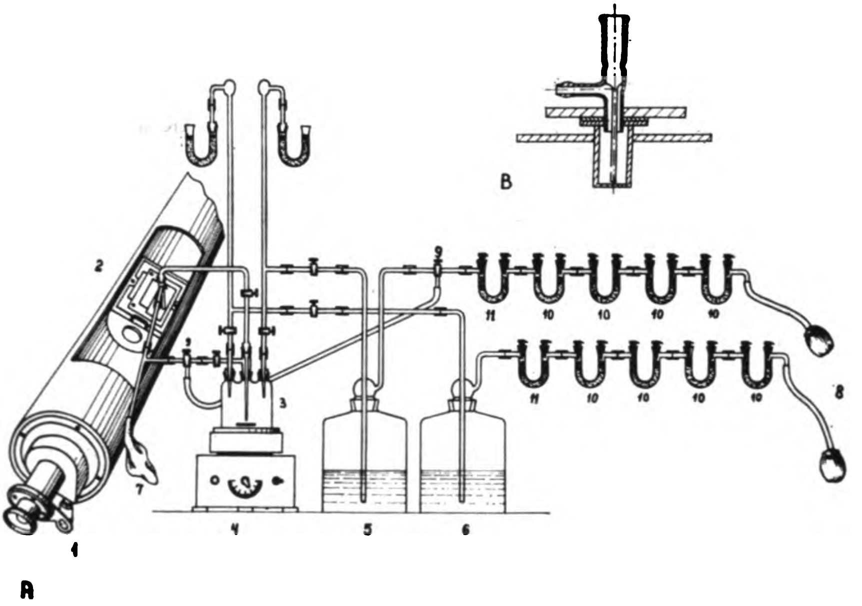

Fig. 3

A. Apparatus for interferometric titration in the absence of atmospheric moisture: 1. — interferometric; 2. — interferometer cuvette; 3. — titration vessel; 4. — magnetic ctirrer; 5. — the solution analysed; 6. — standard solution; 7. — rubber balloon; 8. rubber pumps 9. — three way cock; 10. — U-tube filled with phosphorus pentoxide; 11. — U-tube filled with glass-wool

B. Cross section of the cuvette.

The measurements were done in a cuvette 10.00 *mm* long. The quantity of acetic acid anhydride in the samples was 10 to 55 *mg/ml*. The results of interferometric and thermometric determinations are shown in Table 2.

By this method very good results were obtained in a very short time, and the reproducibility was excellent. This method was even better than the interferometric method for the determination of water. The correlation

TABLE 2

Comparative determinations of acetic acid anhydride by thermometric titration and by the interferometric method using a calibration curve

Sample no.	Termometric titration % anhydride	Interferometric method % anhydride	Difference in %
1	0.99	0.90	—0.09
2	2.00	1.95	—0.05
3	2.70	2.72	+0.02
4	3.24	3.22	—0.02
5	4.24	4.24	0.00
6	5.50	5.46	—0.04

coefficient calculated from the points used to plot the calibration curve is very high (0.9999). In our opinion the difference between these methods with samples which contained small concentrations of acetic acid anhydride came from the uncertainty about the end-point of the thermometric titration.

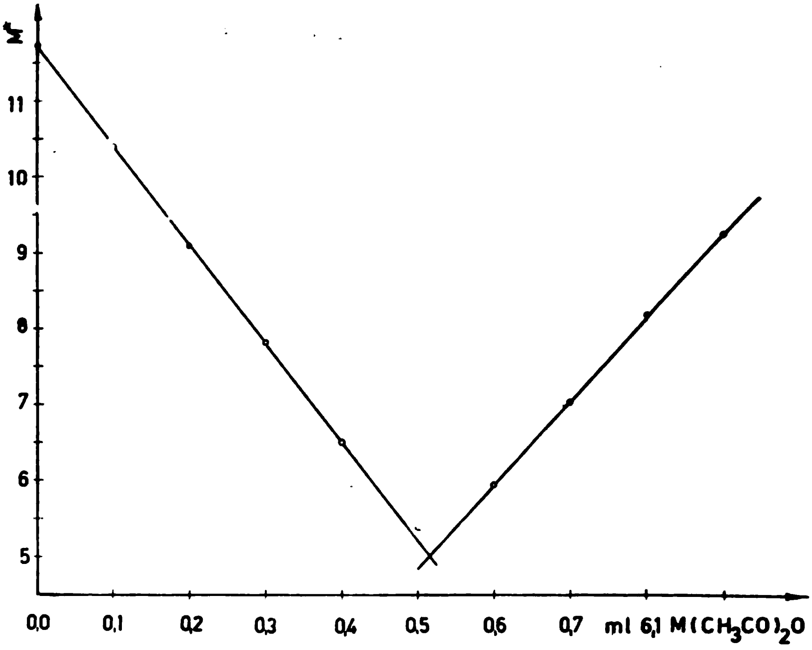

Fig. 4

The curve obtained by interferometric titration of a solution of water containing 0.56% water with 6.1 M solution of acetic acid anhydride in the presence of a drop of 0.05 M $HClO_4$ in acetic acid

* *M* represents corrected reading of the micrometer screw × 10^{-2}

TABLE 3

Results of the Determination of water by interferometric and thermometric titration and by Fischer's method

% H_2O analyzed	*Fischer's method* % H_2O	By the thermometric titration, % H_2O	Interferometric titration in the cuvette		
			No. of deter.	Found *mg* H_2O	Found % H_2O
0.200	0.205	0.211	6	1.98±0.02	0.198
0.380	0.362	0.404	6	3.77±0.01	0.377
0.700	0.709	0.707	6	7.01±0.13	0.701
0.850	0.856	0.868	6	8.46±0.03	0.846
1.100	1.110	1.111	6	10.92±0.15	1.092

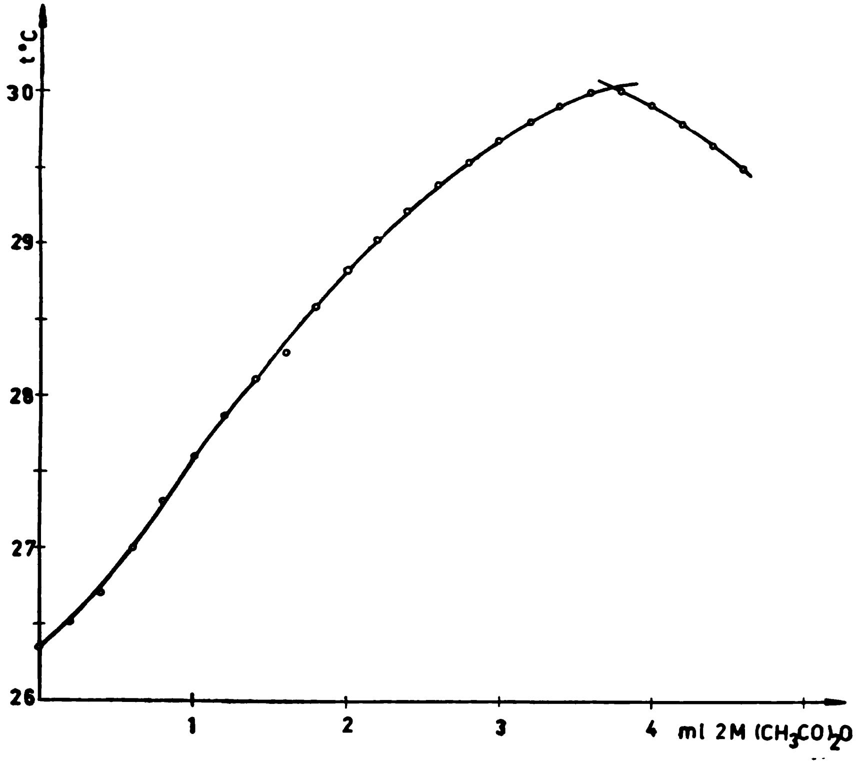

Fig. 5

Shape of the thermometric titration curve: 25 *ml* of 0.56% water solution titrated with 2 M solution of acetic acid anhydride

TABLE 4

Results of the interferometric titration of water in the closed apparatus

% H_2O in analysis	Weight of H_2O in the analysis (*mg*)	Found H_2O in *mg*	Found H_2O in %	Error in %
0.36	41.00	41.09 ± 0.24 (6)*	0.361	—0.001
0.50	68.00	68.18 ± 0.33 (6)	0.502	—0.002
1.00	100.00	99.66 ± 0.61 (6)	0.997	—0.003

* Number of determinations given in parenthesis.

Determination of water and acetic acid anhydride by interferometric titration

The interferometric titrations were done at first in a 20.05 *mm* long cuvette, in which the solutions were mechanically mixed. However, in order to achieve greater accuracy, we subsequently constructed the apparatus shown in Fig. 3. With this apparatus it was possible to weigh out the sample and to add the titrant without exposing them to atmospheric moisture. From the titration vessel, in which the sample was mixed with a magnetic mixer, aliquots were driven over into the cuvette of the interferometer by increasing the air pressure, while the cuvette was emptied by lowering a communicating vessel.

The concentration of the titrant substance was always 10—12 times greater than that of the component under study. In this way the effect of dilution was reduced, so that it was unnecessary to make corrections for the volume increase during titration.

TABLE 5

Results of the interferometric titration of acetic acid anhydride

Sample no.	% of the anhydride in analysis	Weight of anhydride in *mg*	Anhydride found in *mg*	Error in %
1	0.59	5.90	5.85 ± 0.05 (6)*	—0.85
2	0.98	9.80	9.64 ± 0.12 (6)	—1.63

* Number of determinations given in parenthesis

For titration in the cuvette 1—1.5 *ml* of the sample containing 2—11 *mg/ml* water or 6—10 *mg/ml* acetic acid anhydride in acetic acid, was weighed out and a drop of 0.05 M solution of $HClO_4$ in acetic acid was added in order to accelerate the reaction. When the titration was done in the apparatus shown in Fig. 3, the volume of the analysed solution was 10—20 *ml*, and 0.5 *ml* of 0.5 M solution of the catalyst was added. For the thermometric titrations the volume of the sample was 25 *ml*, while the quantity of the catalyst was the same as in interferometric titration. The shape of the titration curve is shown in Fig. 4, and the results of direct interferometric titration of water in the cuvette are shown in Table 3. The titrations gave better results when done in the apparatus, without opening the cuvette between runs, as then it was possible to determine even quite large quantities of water, as may be seen from Table 4, the access of air moisture being prevented. It is therefore possible to obtain quite satisfactory results by means of interferometric titration, but we nevertheless give preference to the calibration curve method, as it is more rapid and simpler.

The titration of acetic acid anhydride in acetic acid was done under the same conditions; the results of some determinations are shown in Table 5.

Finally, some disadvantages of the methods described should be mentioned. The determination of water and acetic acid anhydride after K. Fischer in acetic acid is rather time-consuming. In the thermometric titration, the end-point is determination from the end of the themperature increase during the titration is not quite defined, particularly when small quantities of water are being determined (Fig. 5). Finally, with interferometric titrations the solution in the cuvette must be well protected from atmospheric moisture, and the cuvette well thermostated.

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Original Scientific Paper

REDUCTION OF ARSENIC(III) AT DROPPING MERCURY ELECTRODE

by

MILENKO V. ŠUŠIĆ and MILJAN G. PJEŠČIĆ

The first polarographic observation of As (III) was made by Kačirkova(1) in 1 *M* hydrochloric acid. She obtained two waves with the half-wave potentials —0.3 and —0.6 *V* (SCE). According to her the first wave is the reduction of As (III) to metallic As and the second to arsine. Lingane(2) has also observed the behavior of As (III) in 1 *M* hydrochloric acid in the presence of gelatine, obtaining two waves with the initial potentials —0.4 and —0.9 *V* (SCE). The first wave was prominent and Lingane considered that it corresponded to the reduction of As (III) to metallic As, while the weak second wave was the reduction to arsine. Meites(3) has studied the behavior of As (III) in 1 *M* hydrochloric acid in the absence of peak supressors and obtained slightly different results from the previous authors as regards the quality and height of the waves, ascribing this to the reduction of As (III) via two three-electron reductions. Similar behavior has been found in 0.5 *M* H_2SO_4 and 1 *M* HNO_3(2). Later studies have shown that As (III) is reduced from weakly acid indifferent electrolytes at various pH, such as ascorbic(4) and tartaric acid(5). It has also been shown(6) that As (III) in the presence of chloride ion forms chloride complexes, because of which the half-wave potential changes with the concentration of chloride as well as with solution pH. However, these studies have not clarified the electrode reaction and have not explained the influence of pH and the complex-forming ions on the reaction steps and on the relative positions of the waves.

EXPERIMENTAL

Our studies have shown that from buffered weakly acid chloride solutions two waves of unequal height are obtained. The half-wave potentials of both waves depended on the pH of the medium, while the concentration of chloride ion influenced only the half-wave potential of the first wave, which shows that with chloride ion only one reducible form of arsenic is complexed, the form which is first reduced, that is As (III).

With a change in pH, either in the absence or presence of a constant concentration of chloride ion, the half-wave potentials of both waves changed (Figs 1 and 2.). Hence it is concluded that hydrogen ions take part in both electrode processes.

Tartaric, perchloric or ascorbic acid in the solution acts only as an indifferent electrolyte without affecting the half-wave potential, which means that they do not form complex compounds with As (III). It is suggested by the data in the literature and by our experimental findings that the reduction of As (III) in acid media is irreversible. The data in the cited literature concerning the number of electrons which correspond to the different phases of reduction conflict. In order to determine precisely the

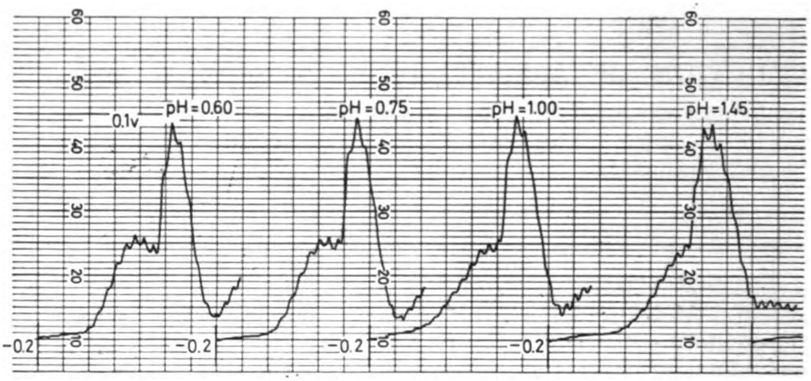

Fig. 1

Differential polarographic polarisation curves $6 \cdot 10^{-4}$ *M* As (III) in 0.91 *M* $HClO_4$ + + 0.05 *M* tartaric acid + 0.001% gelatin at different pH adjusted by means of ammonia

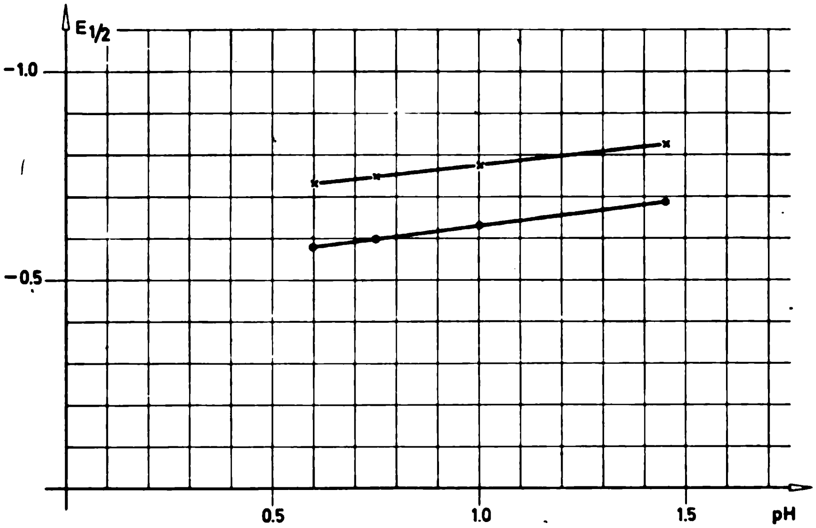

Fig. 2

Dependence of $E_{1/2}$ from Fig. 1 on pH; ● first wave, × second wave number of electrons which take part in the total reduction during which two waves are obtained, we performed microcoulometric[(7)] analysis of a solution of As (III) under conditions when the half-wave potentials of both waves were sufficiently close to appear almost as a single wave, viz. at pH > 2 in the absence of Cl^- ion. By means of electrolysis at dropping mercury electrode of a known volume of 0.5 *mM* solution of As (III) in 0.1 *M* tartaric acid at pH 2.7, at a working potential of the electrode of —1.0 *V* (SCE), we measured the decay of the total diffusion current of both waves at predetermined time intervals during electrolysis. Introducing the measured diffusion currents into the formula

$$n = \frac{I_0 t}{2.303\, C_0 F V \log \dfrac{I_0}{I_t}},$$

where I_0 is the total diffusion current (μA) of both waves at the beginning of electrolysis, I_t the total diffusion current after t seconds of electrolysis, C_0 the initial concentration of As (III) in millimols, and V the volume of the solution in *ml*, it was found from several determinations that the number of electrons, *n*, which take part in the electrodic reaction producing the two waves was 3. This shows that these two waves correspond to reduction to the metallic state. In a similar way but with an adequate interval between the first and the second wave, microcoulometric analysis was done of 0.5 *mM* solution of As (III) in 0.82 *M* HCl + 0.01 *M* tartaric acid at pH 0.85 at a working potential of the electrode 1.1 *V* (SCE). The results, shown in

TABLE I.

Determination of the number of electrons of the first and second wave in reduction of a solution of As (III) *in 0.82* M HCl + *0.01* M *tartaric acid at pH 0.85*

V ml	C_0 mM	I_0 μA	t sec	I_t mm	$\log \frac{I_0}{I_t}$ *)	$\frac{\Delta t}{\Delta \log \frac{I_0}{I_t}}$	n
					First wave		
2	0.5	8	0	40	0	29674	1.07 ± 0.02
			900	37	0.0339		
			1800	34	0.0706		
			2700	32	0.0970		
			3600	30	0.1250		
					Second wave		
2	0.5	32	0	83	0	13267	1.95 ± 0.02
			900	72	0.0618		
			1800	62	0.1267		
			2700	53	0.1948		
			3600	45	0.2659		

*) I_0 is in mm.

Table I, demonstrated that an one-electron electrode reaction corresponds to the first wave and a two-electron reaction to the second.

Considering that the electrodic reduction is an irreversible process, we determined the characteristic transfer coefficients α_1 and α_2 of the first and the second phase of reduction, respectively. Because hydrogen ions are involved in the electrodic reaction, the transfer coefficients were determined at different pH's. From the polarographic curves, according to the procedure of Koutecky(8), it is possible to determine the transfer coefficient from the slope of the line defined by

$$\log \mu = \log \left(\frac{12}{7}\right)^{1/2} \cdot \frac{k_0 t^{1/2}}{D_0^{1/2}} - \frac{\alpha n F}{2.303\, RT} E,$$

where

$f(\mu) = I/I_d$,

D_0 = coefficient of diffusion of the ion, i.e. the reducing species

k_0 = constant of electrodic reaction at electrode potential $E = 0$ with respect to normal hydrogen electrode

t = dropping time of mercury

I_d and I maximum diffusion current and maximum current at electrode potential E, respectively.

The other quantities are standard constants. The values for μ for the corresponding I/I_d ratios are obtained from the table given by Koutecky(8). Values for α_1 and α_2 obtained in this way, at different pH, are given in Tables II and III. It may be seen from the tables that with increasing pH within the observed range both transfer coefficients decreased.

From the slopes of the straight lines in Fig. 2, $\Delta E_{1/2}/\Delta pH = -p/\alpha n\ 0.0591$, we have determined the number of hydrogen ions, p, which participate in different steps of the reduction. The slope was 0.1. Substituting this value into the above formula together with the already determined mean values for αn, for the observed pH range, it was found that $p = 1$ for the first wave, and $p = 2$ for the second wave. Therefore the reduction of As (III) at dropping mercury electrode in the absence of complexing agents at pH 0.5—1.5 should proceed in the following way:

First wave $HAsO_2 + H^+ + e = AsO + H_2O$

Second wave $AsO + 2H^+ + 2e = As + H_2O$

APPARATUS AND REAGENTS

The polarography and pH determinations were done on a Radiometer PO 4d polarograph and a Radiometer PHM22r pH-meter. The reagents used were "Kemika" p.a.

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TABLE II

Transfer coefficient α_1 *(first wave) at different pH;* $6 \cdot 10^{-4}$ *M As (III) in 0.05 M tartaric acid + 0.001% gelatin; pH adjusted with* $HClO_4$

pH	I mm	$\frac{I}{I_d}$	μ	log μ	—E (SCE)	α_1
1.09	22	0.846	4.64	0.6665	0.600	0.75 ± 0.02
	19	0.731	2.49	0.3962	0.640	
	15.5	0.600	1.40	0.1461	0.620	
	12	0.462	0.855	−0.0680	0.600	
	9	0.346	0.547	−0.2620	0.580	
	5	0.192	0.257	−0.590	0.560	
	$I_d = 26$					
1.40	22	0.862	5.160	0.7126	0.685	0.73 ± 0.02
	18	0.706	2.120	0.3263	0.665	
	15	0.588	1.320	0.1206	0.645	
	11.5	0.451	0.821	0.0857	0.625	
	9	0.353	0.563	−0.2495	0.600	
	5.5	0.215	0.293	−0.5531	0.585	
	$I_d = 25.5$					
2.00	21	0.860	5.08	0.7059	0.735	0.69 ± 0.02
	18	0.720	2.38	0.3766	0.715	
	14.5	0.580	1.30	0.1139	0.695	
	11.5	0.444	0.800	−0.0969	0.675	
	8.5	0.340	0.535	−0.2716	0.655	
	6	0.240	0.337	0.4724	0.635	
	$I_d = 25$					
2.85	21	0.857	4.98	0.6972	0.780	0.65 ± 0.02
	17	0.693	2.60	0.4150	0.760	
	13	0.530	1.099	0.0043	0.740	
	9.5	0.387	0.645	−0.1904	0.720	
	7.5	0.306	0.462	0.3354	0.700	
	6.5	0.265	0.382	−0.4179	0.680	
	$I_d = 24.5$					
3.20	20.5	0.854	4.90	0.6902	0.810	0.63 ± 0.02
	18	0.750	2.72	0.4346	0.790	
	14.5	0.604	1.45	0.1614	0.770	
	11.5	0.479	0.911	−0.0405	0.750	
	9	0.375	0.615	−0.2111	0.730	
	7	0.291	0.431	−0.3655	0.710	
	$I_d = 24$					

TABLE III

Ttransfer coefficient α_2 (second wave) at different pH; 6 · 10^{-4} M As(III) in 0.05 tartaric acid + 0.001% gelatin; pH adjusted with $HClO_4$

pH	I mm	$\frac{I}{I_d}$	μ	log μ	—E (SCE)	α_2
1.09	32	0.971	26.6	1.4249	0.855	0.65±0.02
	29	0.879	5.94	0.7738	0.830	
	23	0.697	2.10	0.3222	0.805	
	I_d = 33					
1.40	39	0.975	30.0	1.4771	0.875	0.65±0.02
	36	0.900	7.36	0.8669	0.855	
	30	0.750	2.72	0.4346	0.835	
	18	0.450	0.82	−0.0867	0.805	
	I_d = 40					
2.00	41	0.965	21.9	1.3404	0.905	0.63±0.02
	36.5	0.859	5.04	0.7024	0.880	
	29.5	0.694	2.07	0.3160	0.860	
	20	0.471	0.884	−0.5335	0.840	
	I_d = 42.5					
2.85	43	0.977	35.0	1.5441	0.965	0.60±0.02
	39.5	0.898	7.24	8.8597	0.945	
	34.5	0.784	3.22	0.5079	0.925	
	27.5	0.626	1.54	0.1903	0.905	
	19.5	0.444	0.800	−0.0969	0.885	
	I_d = 44					
3.2	46	0.978	38.8	1.5888	1.005	0.57±0.02
	42	0.894	6.96	0.8426	0.980	
	38	0.809	3.69	0.6570	0.955	
	33.5	0.714	2.30	0.3617	0.945	
	28	0.596	1.32	0.1206	0.930	
	21	0.458	0.845	−0.0731	0.910	
	10	0.213	0.290	−0.5476	0.895	
	I_d = 47					

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Original Scientific Paper

IDENTIFICATION OF β-SITOSTEROL IN OIL FROM THE RADIX AND RHIZOMES OF HELLEBORUS ODORUS BY THIN LAYER CHROMATOGRAPHY*

by

DOBRILA ŽIVANOV-STAKIĆ and MILOŠ MLADENOVIĆ

The phytosterol content of vegetable oils varies from 0.03 to 1.5%⁽¹⁾. Stefanović and Mladenović⁽²⁾ have isolated β-sitosterol from the nonsaponified fraction of the oil from Yugoslav species of *Helleborus*. The product was purified over aluminum oxide. Its melting point (137°C), and those of the acetyl derivate (128°C) and the brome-acetyl derivate and digitonide (235°C) were taken as proof that it was chemically homogenous. Paper chromatography also confirmed this. By thin layer chromatography of the β-sitosterol isolated by Stefanović and Mladenović we always obtained only a single spot. For that reason we have used this substance to prepare a standard solution of β-sitosterol.

Thin layer chromatography is being more and more used in the study of the chemical composition of oils(3,4). It is stated in the literature that lipid chromatograms can be developed with 0.01% solution of fluorescein(4). In our study we combined fluorescein with silicagel G and discovered fluorescent spots under UV lamp.

Thin layer chromatography is used by a great number of authors for the separation and identification of phytosterols(5,6,7,8,9,10,14,15), on silica-gel G, aluminum oxide G or kiselgur G. It is also possible to obtain good separation of phytosterols on silica-gel impregnated with silver nitrate. β-sitosteryl esters have also been separated by thin layer chromatography(11,12).

We used thin layer chromatography for direct identification of β-sitosterol in the oil of the radix rhizome of *Helleborus*, and to identify β-sitosterol isolated from the oil of the radix. To separate β-sitosterol from esterified sterols and glycerides we used seven new developers (S_1—S_7) and two-dimensional chromatography. The developer S_7 has the advantage over the others that it permits excellent separation of the esterified sterols from β-sitosterol. In the other developers the differences in the mobility of esters, although good, are slightly smaller, but the separation of glycerides was on the other hand much better. The oil from the rhizomes contained less glycerides than the oil from the radix, which was the reason why in this oil β-sitosterol was better separated from glycerides.

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To develop the chromatograms we used 10% aqueous solution of phospho-tungstic acid. The red spots of β-sitosterol appeared after heating at 110°C for 10—15 minutes. With Van-Urk's reagent β-sitosterol gave a blue color and the esterified sterols a red.

EXPERIMENTAL

Preparation of the chromatographic plates

Thirty grams of silica-gel G after Stahl was shaken for about one minute with 60 *ml* 0.04% aqueous solution of fluorescein. By means of a Desaga applicator a layer of silica-gel G 0.250 *mm* thick was made on five plates 200 × 200. The plates were than dried at room temperature for about 30 minutes. The plates were activated in a drying chamber at 105—110°C for one hour. We also did comparative runs without the addition of fluorescein, for which the plates were activated at 130°C for one hour.

Developers

For separating and identifying phytosterols from the oil *Helleborus odorus* we tested twenty developer systems. Here we describe only those developers which gave good direct separation of β-sitosterol from the oil of the radix and rhizomes:

S_1 Chloroform-cyclohexane-dioxane	(8 : 4 : 1 *v/v*)
S_2 chloroform-cyclohexane-dioxane	(8 : 4 : 0.5 *v/v*)
S_3 chloroform-cyclohexane-dioxane	(8 : 6 : 1 *v/v*)
S_4 methylene-chloride-tetrahydrofurane	(9 : 1 *v/v*)
S_5 methylene-chloride-tetrahydrofurane	(10 : 1 *v/v*)
S_6 benzene methanol	(99 : 2 *v/v*)
S_7 chloroform-carbonatetrachloride	(9 : 1 *v/v*) and (4 : 1 *v/v*)
S_8 chloroform-acetone	(9 : 1 *v/v*)

Standard solution of β-sitosterol

0.08% solution of β-sitosterol in 96% ethanol. With a micropipette 10 *μl* (8 *μg*) of the solution was put onto the chromatogram at a distance of 3 *cm*. The sensitivity was 1 *μg*.

The same concentration β-sitosterol isolated from the oil of the radix of *Helleborus* by the method of Gracza(13) was also put on the chromatogram. The β-sitosterol was recrystallized from methanol with 20% tetrahydrofurane or from methanol with 3% ethanol. The melting point of the β-sitosterol crystals obtained was 136—137°C.

Preparation of the oil for chromatography

About 0.3 grams of the oil from the radix and rhizomes of *Helleborus odorus* was weight out into a volumetric flask of 25 *ml* which was then filled with ether up to the mark. Then 20 *μl* — 50 *μl* of the ethereal solution was put onto the chromatogram. When greater quantities of the ethereal solution were applied the chromatograms of β-sitosterol were not good. However, with the oil from the rhizomes it was possible to apply as much as 80 μl.

Development of chromatograms

The spots on the chromatograms with fluorescein were detected under a UV lamp. When the chromatograms were exposed to iodine vapour the fluorescence of the background disappeared, only the spots continuing to fluoresce.

The chromatograms without fluorescein were sprayed with 10% solution of phospho-molybdenic acid in ethanol.

The R_f values for β-sitosterol on chromatograms with and without fluorescein are shown in Table 1.

TABLE 1.

Developer	R_f for	
	Silica-gel *G*	Silica-gel *G* with fluorescein
S_1	0.52	0.49
S_2	0.45	0.47
S_3	0.45	0.50
S_4	0.62	0.66
S_5	0.45	0.40
S_6	0.29	0.35
S_7	0.18	0.25
S_8	0.56	0.50

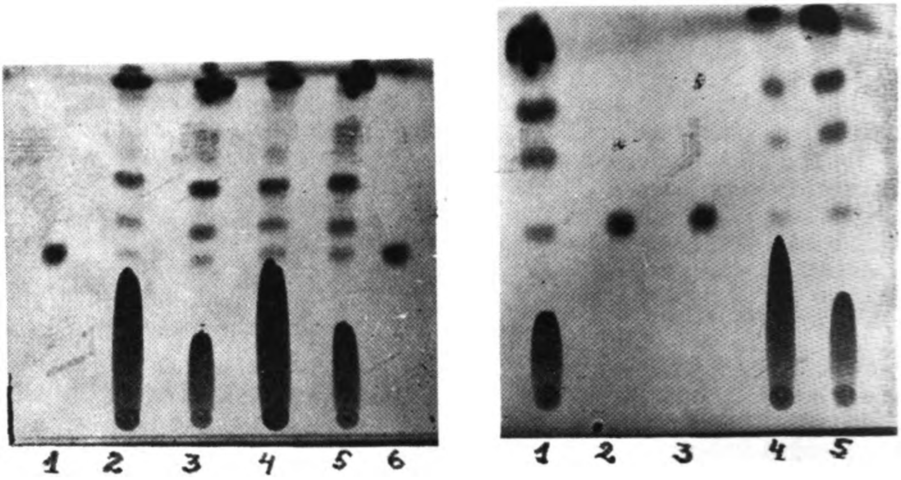
Other staining reactions for steroid substances were also used for developing chromatograms:

1. 10% aqueous solution of phospho-tungstic acid. After 10—15 minutes at 110°C red spots appeared. The intensity of the color increased after standing for 48 hours.
2. Van-Urk's reagent.
   β-sitosterol showed blue, while the other steroids were red.
3. Solution of antimony trichloride in chloroform.

For the demonstration of β-sitosterol in the oil by two-dimensional thin layer chromatography we used the following developers:

A.	direction 1	chloroform 9 acetone 1
	direction 2	chloroform 9 carbon-tetrachloride 1
B.	direction 1	chloroform 16 cyclohexane 8 dioxane 1
	direction 2	chloroform 90 carbontetrachloride 10 dioxane 3

C. direction 1 chloroform 16
cyclohexane 8
dioxane 1
direction 2 chloroform 80
carbontetrachloride 20
dioxane 3



a) b)

Fig. 1

Thin-layer chromatograms of oil of radix and rhizomes of *Helleborus odorus*

a

Developer: S_3;
1 and 6 —β-sitostero (standard)
2 and 4 — oil of radix;
3 and 5 — oil of rhizomes

b

Developer: S_6
2 and 3 —β-sitosterol (standard)
4 — oil of radix
1 and 5 — oil of rhizomes

With two-dimensional chromatography too a single spot was always obtained for β-sitosterol.

The developing time in all the experiments was about 45 minutes, that is until the front of the developer reached a height of 16.5 *cm*.

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Original Scientific Paper

COMPOUNDS OF MANGANESE CHLORIDE WITH VARIOUS METHYLQUINOLINE HYDROCHLORIDES

by

KOSTA I. NIKOLIĆ, KSENIJA R. VELAŠEVIĆ and ANĐELIJA B. ĐUKANOVIĆ

In our earlier studies on the chemical and fluorescent properties a procedure for obtaining some compounds of manganese chloride with pyridine, quinoline and iso-quinoline rings was described(1,2,3). It was found that through the reaction of manganese chloride with the hydrochlorides of these heterocyclic bases two types of compounds are obtained. In one of these the ratio between the hydrochloride and manganese chloride is 1 : 1, and in the other 2 : 1.

In continuation of the study of new compounds with manganese we have synthesized salts of manganese chloride with various methylquinoline hydrochlorides. We have found that methylquinoline hydrochlorides in which the methyl group occupies position 2 or 4 give both types of compound, i.e. compounds in which the ratio between methylquinoline hydrochloride and manganese chloride is 1 : 1 and 2 : 1. The same compounds are also obtained with 2,6-dimethylquinoline hydrochloride. However, with 6- and 7-methylquinoline hydrochloride only 1 : 1 compounds were obtained, while 8-methylquinoline hydrochloride gave only the 2 : 1 compounds.

The composition and structure of these compounds were determined by elementary analysis, UV and IR spectra, potentiometry and electrolysis.

EXPERIMENTAL

Finely powdered crystals of manganese chloride were dissolved in hot ethanol. The corresponding methylquinoline and concentrated hydrochloric acid were added to the solution in excess. After that the solution was slowly evaporated on a water bath. If during the reaction two types of compound were formed, green crystals were the first to crystallize, giving green fluorescence, and then pale-pink crystals which gave red fluorescence.

When both types of compound appeared and we wished to obtain only the green crystals, we used the following procedure. Finely powdered crystals of manganese chloride were dissolved in absolute ethanol and the corresponding methylquinoline was then added in excess to the solution, after which for 3—4 hours dry gaseous hydrogen chloride is blown through. The solution was then slowly evaporated on a water bath to half of the initial volume, and then left to crystalize. Pure crystals were obtained. The purity can also be checked by the fluorescence: the presence of even the smallest quantities of impurities which have a different color of fluorescence can be detected.

The compound in which the ratio between methylquinoline hydrochloride and manganese chloride is 1 : 1 can be obtained by thermal decomposition of the 2 : 1 compound. Heating at 150°C liberates the corresponding methylquinoline hydrochloride, so that the desired compound is obtained.

The absorption spectra were measured on a Beckman model DU 2 spectrophotometer. The cuvettes were 1 *cm* thick. The spectra of the ethanol and water solutions of the compounds were determined.

The spectra obtained were identical to these of methylquinoline in acid medium. The presence of manganese and chlorine ions did not change the position of the maxima in the absorption spectra, which indicates hyperconjugation between the methyl group and the quinoline ring. This decreases the energy of electron transfer, so that the maximums with methylquinoline had slightly longer wavelengths than in quinoline (i.o. 3130 Å). It may be concluded from these observations that in dilute solutions manganese and chlorine were not directly bound to the quinoline ring since this retained its optical characteristics.

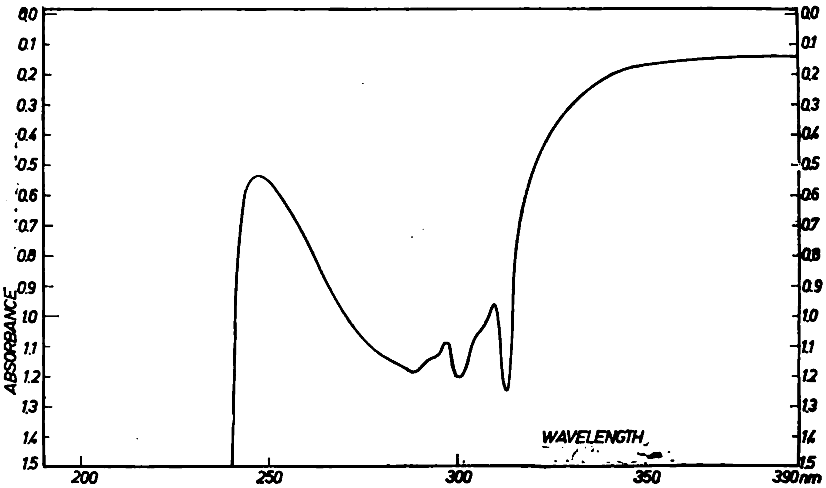

Fig. 1

Absorption spectrum of the compound of manganese chloride and 4-methylquinoline hydrochloride

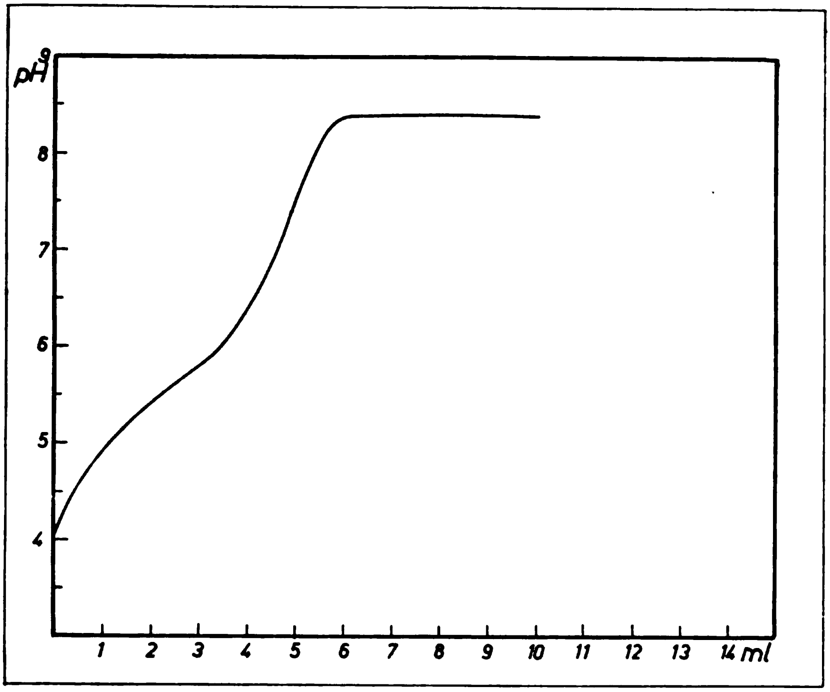

Fig. 2.

Potentiometric titration curve of 0.01 M solution of the compound of manganese chloride and 7-methylquinoline hydrochloride with 0.1 N NaOH

The absorption spectra of methylquinoline are much narrower in basic and neutral than in acid media. The widening of the spectra towards longer waves may be ascribed to the addition of protons to the nitrogen atom. As widening of the spectrum was also obtained with our compounds, we assumed that in dilute solutions quinolinium ions existed. This was confirmed by the violet-blue fluorescence of the solution, due to quinolinum ion and emitted, according to Kneight(4), by a $\pi \rightarrow \pi^*$ electron transition. The absorption spectrum of the compounds of the manganese chloride with 4-methylquinoline hydrohloride, which fluoresced green, is shown in Fig. 1.

The presence of quinolinium ion was also proved by potentiometric titration of solutions of the compounds with 0.1 N solution of sodium hydroxide. The titration curve obtained is shown in Fig. 2.

The first part of the curve corresponds to the neutralization of quinolinium ions. The shoulder on the titration curve lies in the pH range which corresponds to the dissociation constants of methylquinoline bases. The second shoulder is due to the precipitation of manganous ion. By electrolysis of aqueous solutions of the compounds it was found that quinolinium ion moves towards the cathode where it is reduced, so that methylquinoline precepitates in the cathode space.

The infra-red spectra were determined on a Perkin Elmer model 237 grating spectrometer. The substances were examined in tablets of potassium bromide.

The infra-red spectra of all the substances showed characteristic maximums due to the quinoline ring (1500 *cm*$^{-1}$). The characteristic bond for the quinolinium ion was not found in salts in solid state, and therefore we deduced that the $C=NH^+$ bond appears only in dilute solutions. This was also confirmed by the different color of fluorescence of the solution and the solid. The other bands were characteristic only for the given methylquinoline compound and their distribution depended on the position of the methyl groups in the quinoline ring.

On the basis of the elementary analyses we came to the conclusion that there are two types of compound of manganese chloride with the hydrochlorides of quinoline bases. The compounds in which the molecular ratio of the quinoline base hydrohloride and manganese chloride is 1 : 1 are shown in Table I, while the compounds in which this ratio is 2 : 1 are shown in Table II. The color of fluorescence of the compounds and the positions of the fluorescent spectra maximums are also given. These data can be used for the identification of these compounds.

TABLE I

Properties of the 1 : 1 *Compounds*

Compound	Color of the fluorescence	Position of the maximum in the fluorescence spectrum
2-Methylquinoline hydrochloride + $MnCl_2$	Red	620 nm
4-Methylquinoline hydrochloride + $MnCl_2$	Red	620 nm
6-Methylquinoline hydrochloride + $MnCl_2$	Red	620 nm
7-Methylquinoline hydrochloride + $MnCl_2$	Red	620 nm
2,6-Dimethylquinoline hydrochloride + $MnCl_2$	Red	620 nm

It was concluded from the UV and IR spectra that the structure of the compounds was not identical in dilute aqueous solution and the solid state. Apart from quinolinium ions, in dilute aqueous solutions we also detected manganese and chloride ions. Taylor(5), who studied compounds of manganese chloride with pyridine hydrochloride and quinoline hydrochloride, also obtained two types of compound in which the rations were the same as in the compounds of Tables I and II. He hypothesized the following structural formula for these compounds: $QNHMnCl_3$ and $(QNH)_2MnCl_4$ (QN is quinoline). Applying Taylor's hypothesis on the grounds of similar behavior the compounds in Table I should have the structural formula $mQNHMnCl_3$, and these in Table II $(mQNH)_2MnCl_4$ (mQN is methylquinoline).

TABLE II

Properties of the 2 : 1 Compounds

Compound	Color of the fluorescence	Position of the maximum in the fluorescence spectrum
2-Methylquinoline hydrochloride + $MnCl_2$ Ratio 2 : 1	Green	526 nm
4-Methylquinoline hydrochloride + $MnCl_2$ Ratio 2 : 1	Green	543 nm
2,6-Dimethylquinoline hydrochloride + $MnCl_2$ Ratio 2 : 1	Green	526 nm
8-Methylquinoline hydrochloride + $MnCl_2$ Ratio 2 : 1	Red	620 nm

However, Fyfe⁽⁶⁾, on the basis of detailed studies of the structure of manganese chloride compounds with pyridine hydrochloride in concentrated and dilute aqueous solutions, considered that the structure suggested by Taylor could only be a consequence of hydrolysis in dilute aqueous solutions. In concentrated solutions, where there is no hydrolysis, Fyfe assigns these compounds the following formulas: $H_2MnPyCl_3(OH)$ and $H_2MnPy_2Cl_4$ (Py is pyridine). According to these formulas there is no pyridinium ion. Fyfe explains the presence of pyridinium ion in dilute solutions by hydrolysis.

From our studies we conclude that quinolinium ion appeared in the dilute solutions, while the formation of complex ions $MnCl_3$ and $MnCl_4$ was uncertain. They could appear as a result of hydrolysis in dilute solutions. However, as they are not stable, they decompose very easily. The structure given by Fyfe could explain the behavior of our compounds in the solid state, because in that case we did not find quinolinium ion. This hypothesis would be in accordance with the observed differences in the fluorescence of these compounds in dilute aqueous solutions and in the solid state.

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Original Scientific Paper

COULOMETRIC DETERMINATION OF SOME PYRIDINE BASES IN ACETONITRILE

by

KOSTA I. NIKOLIĆ and ZORICA V. ĆUPIĆ

A number of methods have been described in the literature for the determination of pyridine bases(1,2,3,4,5). They make use of different chemical properties of the pyridine ring. In continuation of our work on the application of coulometry in the determination of various compounds we attempted using this method for quantitative analysis of the following pyridine derivatives: 2-, 3- and 4-methylpyridine, 2-, 3- and 4-ethylpyridine, 2,3-, 2,6- and 3,4-dimethylpyridine, 2-methyl-5-ethylpyridine, 2,4,6-trimethylpyridine and 4-n-propylpyridine.

In order to potentiate the alkaline nature of these compounds in comparison with their alkalinity in aqueous solutions, and in order to avoid the effects of solvolysis, the coulometric titration was done in a solution of acetonitrile. Streuli(6) has coulometrically titrated some organic bases in a solution of acetonitrile which contained 0.05 N lithium perchlorate trihydrate, so that the water content in acetonitril was about 0.3%. By anodic oxidation hydrogen ions were formed with which the base was titrated. The end-point was determined by the potentiometric procedure described by Cook, Reilley and Furman(7).

EXPERIMENTAL

Reagents and chemicals:

— Acetonitrile purum "Kemika". The desired degree of purity was achieved by means of the following procedure. The acetonitrile was dried 48 hours over phosphorus pentoxide and then redistilled twice. The degree of purity was checked by means of the boiling point and of the refractive index.

— Lithium perchlorate trihydrate produced by Hopkins & Williams.

— Solution for the anodic space (anolyte): 60 *ml* 0.05 N solution of lithium perchlorate trihydrate in acetonitrile. It is recommended that the solution be prepared just before use, as it decomposes on long standing.

The pyridine bases were products of Koch & Light Labs Ltd. They were purified by distillation. The degree of purity was checked by means of the refractive index. For the coulometric determination we took 0.100 *ml* 1% of acetonitrile solution of the pyridine base (0.100 *ml* contained 10 *mg*). The solution was measured out by means of a microburette with a precision of 0.01 *ml*. The content of pyridine base was determined by using the potentiometric method.

For the electrolytic bridges between the cathodic and anodic spaces we used 5% agar agar in acetonitrile which contained 1% lithium perchlorate in 5% water. With prolonged use the composition of the bridge changed, which necessitated its renewal.

Apparatus:

The d.c. was obtained via an Iskra Kranj B 88 N 5B1 selenium rectifier, which was contained via a variac to a stabilized 220 *V* source. The circuit has already been described(8). The current was adjusted by means of the variac and a 220 Ω variable resistor. With this apparatus it was possible to obtain currents within the range from 1—100 *mA*. However, because of overheating of the electrolytic bridges at high currents we have used currents of 30 *mA*. The current was measured by means of a Chauvin Arnoux milliampermeter with a precision of 0.2 *mA*/scale division. The time was measured by means of a Mashpriborintorg chronometer with a precision of 0.1 second.

The anode was a platinum plate with dimensions 10 × 2 *cm* and the cathode a 4 × 1 *cm* platinum plate.

The end-point was determined potentiometrically. The potential of a G 200 B glass indicator electrode was measured on a Radiometer 22 pH-meter. A saturated calomel electrode was used as the standard electrode. It was immersed in a saturated solution of potassium chloride which was connected to the titrated solution via an electrolytic bridge.

All the electrical instalations were well grounded in order to avoid interference.

Procedure:

The end-point was determined by titrating the solution up to a certain potential. By studying the change of the potential as a function of the time of generation of hydrogen ions in the anolyte we came to the conclusion that these changes were greatest in the range from 300 to 350 *mV*. For that reason we chose 315 *mV* as the end-point of titration.

Before the addition of the solution to be tirated current was passed through the anolyte until the potential reached 315 *mV*. Then 0.100 *ml* acetonitrile solution of the pyridine base was added to the anolyte, which caused a change of the potential. In order to reestablish the potential of 315 *mV*, which corresponded to the end-point, the current was passed through the solution and the time measured. Near the end-point the current was reduced in order to obtain the desired potential as accurately as possible. After passing the current one should always wait about 5 minutes before measuring the potential.

The quantity of the pyridine compound was calculated by Faraday's law.

DISCUSSION

Our preliminary studies had shown that there was no anodic oxidation of the pyridine compounds or their neutralization products so that hydrogen ion was produced with 100% current efficiency. Because of that we were able to apply the procedure used by Streuli to the coulometric determination of the pyridine bases under study.

The results are shown in the table.

TABLE I

Titrated Substance	Taken (*mg*)	No. of titration	Coulometric titration
2-Methylpyridine	10.0	6	9.96±0.02
3-Methylpyridine	10.0	6	9.97±0.02
4-Methylpyridine	10.0	6	9.96±0.01
2-Ethylpyridine	10.0	6	9.97±0.02
3-Ethylpyridine	10.0	6	9.97±0.01
4-Ethylpyridine	10.0	6	9.96±0.01
2,3-Dimethylpyridine	10.0	6	10.06±0.02
3,4-Dimethylpyridine	10.0	6	10.06±0.01
2,6-Dimethylpyridine	10.0	6	10.05±0.01
2-Methyl-5-ethylpyridine	10.0	6	9.96±0.02
4-n-propylpyridine	10.0	6	10.01±0.01
2,4,6-Trimethylpyridine	10.0	6	10.03±0.01

It is concluded from the results that the coulometric method can be applied for the determination of these pyridine bases. The measurements were reproducible and the deviations small.

During the determination great care must be taken about the volume of the titrated solution which is added If it is too great, potential changes occur due to dilution, which causes errors in the end-point potential.

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Original Scientific Paper

OSCILLOGRAPHIC-CHRONOPOTENTIOMETRIC TITRATION

I. PRINCIPLE OF THE METHOD*

by

ĐORĐE K. STEFANOVIĆ, VILIM J. VAJGAND and TIBOR A. KIŠ

Amperometric, biamperometric and potentiometric titrations at constant current(2—6) are usually done with D.C. but they can also be done by with voltage a.c., of about 10 *mV*. Thus, under the name of "polarization titration", Franck(7) in fact described a dead-stop method with superimposed sinusoidal a.c., which Laitinen and Hall(8) later improved by using square-wave oscillations. Juhász(9) has developed a modification of the amperometric titration in which the potential changes are measured at constant alternating current. In these methods low current and voltage (10—20*m V*) A.C. passes through the system.

Oscillations of a relatively high voltage of 1—2 *V* are mainly used in oscillation polarography for studying the reversibility of electrodic processes, for qualitative and less frequqently for quantitative analysis. They have also been used for the determination of the end-point of oscillo-polarographic(10—13), comparative (14—16) and dilution titrations(17). In oscillo-polarographic titration the depolarizer is determined, while the disappearance of its notch on the cyclogram denotes the end-point. In comparative titration the notch of the depolarizer solution is recorded, while a standard solution of the same depolarizer is added to the second solution, which contains only the electrolyte, until the notch of the second solution becomes the same as that of the test solution. In dilution titrations a solution of a depolarizer is titrated with an indifferent electrolyte until the notch disappears. The relative errors in all these titrations are quite high, amounting to 5 to 10%.

By using higher voltage polarization a.c. new possibilities were opened for the application of alternating current in titration. Their investigation was the aim of the present study. The results have shown that by superimposing an alternating current of relatively high voltage in potentiometric titrations it is possible to develop a new method of end-point determination. The principle of the method is as follows:

A platinum indicator electrode was immersed in the titrated solution and connected to a saturated calomel electrode of large surface area by means

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* Communicated at the International Symposium on Instrumental Analytical Chemistry in Budapest, 1966.(1)

of an electrolytic bridge. This galvanic element was polarized by means of an a.c. voltage of 1—2 V (Fig. 1)(18). The high series resistance of 450 K Ω ensured constancy of the alternating current when the EMF of the galvanic element changed during titration. Signals were taken via a derivation circuit (1 K Ω and 0.33 uF) and fed to an oscillograph. Oscillograms presented on the screen showed the changes of the a.c. voltage during titration, i.e. the derivative $dE/dt = f(t)$.

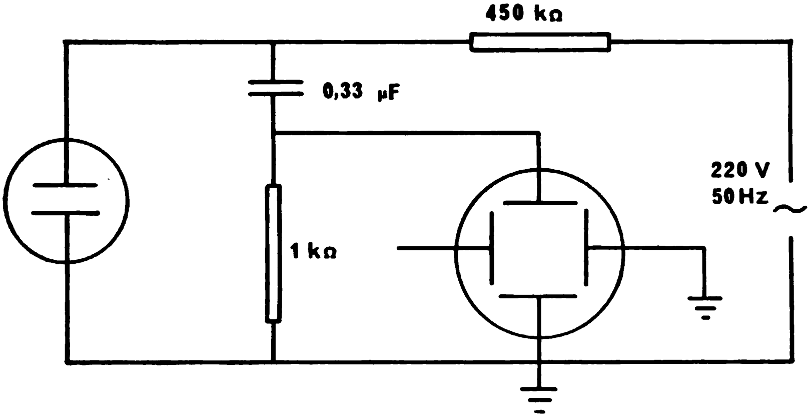

Fig. 1

Diagram of the equipment for oscillographic chronopotentiometric titrations

Before the end-point the a.c. voltage oscillated mainly around the potential of the d.c. of the indicator electrode (Fig. 2, potential A). It was adjusted so that the time function of the a.c. potential ($E = f(t)$) did not reach the separation potential of the indicator ions before the equivalence point (Fig. 2, potential C). Because of that ions did not separate at the indicator electrode, the electrode remained in polarized state, and hence the oscillogram was sinusoidal (Fig. 2, curve a).

Because of the sudden change in concentration of the titrated ions at the end-point, the potential of the d.c. of the indicator electrode also changed considerably (Fig. 2, potential B). Then the a.c. voltage oscillated around the newly established d.c. potential (Fig. 2, potential B). Because of this change of potential, the amplitude of oscillations went over the separation potential of the indicator ions and they discharged at the microelectrode, which was thus depolarized, Faradic currents appeared and the phase of the alternating current changed. As a result the shape of the oscillogram suddenly changed (Fig. 2, curve b): this was used for determinating the end-point of the titration (Fig. 3).

Since we determined the end-point mainly by the simultaneous change of the d.c. potential and the a.c. waveform we have suggest that the such method be called oscillographic chronopotentiometric titration(1,19–21).

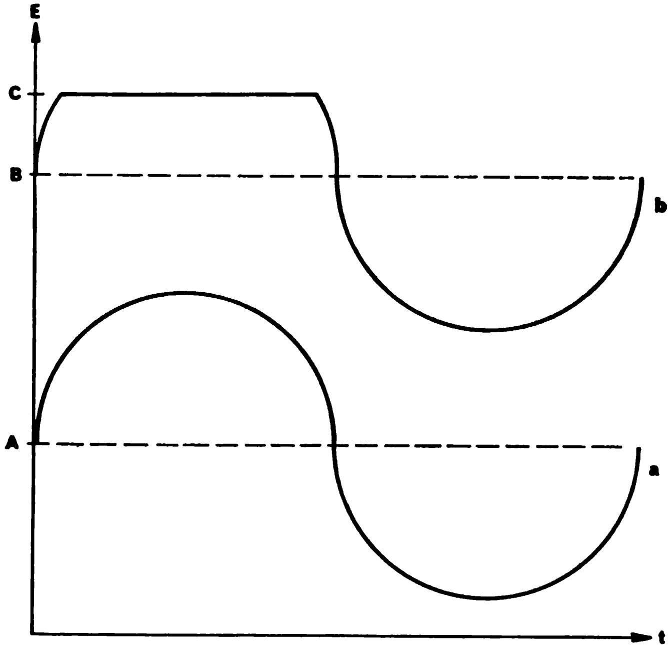

Fig. 2

AC potential waveform. E = f(t) *E* = d.c. potential of the indicator electrode. *A* — before, and *B* — at the titration end-point; *C* — deposition potentical of the indicator ions; *t* — time; *a* — shape of oscillogram before, and *b* — at the end-point

By using a suitable indicator ion and the corresponding amplitude of the alternating current we have succeeded in determining the end-point by this method in acid-base, precipitation, redox and complexometric titrations.

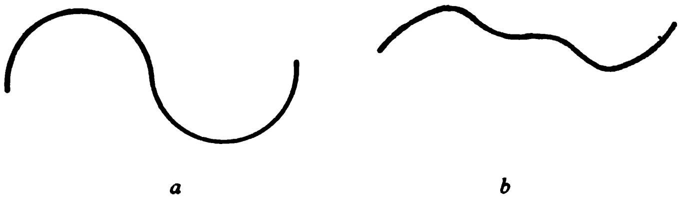

Fig. 3

Change of the derivative dE/dt = f(t) in oscillographic chronopotentiometric titrations using sinusoidal oscillations. *a* — oscillogram before, and *b* — at the titration end-point

The presence of ions whose separation potential was higher than the potential of separation of indicator ions (Fig. 2, potential *C*) does not interfere with the titration. Thus, for example, arsenic (III) was without difficulty titrated against potassium-bromate in the presence of an ionic mixture of alkali and alkaline-earth metals: aluminum, iron (III), manganese (II), nickel, cobalt (II), zinc, cadmium, bismuth and copper (II), using bromide ion as the indicator.

The relative errors and standard deviations of the results of oscillographic chronopotentiometric titrations were approximately within the limits of the errors in the corresponding usual potentiometric titrations.

The new method of end-point determination has all the advantages and limitations of the common potentiometric methods. It is not necessary to plot graphs or to calculate the end of titration, the end-point being determined visually from the distortion of the oscillogram.

In future papers we shall report on investigation of the influence of various factors on the oscillogram distortion, i.e. on the accuracy of the determination, and on the procedures for some acid-base, precipitation, redox and complexometric determinations.

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Original Scientific Paper

POLAROGRAPHIC DETERMINATION OF INDIUM IN THE PRESENCE OF CADMIUM*

by

SRETEN M. MLADENOVIĆ, MILADIN VESKOVIĆ and BOŽIDAR FILIPOVIĆ

The number of indifferent electrolytes in which indium can be determined polarographically is relatively great. The half-step potential of indium in the majority of indifferent electrolytes lies within the range 0.45 *V* to —0.80 *V* relative to saturated calomel electrode(1). The ions of a number of metals, and primarily the ions of lead, thalium, tin and cadmium, are reduced at the same or approximately the same potentials as the cadmium-ions(1).

Considering the value of the half-step potential(1) it may be concluded that the simultaneous polarographic determination of indium, lead, thallium, tin and cadmium in almost all these electrolytes is unreliable or impossible, because of the similar or identical reduction potentials of the ions of these metals.

The obstacles to polarographic determination of indium in the presence of lead, tin, thallium and other metals, but not in the presence of cadmium, can be avoided by the method described by Kriukova, Siniakova and Aref'eva(1).

For the simultaneous determination of indium and cadmium polarographic determination in 0.1 M acetate buffer at pH 4.7 is recommended(1); in this electrolyte the common wave of indium and cadmium is first recorded, and after the addition of fluoride to the electrolyte cadmium is determined polarographically; indium is determined from the difference.

Treindl(2) has suggested a solution of sodium-iodide as the indifferent electrolyte for the polarographic determination of indium in the presence of cadmium. Because of the small difference between the reduction potentials of the ions of indium and cadmium in sodium-iodide we did not obtain reliable and valid results.

Using calcium-carbonate as a collector of indium from a solution with pH < 5 we obtained quantitative separation of indium from cadmium. In the precipitation of ferric hydroxide by means of ammonium hydroxide in the presence of ammonium salts it is not possible to separate cadmium quantitatively from the indium completely separated from the solution by

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* This paper was communicated at the 2nd Yugoslav Congress on Pure and Applied Chemistry, held in Belgrade from 16 to 19 June, 1966.

the ferric hydroxide collector. This conclusion was confirmed by a great number of experiments. In all experiments we used a Radiometer PO4 polarograph.

The influence of cadmium was studied by means of polarographic determination of indium in the presence of cadmium⁽¹⁾ without the separation of indium by means of calcium-carbonate. The results of these experiments are shown in Table 1.

TABLE 1.

Influence of cadmium on the wave height of indium.
Indifferent electrolyte: 10 ml 6 N HCl + 1 ml 0.5% gelatin.

Content (*mg*)		Wave height in *mm*	
Indium	Cadmium	without $CaCO_3$	with $CaCO_3$
0.19	0	34.0	34.0
0.19	1.00	38.0	34.0
0.19	2.00	38.0	34.0
0.19	3.00	39.0	34.0
0.19	4.00	39.0	34.0
0.19	5.00	39.0	34.0

The polarographic waves of indium in the presence of cadmium, without the action of a calcium-carbonate solution, as shown by the results in Table 1, were about 10% higher than in the absence of cadmium. When calcium carbonate was used to separate indium from various amounts of cadmium the heights of the polarographic waves were always equal.

The linear dependence of the waves height on the concentration of indium was investigated on samples with copper, zinc, lead, cadmium, iron and different quantities of indium. In these experiments indium was also separated from cadmium by means of calcium-carbonate. The results of the experiments are shown in Table 2.

TABLE 2.

Heights of polarographic waves in dependence on the quantity of indium.
Sample: 0.14 g Zn + 0.34 g Cu + 0.02 g Cd + 0.012 g Pb + 0.01 g Fe + In.
Indifferent electrolyte: 10 ml 6 N HCl + 1 ml 0.5% gelatin.

Indium (*mg*)	Wave heights *mm*
0.19	14.0
0.38	27.5
0.57	42.0
0.76	57.0
0.95	71.0

The results in Table 2, and the graph (Fig. 1) show the existence of a linear correlation between the wave height and the quantity of indium, i.e. that cadmium and the other metals were quantitatively separated from indium.

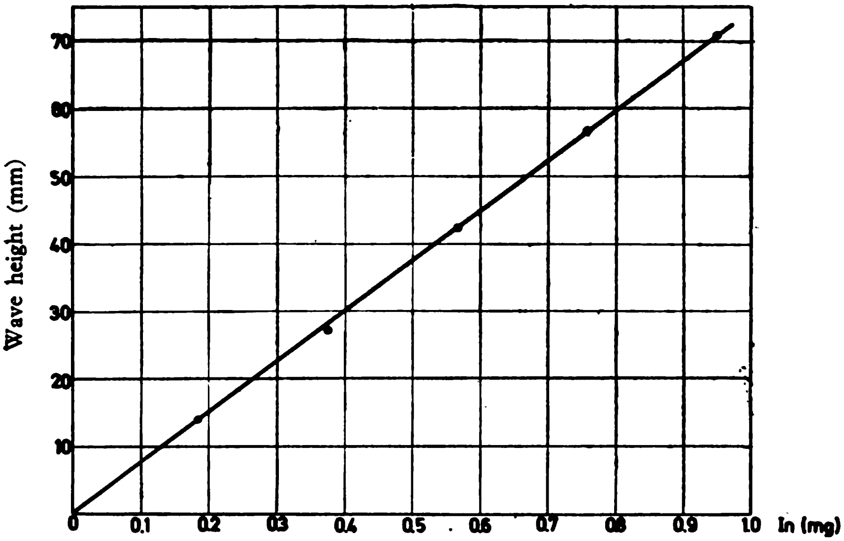

Fig. 1

Dependence of wave height on indium concentration.

The waves height in hydrochloric acid as the indifferent electrolyte depended on the concentration of hydrochloric acid, as shown by the results in Table 3.

TABLE 3

Effect of the concentration of hydrochloric acid on the polarographic wave height
Quantity of indium: 0.19 mg

Volume of the indifferent electrolyte: 10 ml × N HCl + 1 ml 0.5% gelatin

Concentration of hydrochloric acid	Wave height in *mm*
1 N	7.0
2 N	12.0
3 N	24.0
4 N	30.0
5 N	32.0
6 N	33.0
7 N	35.0
8 N	34.0

With increasing hydrochloric acid concentration the wave height increased, up to a concentration of 7 N.

The results of our experiments and the already existing method⁽¹⁾ were used as the basis for a determination of indium in the presence of cadmium in the sediment of roasted floatation concentration of zinc after its exposure to the action of a base, and in zinc oxide in which the indium content was less than 0.1%. The procedure is as follows:

1000 grams of the sample is weighed and put into a 400 *ml* beaker, and the sample dissolved with 20 *ml* of conc. hydrochloric acid and 2—3 *ml* of conc. nitric acid. After dissolution of the sample about 100 *ml* of water is added and the solution gently warmed. By means of Ammonium hydroxide in the presence of ferric ion indium hydroxide $In(OH)_3$ is precipitated. If there is no iron in the solution, 10 *mg* of iron in the form of ferric chloride is added.

The precipitated hydroxides of indium and iron are kept 15 minutes on a sand bath, after which they are filtered through filter paper (black band). The precipitate is well washed with 1% solution of ammonium-chloride and than with warm water. It is then dissolved with warm conc. hydrochloric acid, and the solution collected in the beaker in which the precipitation was done. The resulting solution is evaporated to dryness, after which 10 *ml* of conc. hydrobromic acid and 1 *ml* of bromine are added. The solution is evaporated to dryness. The dry residue is dissolved in 10 *ml* 5 N hydrobromic acid with gentle warming. To the cooled solution an amount of sodium thiosulfate crystals is added sufficient to cause disappearance of the color; after that a few more crystals of sodium thiosulfate are added. After 5 minutes the solution is filtered through a thick filter paper (blue band) and a separation funnel. The beaker and the precipitate are washed with 10 *ml* 5 N hydrobromic acid each, and the acid is collected in the separation funnel. Then 30 *ml* of dietyl-ether is added via the separation funnel. After 2 minutes extraction the ethereal layer is decanted into another separation funnel, and from the water layer indium is again extracted. In the other separation funnel, containing both ethereal layers, indium is reextracted twice with 25 *ml* of hydrochloric acid (1 : 1) and 2 *ml* of 2% hydrogen perioxide for 2 minutes each time. The aqueous hydrochloric acid layers are united, mildly warmed and neutralized with 25% ammonium hydroxide until mildly acid according to "universal" indicator paper. The mildly acid solutions are transferred to a separation funnel. Calcium carbonate is added in small quantities with continuous mixing until the solution becomes saturated and calcium carbonate precipitates; at the moment of precipitation the pH of the solution should be about 5. After shaking for half an hour the precipitate is filtered through thin filter paper. After washing, the precipitate which contains indium is dissolved with warm hydrochloric acid (1 : 1). The solution is evaporated to dryness, and 10 *ml* of hydrochloric acid ($\sim$ 6N) and 1 *ml* of 0.5% gelatin are added to the cooled dry residue. After the introduction of hydrogen, indium is determined polarographically in the solution obtained.

Another sample is prepared in absolutely the same way, at the same, in which before dissolution a quantity of a standard indium solution which corresponds approximatively to the quantity expected in the test sample is added.

The accuracy of the method for the determination of indium in the presence of cadmium in the precipitate of roasted floatation concentrate of zinc after exposure to the action of a base, and in zinc oxide, is confirmed by the excellent reproducibility of the results.

By means of this method it is definitely possible to separate indium from cadmium, lead, tin, thallium and other metals. It is therefore recommended primarily for the determination of indium in the presence of cadmium.

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Original Scientific Paper

A STUDY OF INVERTASE FROM A THERMOTOLERANT STRAIN OF *SACCHAROMYCES CEREVISIAE*

by

VESELINKA M. GALOGAŽA

Part I

In 1937 Sizer(1) determined the activation energy of saccharose inversion in the presence of invertase and found that its mean value in the temperature range between 0 and 40°C was 11000—11500 *cal/mol.* He also observed(2) that invertase in the viable cells of baker's yeast, and also in dead but non-cytolyzed cells, had an activation energy in the temperature range from 0° to 17°C of 10700 *cal/mol,* while in the range below (*sic*) 17°C the activation energy was 8300 *cal/mol.* As a measure of invertase activity at different temperatures he took the rate constant of the first order reaction which initiates, according to his findings(3), after 12% inversion.

The existence of two activation energies, or an inflection on Arrhenius's line (which was found by Sizer during his work on invertase from baker's yeast) has also been found for many other enzymes: for lipase the inflection is at 0°C(4), for urease at a certain redox potential at 22°C(5), and for fumase it depends on the difference of pH from the optimum(6).

This is explained by the fact that the two rate constants which characterize the kinetic steps of the compound reaction of enzyme action often change with temperature, so that in one temperature range the first step is slower, and in another range the second is slower. For that reason there are two activation energies, always associated with the slower process(7). Another proposed explanation is that temperature influences the spatial relationship of active groups in the active segment of the enzyme molecule and the stability of the bonds between these groups and the corresponding atoms in the substrate molecule by means of which the active complex is formed(8–10).

The aim of the first part of this work was to study whether invertase from the yeast *Saccharomyces cerevisiae* which has been acclimatized to 40°C over several years shows different thermodynamics of the activation process in comparison with invertase from a yeast which was not thermophilized.

The enzyme activity at different temperatures was determined on the unpurified clear solution after autolysis of the thermophilized yeast. The activation energies were compared in tests performed with invertase from brewer's yeast which, in order to liberate the enzyme from the cells, was treated in the same way as the thermotolerant strain of *Saccharomyces cerevisiae*. In order to verify whether the other soluble constituents of the cell affect the activation energy, the same experiments were done using a liquid preparation of invertase of L. Light Co., Ltd., England.

In all experiments the activity was determined at temperatures at which it was certain that invertase was not inactivated during the experiment of inversion.

It was found that the inversion of saccharose by invertase does not follow the same kinetic law over the entire concentration-time range, and that the size of the different ranges depends on the enzyme concentration and the initial concentration of saccharose(1,11,12). We found that the reaction kinetics of inversion was zero order up to 30% inversion when the initial concentration of saccharose in the solution was 6 *g*/100 *ml*. In experiments with the liquid commercial invertase and the unpurified autolyzate of brewer's yeast the zero order kinetics was observed from the beginning of reaction, while in the experiments with unpurified autolyzate of yeast from acclimatized *Saccharomyces cerevisiae* it was observed after an individual period of stagnation (until 2% inversion). For that reason we decided to use the slope of the straight part of the concentration-time curve, that is the constant rate of inversion in this stage of the reaction, as a measure of activity.

EXPERIMENTAL

Production of yeast biomass

1. *Thermophilized strain of Saccharomyces cerevisiae*. The biomass of thermophilized yeast was produced by multiplying the culture first in test-tubes for 48 hours and then in 1 liter flasks for 36 hours. The multiplication medium contained an extract of boilt commercial yeast (200 *g*/*lit*), saccharose (100 *g*/*lit*) and diammoniumphosphate (1 *g*/*lit*), the pH being adjusted to 5.5. Multiplication was continued in a fermentor for 8 hours with the addition of culture medium and salt solution under aerobic conditions at pH 4.8—5.1.

All multiplications were done at 40°C.

2. *Brewer's yeast* produced by "7 Juli", Beograd, was washed several times in water, plasmolyzed and then filtered under pressure.

Preparation of the invertase solution

Active autolysate was prepared by using the method of rapid autolysis(14): 100 *g* of yeast is treated with 10 *ml* of toluol for 3 hours at room temperature, diluted with 100 *ml* of water, the pH adjusted to 5.8, and then the mixture kept at a temperature of 30°C for 24 hours. The pH is then adjusted to 4.7 (optimum pH) and the suspension freed of cell remnants by centrifuging.

The cloudy solution after centrifugation was filtered through a layer of Supercell-Dekalit until a clear solution was obtained. The liquid was then diluted with water to an invertase concentration at which the reaction rate is such that it can be observed with sufficient accuracy.

It was found that after 30 days at +5°C this solution did not lose any of its initial invertive activity. Sterility of the solution during this time was maintained by the presence of toluol.

Purification of saccharose

Saccharose was obtained by purification of commercial saccharose with active carbon, and after removal of the carbon, crystallization from the syrup after the addition of a mixture of alcohol and ether.

Preparation of the buffer solution

Acetate buffer with a pH 4.7, prepared by the method of Michaelis(14) was used in order to optimize the pH for inversion.

Determination of invertase activity at different temperatures

Invertase activity was determined by measuring the inversion in a saccharose solution of initial concentration 6 *g/100 ml*. The temperature kept constant in a water thermostat to an accuracy of =0.02°C. Inversion was initiated by adding a certain volume of active solution (the solution obtained after autolysis or a solution of the enzyme) to the saccharose solution containing acetate buffer. After predetermined time intervals 20 *ml* was transferred by means of a pipette into vessels each containing 2 *ml* of 0.6 N solution of sodium hydroxide which inactivated the enzyme. As the solution turned cloudy because of the action of the sodium hydroxide, the samples were filtered through dry filter paper. The rotation of the sodium light was read on a polarimeter after the samples had stood for at least 30 minutes after inactivation in order to allow the establishment of a constant rotation. All the rotation measurements were done at 20°C.

Two parallel experiments were done for each temperature.

The initial rotation of the solution was determined by taking a sample in each experiment under identical conditions but containing water instead of active enzyme solution.

RESULTS AND DISCUSSION

Figures 1 and 2 show the course of inversion at different temperatures using invertase from the autolysate of brewer's yeast and from the autolysate of the thermotolerant strain of *Saccharomyces cerevisiae*. The inversion with the liquid commercial invertase is represented by a straight line from the beginning of the reaction, the same as inversion using the autolysate of brewer's yeast, for which reason it is not separately presented.

Tables 1, 2 and 3 show the constant rate of inversion $v(^{c}/min)$ and the data necessary for the determination of the activation energy.

Activation energies E *cal/mol* (determined graphically, Fig. 3) are:

For brewer's yeast invertase

E = 8300 *cal/mol* for temperatures above 21.3°C
E = 11000 *cal/mol* for temperatures from 0° to 21.3°C.

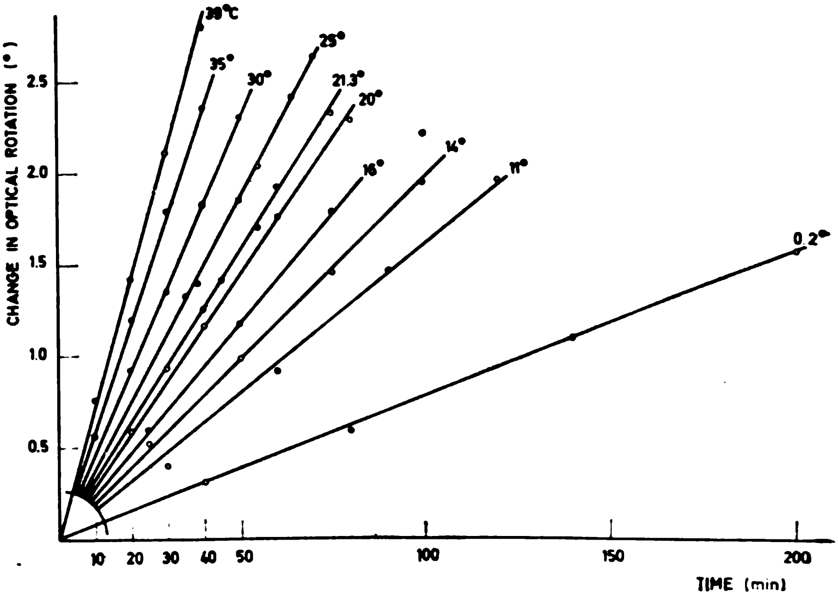

Figure 1
Invertase of brewer's yeast

For invertase from the termotolerant strain of Saccharomyces cerevisiae

E = 8200 *cal/mol* for temperatures above 21.7°C
E = 11400 *cal/mol* for temperatures from 0° to 21.7°C.

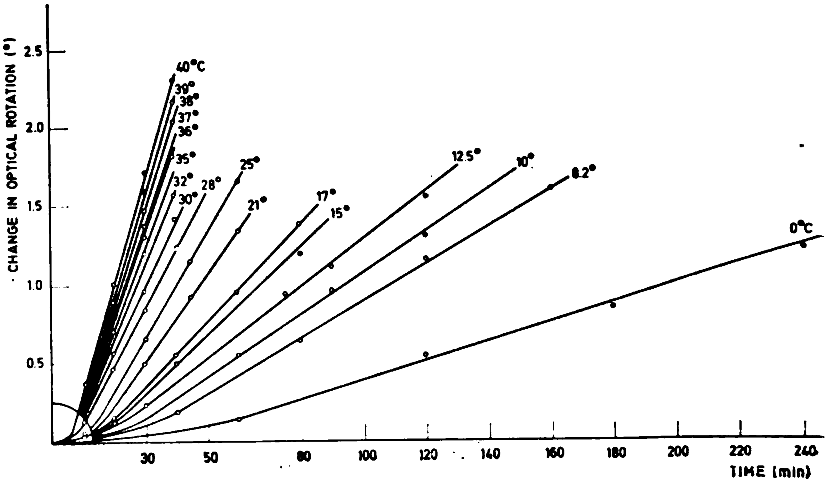

Figure 2
Invertase of thermotolerant strain S. Cerevisiae

TABLE 1

Brewer's yeast

Temperature (°C)	$1/T \cdot 10^3$ (1/°K)	$v \cdot 10^3$ (°/*min*)
0.2	3.660	7.65
11.0	3.521	16.3
14.0	3.484	19.6
16.0	3.460	23.4
20.0	3.413	29.0
21.3	3.398	31.4
25.0	3.356	37.6
30.0	3.300	46.2
35.0	3.247	59.0
39.0	3.205	70.0

For the commercial invertase

E = 7700 *cal/mol* for temperatures above 21.5°C

E = 11100 *cal/mol* for temperatures from 0° to 21.5°C.

TABLE 2

Thermotolerant strain of Saccharomyces cerevisiae

Temperature (°C)	$1/T \cdot 10^3$ (1/°K)	$v \cdot 10^3$ (°/*min*)
0	3.663	6.00
8.2	3.556	12.10
10	3.534	13.11
12.5	3.503	14.78
15	3.472	18.50
17	3.448	20.67
21	3.401	27.78
25	3.356	33.33
28	3.322	38.67
30	3.300	42.33
32	3.279	48.00
35	3.247	53.67
36	3.236	54.00
37	3.226	56.00
38	3.215	57.67
39	3.205	61.00
40	3.195	67.3

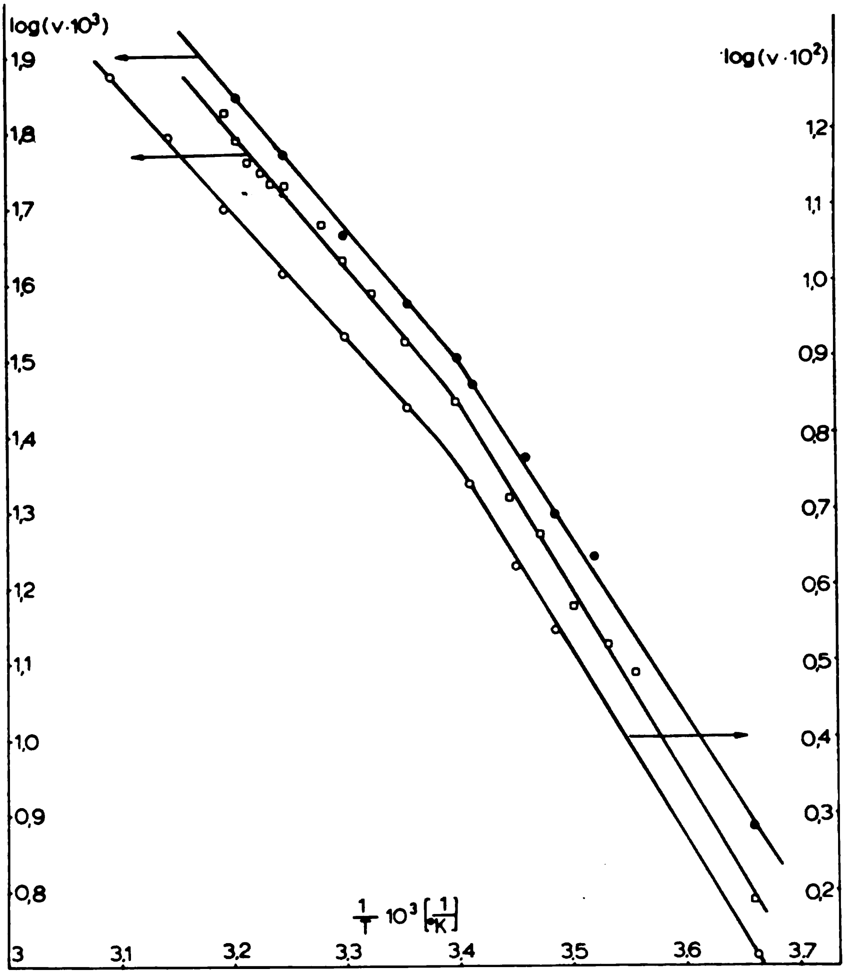

Figure 3

Energy of activation of invertase

● — Brewer's yeast (8.3; 11.0 *kcal/mol*)
□ — S. cerevisiae thermotol. (8.2; 11.4 *kcal/mol*)
○ — Commercial invertase (7.7; 11.1 *kcal/mol*)

Part II

In the second part of this study we compared the course of liberation of invertase from the cells of the thermotolerant strain of *Saccharomyces cerevisiae* during autolysis with that from cells of the same yeast cultivated at 30°C, and the yeast obtained from the brewery. Our aim was to find out whether thermophilization affected the rate of liberation of this enzyme during autolysis and plasmolysis in the presence of toluol.

TABLE 3

Commercial invertase (L. Light Co. LTD)

Temperature (^{0}C)	$1/T \cdot 10^3$ ($1/^0$K)	$v \cdot 10^3$ (^{0}/*min*)
0.2	3.666	1.30
13.9	3.486	3.48
16.9	3.450	4.23
20	3.413	5.42
25	3.356	6.86
30	3.300	8.56
35	3.247	10.34
40	3.195	12.58
45	3.145	15.60
50	3.096	18.93

Similar experiments, but with non-thermophilized yeasts, that is with several kinds of baker's yeast, brewer's yeast and saké yeast at an autolysis temperature of 25°C were done by Y. Yusa and S. Enokida(15), who found that for all kinds of yeast the maximum inversion was obtained after 72 hours of autolysis.

It has been found that the quantity of some yeast enzymes significantly decreases during thermophilization. Because of the reduced solubility of oxygen at higher temperature, systems are formed which allow more intensive anaerobiosis (fermentation enzymes and hydrolases) to compensate for the deficiency in the enzymes of aerobic respiration, which are, furthermore, sensitive to higher temperatures(19).

It was found that thermophilization of *Candida pseudotropicalis* at increasing temperatures reduced the quantity of hexokynase(16); thermophilization of *Saccharomyces cerevisiae* reduced the quantity of dehydrogenase by 1.5 to 2 times(17), and the quantity of catalase by 2.5 to 3 times(18), while the maltase of a thermotolerant strain of *Saccharomyces cerevisiae* cultivate on malt extract as the substrate was 42% more active than that of a normal strain(19).

In order to determine whether thermophilization changes the amount of invertase or its activity, and to what extent, the experiments with autolysis were also used to determine total invertase activity in the cells of both strains of *Saccharomyces cerevisiae,* and of the brewer's yeast.

As a measure of the liberation of invertase from the cells we used the inversion activity of the clear solution obtained after the removal of cells and their insoluble parts from the suspension, while the inversion activity of the suspension in which all autolysis and plasmolysis had taken place was used as a measure of the total content of invertase.

Enzyme activity was expressed in terms of constant inversion rates measured at 30°C under identical experimental conditions.

In view of the already established fact that the inversion activity per unit dry weight showed great differences for the yeasts under study, in order to measure the rates within approximately the same range of inversion in all cases, after autolysis the suspension was diluted with water in different ratios. For the same reason, the autolysis itself was done with different dilutions; with the wet brewer's yeast and *Saccharomyces cerevisiae* cultivated at 30°C the weight ratio of yeast to water was 1 : 3, while with the termotolerant strain it was 1 : 2.

EXPERIMENTAL

The biomass of *Saccharomyces cerevisiae* was obtained by multiplication of a pure culture according to the procedure described in Part I of this paper. Brewer's yeast was obtained from the factory "7 Juli", Beograd.

Autolysis was done according to instructions for rapid autolysis of yeast: to each 10 *g* of yeast 1 *ml* of toluol was added, and the mixture stirred for 3 hours at room temperature. It was then diluted with water in the required ratio and the pH adjusted to 5.8, which is the optimum pH for autolysis under these conditions.

The suspension was than put into a thermostat, in a container preventing evaporation, and after predetermined time intervals of several hours samples of the homogeneous suspension were taken by means of a pipette and put into measuring cylinders; the pipette was washed out with distilled water. A solution of acetate buffer, pH adjusted to 4.7 by adding dilute acetic acid, was added to the measuring cylinder which was then filled up with distilled water. The clear solution obtained by filtration was used for the determination of inversion activity at 30°C. The conditions of inversion and the method of determining the activity have been described in the first part of this paper.

In each experiment the content of solids in 10 *ml* of suspension was determined before autolysis, so that all the activities are expressed as constant inversion rates in °/*min* per *g* dry weight of yeast.

In each experiment of autolysis the activity of the solution was also determined after 3 hours of treatment with toluol and dilution with water but before exposure to the temperature of autolysis. The total inversion activity of the yeast was measured after certain time intervals by taking samples in the described way, but without removal of the solid cell remnants by means of filtration. After exposure of a solution of saccharose to the action of this suspension, to obtain better clearing, the test samples were inactivated, but instead of sodium hydroxide solution this was done with 2 *ml* of lead acetate solution to which anhydrous sodium carbonate was added after pouring in the sample.

All three kinds of yeast were analysed: nitrogen content was determined by Kjeldahl, ash and P_2O_5 by volumetric methods.

RESULTS AND DISCUSSION

The analyses of the three kinds of yeast may be seen in Table 4.

The content of nitrogen and phosphorus shows that the composition of the cell was within the limits of normal, that is that during multiplication there was no deficiency of nitrogen or phosphorus.

TABLE 4

Yeast	% (of dry weight)		
	Nitrogen	Ash	P_2O_5
Brewer's yeast	9.64	7.85	4.04
Saccharomyces cerevisiae (cultivated at 30°C)	7.67	7.92	3.95
Saccharomyces cerevisiae (cultivated at 40°C)	6.80	7.75	3.00

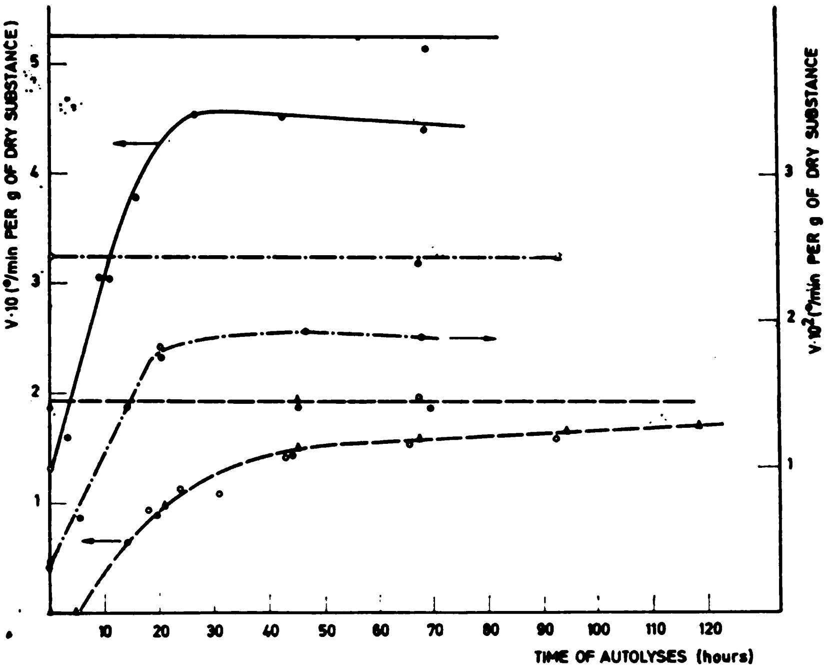

Figure 4

Autolysis t = 30°C

——— Brewer's yeast
— — — S. cerevisiae
.—.—. S. cerevisiae thermotol.

● I run
○ II run
△ III run

Tables 5, 6 and 7 show the constant inversion rates calculated per *g* of dry weight, for different times of autolysis and all three kinds of yeast.

The course of autolysis at 30°C for all three yeasts is shown in Fig. 4. The inversion rates per *g* of dry weight are shown on the ordinate, and the duration of autolysis in hours on the abscissa.

TABLE 5

Brewer's yeast
Temperature of autolysis: 30°C

Duration of autolysis (hours)	v. 10 (°/min g dry weight)
0	1.31
3.5	1.61
8	3.07
10.5	4.05
12	3.80
26	4.55
42	4.55
68	4.41
68	5.15 (suspension)

The activity at 0 hours of autolysis refers to the solution after 3 hours of treatment with toluol and represents the initial point of the graph. The maximum activity which could be obtained from the entire autolysate is shown by the straight line.

The maximum inversion activity of the brewer's yeast was $5.25 . 10^{-1}$ ^{c}/*min* per *g* dry weight. Treatment with toluol released 22% of the invertase from the cells, and after about 25 hours 88% of the invertase went into solution. This percentage was not further increased with prolongation of the autolysis.

The activity of the suspension of the thermotolerant *Saccharomyces cerevisiae* was $2.45 \cdot 10^{-2}$ °/*min* per *g* dry weight. After treatment with toluol 13% of the invertase was released into solution, and after 25 hours the maximum percentage (81%) of autolysis was reached, as regards the quantity of invertase, which was not further increased by prolongation of the autolysis.

The maximum activity of invertase from *Saccharomyces cerevisiae* cultivated at 30°C was $1.93 \cdot 10^{-1}$ °/*min* per *g* dry weight. The cells of this yeast were the most resistant to the release of invertase under the influence of toluol and heat. Under the influence of toluol alone no invertase at all was released; after approximately 70 hours of autolysis 85% had gone into solution, which was not increased by further autolysis.

Figure 5 shows the course of autolysis of the thermotolerant strain at three different temperatures: 30, 36 and 40°C. The maximum percentage of invertase in solution was not higher at the higher temperatures (36 and 40°C), because along with autolysis there is a parallel process of thermal inactivation, as may be seen from shape of the corresponding curves in the graph.

TABLE 6

Thermotolerant strain of Saccharomyces cerevisiae
Temperature of autolysis: 40°C

Duration of autolysis (hours)	v. 10^2 (°/min g dry weight)
0	0.34
5	1.29
20	1.46
45	1.18
70	0.99

Temperature of autolysis: 36°C

Duration of autolysis (hours)	v. 10^2 (°/min *g* dry weight)
0	2.45 (suspension)
0	0.32
4	0.88
8	1.14
18.5	1.41
27	1.47
44.5	1.17
54	1.22
72	1.03

Temperature of autolysis: 30°C

Duration of autolysis (hours)	v. 10^2 (°/min *g* dry weight)
5.5	0.64
14	1.41
20	1.76
20	1.83
46	1.93
67	1.88
67	2.39 (suspension)

Figure 6 compares autolysis at 30°C, expressed in terms of released invertase as a percentage of total invertase, for all three yeasts.

The course of invertase release by the thermotolerant strain and brewer's yeast is similar; in the cells of the thermotolerant strain a greater proportion of the invertase firmly bound to the cell structure. The yeast from *Saccharomyces cerevisiae* cultivated at 30°C released invertase much more slowly than brewer's yeast and the amount of invertase which it was possible to extract from it under these conditions was less. However with the thermotolerant strain this was still less.

As regards the invertase which is firmly bound to the cell wall there is an opinion⁽²⁰⁾ that in the production of the enzyme first an insoluble

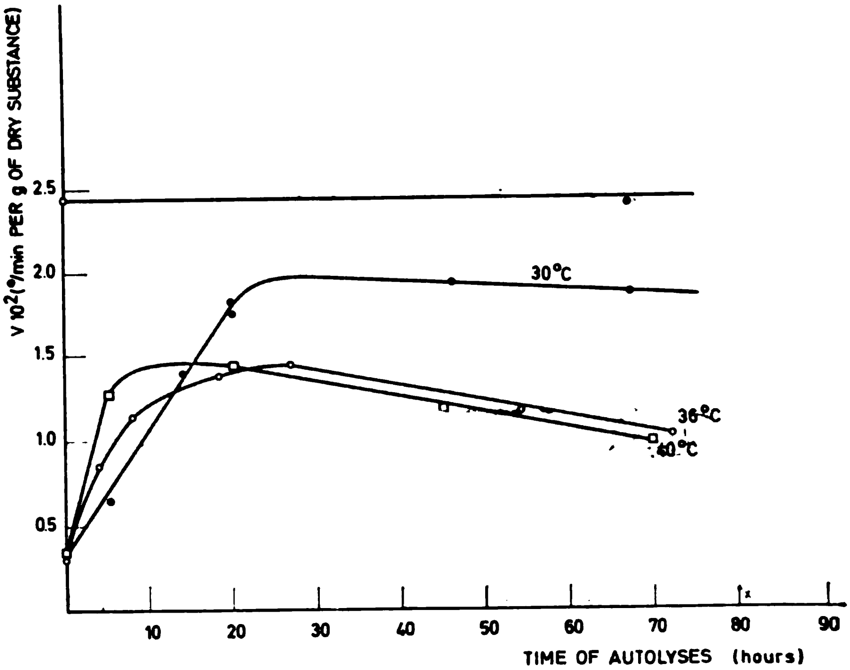

Figure 5

Autolysis of S. cerevisiae thermotol.

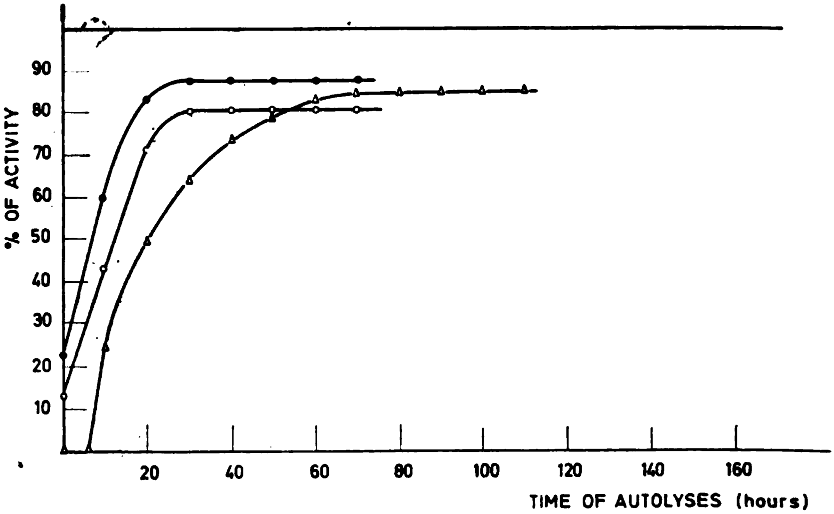

Figure 6

Invertase activity

● Brewer's yeast
△ S. cerevisiae
○ S. cerevisiae thermotol.

TABLE 7

Saccharomyces cerevisiae propagated at 30°C

Temperature of autolysis: 30°C

Duration of autolysis (hours)		v. 10 (°/min *g* dry weight)
1st run	0	1.89 (suspension)
	0	0
	5	0
	21	0.99
	45	1.55
	45	1.97 (suspension)
	69	1.66
	94	1.67
	118	1.69
2nd run	0	0
	18	0.97
	24	1.14
	43	1.40
	67	1.61
	67	1.98 (suspension)
3rd run	9	0.35
	20	0.89
	31	1.07
	44.5	1.41
	92	1.59
	45	1.87 (suspension)
	69	1.87 (suspension)

enzyme is formed, most of which becomes soluble under the influence of enzymes like papain, while about 15% remains bound to the cell wall in insoluble form. According to our results, this proportion is increased by thermophilization from 15 to 19%.

The content of invertase in the thermotolerant strain of *Saccharomyces cerevisiae,* determined in the above way, is about 21 times smaller than in brewer's yeast, and about 8 times smaller than in the same yeast before thermophilization, or the invertase is that much less active.

Since increasing the temperature from 30 to 40°C increased the rate of inversion by less than twice (Part I of this study), and since the content of invertase is reduced 8 times by thermophilization, it follows that the ability of the yeast living at 40°C to hydrolyse saccharose is 4 times less.

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Original Scientific Paper

POLAROGRAPHIC DETERMINATION OF LEAD IN THE PRESENCE OF TIN*

by

SRETEN N. MLADENOVIĆ and MILENKO GEMOVIĆ

The method(1) for the determination of lead in zinc cannot be used if the zinc contains tin, because of superposition of the waves of lead and tin.

The other polarographic method for the determination of lead(2) in the presence of cadmium and zinc, in which lead is first precipitated in the presence of a strontium sulphate collector and after dissolving the precipitate with complexon III lead is determined polarographically, is rather time consuming.

On the basis of the fact that in acid solutions of complexon III tin forms more stable complex compounds than lead, we have developed a method for rapid polarographic determination of lead in the presence of tin and large quantities of zinc.

In all determinations a Radiometer PO4 polarograph was used.

The results of polarographic determination of lead in acid solution of complexon III are shown in Table 1.

TABLE 1

Indifferent electrolyte:

10 *ml* conc. HCl/*lit* + 75 *g* KCl/*lit* + 10 *g* complexon III/*lit* + 0.2 *g* gelatin/*lit*

Lead *mg*/10 *ml*	Wave height in *mm*
0.10	42.0
0.20	85.0
0.30	127.0
0.40	168.0
0.50	209.0

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* Communicated at the 2nd Yugoslav Congress for Pure and Applied Chemistry, Belgrade, 16—19 June, 1966.

The results in Table 1 show that lead does give waves in acid chloride electrolyte in the presence of complexon III and that there is a linear correlation between the amount of lead and the step height. The concentration of hydrochloric acid in the indifferent electrolyte influences this height, as seen from Table 2.

TABLE 2

Influence of the concentration of hydrochloric acid on the height of the lead wave:

Indifferent electrolyte: *x ml* conc. HCl/*lit* + 75 *g* KCl/*lit* + 10 *g* complexon III/*lit* + + 0.2 *g* gelatin/*lit*;

Volume of indifferent electrolyte: 10 *ml.*

x	Wave height (in mm)		
	0.20 *mg* Lead	0.30 *mg* Lead	0.40 *mg* Lead
2.5	2.6	3.9	5.1
5.0	38.0	57.5	76.0
10.0	85.0	127.0	169.0
20.0	80.0	121.0	161.0
40.0	80.0	119.0	160.0

It is concluded from the results in Table 2 that for the same quantity of lead the wave height increases with increasing concentration of hydrochloric acid up to x = 10 *ml/lit* or ~ 0.12 N HCl.

It is concluded from the polarogram (Fig. 1) that the waves of lead and tin in this electrolyte are well resolved. The half-wave potential of lead relative to the saturated calomel electrode is ~ —0.45 *V*, and of tin ~ —0.65 *V*. Although the amount of tin was 20 to 100 times greater than that of lead, the steps of tin are smaller than those of lead, which is explained by the formation of a complex of tin with complexon III.

Step heights in the polarographic determination of lead in the presence of tin in an acid indifferent electrolyte with complexon III and without it are shown in Table 3.

It is concluded from the results in Table 3 that in the indifferent electrolyte with complexon III the wave height is proportional to the quantity of lead. Because of superposition of the waves of lead and tin in the indifferent electrolyte without complexon III it is not possible to calculate the quantity of lead.

In the polarographic determination of both pure lead and of lead in the presence of tin in the indifferent electrolyte with complexon III the wave height of lead increases with increasing concentration of hydrochloric acid up to a concentration of 10 *ml/lit.* The influence of the hydrochloric acid concentration on the wave height for the same quantity of lead in the presence of tin is shown in Table 4.

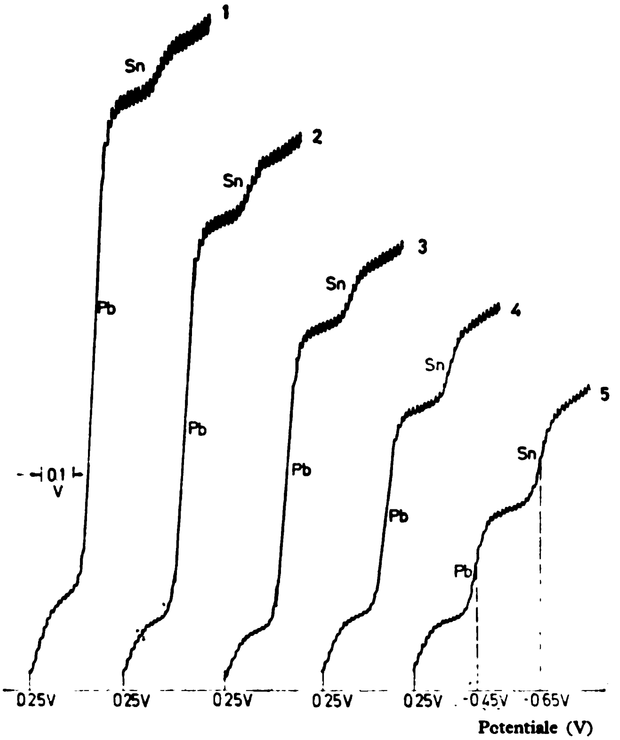

Figure 1

Indifferent electrolyte: 10 *ml* conc. HCl/*lit* + 75 *g* KCl/*lit* + 10 *g* complexon III/*lit* — 0.2 *g* gelatin; volume of indifferent electrolyte: 10 *ml*

1) 10 *mg* Sn + 0.5 *mg* Pb; 2) 10 *mg* Sn + 0.4 *mg* Pb; 3) 10 *mg* Sn + 0.3 *mg* Pb; 4) 10 *mg* Sn + 0.2 *mg* Pb; 5) 10 *mg* Sn + 0.1 *mg* Pb.

TABLE 3

Indifferent electrolyte: 10 *ml* conc. HCl/*lit* — 75 *g* KCl/*lit* — 0.2 *g* gelatin/*lit* — 10 *g* complexon III/*lit* or without it; volume of indifferent electrolyte: 10 *ml.*

Lead in *mg*/10 *ml* of indifferent electrolyte	Tin (II) in *mg*/10 *ml* of indifferent electrolyte	Wave height in the indifferent electrolyte	
		with complexon III	without complexon III
0.10	4.0	30.0	47.0
0.20	4.0	61.0	80.0
0.30	4.0	91.0	105.0
0.40	4.0	119.0	133.0
0.50	4.0	150.0	162.0

It is concluded from the results in Table 4 that from the point of view of economy and sensitivity of the method, the optimum concentration of hydrochloric acid is 10 *ml* per liter of electrolyte (—0.12 N HCl).

TABLE 4

Indifferent electrolyte: x ml conc. HCl/*lit* + 75 *g* KCl/lit + 10 *g* complexon III/lit + + 0.2 *g* gelatin/lit; volume of the indifferent electrolyte: 10 *ml*.

x	Tin in *mg*/10 *ml* of indiff. electrolyte	Wave height, in mm.		
		0.20 *mg* of lead	0.30 *mg* of lead	0.40 *mg* of lead
2.5	1.0	3.1	4.5	6.0
5.0	1.0	29.0	44.0	59.0
10.0	1.0	61.0	91.0	121.0
20.0	1.0	60.0	90.0	120.0
40.0	1.0	61.0	90.0	120.0

The results of our experiments show that it is possible to determine lead in the presence of tin by polarography in acid chloride indifferent electrolyte with complexon III. This fact has already been used for the determination of lead in the presence of tin in zinc.

In the polarographic determination of lead in zinc with a certain amount of tin in acid chloride indifferent electrolyte with complexon III, the undesirable effect of tin is removed, which is not the case in polarographic determination of lead according to the ASTM method(1).

Our new procedure for the determination of lead in zinc which contains tin is simple:

1.000 *g* of zinc is dissolved in a 100 *ml* beaker with 10 *ml* of hydrochloric acid (1 + 1), and the solution is evaporated to dryness. Then 10 *ml* of the indifferent electrolyte is poured over the cooled dry residue. The electrolyte composition is: 10 *ml* HCl/*lit* + 75 *g* KCl/*lit* + 10 *g* complexon III/*lit* + 0.2 *g* gelatin.

After the introduction of hydrogen lead is determined in the solution by polarography. Another sample of 1.000 *g* of zinc is treated in an absolutely identical way, but before dissolution the amount of lead which is expected in the zinc is added.

The reproducibility of the determinations of lead from different samples of zinc to which a variable quantity of tin had been added shows that the method can be successfully used for the determination of lead in zinc which contains tin.

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Original Scientific Paper

POLAROGRAPHIC DETERMINATION OF COPPER IN THE PRESENCE OF CADMIUM AND ZINC*

by

SRETEN N. MLADENOVIĆ

Colorimetric methods for the determination of copper using the sodium salt of diethyldithiocarbamate, cupral(1, 2), are usually applicable for solutions which do not contain more than 1 *mg/lit* of copper and have a high content of cadmium and zinc (60 *g/lit* of each). Besides cadmium and zinc these solutions also contain a lot of sulfuric acid (100 *g/lit*). In solutions with so small a concentration it is not possible to determine copper polarographically without increasing its concentration.

It is not possible to increase the concentration of copper in an electrolyte for the determination of cadmium which also contains zinc by evaporation: during evaporation, because of its saturation in the salts of cadmium and zinc, the electrolyte rapidly turns into a syrupy mass without obtaining the desired concentration of copper.

Copper can be precipitated, i.e. concentrated from solutions with a high content of cadmium and zinc by means of a certain amount of cadmium sulfide. The solubility product of aqueous solution of cadmium sulfide, L_{CdS}, at 18°C is $3.6 \cdot 10^{-29}$; that of cupric sulfide, CuS, at 18°C is $8.5 \cdot 10^{-45}$.

In the presence of cupric sulfide and cadmium sulfide the activity of sulfide ion, $a_{S^{2-}}$, is given by the formula

$$a_{S^{2-}} = \frac{L_{CdS}}{a_{Cd^{2+}}} = \frac{L_{CuS}}{a_{Cu^{2+}}} \tag{1}$$

The activity of cupri ion, $a_{Cu^{2+}}$, in a solution in the presence of sulfide is calculated from equation (1):

$$a_{Cu^{2+}} = \frac{L_{CuS} \cdot a_{Cd^{2+}}}{L_{CdS}} \tag{2}$$

Equation (2) shows that the activity of cupric ion, that is the concentration of copper in a solution of cadmium sulfide, depends on the ratio of the solubility products of cupric sulfide and cadmium sulfide, $\frac{L_{CuS}}{L_{CdS}}$,

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* Communicated at the 2nd Yugoslav Congress for Pure and Applied Chemistry, Belgrade, 16—19 June, 1966.

and on the activity of cadmium ion in the solution. As this ratio is very low ($\sim 24 \cdot 10^{-17}$ at 18°C), the concentration of cupric ions in the solution in the presence of cadmium sulfide after the establishment of the equilibrium

$$CdS + Cu^{2+} \rightleftarrows CuS + Cd^{2+} \qquad (3)$$

will be practically independent of the cadmium ion concentration.

Complete precipitation of copper by means of cadmium sulfide depends on the rate of decomposition of cadmium sulfide, that is on the rate of formation of cupric sulfide. To obtain complete precipitation it is essential that the amount of precipitated cadmium sulfide be greater than the equivalent amount of copper in the solution.

In solutions in which there is much more cadmium than copper, all the cadmium is not necessarily precipitated in the form of sulfide; an amount of cadmium sulfide in excess of the equivalent amount of copper is sufficient to precipitate all the copper in the form of sulfide and to act as a good collector for the copper sulfide(3). The separation of copper from larger amounts of cadmium and the concentration of copper are based on this property.

Polarographic determinations of copper after dissolution of the precipitate of cadmium and copper sulfide confirm the possibility of total precipitation of copper with cadmium as the collector.

Table 1 shows the polarographic wave heights of copper after the dissolution of cadmium and copper sulfide precipitated with 5 *ml* of 5% solution of sodium sulfide in 100 *ml* of solution in the presence of 100 *mg* of cadmium.

TABLE 1

Indifferent electrolyte: KCl (1 : 1)
Volume of indifferent electrolyte: 16.0 ml.

Copper, *mg*	Wave height, *mm*
0.5	9.0
1.0	18.0
2.0	36.5
3.0	54.0
4.0	71.5
5.0	90.5

It may be concluded from the results shown in Table 1 that the wave height of copper is proportional to the quantity of copper in the solution.

The results in Table 2 represent the wave heights of copper after the dissolution of cadmium and copper sulfide precipitated with 5 *ml* of a 5% solution of sodium sulfide from 100 *ml* of a solution containing 6 grams of cadmium.

It is concluded from the results shown in Table 2 that it is also possible to quantitatively separate copper from solutions contain high concentrations of cadmium.

TABLE 2

Indifferent electrolyte: HCl (1 : 1)

Volume of indifferent electrolyte: 16.0 ml

Copper, *mg*	Wave height, *mm*
0.5	7.0
1.0	13.0
2.0	26.0
3.0	39.5
4.0	52.0
5.0	65.0

The experiments of Table 3 show that it is possible to quantitatively separate copper from solutions which contain 6 grams of cadmium and zinc by using 5 *ml* of 5% solution of sodium sulfide. After the dissolution of the sulfide, copper is determined polarographically. Wave heights are shown in Table 3.

TABLE 3

Indifferent electrolyte: HCl (1 : 1)

Volume of indifferent electrolyte: 16.0 ml

Copper, *mg*	Wave height, *mm*
0.5	7.0
1.0	14.0
2.0	28.0
3.0	41.5
4.0	56.5
5.0	70.5

Quantitative precipitation of copper from solution which contain a lot of cadmium and zinc by sodium sulfide was also checked by the colorimetric determination of copper (cupral method⁽²⁾) in the filtrate after precipitation of the sulfide. The greatest amount of copper found in the filtrate was 5 γ or $<1\%$, which is less than the usual error in polarographic determinations.

In electrolytes for the production of cadmium which contain about 60 grams of cadmium and the same of zinc per liter, after the precipitation with sodium sulfide and dissolution of the precipitate it is possible to determine copper reliably. Considering that this procedure takes longer than the colorimetric determination of copper, it is only applied when the concentration of copper in the solution exceeds 1 *mg/lit.*

The procedure itself for the determination of copper in the presence of cadmium and zinc is as follows:

100 *ml* of cadmium electrolyte is diluted with water to 200 *ml* and the pH adjusted (pH = 0—1). To this electrolyte 5 *ml* of 5% solution of sodium sulfide is added dropwise with constant stirring. Then the solution is heated with continuous stirring. After cooling the solution is filtered through thick filter paper and the precipitate washed with cold water. The precipitate together with the filtrate is transfered to the beaker in which the precipitation was done, the precipitate then being dissolved with about 20 *ml* of hot hydrochloric acid (1 : 1) with the addition of 2 *ml* of concentrated nitric acid. The solution is then filtered through filter paper of medium thickness and the filter paper washed with hot water. The filtrate is evaporated to dryness. 15.0 *ml* of hydrochloric acid (1 : 1) and 1.0 *ml* of 0.5% solution of gelatin are added to the dry residue. Finally, after the introduction of hydrogen into the electrolyte, copper is determined by polarography. Another sample is run in exactly the same way with 100 *ml* of the cadmium electrolyte, to which a predetermined amount of copper is added before the dilution whith water.

This procedure for concentrating copper from a solution with a lot of cadmium by means of cadmium sulfide, which is more soluble than copper sulfide, can be used as a model for the concentration and separation of traces of metal in the presence of large amounts of another metal if:

a. both metals form poorly soluble compounds with the same reagent and
b. the solubility product of the compound of the trace metal is much smaller than that of the compound formed by the other metal.

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Original Scientific Paper

THE MECHANISM OF FORMATION OF NEW PHASES IN THE SILICON-MANGANESE SYSTEM

by

MIODRAG Đ. JANČIĆ and LJILJANA M. RADONJIĆ

I. INTRODUCTION

The formation of new phases (intermetalic compounds) in the solid phase by reactive diffusion is today a subject of intensive research. Although reactions in the solid phase have been used for the treatment of various materials for a long time, there is no complete theoretical explanation of this complex phenomenon.

In his studies of binary metal-gas systems Arkharov(1–5) defined the basic characteristics of the mechanism of reactive diffusion. Rodigin(6) and Borisov(7) have given the mathematical interpretation of reactive diffusion in a binary system producing an arbitrary number of phases. They also give the concentrations distribution of the diffusing components, the speed at which the boundaries move due to diffusion through each of the monophasic layers, and the chemical reactions in the solid phase. Janssen(8) studied reactive diffusion and the Kirkendall effect in the nickel-aluminum system, but only from the kinetic point of view and not from the aspect of the mechanism.

As far as can be seen from the literature neither the mechanism nor the kinetics of the formation of new phases in the transition metal (Mn)-semiconductor (Si) system have so far be studied.

The main aim of the present study was to determine the mechanism of formation of new phases in this system of intermetallic compounds, at the contact of two components, one of which is a single crystal with a known orientation. On this simple system it is easier to determine which factors determine the mechanism of reaction in the solid state. Our work in the Si-Mn system is part of a study of the mechanism of reactive diffusion in the silicon-transition metal (Mn, Cr, Ni, Fe) system which was chosen because of the characteristic electron configuration of the transition metals — an unifilled d-level which overlaps with the s-level, or in quantum mechanical terms, the *s* and *d* states have the same wave functions. By studying the solid state reaction of the silicon-transition system metal it should be possible to determine how the degree of the incompleteness of the d-level affects the mechanism and rate of reaction and also the main characteristics of the mechanism of reactive diffusion.

During this work a new technique for the preparation of the diffusion pair was developed. The kinetics of growth of new phases and the calculation of the diffusion coefficients have already been described⁽⁹⁾.

The diffusion pairs were analyzed metallographically by means of X-ray phase analysis and by measuring the microhardness. The concentrations at the phase boundaries and the concentration profiles of each phase, which are necessary for the calculation of the diffusion coefficients of the components, were obtained by means of an electronic probe.

2. EXPERIMENTAL

Preparation of the samples

The silicon 9N was in the shape of a parallelepiped 10 × 5 × 2 *mm* and the electrolytic manganese 4.5 N in granular form.

Silicon plates of orientation (111) and (100) were polished, and soaked in manganese in evacuated (5×10^{-3} *mm* Hg) quartz ampules. The diffusion experiment was run at the following temperatures: 700, 800, 900, 1000, 1050 and 1100°C, for a time of from 1 to 6 hours.

The samples were metallographically prepared by soaking in metacrylate and after careful working etched with 10% HF in alcohol.

X-ray diffraction, measurement of microhardness and the electronic probe

The occurrence of new phases after microscopic examination was detected by means of X-ray phase analysis. The samples were ground in a mortar and the powder was soaked into capillaries. The diffraction was done with CuK-α radiation using an Ni filter.

The microhardness was measured on a Reichert indenter. A loading of 80 *g* was applied for 10 seconds. Because of cracks in the newlycreated phases and because of their brittleness the measurements were rather difficult and on some samples even impossible.

3. RESULTS

After the diffusion treatment at high temperature the samples had a matt grey color and were very brittle.

The results of microscopy, X-ray diffraction and the electronic probe tests are shown in Table 1.

TABLE 1

Results for the interdiffusion zone

System		Number of layers	Date of X-ray and elec. probe analysis	Position of marker
MnSi	700 — 1000	2	1. Outer layer Mn_5Si_3 2. Inner layer $MnSi_2$	Between layers
	1000 — 1100	2 or 3	1. Outer layer Mn_5Si_3 2. Middle layer MnSi 3. Inner layer $MnSi_2$	Between layers

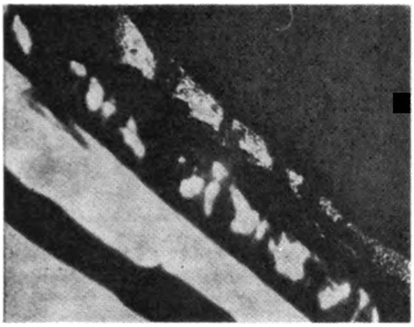

Figure 1

Si-Mn diffusion pair after 5 hours at 1000°C; magnification × 316

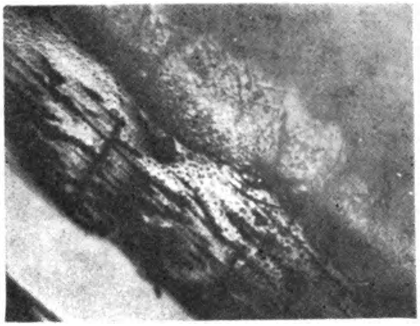

Figure 2

Si-Mn diffusion pair after 4 hours at 900°C; magnification × 316

The marker (tungsten wire Ø 7 microns) is between the outer and the inner layer

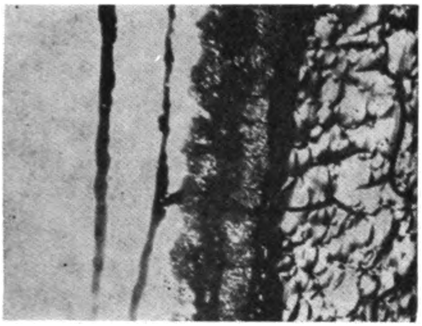

Figure 3

Si-Mn diffusion pair after 6 hours at 1100°C; magnification × 316

Microscopic studies

On the microscopic section the stratified character of the products of reactive diffusion was clearly visible. In the temperature range between 700 and 1000°C there were two layers (Figs. 1 and 2). The outer layer was bright, compact, and the inner one darker, finely crystalline and fissured and in good contact with the base.

At 1000 and 1100°C three layers occurred. The third layer was very thin (Fig. 3) and difficult to analyse. The thickness ratio of the layers changed with increasing temperature. The first layer became thicker while the second became more compact and coarsely crystalline. The results of kinetic studies of this system have already been reported(9).

X-ray analysis and microhardness measurements

The influence of the Si base orientation on the newly-formed phases was studied by the Laue method. Figures 4 and 5 show the diffraction patterns of the layer at the initial stage of growth and the diffraction pattern of the silicium itself.

It is seen from Figs. 4 and 5 that the diffraction patterns are almost identical, which is proof that the newly-formed phase has the same structure and grows in the (111) direction of the silicon. This growth of the base soon ceases and further layers become polycrystalline. Only the strongest lines and those whose existence was doubtful are indicated.

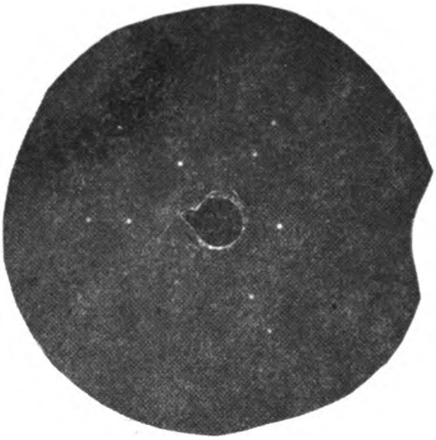

Figure 4

Diffraction pattern of silicon single crystal

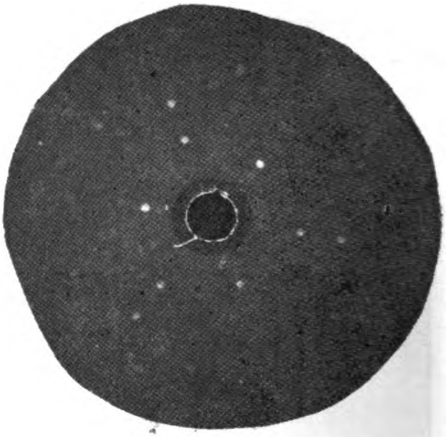

Figure 5

Diffraction pattern of the interdiffusion zone after 30 minutes at 900°C

The microhardness of the measurements newly formed phases are shown in Table 2. It is seen that there is quite a difference between the phases as regards microhardness (mean values of five measurements).

TABLE 2

Microhardness of the layers formed

t°C	Layer I (kg/*mm*²)	Layer II (kg/*mm*²)
900	1100	950
1000	1010	960
1100	910	960

At the highest temperature, 1100°C, there was a decrease of microhardness. The accuracy of these measurements was not great because of the great brittlness of the layers (the impressions were of rather irregular shape so that the possibility of error was also greater). The hardness was calculated according to the formula

$$H_{\mu} = 1854 \frac{P}{d^2} \text{ kg}/mm^2$$

P = force in grams

d = diameter of the impression multiplied by the coefficient k = = 0.16145 (value in microns).

Results with the electronic probe

The concentration profile of the components in the interdiffusion zone was determined and the identification of the newly-formed phases checked from the recordings made with an electronic micro-probe of silicium and manganese (Figs. 6 and 7).

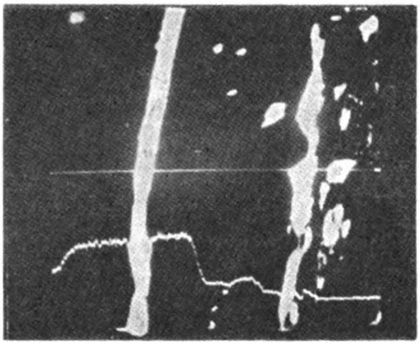

Figure 6

Distribution of Si in the interdiffusion zone

Figure 7

Distribution of Mn in the interdiffusion zone

The diffusion coefficients of the components through the newly-formed phases (at 1000°C for 5 hours) were calculated by the method suggested by Borisov$^{(7)}$ from the equilibrium state diagram of Si-Mn and the concentrations distribution curve of silicium and manganese in the interdiffusion zone (Figs. 6 and 7). The calculated values (D δ) for silicium and manganese through the different phases were:

$$(D_1 \delta_1)^{Mn}_{Mn_5Si_3} = 1.02 \times 10^{-7} \% \; cm^2/sec$$

$$(D_2 \delta_2)^{Mn}_{MnSi} = 5.31 \times 10^{-8} \quad ,,$$

$$(D_3 \delta_3)^{Mn}_{MnSi_2} = 4.07 \times 10^{-8} \quad ,,$$

$$(D_1 \delta_1)^{Si}_{MnSi_2} = 3.05 \times 10^{-8} \quad ,,$$

$$(D_2\,\delta_2)^{\mathrm{Si}}_{\mathrm{MnSi}} = 2.71 \times 10^{-8} \qquad ,,$$

$$(D_3\,\delta_3)^{\mathrm{Si}}_{\mathrm{Mn_5Si_3}} = 1.39 \times 10^{-8} \qquad ,,$$

The formation of phases Mn_3Si_5 ($MnSi_2$) and Mn_5Si_3 was observed at all temperatures, while MnSi formed in only some samples. The samples from 700°C were not investigated. The concentration values obtained approximately corresponded to the stoichiometric formula. Considerable deviations from stoichiometry were observed with $MnSi_2$(12). This has already been studied and according to some authors(10) a phase of the formula $MnSi_2$ does not even exist, but rather $MnSi_{1.7}$, which is explained by the existence of vacancies in the sublattice of silicium (111). However, this hypothesis has not yet been proved.

4. DISCUSSION

In order to elucidate the basic characteristics of the mechanism of formation of intermetalic compounds in the silicium-manganese system from the experimental data, two fundamental problems must first be solved:

1. the mechanism of formation of different phases in the interdiffusion zone, the degree of participation of the components in these phases;
2. in which crystallographic elements of the lattice does the diffusion movement of the components occur; does an atom of a given component move only via vacancies of its own sublattice or can it also use vacancies of other components?

As already reported(9), the growth of the new phases obeys the parabolic law, which is a proof that the rate of formation determines the diffusion process (sic).

The mechanism of reactive diffusion is determined mainly by three factors: 1. — the ratio of the dimensions of the diffusing particles; 2. — the crystall geometry of the reaction products; 3. — the nature of the forces which bind the components of the system(3).

The transition metals form with silicium a mixed, iono-homeopolar bond(13). The degree of participation of the components in the diffusion process depends on the relative contribution of the homeopolar bond.

It is known that manganese more than any other transition metal forms "ionic bonds" with silicium(14). The homeopolar bond between Si and Mn is realized by an electron exchange, p-electrons of Si completing the d-level of manganese. The elementary function of diffusion causes a redistribution of the electronic density such that Si gives up some of its electrons to the neighboring manganese atoms. In this way a "positive" silicium ion is formed, which can occupy a metal vacancy. The local redistribution of electronic density preserves the electrical neutrality of the atomic complex surrounding the silicium ion in a vacancy of the manganese sublattice.

Thus silicium can diffuse not only via vacancies of its own sublattice but also via those of the manganese sublattice. This effect increases with the increasing contribution of the homeopolar bond, together with the increasing number of defects in the cationic sublattice, i.e. the number of possible vacancies for the migration of silicium atoms (or ions). All this brings about the diffusion of silicium.

With increasing contribution of the homeopolar bond the positive charge of the manganese decreases, which means that the ionic radius increases and the diffusion mobility decreases. The great diffusion mobility of manganese in the Si-Mn system is explained by the greater proportion of ionic bond which facilitates diffusion.

From analysis of the structural characteristics of the newly-formed intermetalic compounds it may be concluded that diffusion is double. This is indicated by the position of the marker, the presence of growth texture in the outer layer, traces of stresses during the formation of phases, and by the double layer interdiffusion zone.

Silicium diffuses through the layers towards the outer surface of the sample (evidence for this is the presence of texture in the outer layer, fissures in the zone next to the base, position of the marker), where free growth of the crystals occurs. Because of the migration of silicon from the inner layer next to the base, this layer becomes porous (Fig. 2). Manganese diffuses through the interdiffusion zone towards silicium and the inner layer grows at the boundary of the silicium and the interdiffusion zone. This layer is sandwiched between solid phase, and because of the difference in the dimensions of the unit cells it becomes stressed from the very beginning, which causes rupturing and the formation of a finely crystalline structure. Recrystallization and growth of the granules within the layer was not observed.

The relative contributions of manganese and silicium to the diffusion through the interdiffusion zone change with temperature. At high temperatures (Fig. 3) the rate of diffusion of manganese was higher that that of silicium, so that the inner layer, growing by the manganese diffusion, became thicker than the outer one. At lower temperatures (Figs. 1 and 2) the layer thickness ratio was approximately the same, which means that the diffusion rates of silicium and manganese were about the same.

It is hypothesized that the compound Mn_3Si_5 is formed on the surface of the silicium during the initial phase of the process. This thin layer has the same structure as the Si base, as evidenced by its diffraction pattern (Fig. 4). Later on manganese diffuses through the Mn_3Si_5 phase towards its boundary with silicium, and silicium diffuses towards the outer boundary of the Mn_3Si_5 and with the manganese forms Mn_5Si_3.

It may be concluded from the microhardness values (Table 2) that Mn_3Si_5 has more ionic bonding than Mn_5Si_3. This can be explained in terms of the greater statistical weight of the configuration sp^3 in the compound Mn_3Si_5. The stabilization of the sp^3 configuration of silicium is contributed to by the influence of the s^2 electrons of manganese. Manganese has a low microhardness because of the great contribution of non-localized electrons to the bond, regardless of the great stability of the d^5 configuration, as the hardness decreases with decreasing number of non-localized electrons.

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Original Scientific Paper

OSCILLOGRAPHIC-CHRONOPOTENTIOMETRIC TITRATION. II.*

INFLUENCE OF DIRECT CURRENT AND OF THE COMPOSITION OF THE TITRATED SOLUTION ON THE ACCURACY**

by

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and TIBOR A. KIŠ

In oscillographic-chronopotentiometric titration the end-point is determined from the sudden distortion of oscillogram(1). The larger and better visible the distortion the greater is the accuracy of determination. From the principles of the method(1) it ensues that the magnitude of the distortion depends on many factors: the change of the d.c. potential of the indicator electrode at the end-point, composition of the titrated solution, parameters of the alternating current circuit, the electrodes, etc.

The aim of the present experiments was to study the influence of the first two factors in the titration of arsenic (III) with potassium bromate, their influence also having been theoretically predicted.

According to the principles of oscillographic-chronopotentiometric titration(1) the magnitude of the oscillograph distortion is directly proportional of the change in the d.c. potential of the indicator electrode. It is known from ordinary potentiometry that the potential change is inversely proportional to the direct current. We therefore tried to determine the end-point by the oscillographic-chronopotentiometric method: *a* — when a high direct current is flowing through the system (amperometric titration with superimposed low and high voltage a.c.), *b* — when the direct current is zero (potentiometric titration with superimposed high voltage a.c.), and *c* — at a low direct current.

In ordinary potentiometric titration the change in the indicator electrode d.c. potential at the end-point is directly proportional to the concentration of the titrated substance and to the concentration of the standard solution, for which reason we assumed that the magnitude of the oscillographic distortion would be greater at higher concentrations of titrated substance of the standard solution.

From the principle of this method of end-point determination(1) it is possible to predict that by using higher concentrations of indicator ions

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* Part I: see reference 1.

** Communicated at the International Symposium on Instrumental Analytical Chemistry, Budapest, 1966(2).

the microelectrode should get more depolarized at the end-point. Furthermore, a stronger Faradic current should be generated, which would increase the a.c. phase shift and the distortion of the oscillogram.

EXPERIMENTAL

Preparation of standard solutions

0.1 N solutions of potassium bromate and arsenic trichloride were prepared by the usual methods(3, 4) and standardized by potentiometric titration.

Instruments

For potentiometric titrations the instruments used were: a PHM 22p pH-meter, a TTA 1 titration set, a K 100 calomel electrode and P 101 platinum electrode, all produced by Radiometer.

The apparatus for oscillographic-chronopotentiometric titrations(5) is shown in Fig. 1 of Part I(1): the voltage of the a.c. source was adjusted by means of an ST 11 N variable transformer produced by the Institute of Electrocommunications in Ljubljana. A Philips GM 5653 and an Avala KO 701 oscillograph were used. The electrodes were a round platinum microelectrode with a diameter of 1 *mm* and a calomel electrode with a mercury surface area of about 10 cm^2.

The titration procedure

Into a 250 *ml* glass 5—25 *ml* of 0.1 N solution of arsenic-trichloride was measured by means of a burette, and 25 *ml* of distilled water, 15 *ml* of concentrated hydrochloric acid and 0.5 *g* of potassium bromide were added. The solution was titrated with 0.1 N standard solution of potassium bromate until sudden distortion of the oscillogram took place.

1. *Influence of the direct current*

In amperometric titration the diffusion current changes at constant potential; in potentiometric titrations it is the potential of the indicator electrode which changes, at constant current (usually zero), while in the third kind of titration both the potential and the current change. All these titrations were done with superimposed a.c. to determine the end-point by means of the wave form distortion.

a) *Amperometric titrations with superimposed alternating current*

These determinations were done with the apparatus shown in Fig. 1. The electrodes were short-circuited through a galvanometer, for simultaneous ordinary amperometric titration and observation of the derivative oscillograms. Determinations were done with superimposed a.c. of low (20 *mV*) and high (2 *V*) voltage.

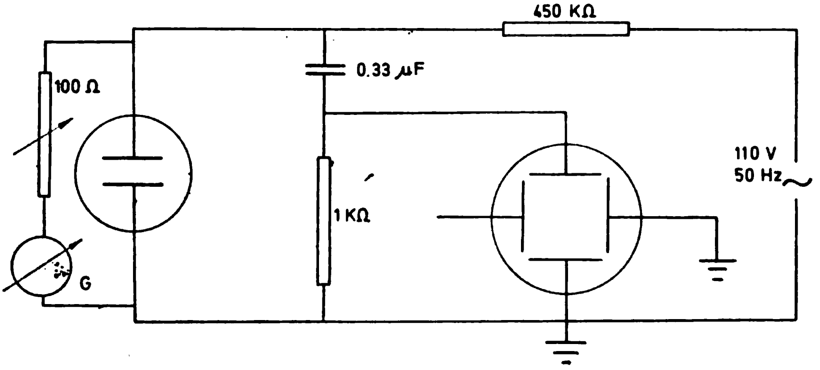

Figure 1
Circuit diagram of the equipment for amperometric titration with superimposed alternating current
G = Multiflex galvanometer

Low voltage a.c.

At an a.c. source voltage of 110 *V* and a series resistance of 450 KΩ the amplitude of the alternating current (about 20 *mV*) did not reach the separation potential of bromide ions before the end-point (Fig. 2, curve *a*, of Part I(1), so that the oscillogram was a regular sine wave.

At the end-point there was a sudden rise of the direct current while the potential of the indicator electrode hardly changed (only about 10 *mV*). Because of that the zero oscillation potential (Fig. 2, potential *A*, of Part I(1)) remained unchanged. The a.c. potential did not reach the potential of separation of bromide ions (Fig. 2, potential C, of Part I(1)), the oscillograms did not change, and it was therefore not possible to use them for the determination of the end-point.

High voltage a.c.

By increasing the oscillation amplitude (by increasing the a.c. voltage and decreasing the series resistance) or by changing the zero potential by superimposing a direct voltage on the galvanic cell, the potential of separation of bromide ions was reached before the end-point of titration, which was reflected in "denting" of the $\frac{dE}{dt}$ curves. Similar dents were obtained in precipitation titration of zinc with potassium ferrocyanide. However, in these "oscillographic titrations"(6,7) the changes of the derivative wave form at the end-point were not clear and the accuracy was mainly within the limits of "oscillographic-polarographic" titrations with a relative error of 3—5.

b) *Potentiometric titrations with superimposed alternating current*

In order to achieve a sudden and great change of the rotating platinum microelectrode potential at the end-point we used the already described apparatus and procedure for potentiometric titration with superimposed alternating current (Fig. 1 in Part) I). The changes in the oscillogram at the end-point (Figs. 2 and 3 in Part I⁽¹⁾) were very sudden and marked, the results being therefore satisfactory, that is within the accuracy limits of ordinary potentiometric determinations.

c) *Superimposed a.c. in titrations where both the indicator electrode potential and the d.c. change*

These titrations were done by means of the apparatus shown in Fig. 1, the only difference being that the series resistance was much greater than 100 Ω while the d.c. potential changes of the galvanic cell were measured with a vacuum-tube voltmeter. Because in these determinations a direct current flowed through the galvanic cell, the indicator electrode potential changed less at the end-point than in ordinary potentiometric titrations. Because of the smaller potential changes (Fig. 2, potential difference *B-A*, of Part I⁽¹⁾) the oscillogram distortions caused by it were also less marked. As these titrations were less accurate they were not further studied.

2. *The influence of the composition of the titrated solution*

The influence of the bromide ion concentration. In accordance with the principle of oscillographic-chronopotentiometric titration⁽¹⁾, with increasing concentration of bromide ions the distortion of the dE/dt waveform also increased. The concentration of potassium bromide was increased from 0.05 N, which is the concentration used in ordinary potentiometric visual indicator titrations, to 5 N. The oscillographic distortion occurred more suddenly and was more pronounced and therefore the results of the determinations were better (Table 1).

TABLE 1

The influence of the composition of the titrated solution on the accuracy of oscillographic-chronopotentiometric titrations of arsenic (III) with potassium bromate using platinum indicator microelectrode (sphere Ø 1 mm), SCE, 450 KΩ resistance, 0.33 μF capacitance and 220 V (sic) 50 c/s sinusoidal a.c. (Fig. 1 and 3). The results represent mean values of 68 determinations of 10—100 mg of arsenic in 100 ml titrated solution

Potassium bromide	Potassium bromate	Hydrochloric acid	Relative error in %	Average deviation in %
0.001 N	0.1 N	5 N	+0.8	0.61
0.1 N	„	„	—0.1	0.43
5 N	„	„	+0.04	0.26
„	„	„	+0.10	0.54
„	1 N	„	+0.03	0.19
„	0.1 N	2	—0.26	0.63
„	„	5	—0.05	0.37
„	„	10	+0.11	0.63

The influence of the concentration of arsenic (III) and potassium bromate. Since the wave form distortion is also due to a jump in the d.c. potential of the indicator electrode at the end-point, greater distortions were obtained with greater potential changes, that is when higher concentrations of arsenic (III) were titrated with higher concentrations of the standard solution of potassium bromate. 1 N potassium bromate gave better results than 0.5 N and 0.1 N solutions (Table 1). It was not possible to do titrations with 0.01 N solution with satisfactory accuracy, though by using a more sensitive oscillograph it might be possible.

The influence of the concentration of hydrochloric acid. For potentiometric titration of arsenic (III) with potassium bromate various authors recommend different concentrations of hydrochloric acid. Győry(8) determined arsenic (III) in 0.25 N to 1 N hydrochloric acid in the presence of methyl orange as the indicator. Nissenson and Mittasch(9) accelerated the reaction of arsenic (III) with potassium bromate by heating at 50—60°C. Other authors recommend even greater concentrations of the acid : 2 N(10) and 3.5 N(11). Smith and May(12), using indigo carmine or naphthol-blue-red as the indicator, recommend 1.6 N, 3.5 N, and 6 N hydrochloric acid(12). Zintl and Wattenberg(4) used 1.2 N acid, and for the titration of 10^{-4} N solution of arsenic (III) they used 3 N hydrochloric acid(13).

We varied the concentration of hydrochloric acid from 2 N to 10 N; it was found that the best results were obtained with concentrations from 4 N to 6 N (Table 1).

The influence of other ions. The presence of ions which do not react with potassium bromate, arsenic (III), potassium bromide and bromine, and whose separation potential is reached before the end-point outside the oscillation amplitude (Fig. 2, curve *a*, of Part I(1)), did not interfere with the determination of arsenic (III) with potassium bromate. For example, the presence of a mixture of cations of alkali metals and lanthanides, aluminum, iron (III), manganese (II), nickel (II), cobalt (II), zinc, cadmium, bismuth and copper did not interfere with the determination.

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Original Scientific Paper

EFFECT OF INSULIN ON THE METABOLISM OF PROTEINS, LIPIDS AND GLUCIDES. XI.

EFFECT OF SUCCESSIVE HYPERINSULINEMIAS ON RAT LIVER GLYCOGEN LEVEL

by

JELENA J. BOJANOVIĆ, PREDRAG P. MILOŠEVIĆ, RUŽICA M. KOVAČEVIĆ and OLGA ĐORĐEVIĆ-ČAMBA

During the fifty years for which the hypoglycemic effect of insulin has been known(1, 2) numerous aspects of insulin's action on the carbohydrate metabolism have been discovered and explained. In 1925 Cori(3) found that insulin induces an increase in liver glycogen, which was subsequently observed by other authors as well(4, 5). Many studies which followed this discovery aimed to establish whether the increase of hepatic glycogen was due to decreased mobilization or increased storage of glucose. Some light has been thrown on the problem by the papers of Bouckaert and co-workers(6) and Bearn and co-workers(7), in which it is confirmed that insulin has a direct effect both in increasing storage and in reducing release of glucose into the circulation. However, *in vitro* experiments with labeled glucose showed that much more comprehensive research is necessary for the clarification of the problem, as this effect of insulin is not constant but depends on the concentration both of the administered insulin and of the glucose present(8–12).

The need to answer this, among the many other questions which ensue, led to the opening of a new chapter in the enzymatic regulation of the carbohydrate metabolism(13–17). Together with attempts to elucidate the action insulin on the metabolism of carbohydrates from this aspect, many other facts were discovered with regard to the action of insulin on the glucose metabolism(17–20), while the studies of Krahl and co-workers(21–23) raised the question of the influence of a number of factors on carbohydrate metabolism. On the other hand the question was also raised of the metabolic interaction of carbohydrates, proteins and lipids in hyperinsulinemia. Studies of this aspect of the problem have been done mainly with single injections of insulin, and it was mainly the direct effect which was observed, while more recently attention is being paid to the states caused by successive hyperinsulinemias, and besides the direct effect the prolonged effect of insulin is also be ingvestigated(24–29). In this context we have also studied the effect of insulin on the liver glycogen level of rats given large daily doses of insulin. In this paper we report the results of experiments on the prolonged effect of insulin after successive hyperinsulinemias, 24 hours after its administration.

MATERIAL AND METHODS

Experimental were done on pure-bred white rats (male), weight from 210 to 230 *g*, kept under constant conditions.

The animals were given daily deep intramuscular injections of 25 units of crystalline insulin per 1000 *g* of body weight. The hypoglycemic state was interrupted after 90 minutes by intraperitoneal injection of 10 *ml* of physiological glucose, solution, after which the animals were fed. Twelve hours before killing the food was withdrawn. Rats were killed after the first, fifth, tenth and fifteenth shock by decapitation. The liver tissue was weighed fresh and immediately hydrolysed with alkaline hydroxide (300 *mg* of tissue: 10 *ml* 30% KOH) by heating for 20 minutes at boiling. From the cooled hydrolyzate glycogen was precipitated by adding 96% ethanol, then dissolved in redistilled water and determined by the spectrophotometric method of Seifert(30). The concentration of glycogen was expressed per 100 *g* of fresh tissue.

RESULTS

The liver glycogen concentration of seven non-treated rats was between 4828 and 4459 *mg*%, mean value 4588 ± 113 *mg*%, which was taken as the normal value.

In the group (seven rats) given only one insulin shock a slightly higher liver glycogen than normal was found. The values ranged from 5101 to 4918 *mg*%, mean value 5015 ± 73 *mg*%, which was 9% greater than the normal value. The difference is statistically highly significant ($p < 0.001$).

TABLE 1

Content of glycogen in rat liver 24 h after successive insulin administration

	N	Insulin administrations No. of			
		1	5	10	15
No.	7	7	7	7	7
R	4828—4459	5101—4918	3696—3167	2299—1928	4910—4756
M	4588	5015	3342	2059	4839
SD	113	73	183	128	49
SE	43	27	69	49	3
CV%	2.5	1.4	5.4	6.2	1.0
a		+9	—28	—56	+5
b		p<0.001	p<0.001	p<0.001	p<0.001

No. — number of cases
R — range of values
M — mean value
SD — standard deviation
SE — standard error
CV% — coefficient of variation
a — % increase relative to the normal value (N)
b — level of significance of changes.

In the group (seven rats) which got five insulin shocks on five successive days, 24 hours after the last shock the glycogen concentration was 28% down on the normal value. The values ranged from 3696 to 3167 *mg*%, mean value 3342 ± 183 *mg*%. The difference is statistically highly significant ($p < 0.001$).

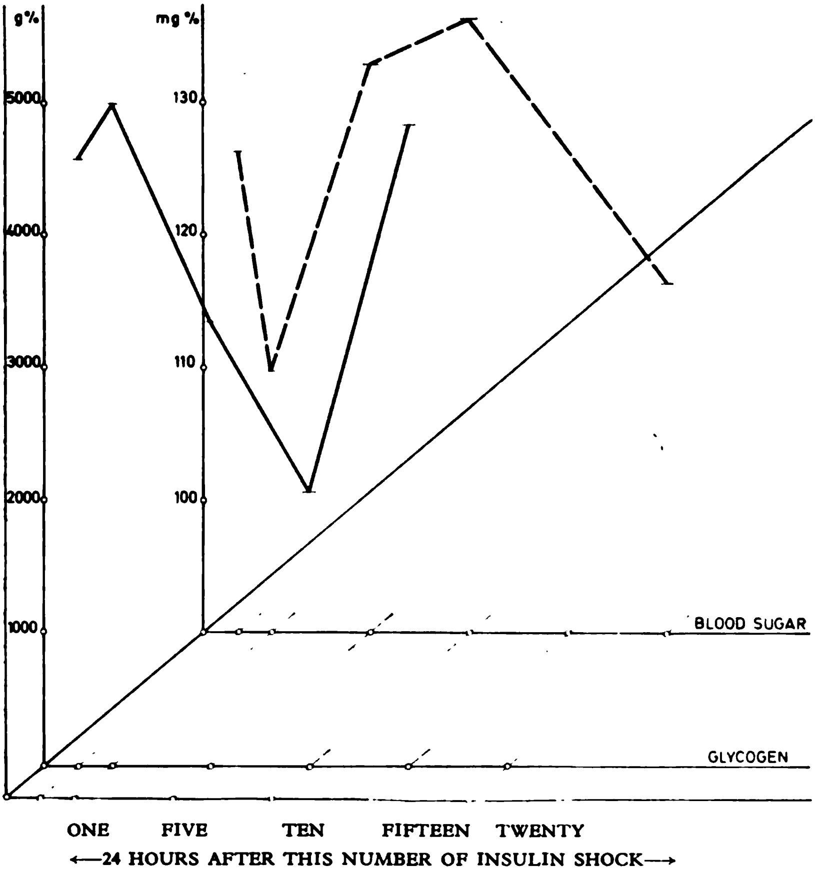

Figure 1

Glycogen (and glucose (7)) in rat liver 24h after successive insulin administration

In the group which got ten insulin shocks on ten successive days (seven rats), 24 hours after the last shock the glycogen was very low, 56% down on the normal value. The values ranged from 2299 to 1928 *mg*%, mean value 2059 ± 128 *mg*%. The difference is statistically highly significant ($p < 0.001$).

In the group of seven rats killed 24 hours after fifteen successive shocks glycogen values were higher than those found in untreated animals. The values ranged from 4910 to 4756 *mg*%, mean value 4839 ± 49 *mg*%. The difference is statistically highly significant ($p < 0.001$).

DISCUSSION

In analyzing the effect of insulin attention was paid to the direct effect, which is manifested a short time after the administration of insulin, and to the prolonged effect, i.e. changes occurring after several hours. While the direct effect is most marked in the muscles, adipose tissue and the tissue of the mammary gland, it is considered that the prolonged effect has a direct influence on liver processes. However, it is necessary to note that far less is known about this phase of the effect of insulin than the immediate effect.

Research on the influence of successive administration of great quantities of insulin on proteins, amino acids and nucleic acids(24–29) has shown that with daily repetition of hyperinsulinemia both the immediate and the prolonged effect change and often differ significantly from the effect of a single injection. This is confirmed by our results for the prolonged effect on liver glycogen of rats given great quantities of insulin daily for 15 days.

The high level of glycogen observed 24 hours after the first injection of insulin could be a result of the marked anabolic effect of insulin (direct) on liver glycogen(31). It is certain that the large amount of glucose given in order to interupt the hypoglycemic shock contributed to the high level, since according to *in vitro* experiments liver glycogen always increases if glucose is present in the perfusing fluid(32). It would seem that the great fall in glycogen concentration observed 24 hours after the fifth, and particularly after the tenth successive shock, is in contradiction with the generally accepted view on the establishment of optimum functions at the hepatic level under prolonged insulin action(32). However, the fact that with the fifth, and even more so with the tenth insulin shock the direct effect is most marked in the synthesis of proteins(24) and nucleic acids(29) permits the hypothesis that increased liver energy requirements step up glucogen consumption, with exhaustion of its pools, so that even after several hours its level is low. Nevertheless, it is not possible to rule out here other possibilities which can influence the level of glycogen several hours after the administration of insulin. Above all, the data on proteins and nucleic acids 24 hours after the fifth and the tenth shock show that at that time the anabolic processes were not stimulated(24, 29), probably due to the secondary consequences of insulin, which could also prevent the normalization of the glycogen level. This is also born out by the blood sugar, which throughout the entire period of observation was in strictly reciprocal correlation with the glycogen content, that is 24 hours after the fifth and the tenth shock the values were greater than normal(26, 33).

After fifteen successive insulin shocks the glycogen level was near normal which, considering the high level of proteins in circulation at that time⁽²⁴⁾, supports the hypotheses put forward to explain the prolonged effect on liver glycogen. However, the return of the glycogen values to normal after fifteen successive hyperinsulinemias does not mean that the mechanisms established after prolonged administration of such great quantities of insulin and glucose are normal in all phases.

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Original Scientific Paper

INFLUENCE OF ACTIVATOR CONCENTRATION ON THE FLUORESCENT PROPERTIES OF AgCl(Mn^{++}) SINGLE CRYSTALS

by

MITA M. SKOROBRIJIN

According to the literature(1) AgCl has the crystal structure of NaCl with $a_0 = 5.547$ Å. It is known from the theory of luminescence that chemically pure crystal bodies, in the absence of a defect in their crystal lattice, do not produce luminesce light. For luminescence to occur it is necessary that a luminescent center is formed in the crystal. In our case these are manganese ions, which are therefore often called activators.

AgCl(Mn^{++}) was prepared in the chemistry lab of the department of General Physics of the School of Mathematical and Physical Sciences in Prague according to instructions already described(2) and with the concentrations shown in Table 1.

TABLE 1

Shift of the intensity maximum (I_{max}) with increasing activator concentration at different temperatures

Activator concentration in mol %	λ[A]			
	$t_1 = -196^{\circ}C$	$t_2 = -183^{\circ}C$	$t_3 = -140^{\circ}C$	$t_4 = -90^{\circ}C$
AgCl/pure	4820	4820		
$C_1 - 0.001$	4860	4880	4920	5120
$C_2 - 0.01$	4870	4950	4980	4740
$C_3 - 0.1$	5050	5100	red	red

Besides these samples we also used a pure sample of silver chloride single crystals, or more precisely, in this sample the impurities were of the order of 10^{-4} *mol*%. The size of the samples was 20 × 10 × 0.2 *mm*.

The experimental apparatus was the same, apart from slight changes, as described in a previous paper(3). An HBO-200 mercury lamp was used for excitation, the light from the lamp passing through an interference filter whose transparency was a maximum at $\lambda = 365\ m\mu$. In the measurements done at the temperature of liquid air or liquid nitrogen the sample was put directly into the liquid. In other measurements the temperatures were checked by means of termocouples. The intensity of fluorescence was recorded via a FEU-35 photomultiplier of Soviet origin, which was fed through an amplifier to an eKN-type compensating recorder of East German origin. Wavelengths were determined on a quartz spectrograph, whose reciprocal linear dispersion within the interval from 4000 to 7000 Å was about 15 Å/*mm*⁽⁴⁾.

RESULTS

According to the literature⁽⁵⁾ Randall was the first to study the luminescent properties of AgCl. It is reported in the same paper that Golub⁽⁶⁾ found that AgCl and AgBr crystals show two absorption maximums, at about $\lambda_1 = 4800$ Å and $\lambda_2 = 6400$ Å. This is also the case with AgCl(Mn^{++}). At low temperature, $t_1 = -196°C$ and $t_2 = -183°C$, all the samples had a strong blue-green fluorescence. With increasing temperature the maximum shifted towards longer wavelengths. It also shifted towards longer wavelengths with increasing concentration of the activator at the same temperature. This was especially noticeable with the samples containing the highest concentration of the activator.

There was an exception to this rule with the concentration $C_2 = 0.01$ mol%, at which the intensity of fluorescence suddenly increased at the highest temperature measured, while the wavelength dropped right down to 4740 Å.

As regards the intensity of fluorescence, it was found that it decreased with temperature, except in the case described, and at —80°C there was no longer any fluorescence whatsoever. Unfortunately, because of low small intensity light and the insensitivity of the photomultiplier for the red range, it was not possible to measure the wavelengths accurately for the concentration $C_3 = 0.1$ mol% at temperatures —140°C and —90°C. The low intensity was due to temperature quenching.

Under constant experimental conditions (temperature, photomultiplier voltage, slit width of the spectrograph etc., the intensity decreased with the activator concentration, and it was concluded that the optimum concentration is smaller than C_1. Table 2 shows the dependence of the relative intensity (I_{rel}) on the activator concentration for fluorescence at the temperature of liquid nitrogen, while the graph (Fig. 1) shows the same at the temperature of liquid air.

TABLE 2

Change of I_{max} with activator concentration at —196°C

Activator concentration in mole %	C_1 0.001	C_2 0.01	C_3 0.1
I_{rel}	26.7	22.8	17.5

The measurements of excitation spectra showed that the fluorescence intensity maximum was at λ = 3650 Å for the integral fluorescence. When

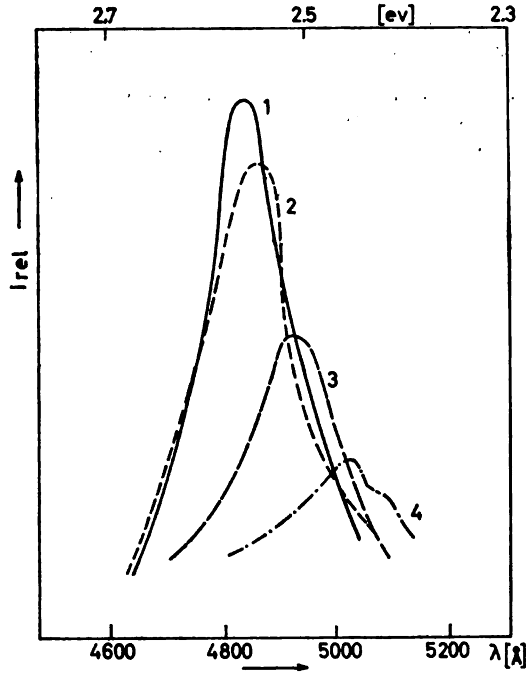

Figure 1

Dependence of I_{rel} on concentrations at —183°C

1) ——— AgCl
2) — — — AgCl + 0.001 (mol%act.)
3) — — AgCl + 0.01 (mol%act.)
4) —.—.— AgCl + 0.1 (mol%act.)

the green fluorescence was isolated I_{max} was at λ = 3500 Å. The green fluorescence was isolated by means of a VG-9 filter, designated according to Schott. In these measurements we used a hydrogen lamp produced by Zeiss, whose light passed through a monochromator with a sodium chloride prism.

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Original Scientific Paper

KINETICS OF FORMATION OF NEW PHASES IN THE SYSTEM SILICIUM-MANGANESE

by

MIODRAG Đ. JANČIĆ and LJILJANA M. RADONJIĆ

1. INTRODUCTION

The purpose of the present study was to obtain quantitative data on the kinetics of growth of new phases in the Si-Mn system, to mathematically interpret the kinetic curves and to calculate the diffusion characteristics of the components participating. Considering that the intermetallic compounds are here formed by diffusion, we have used the term "reactive diffusion".

In order to obtain new phases in the Si-Mn system a new technique for preparing the diffusion pair was developed. The kinetics of growth of the new phases was studied at different temperatures. The diffusion characteristics of the components participating in the reactive diffusion were calculated from the results obtained by means of an electronic probe.

The diffusion pairs were analyzed metallographically. The concentration of components at boundaries of phases and the concentration profile of each phase, which are necessary for calculating the diffusion characteristics, were determined by means of the electronic probe and X-ray analysis.

2. EXPERIMENTAL

2.1. *Preparation of the diffusion pair*

We used a single crystal of silicium 9N in the shape of a parallelepiped 6 × 4 × 2 *mm* and electrolytic manganese 4.5 N in granules.

Plates of silicon with the orientation (111) and (100), previously polished, were soaked with manganese in evacuated quartz ampules (5×10^{-8} *mmHg*). The diffusion treatment was done in a resistance furnace at temperatures 800, 900, 1000 and 1100°C, from 1 to 6 hours.

The resulting samples were metallographically prepared by soaking in metacrylate and, after careful working of the face parallel to the direction of diffusion, etched with 10% HF in alcohol. The thickness of layers was measured on a MIKA microscope (magnification 21 × 2.5 × 6).

2.2. *X-ray analysis*

New phases was sought by means of X-ray phase analysis. The photographs were taken in a Ø 56 *mm* camera with CuK-α radiation and an Ni filter.

The influence of the orientation of the silicium on the kinetics of growth and the perfection of new phases was examined by means of the Laue method.

3. RESULTS

3.1. *Kinetic measurements*

After diffusion treatment at lower temperatures the shape of the sample underwent a slight change and lacked metallic lustre. At higher temperatures the edges were rounded and the samples brittle.

The results of kinetic measurements are shown in Figs. 1 and 2. The thickness of the interdiffusion zone formed in the process of reactive diffusion was measured in the direction of diffusion. It may be seen from the graphs (Figs. 1 and 2) that the rate of formation of new phases obeyed the parabolic law. There were deviations from parabolic growth only during the initial stage of the reaction.

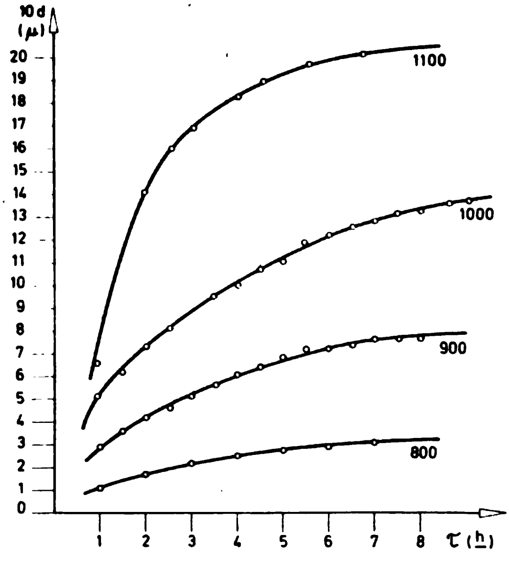

Figure 1

Dependence of the thickness of the interdiffusion zone on annealing time *t*

The general expression for the rate of growth of the interdiffusion zone with several phases is given by the equations(1, 2):

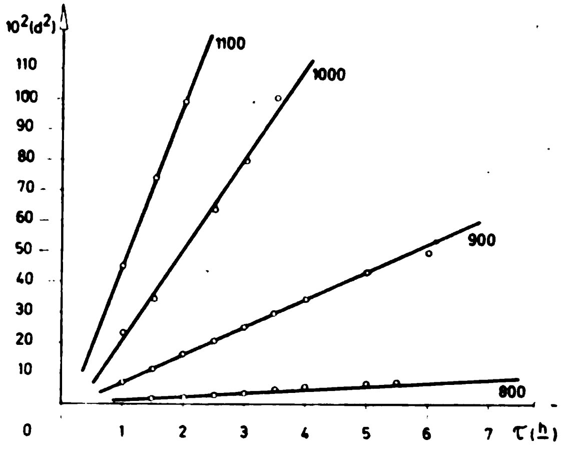

Figure 2

Dependence of the thickness of the interdiffusion zone on *t*

$$Q = \sqrt{t}\ \sum_i g_i\,(k_i - k_{i-1}) \tag{1}$$

$$Q = t^n \sum_i g_i\,(k_i - k_{i-1}), \tag{1a}$$

or for a given phase:

$$g_i = \sqrt{t}\ k_i \tag{2}$$

k = rate constant of the reaction
t = duration of the diffusion treatment
Q, *g* = weight (or thickness) of the interdiffusion zone or of an individual phase

Equations (1) and (2) also hold for the thicknesses of the newly-formed phases, only the constant *k* has different dimensions. Thus the rate of formation of a given phase can be expressed as

$$d_i = \sqrt{t}\ k_i = k_i t^n \tag{2a}$$

The parabolic time law of growth can be expressed in a form which shows the relation between the kinetic constant and the diffusion coefficient:

$$d_i\,(t) = 2\,\xi\,\sqrt{D_i t} \tag{2b}$$

ξ = constant number
D_i = diffusion coefficient.

Since the growth of all phases was found to follow the parabolic time law, the growth constant k_i of the interdiffusion zone was calculated from equation (2a).

The determination of *k* and checking that the exponent *n* in equation (2a) was 1/2 were done by the method of least squares.

In order to be able to apply statistical analysis of the results to equation (2a) it was necessary to express it in linear form⁽³⁾. The following expression is obtained:

$$\log d = \log k + \mathrm{N} \log t$$

Writing

$$\log d = \mathrm{Y}$$
$$\log k = B$$
$$\log t = X$$

we have

$$X = nX + B \tag{3}$$

k and *n* in equation (2a) were calculated from the expressions⁽³⁾

$$n = \frac{\mathrm{N}\, \Sigma\, \mathrm{X_i Y_i} - \Sigma\, \mathrm{X_i} \Sigma\, \mathrm{Y_i}}{\mathrm{N}\, \Sigma\, \mathrm{X_i^2} - (\Sigma\, \mathrm{X_i})^2}$$

$$B = \frac{\Sigma\, \mathrm{Y_i} \Sigma\, \mathrm{X_i}^2 - \Sigma\, \mathrm{X_i}\, \Sigma\, \mathrm{X_i Y_i}}{\mathrm{N}\, \Sigma\, \mathrm{X_i}^2 - (\Sigma\, \mathrm{X_i})^2} \,.$$

An example for the results at 900°C is shown in Table 1. *n* and *k* were calculated from the tabulated values. Figure 3 shows log *k* against 1/T, and Table 2 shows the calculated *k* and *n*.

TABLE 1

Statistical analysis of the measured values

N	T (h)	$d \cdot 10^4$ (cm)	log t = X	log d = Y	X^2	XY
1	1	28	0	1.447	0	0
2	1.5	35	0.176	1.544	0.0318	0.2720
3	2	42	0.301	1.613	0.0910	0.4850
4	2.5	46	0.394	1.663	0.1560	0.6550
5	3	51	0.477	1.707	0.2280	0.8150
6	3.5	55	0.544	1.541	0.2960	0.9500
7	4	59	0.602	1.771	0.3640	1.0700
8	5	66	0.698	1.795	0.490	1.2700
9	6	70	0.778	1.845	0.6020	1.4340
			$\Sigma X_i = 3.970$	$\Sigma Y = 15.146$	$\Sigma X_i^2 = 2.590$	$\Sigma X_i Y_i = 6.9510$

TABLE 2

Calculated values of k and n

t (°C)	800	900	1000	1100
$k \cdot 10^3$	1.12	2.11	4.01	8.11
n	0.501	0.510	0.598	0.502

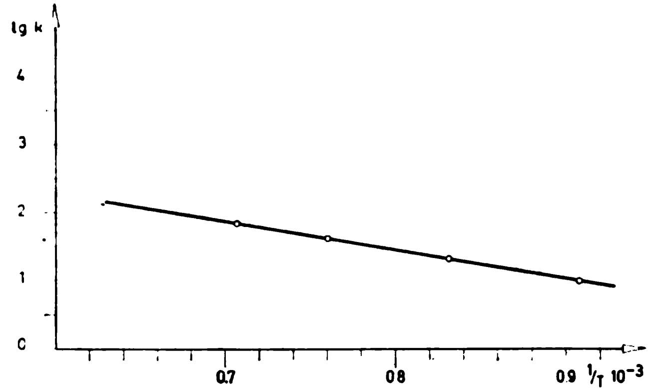

Figure 3

Temperature dependence of the logarithm of the parabolic constant

3.2. *Calculation of the diffusion characteristic* $(D_i\delta_i)$

The diffusion characteristics $(D_i\delta_i)$, which is used instead of the diffusion coefficient in diffusion through a phase of stoichiometric composition, was calculated by the method of Borisov(4). Solving Fick's second equation and using the expression for the mass balance the following equation is obtained:

$$2(D_i\delta_i)t = M(y_i' - y_i) \tag{4}$$

M = integral diffusion flux
t = duration of annealing
D_i = diffusion coefficient
δ_i = concentration difference within the layer
$y_i' = y_i$ — layer thickness.

The integral diffusion flux M is calculated from the graphs of the distribution of components through the different phases. The concentration distribution curves for silicium and manganese were obtained by means of the electronic probe (Fig. 4). From them it was possible to calculate $(D_i\delta_i)$ for both components. Figure 5 shows schematically the distribution curve of silicium through the interdiffusion zone after annealing fat 1000°C for 3 hours.

Data:

$c_1 = 76.52\%$ $c_2 = 66.16\%$ $c_3 = 49.44\%$ Mn
$c_1' = 76.52\%$ $c_2' = 66.16\%$ $c_3' = 49.44\%$ Mn
$\delta_1 = 0$ $\delta_2 = 0$ $\delta_3 = 0$
$y_1 = 0$ $y_2 = 36$ $y_3 = 56;\ y = 98$
$\Delta_1 = y_i - y_{i-1}$ $\Delta_2 = 10.36$ $\Delta_3 = 16.72$

$$M_1 = \Delta_2 y_2 + y_2 c_2 + (y - y_3) c_3$$
$$M_2 = 6154.4 \,.\, 10^{-4}\%\ cm$$
$$M_2 = 5781.44 \,.\, 10^{-4}\%\ cm$$
$$M_3 = 2076.48 \,.\, 10^{-4}\%\ cm$$

$$(\delta_1 D_1)\frac{\mathrm{Mn}}{\mathrm{Mn_5Si_3}} = \frac{36 \cdot 0.615 \cdot 10^{-8}}{2.16} = 10.2 \cdot 10^{-8}\%\ cm^2/sec$$

$$(\delta_2 D_2)\frac{\mathrm{Mn}}{\mathrm{MnSi}} = \frac{20 \cdot 0.578 \cdot 10^{-8}}{2.16} = 5.3 \cdot 10^{-8}\%\ cm^2/sec$$

$$(\delta_3 D_3)\frac{\mathrm{Mn}}{\mathrm{MnSi_2}} = \frac{42 \cdot 0.208 \cdot 10^{-8}}{2.16} = 4.07 \cdot 10^{-8}\%\ cm^2/sec$$

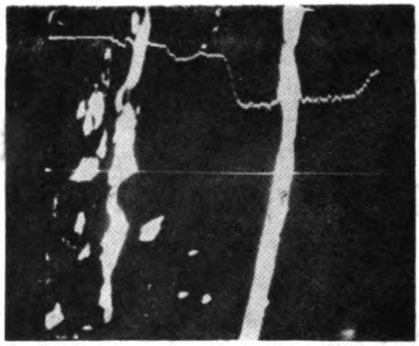

Figure 4

Distribution of silicium in the interdiffusion zone after 3 hours at 1000°C

The diffusion characteristics of silicium for different phases were calculated in a similar fashion. The following values were obtained:

$$(\delta_1 D_1)\frac{\mathrm{Si}}{\mathrm{MnSi_2}} = 3.05 \cdot 10^{-8}\%\ cm^2/sec$$

$$(\delta_2 D_2)\frac{\mathrm{Si}}{\mathrm{MnSi}} = 2.71 \cdot 10^{-8}\%\ cm^2/sec$$

$$(\delta_3 D_3)\frac{\mathrm{Si}}{\mathrm{Mn_5Si_3}} = 1.39 \cdot 10^{-8}\%\ cm^2/sec$$

Because we did not have the necessary concentration distribution curves the diffusion characteristics were only calculated for a single annealing temperature.

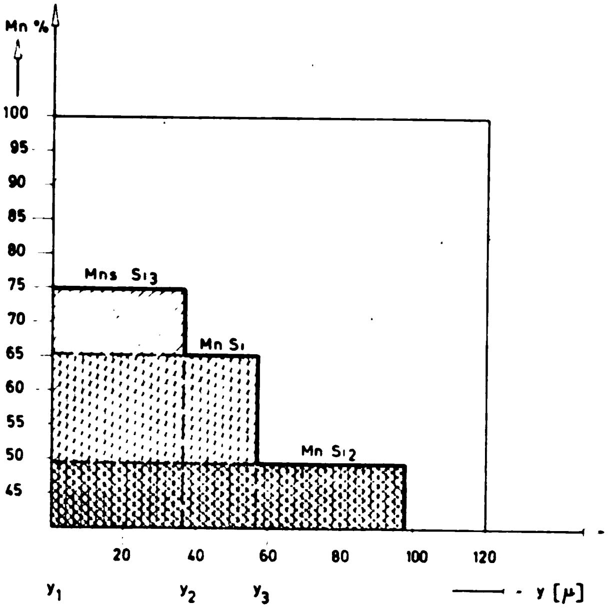

Figure 5

Schematic representation of the concentration profile for silicium in the interdiffusion zone after 3hr at 1000°C

4. DISCUSSION

The kinetics of formation of the new phases is determined by the rate of chemical reaction and the diffusion of atoms through the phases formed. When the diffussion is slow the rate of formation of new phases is determined by it. The parabolic dependence of the rate of formation of new phases is a proof that reaction rate is diffusion-determined. The deviations from this dependence observed at the beginning of the process were probably due to the very small thickness of the interdiffusion zone so that the diffusion was fast and did not determine the rate of reaction, this being determined by the chemical reaction⁽⁵⁾.

Both silicium and manganese participate in the formation of the new phases, $MnSi_2$ and Mn_5Si_3⁽⁶⁾. It may be seen from the diffusion characteristics ($\delta_i D_i$) that the diffusion rate of manganese through the Mn_5Si_3 is approximately eight times greater, and through $MnSi_2$ half the rate of silicium. However, at lower temperatures (below 1000°C) the diffusion rate of the components is approximately the same, as is seen from the relationship of the thicknesses of $MnSi_2$ and Mn_5Si_3. The increase of the values with increasing temperature may also be seen from the reaction rate constants (Table 2).

The rate of formation of new phases also depends on the orientation of the silicium. The rate of growth in the direction of the (111) plane is about 1.2 times greater than in the (100) direction, as is seen from the thickness of the interdiffusion zone. This is ascribed to the favorable crystallographic conditions for the growth of $MnSi_2$ on the (111) plane. As shown by the Laue method, in the initial stage of the process the $MnSi_2$ phase is modelled on the Si base but later it changes and a polycrystaline interdiffusion zone is obtained. This was expected because of the different crystal structure of silicium and the newly-formed phases (primarily of $MnSi_2$ which is next to the base).

The dependence of the kinetic constant k on the temperature of reactive diffusion is plotted as $\log k$ — 1/T (Fig. 3). It may be seen that this is a straight line, which is another proof of the parabolic rate of formation of new phases in this system.

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Original Scientific Paper

ULTRAVIOLET SPECTRA OF SOME ORGANOPHOSPHOROUS INSECTICIDES IN DIFFERENT SOLVENTS

by

JELENA B. JORGOVIĆ-KREMZER

Together with the increasing importance, production and application of organophosphorous insecticides, and of pesticides in general, there is an increasing need for their study. This need is today very great. From the moment the organophosphorous preparations are produced until the consumption of the foodstuffs which are treated with them, their qualitative and quantitative chemical analysis is constantly required.

Investigations of organophosphorous pesticides are rather complicated, parcticularly in biologic material. On the one hand it is often necessary to separate even microquantities of the substance in a pure state. On the other hand, many of these preparations rapidly decompose. Because of this the analytical methods for their determination must be specific and sensitive, reproducible, and relatively rapid and simple.

Ultraviolet spectrophotometry fulfils most of these conditions. It is rapid, very sensitive and suitable for the determination of microquantities. It is strictly specific, as it concerns the entire, unaltered molecule of the insecticide, in contrast to many other methods which are based on the determination of their degradation product. It has found successful application in the study of many organic compounds. However, it is less used in the study of organophosphorous insecticides. In the literature at our disposal there is information on the ultraviolet absorption spectra of only some organophosphorous compounds[1–6]. The aim of the present study was to determine the shape of the absorption curve in the ultraviolet for several more organophosphate preparations. As the ultraviolet spectrum also depends on the solvent, the other aim of the study was to examine the influence of different solvents on the shape of the absorption curve and to study how the absorption changes with changing polarity of the solvent.

The solvents were mainly chosen according to the solubility of the substance under study, and according to their availability and applicability in a study of this kind.

MATERIAL AND METHOD

Four organophosphorous insecticides were chosen for study. Chemically pure active substances were obtained directly from the firms which produce them.

Substances

Menazon, pure, Plant Protection (England). This is a white, crystalline substance with a characteristics, very faint smell of mercaptan. Melting point 160—162°C.

Morphothion, pure, Sandoz (Switzerland). White, crystalline substance with a faint smell of mercaptan. Melting point 63°C.

Formothion No. 2110, Sandoz (Switzerland). A viscous oil, of pale yellowish color, with a faint smell of onions.

Thiometon, dist., Sandoz (Switzerland). Colorless oil with a strong unpleasant odour.

Solvents

Ethanol, absolute, p.a. "Reanal".
N-hexane, purum, "Fluka".
Petroleum ether, b.p. 55—72°C.
Acetone, p.a. "Kemika", mixed with water (double-distilled) 1 : 1.

Apparatus

Mettler analytical balance, type B.

Unicam Sp. 500 spectrophotometer: calibrated with ethanol solutions of maleinic acid and toluol. The voltage of the power supply was checked before and after the readings. The silica-gel desiccant was regularly checked and dried. The measurements were done in quartz cuvettes of 1 *cm*^{3}.

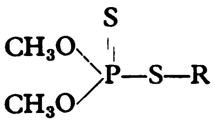
Solutions

A quantity of the substance was weighed with a precision of 0.01 *mg*. First a basic solution of approximately 4×10^{-4} M was made, and from it a series of solutions of lower concentrations.

For a series of concentrations of all solutions the absorption was measured at wavelengths from 190 to 280 *nm* and the ultraviolet absorption spectra curves plotted.

RESULTS AND DISCUSSION

All the compounds under study are thiophosphate esters with the structural formula

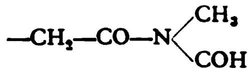
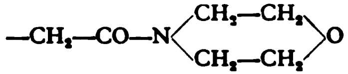
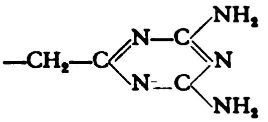


$$(CH_3O)_2P(=S)-S-R$$

They differ only in the acyl part of the molecule, towards the radical R. Table 1 shows the differences, defining in each case the nature of R.

TABLE 1

Structural differences of the compounds

Substance	R
Thiometon	$—CH_2—CH_2—S—CH_2—CH_3$
Formothion	 $—CH_2—CO—N\begin{smallmatrix}CH_3\\COH\end{smallmatrix}$
Morphothion	
Menazon	

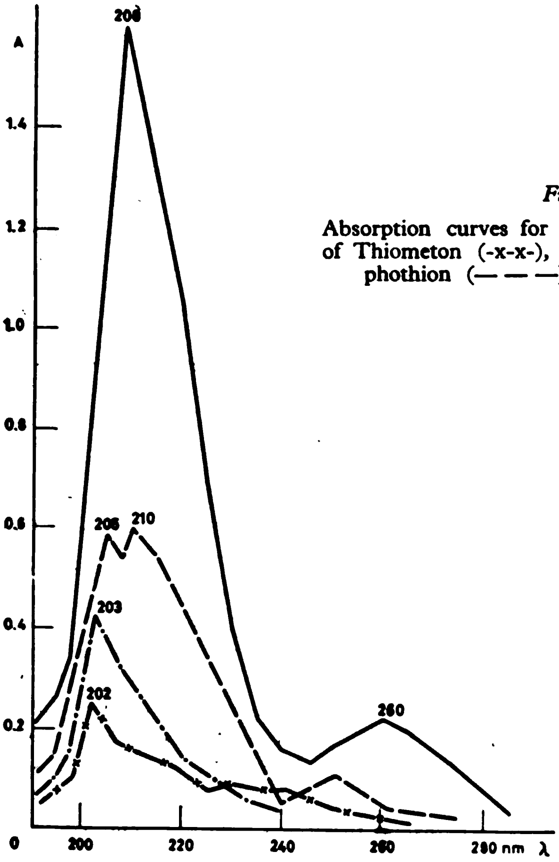


Figure 1

Absorption curves for 5 × 10-⁵ M ethanol solutions of Thiometon (-x-x-), Formothion (—.—.—), Morphothion (— — —) and Menazon (———).

It is seen from Table 1 that the differences are manifested in the presence of a thioethylether part in Thiometon, N-methylformoilacetyl in Formothion, an acetyl-morpholin ring in Morphothion and a methyldiaminetriazine ring in Menazon. The molecule of Menazon (triazine ring) contains the greatest number of groups determining ultraviolet absorption.

The ultraviolet absorption of the ethanol solutions shows that all the preparations have a sharply defined absorption maximum at wavelengths between 202 and 208 *nm* (Fig. 1). Considering that all these compounds have part of their molecule in common (see the structural formula), it may be hypothesized that this part of the spectrum corresponds to that part of the molecule. It is seen from the curve in Fig. 1 that the absorption of maximum of Thiometon, whose acyl group R is an aliphatic radical without double bonds, occurs at the lowest wavelength, 202 *nm*. With increasing number of functional groups in this other part of the molecule there is a progressively increasing displacement of the absorption maximum towards greater wavelengths. The solution of Menazon, which contains a triazine ring, showed the greatest displacement, being at 208 *nm*.

Solutions of Morphothion and Menazon had another absorption maximum, at 210 *nm* and 260 *nm*, respectively. This second part of the spectrum certainly corresponded to the *R*-part of the molecule. In Morphothion this is the Morpholine ring, and in Menazon the triazine ring. With Formotion and Thiometon there was no second maximum, R being the aliphatic radical. There are similar examples in the literature(1, 2, 4, 7). Only two of them will be cited here. Parathion, whose acyl part *R* is a *p*-nitrophenyl radical, has the first absorption maximum at 205 *nm* and the second at 265 *nm*. Asuntol (Co-Ral)(6), a thiophosphate ester whose radical *R* is a benzopyrene ring, shows another absorption maximum at 290 *nm* and 315 *nm*, and probably a third in the interval 202—208 *nm*, not yet measured.

Solutions of the different substances in the same solvent showed marked differences in absorption. For ethanol solutions of the same concentration of 5×10^{-5} M, Menazon showed the greatest absorption value — 1.600, followed by Morphothion — 0.592, Formothion — 0.428, and Thiometon — 0.245. The same regularity was seen with Morphothion, Formothion and Thiometon in other solvents (Table 2). Since an increase of the number of chromofor groups in a molecule (double bonds, and particularly the aromatic ring) produces the hyperchromic and bathochromic effect, i.e. increased absorption and a shift of the absorption maximum towards the visible part of the spectrum, it is clear that the observed regularity in the ultraviolet absorption of the compounds is a consequence of their molecular structure.

Investigation of the ultraviolet absorption of Thiometon, Formothion and Morphotion* in different solvent revealed absorption maxima in all cases (Figs. 2, 3 and 4). It is seen from the curves in Figs. 2, 3 and 4 that the maximum is displaced towards greater wavelengths when the solvent is changed from polar to non-polar. With ethanol solutions the maxima are at 202, 203, 205 and 210 *nm*. With the solutions in the acetone-water

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* Menazon dissolved well only in ethanol. In the other three solvents it is hardly soluble.

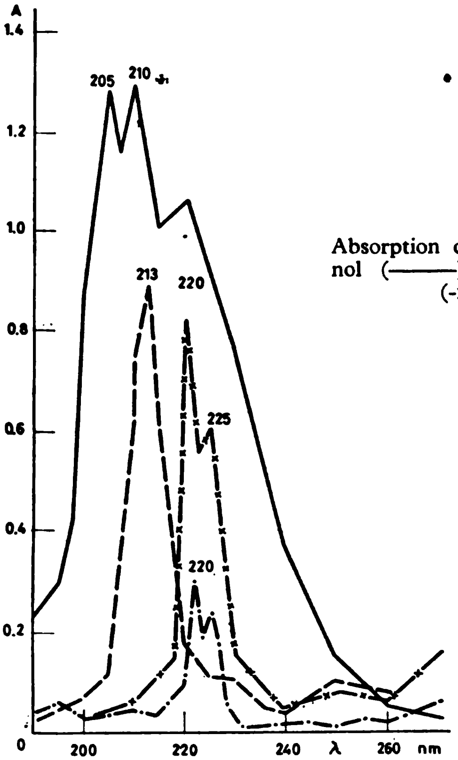

Figure 2

Absorption curves from 2×10^{-4} M solutions in ethanol (———), acetone (— — —), petroleum ether (-x-x-) and n-hexane (—.—.—.)

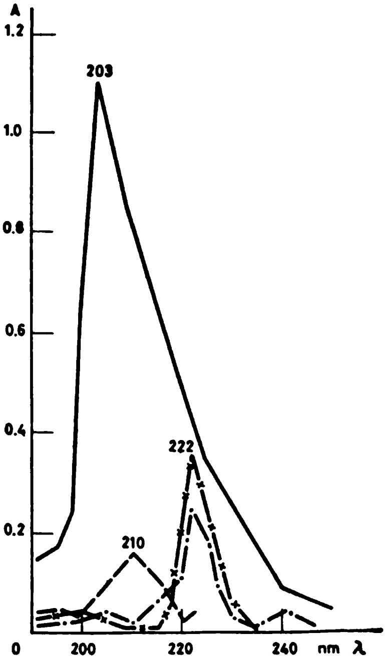

Figure 3

Absorption curves of 2×10^{-4} M solutions of Formothion in ethanol (———), acetone (— — — —), petroleum ether (-x-x-) and n.hexane (—.—.—.—).

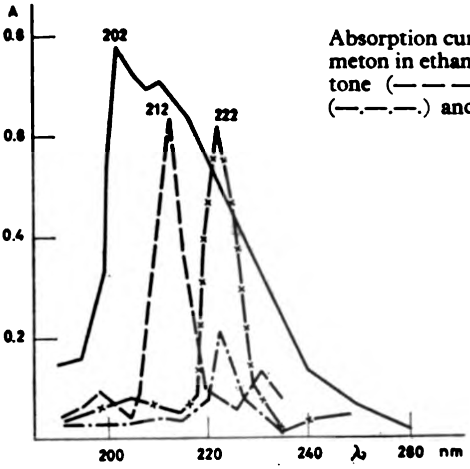

Figure 4

Absorption curves of 1.84 × 10^{-4} M solution of Thiometon in ethanol (————), 2 × 10^{-4} M solution in acetone (— — — —), 2 × 10^{-4} M solution in n-hexane (—.—.—.) and a saturated solution in petroleum ether (x-x-)

mixture they are at 210 *nm* and 213 *nm*, while in petroleum ether and n-hexane they are further displaced to 220 nm and 222 nm, respectively.

By further examination of the absorption curves it may be observed that with a change of the solvent, the concentration of the solution remaining unchanged, the absorption values changed markedly, as also seen from Table 2.

TABLE 2

Absorption maxima for 2 × 10^{-4} M solutions in different solvents

Solvent	Morphothion	Formothion	Thiometon
Ethanol	1.284	1.110	0.780
Acetone	0.880		0.640
Petroleum ether	0.820	0.360	0.620*
n-Hexan	0.310	0.250	0.210

* A saturated solution whose concentration was about 4 × 10^{-4} M at room temperature.

The results in Table 2 show that for all the substances the absorption was greatest in ethanol solutions, followed in order by acetone-water, petroleum ether, and *n*-hexane, which last is a typical non-polar compound with a zero dipole moment. In comparison with the other solvents, therefore, *n*-hexane showed the most marked hypochromic effect.

It has already been shown(6) that the absorption of ethanol solutions of Menazon, Morphothion and Thiometon is linearly dependent on the concentration. The equation of the straight line is $y = ax$. In quantitative analysis the concentration can be calculated from the formula $c = A/f$.

If the absorption of petroleum ether solutions of Morphothion from 1 × 10^{-5} M to 2 × 10^{-4} M, measured at 220 nm, at the absorption maximum, is plotted against concentration, it is seen that all the points lie on a straight line (Fig. 5). Thus the validity of the Lambert-Beer law for the given case is confirmed.

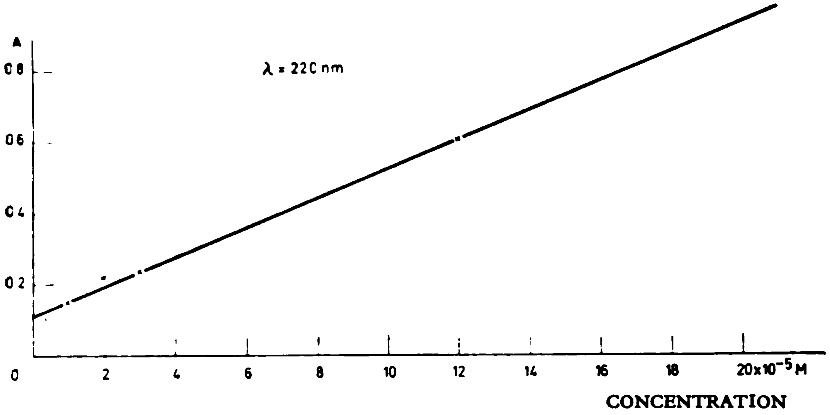

Figure 5

Absorption of petroleum ether solution of Morphothion against concentration

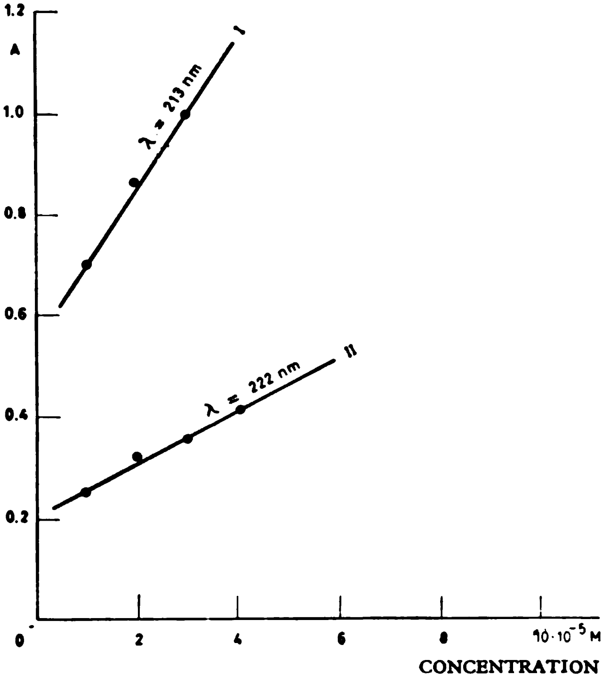

Figure 6

Absorption as a function of concentration for solutions of Morphothion in acetone (I) and n-hexane (II)

A linear relationship between absorption and concentration was also found for solution of Morphothion in acetone from 1×10^{-4} M to 4×10^{-4} M and in *n*-hexane from 1×10^{-4} M to 4×10^{-4} M (Fig. 6).

When using ultraviolet spectrophotometry for quantitative determination of concentration it is necessary to plot an analytical curve, which gives concentration directly from the measured absorption. The analytical curves obtained in the present study are shown in Figs. 5 and 6.

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Original Scientific Paper

FRAMES OF REFERENCE IN THE STUDY OF DIFFUSION IN BINARY SYSTEMS

by

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I. GENERAL TERMS

1. *Frame of Reference.* A reference coordinate system or frame of reference is a chosen coordinate system relative to which the flow of a mixture or a species is considered. The frame of reference can be locally fixed in the space which contains the mixture for a differential volume dV, or it can move at some velocity relative to some other frame of reference. To determine its position and velocity it should be associated with some parameter of the mixture through which a phenomenon is being examined. Then a local frame of reference can be set up relative to the center of gravity, center of volume, or center of moles of the mixture. In a multicomponent system the frame of reference can be associated with one of the components (usually the solvent), relative to which the transport of the other components is considered. The choice of the reference frame will greatly depend on the phenomenon to be studied, and on how and whether velocities, concentrations, etc. which define the frame of reference can be determined.

2. *Velocity of the Reference System.* The frame of reference may move with respect to some other system. If a multicomponent mixture is studied, the frame of reference coincides with the local center of gravity, center of volume, etc. Then the frame of reference moves at the velocity of the corresponding local center. Often it is necessary to observe two frames of reference at the same time. Their different velocities can be compared with respect to a third frame of reference which is fixed with respect to them (*sic*); this is usually the case with the reference frame of the cell in which a diffusion experiment is conducted. For example, if the velocity w_{mo} of the mass frame of reference (m) relative to the volume frame of reference (o) is sought, it can be derived from the velocity of the mass frame of reference relative to the reference frame of the cell (w_{mc}) and that of the volume frame of reference relative to the frame of the cell (w_{oc}), i.e.:

$$w_{\mathrm{mo}} = w_{\mathrm{mc}} - w_{\mathrm{oc}} \tag{1}$$

It must be remembered that the velocity of a given frame of reference as a rule can change with both position and time.

3. *Diffusion and Bulk Flow Fluxes.* — Diffusion fluxes occur when the velocities of molecular transport of the components in a mixture with respect to the selected frame of reference for the mixture are different. The "diffusion velocity" is the statistical mean velocity of the components relative to the mean velocity of the frame of reference, while the velocity of the frame of reference relative to the fixed system correspond to bulk flow. Table 1 shows diffusion velocities in various frames of reference.

TABLE 1

Diffusion velocity of species *i* $w_i - w^a$	Velocity of the system w^a	Concentration a	Frame of reference
$w_i - w$	w	$g_i\ (\varrho_i)$	m
$w_i - w'$	w'	$x_i\ (\varrho_i')$	M
$w_i - w^0$	w^0	$\bar{v}_i$	o
$w_i - w^r$	w^r	δ_{ik}	r

m = mass, *M* = molar, *o* = volume, *r* = frame of reference relative to one of the system components, δ_{ik} = Kronecker delta function.

Diffusion flux of component *i* whose diffusion velocity relative to the mean velocity of the frame of reference is determined, can be defined by the equation

$$j_i^a = a(w_i - w^a) \tag{2}$$

Diffusion fluxes defined in this manner are presented in Table 2 for various frames of reference.

Bulk flow flux means the amount of mixture or of a component which in unit times moves through a surface fixed relative to the frame of reference of the cell. The bulk flow flux N for a multicomponent mixture can be written

$$N = \sum_{i=1}^{n} N_i \tag{3}$$

where N and N_i are in mass units.

II. RELATIONS BETWEEN BULK FLOW AND DIFFUSION FLUXES

In the experimental measurement of diffusion in multicomponent systems diffusion fluxes can be defined in various frames of reference as shown in Table 2. Different fluxes, however, have different uses and importance in engineering calculations. The molar and mass bulk flow fluxes

N_1' and N_1 can be measured in the laboratory as they are defined in an external fixed frame of reference. The mass and molar diffusion fluxes j_i and J_i' are measures of the rate of diffusion. They are in frequent use for measuring the diffusion in cells with porous membranes. The fluxes j_i' and J_i are less used because the units of transport are not relative to the corresponding velocities of the frames of reference. The fluxes j_i° and J_i° are also often used, because the laws of the conservation of mass, energy and momentum for continuous media are expressed with respect to the volume frame of reference. Also used in experimental measurements on mixtures in which the transport of solutes is observed relative to the solvent are the fluxes relative to a component, j_i^r and J_i^r. However, it should always be kept in mind that the diffusion fluxes cannot be measured directly in cells with a porous membrane. They are functions of the diffusion velocities, not measurable in the laboratory with an external fixed frame of reference, and so for their determination special methods have been developed.

To find out the relations between different fluxes in various frames of reference (our considerations will center only on some more important relations), the law of the conservation of mass, which applies to every frame of reference, will be taken first. For the mass frame of reference this law is

$$j_1 + j_2 + \ldots = \sum_{i=1}^{n} j_i = 0 \tag{4}$$

i.e. the sum of diffusion mass fluxes in binary and multicomponent mixtures is zero. Also, for the molar and volume frames of reference

$$\sum J_i' = 0$$

$$\sum I_i^0 = 0$$

To obtain the relation between the mass bulk flow flux N_1 in the fixed frame of reference of the cell and the diffusion flux j_i in the mass frame of reference, we start from the equation defining the diffusion flux (2), which, applied to the given frame of reference, may be written

$$j_1 = \rho_1 (w_1 - w) \tag{5}$$

or

$$\rho_i w_i = j_i + \rho_i w = j_i + w \rho \frac{\rho_1}{\rho} \tag{6}$$

where the velocity can be generalizeed by Eq. (1). Summing Eq. (6) over all components and using Eq. (4) and the equation defining the mixture

$$\rho = \sum_{i=1}^{n} \rho_i \qquad (7$$

the expression for the velocity of the mass frame of reference is obtained:

TAB

Quantity	With respect to stationary axes	With respect to w
Velocity of species 1 $\left[\frac{cm}{s}\right]$	w_1	w_1-w
Mass flux of species 1 $\left[\frac{g}{cm^2 s}\right]$	$N_1=\rho_1\cdot w_1$	$j_1=\rho_1(w_1-w)$
Molar flux of species 1 $\left[\frac{g\,mol}{cm^2 s}\right]$	$N'_1=\rho'_1\cdot w_1$	$J_1=\rho'_1(w_1-w)$
Volume flux of species 1 $\left[\frac{cm^3}{cm^2 s}\right]$	$N^0_1=\rho_1 . \bar{v}_1 . w_1=\rho'_1 . \bar{v}'_1 . w'_1$	$I_1=\rho_1 . \bar{v}_1(w_1-w)$
Sum of mass fluxes $\left[\frac{g}{cm^2 s}\right]$	$N=\sum_i N_i=\rho . w$	$\sum_i j_i=0$
Sum of molar fluxes $\left[\frac{g\,mol}{cm^2 s}\right]$	$N'=\sum_i N'_i=\rho' . w'$	$\sum_i J_i=\rho'(w'-w)$
Sum of volume fluxes $\left[\frac{cm^3}{cm^2 s}\right]$	$N^0=\sum_i \rho_i w_i \cdot \bar{v}_i$	$\sum_i I_i=w^0-\rho v . w$
Fluxes in terms of N_1 and N_2	$N'_1=\frac{N_1}{M_1}$; $N'_2=\frac{N_2}{M_2}$	$j_1=N_1-(N_1+N_2)g_1$
Fluxes in terms of N'_1 and N'_2	$N_1=M_1 . N'_1$; $N_2=M_2 . N'_2$	$J_1=N'_1-\left(N'_1+\frac{M_2}{M_1} . N'_2\right)g_1$
Fluxes in terms of N^0_1 and N^0_2	$N_1=\frac{N^0_1}{\bar{v}_1}$; $N'_1=\frac{N^0_1}{\bar{v}'_1}$	$I_1=N^0_1-\left(N^0_1+\frac{\bar{v}_1}{\bar{v}_2}N^0_2\right)g_1$
Fluxes in terms of j_1 and w	$N_1=j_1+\rho_1 . w$	$J_1=\frac{j_1}{M_1}$
Fluxes in terms of J'_1 and w'	$N'_1=J'_1+\rho'_1 \cdot w'$	$J_1=\frac{M_2}{M_s}\cdot J'_1$
Fluxes in terms of I^0 and w^0	$N^0_1=I^0_1+\rho_1\bar{v}_1 w^0$	$I_1=\frac{\rho_2}{\rho}I^0_1$

Symbols

a — concentration in terms of which the reference frome is defined
D_i — diffusion coefficient (defined by Eq. (20))
g_i — mass fraction of species *i*
I_i — volume diffusion flux of species *i*
J_i — molar diffusion flux of species *i*
j_i — mass diffusion flux of species *i*
M_i — molecular mass of species *i*
M_s — molecular mass of the mixture
N_i — mass bulk flow flux of species *i* in fixed system
N'_i — molar bulk flow flux of species *i* in fixed system
v — specific volume of the mixture
v′ — molar volume of the mixture
$\bar{v}_i$ — partial mass volume of species *i*
$\bar{v}'_i$ — partial molar volume of species *i*

L E 2

With respect to w′	With respect to w°	With respect to wʳ
$w_1 - w'$	$w_1 - w^0$	$w_1 - w^r$
$j'_1 = \rho_1 (w_1 - w')$	$\overset{0}{j}_1 = \rho_1 (w_1 - w^0)$	$j^r_1 = \rho_1 (w_1 - w^r)$
$J'_1 = \rho'_1 (w_1 - w')$	$\overset{0}{J}_1 = \rho'_1 (w_1 - w^0)$	$J^r_1 = \rho'_1 (w_1 - w^r)$
$I'_1 = \rho'_1 \, . \, \overline{v}_1 (w_1 - w')$	$\overset{0}{I}_1 = \rho_1 \overline{v}_1 (w_1 - w^0)$	$I^r_1 = \rho_1 \, . \, \overline{v}_1 (w_1 - w^r)$
$\sum_i j'_i = \rho (w - w')$	$\sum_i \overset{0}{j}_i = \rho (w - w^0)$	$\sum_i j^r_i = \rho (w - w^r)$
$\sum_i J'_i = 0$	$\sum_i \overset{0}{J}_i = \rho' (w' - w^0)$	$\sum_i I^r_i = \rho' (w' - w^r)$
$\sum_i I_i = w^0 - \rho' \, . \, v' \, . \, w'$	$\sum_i \overset{0}{I}_i = 0$	$\sum_i I^r_i = w^0 - \rho v \, . \, w^r$
$j'_1 = N_1 - \left(N_1 + \frac{M_1}{M_2} N_2\right) x_1$	$\overset{0}{j}_1 = N_1 - \rho_1 (\overline{v}_1 \, . \, N_1 + \overline{v}_2 \, . \, N_2)$	$j^r_1 = N_1 - \frac{\rho_1}{\rho_r} N_r$
$J'_1 = N'_1 - \left(N'_1 + N'_2\right) x_1$	$\overset{0}{j}_1 = N'_1 - \rho'_1 \; (\overline{v}_1 N'_1 + \overline{v}_2 \, . \, N'_2)$	$J^r_1 = N'_1 - \frac{\rho'_1}{\rho'_r} N'_r$
$I'_1 = N^0_1 - \left(N^0_1 + \frac{\overline{v}'_1}{\overline{v}'_2} N^0_2\right) x_1$	$\overset{0}{I}_1 = \overset{0}{N}_1 - (\overset{0}{N}_1 + \overset{0}{N}_2) \rho_1 \, . \, \overline{v}_1$	$I^r_1 = N^0_1 - \frac{\rho_1 \overline{v}_1}{\rho_r \overline{v}_r} \; . \, N^0_r$
$j'_1 = \frac{M_8}{M_2} j_1$	$\overset{0}{j}_1 = \rho \, . \, \overline{v}_8 \, . \, j_1$	$j^r_1 = j_1 - \frac{\rho_1}{\rho_r} j_r$
$j'_1 = M_1 \, . \, J'_1$	$\overset{0}{J}_1 = \rho' \; . \; \overline{v}'_2 \, . \, J'_1$	$J^r_1 = J'_1 - \frac{\rho'_1}{\rho'_r} \, . \, J'_r$
$I'_1 = \frac{\rho'_2}{\rho'} I^0_1$	$\overset{0}{j}_1 = \frac{I^0_1}{\overline{v}_1}$	$I^r_1 = I^0_1 - \frac{\rho_1 \overline{v}_1}{\rho_r \overline{v}_r} I^0_r$

w — velocity of the frame of reference
w_i — velocity of species *i* in fixed system
x_i — molar fraction of species *i*
y — distance
ρ — mass density of the mixture
ρ' — molar density of the mixture
ρ_i — mass density of species *i*
ρ'_i — molar density of species *i*

Subindex:

r — denotes species *r*

Superscript:

′ — *A* prime denotes the molar frame of reference
° — denotes the volume frame of reference
r — denotes the frame of reference relative to species *r*

$$w_{\mathrm{mc}} = w = \frac{1}{\rho}(\rho_1 w_1 + \rho_2 w_2 + \ldots) = \frac{1}{\rho}\sum \rho_i w_i \tag{8}$$

Since the mass bulk flow fluxes are defined by

$$\mathrm{N}_i = \sum_{i=1}^{n} {}_i w_i \tag{9}$$

from Eqs. (6), (8) and (9), we obtain

$$\mathrm{N}_i = j_i + g_i \sum_{i=1}^{n} \mathrm{N}_i \tag{10}$$

where g_i signifies the mass fraction of species i in the mixture. From this equation it may be concluded that the mass bulk flow flux N_i in the frame of reference of the cell is made up of the sum of the two fluxes:

$g_i \sum_{i=1}^{n} N_i$ = mass flux of component i resulting from the flow of the mixture relative to the frame of reference of the cell

j_i = mass diffusion flux, defined by Eq. (6), which is related to the flow of a the mixture if its flow velocity is the velocity of the mass frame of reference (Eq. (8)).

Eqs. (6) and (10) are laws expressed in the frame of reference of the cell, Eq. (6) in terms of velocity and Eq. (10) of flux.

By analogy, for the molar frame of reference

$$w'_i \rho'_i = J'_i + w'\rho' \frac{\rho'_i}{\rho'} \tag{11}$$

and

$$N'_i = J'_i + x_i \sum_{i=1}^{n} N'_i \tag{12}$$

where ρ_i' = molar density of species i
ρ' = molar density of the mixture
x_i = molar fraction of species i

Also important in experimental work is the relation between mass fluxes in the reference frame of the cell and in the volume frame of reference. Again starting from Eq. (2) we have

$$j_i^0 = \rho_i (w_1 - w^0) \tag{13}$$

or

$$\rho_i w_i = j_i^0 + \rho_i w^0 \tag{14}$$

Multiplying Eq. (14) by the partial mass volume v_i

$$\rho_i \bar{v}_i w_i = \bar{v}_i j_i^0 + \rho_i \bar{v}_i w^0 \tag{15}$$

and use the relation for the mixture

$$\sum_{i=1}^{n} \rho_i \bar{v}_i = 1 \tag{16}$$

we get

$$(\bar{v}_1 j_1^0 + \bar{v}_2 j_2^0 + \dots) = \sum_{i=1}^{n} \bar{v}_i j_i^0 = 0 \tag{17}$$

i.e. the law of the conservation of mass in the volume frame of reference, which makes it evident that the fluxes j_i° are not independent. From Eqs. (15) and (17), the velocity of the volume frame of reference is obtained:

$$w_{oc} = w^0 = \bar{v}_1 w_1 + \bar{v}_2 w_2 + \dots = \sum_{1}^{n} \bar{v}_i w_i \tag{18}$$

and the desired relation between N_i and j_i° is obtained using (9), (15) and (18):

$$N_i = j_i^0 + \rho_i w^0 = j_i^0 + \rho_i \sum \bar{v}_i N_i \tag{19}$$

In a similar way the other relations between bulk flow fluxes and diffusion fluxes can be derived. Table 2 presents all these relations for a binary mixture.

Diffusion fluxes are experimentally expressed by Frick's First Law, which for diffusion in an ideal binary mixture (and also for multicomponent mixture without interactions between concentration gradients) gives the relation between the flux of species i with respect to the mass frame of reference due to motive force gradient, in terms of the transport coefficient:

$$j_i = -D_{ik} \frac{d\rho_i}{dy} \tag{20}$$

where the transport coefficient D_{i_k} is the diffusion coefficient defined in the same frame of reference. However, it is often necessary to represent various processes in frames of reference in which the diffusion flux, as defined by Eq. (20), does not give an experimentally measurable coefficient of diffusion (mass, molar frames of reference). Then it is necessary to set up relations between the diffusion flux in the frame of reference in which the phenomenon considered and the diffusion flux in the frame in which the quantities dependent on that flux can be determined experimentally (the volume frame of reference).

For the present the relation between the mass diffusion flux j_i defined in the mass frame of reference and the mass diffusion flux j_i° in the volume frame of reference will be singled out:

$$j_i = j_i^0 + \rho_i \sum_{i=1}^{n} \bar{v}_i j_i \tag{21}$$

i.e. the mass diffusion flux of species i in the mass frame of reference equals the sum of the mass diffusion flux of this species in the volume frame of reference and the flux of species i caused by the bulk flow of mass in the mass frame of reference. Here the motion of the volume frame of reference with respect to the mass frame of reference is observed, i.e. j_i° is the true diffusion flux and the j_i ($i = 1, 2, \ldots$) originate from the bulk flow in relation to the same frame of reference.

Eq. (21) can be simplified by using relation (8) and Eqs. (11) and (18), giving for the case of a binary system

$$j_i^0 = \rho \bar{v}_k j_i \qquad i, k = 1,2 \tag{22}$$

In a similar manner the other relationships between the diffusion fluxes can be derived. They are reviewed in Table 2.

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Original Scientific Paper

PHOTOLUMINESCENCE OF YOHIMBINE BORIC ACID PHOSPHOR

by

ŽELJKO A. KUĆER, BOŠKO J. DRAŠKOVIĆ and ILIJA Đ. BURIĆ

Yohimbine boric acid phosphorus excited with light of 366 nm manifests very strong luminescence(1). The parameters of the luminescence which were investigated in the present study (luminescent spectra, decay law of the phosphorescence, temperature quenching of phosphorescence) confirmed certain general rules concerning the luminescence of boric acid phosphors.

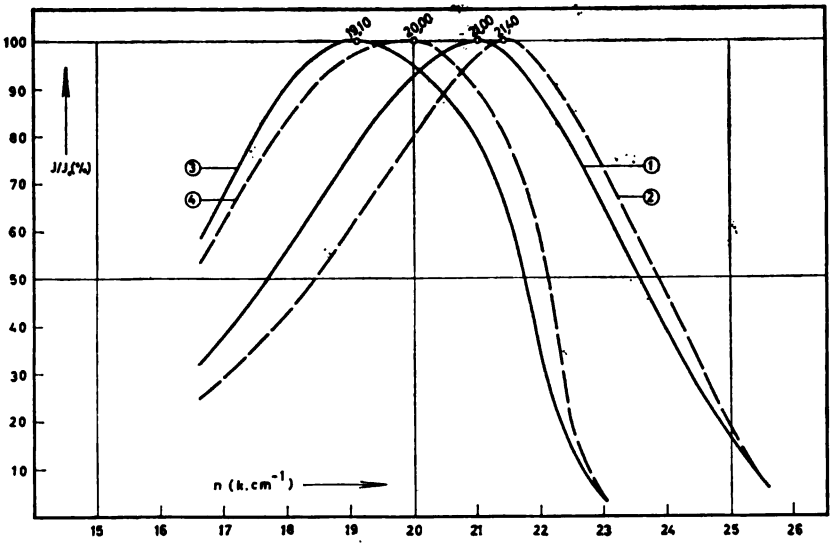

Figure 1

Phosphorescent and integral luminescent spectra of boric acid phosphor activated by yohimbine (activator concentration ranging from 10^{-3} to 10^{-5} *g/g*): *a* — integral luminescence: curve 1 (20°C), curve 2 (—183°C); b — phosphorescence: curve 3 (20°C), curve 4 (—183°C)

Phosphors were prepared with different concentrations of the activator (from 10^{-3} to 10^{-5} *g/g*) by the known methods(2, 3). All the phosphors were studied in a single piece of the same dimensions (thickness 1 *mm*).

The luminescent spectra were measured by means of a spectral photometer. The exciting source was a high pressure Hg-lamp with a 2 *mm* BG 12 + 2 *mm* UG 2 filter (Schott) for selection of the 366 *nm* line. The same apparatus was used to study the temperature quenching of phosphorescence. The mean life of phosphorescence was measured by means of an apparatus with synchronized apertures for the exciting and phosphorescent radiation(1).

The luminescent spectrum of yohimbine boric acid phosphor excited with light of 366 *nm*, is composed in general of two components which correspond respectively to the transitions between states of the same multiplicity (with a very short mean life and shorter wavelength — fluorescence) and the states of different multiplicity (with a long mean life and longer wavelength — beta-phosphoresence). Fig. 1 shows the relative energy distribution of the integral luminescence* and the beta-phosphorescence of this phosphorus.

The fluorescence was pale blue; the phosphorescence was green, very strong and of long duration. The spectra consisted of a single wide band with a marked maximum. The investigated range of activator concentration from 10^{-8} to 10^{-5} *g/g* did not influence the position and shape of the spectra but only the intensity of luminescence. At low temperature both spectral bands were shifted towards shorter wavelengths (Table 1).

TABLE 1

Spectrum of luminescence

Activator concentration *(g/g)*	Maximum *(k.cm^{-1})*			
	Integral spectrum		Phosphorescence spectrum	
	20°C	—183°C	20°C	—183°C
10^{-8}—10^{-5}	21.00	21.40	19.10	20.00

Starting from the scheme of Jablonsky(4), in view of the shape of the spectrum, it may be concluded that the metastable level which defines the beta-phosphorescence relative to the ground state, is very near the first excited level from which the transition to the ground state is allowed. At higher temperatures one would expect the appearance of alfa-phosphorescence. However, this transition does not take place, which shows that the energy level scheme of yohimbine boric acid phosphor is somewhat different from that postulated and developed by Lewis, Kasha and co-workers(5-7).

The phosphorescent intensity decreased with time according to an exponential law independently of the activator concentration (Fig. 2). The activator concentration also did not influence the mean life of phosphorescence. Lowering the temperature greatly increased the mean life (Table 2),

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* Integral luminescence means the superposition of fluorescence and phosphorescence.

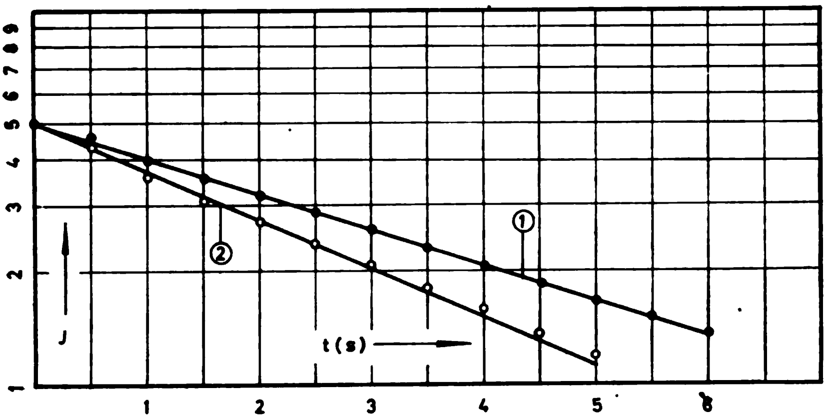

Figure 2

Phosphorescence decay (activator conc. ranging from 10^{-3} to 10^{-5} *g/g*): curve 1 (—183°C), curve 2 (20°C)

TABLE 2

The mean life of phosphorescence

Activator concentration (*g/g*)	*τ (sec)*	
	20°C	—183°C
10^{-3}—10^{-5}	3.50	4.60

due to the influence of temperature on the density of the oscillatory levels of the ground state and the metastable state.

With increase of temperature the phosphorescence was quenched (Fig. 3). Its intensity started to decrease at 50°C and followed the Mott-Seitz formula:

$$I = \frac{I_0}{1 + C_1 \exp\left(-\frac{C_2}{T}\right)},$$

where:

I_0 = initial intensity (approximate)
I = intensity at temperature
T = absolute temperature
C_1, C_2 = constants

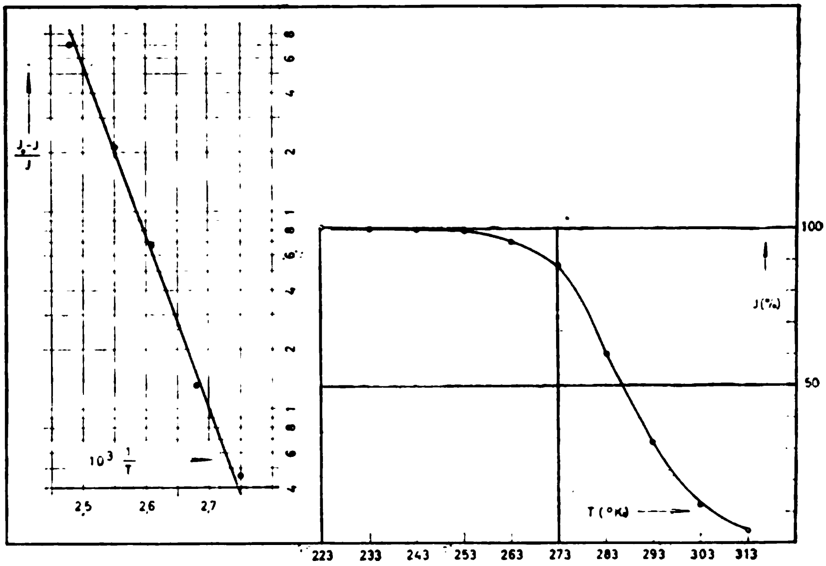

Figure 3

Temperature quenching of phosphorescence of yohimbine boric acid phosphor (activator conc. 10^{-3} to 10^{-5} *g/g*); auxiliary graph: verification of the Mott-Seitz formula

The values of the constants are: $C_1 = 2.29 \cdot 10^{22}$, $C_2 = 1.99 \cdot 10^4$ (°K) (Fig. 3, auxiliary graph).

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Original Scientific Paper

SOME FACTORS INFLUENCING THE CRYSTALLIZATION OF ALUMINUM-III-FLUORIDE FROM SUPERSATURATED SOLUTIONS*

by

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The classical procedure for obtaining aluminum-III-fluoride is based on a reaction between hydrofluoric acid and aluminum hydroxide according to the formula

$$3HF + Al(OH)_3 \rightarrow AlF_3 + 3H_2O \qquad (I)$$

Besides this procedure, which was also the first to be applied in industry during recent years another procedure has been used which produces aluminum-III-fluoride from the cheaper silico-hydrofluoric acid(1), according to formula

$$H_2SiF_6 + 2Al(OH)_3 \rightarrow 2AlF_3 + SiO_2 + 4H_2O \qquad (II)$$

In these procedures, which are done in aqueous solutions, aluminum-III-fluoride is first obtained in the form of a metastable supersaturated solution(1). From these solutions, by means of crystallization under appropriate conditions, $AlF_3 . 3H_2O$ is obtained. The trihydrate is then dehydrated to anhydrous AlF_3, which is used as a solvent.

Two structurally different forms of $AlF_3 . 3H_2O$ are often mentioned in the literature: α-form, which is soluble and has a tendency to form metastable supersaturated solutions, and β-form, which is practically insoluble and stable. During crystallization at favorable temperatures the soluble α-aluminum-fluoride is converted irreversibly into the insoluble β-form. According to Ehret and Frere(2) at 25°C only 0.41% β-AlF_3 dissolves.

Crystallization is an important part of the so-called wet procedures for obtaining aluminum-III-fluoride. Therefore, in the present study we tried to determine the optimum conditions for this crystallization.

According to the literature, for the crystallization of 80% to 90% of $AlF_3 . 3H_2O$ from supersaturated solution with vaccination, heating and mixing for 4 to 6 hours is needed, and according to some authors even as long as 20 hours(1, 3, 4, 5, 6).

Of the factors which can influence the crystallization, in the present study we investigated the concentration of the solution, the pH and the temperature.

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INFLUENCE OF SOLUTION CONCENTRATION ON THE CRYSTALLIZATION OF $AlF_3 . 3H_2O$

The supersaturated solution of aluminum-III-fluoride obtained by reaction between H_2SiF_6 and hydrated alumina (in a deficit of 5%), contained after the removal of the SiO_2 precipitate 184 *g* of $AlF_3 . 3H_2O$ in 500 *ml* solution, or 18.08% AlF_3. In this reaction a gelatinous precipitate of silicic acid is formed, and because of adsorption on the precipitate there may be a considerable loss of aluminum-III-fluoride on separation of the precipitate from the solution for crystallization. In order to cut down losses it is necessary to wash the SiO_2 precipitate thoroughly with water, and to add this to the filtrate. The precipitate was washed with about 500 *ml* of water, thus dubling the volume of filtrate to 1000 *ml*.

In order to study the influence of this great dilution, solutions of the following concentrations were crystallized under the same conditions (with regard to temperature, quantity of vaccine etc.):

a) partially evaporated solutions (before the appearance of the first crystals), the concentration of which was 21.6% AlF_3;

b) undiluted solutions, without water from the rinsing, the concentration of which was 18.08% AlF_3;

c) solutions diluted with water from rinsing of the SiO_2 precipitate, concentration 10.04% AlF_3.

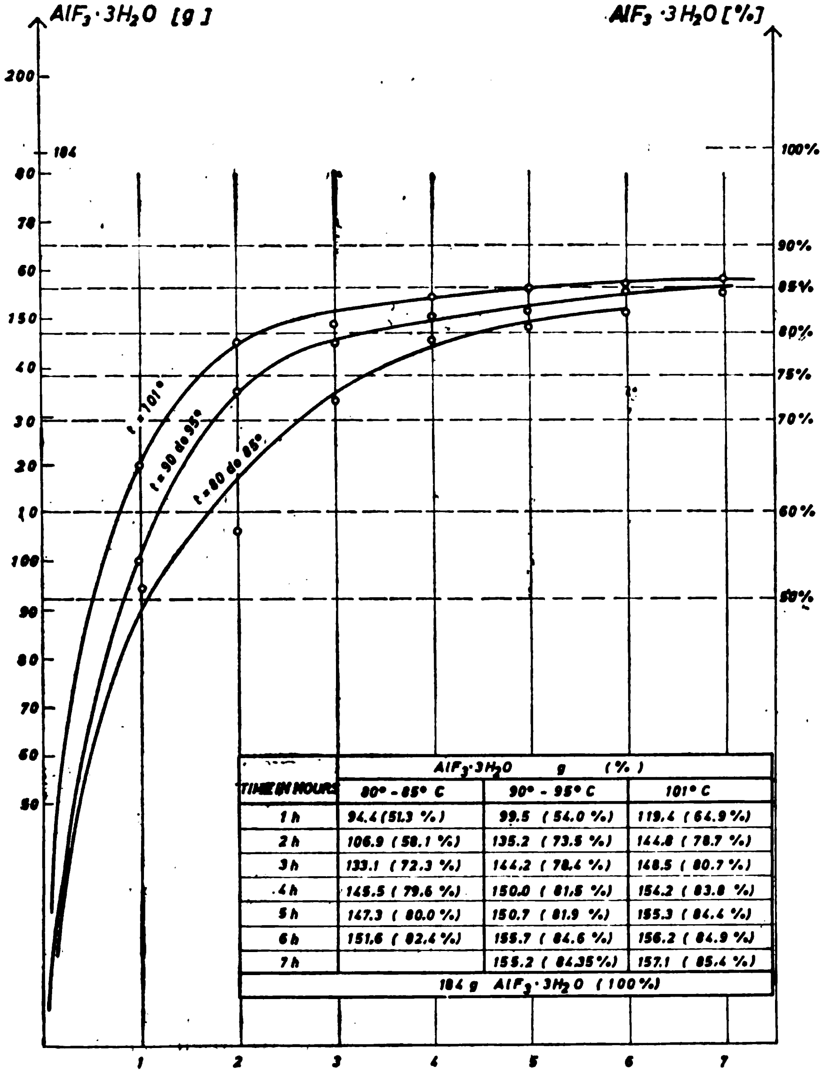
In all three case almost the same quantities of $AlF_3 . 3H_2O$ crystals were obtained during the same time of four hours. In fact, in all three cases the solution was highly supersaturated, considering the poor solubility of β-AlF_3. It is possible that the influence of concentration would have manifested itself only at much higher concentrations, but this possibility was not investigated in the present study. Hence, it may be concluded that in supersaturated solutions of concentration 10% AlF_3 or more the initial concentration of the solution has practically no influence on the rate of crystallization.

Two important conclusions with practical implications can be derived from these observations. First, there is no need to evaporate the solution of aluminum-III-fluoride obtained according to reaction II, as this does not accelerate the crystallization. During evaporation some undesired effect may even occur, such as precipitation the monohydrate $AlF_3 . H_2O$ in the form of a hard crust which becomes cemented to the bottom of the vessel. Secondly, it is possible to dilute the solution of aluminum-III-fluoride obtained according to reaction I to half-strength with water from rinsing the SiO_2 precipitate, without fear that the crystallization will be slowed down.

INFLUENCE OF SOLUTION pH ON THE CRYSTALLIZATION

The solution of aluminum-III-fluoride obtained according to reaction II is acid. If silico-hydrofluoric acid and aluminum hydroxide are taken in the stoichiometric ratio, the pH of the filtrate after removal of the SiO_2 precipitate is about 2.5. With an excess of 5% $Al(OH)_3$ the pH is about 3, and with a deficit of 5% $Al(OH)_3$ it is about 1.

We established experimentally that the rate of crystallization increased with increasing acidity. Furthermore the crystals of $AlF_3 . 3H_2O$ obtained from highly acid solution, pH $\sim$ 1, had the lowest content of inpermissible impurities: Si, P, and Fe. The addition of concentrated hydrochloric acid to the filtrate, in order to accelerate crystallization, had practically no positive effect.



TIME IN HOURS	$AlF_3 \cdot 3H_2O$ g (%)		
	80° - 85° C	90° - 95° C	101° C
1 h	94.4 (51.3 %)	99.5 (54.0 %)	119.4 (64.9 %)
2 h	106.9 (58.1 %)	135.2 (73.5 %)	144.8 (78.7 %)
3 h	133.1 (72.3 %)	144.2 (78.4 %)	148.5 (80.7 %)
4 h	145.5 (79.6 %)	150.0 (81.5 %)	154.2 (83.8 %)
5 h	147.3 (80.0 %)	150.7 (81.9 %)	155.3 (84.4 %)
6 h	151.6 (82.4 %)	155.7 (84.6 %)	156.2 (84.9 %)
7 h		155.2 (84.35 %)	157.1 (85.4 %)
184 g $AlF_3 \cdot 3H_2O$ (100 %)			

Figure 1

Amounts of $AlF_3.3H_2O$ crystals obtained by crystallization at different temperatures

INFLUENCE OF TEMPERATURE ON THE CRYSTALLIZATION OF $Al_3.3H_2O$

Various authors give different temperatures favorable for the crystallization of $AlF_3 . 3H_2O$ from supersaturated solutions. Temperatures most frequently mentioned are between 78° and 98°C.

The amount of $AlF_3 \cdot 3H_2O$ crystals obtained after each hour of crystallization was determined at the following temperatures:

a) $t = 80°$ to 85°C
b) $t = 90°$ to 95°C
c) $t = 101°C$ (the boiling point of the solution).

The solutions for crystallization were pH ~ 1, as they were obtained with a deficit of 5% $Al(OH)_3$ relative to the stoichiometric quantities for equation II. Water from rinsing the SiO_2 precipitate was added to them, so that their volume was twice greater than that of the filtrate. Fifty grams of $AlF_3 \cdot 3H_2O$ crystals were added to each solution, which was about 27% of the expected quantity of crystals. The crystallization was done in a flask with reflux condenser, with continuous mixing.

The results are shown graphically in Fig. 1. The greatest rate of crystallization was obtained at 101°C, that is at the boiling point of the solution. At this temperature about 79% of the total amount of aluminum-III-fluoride crystallized from the solution in two hours, and nearly 84% in four hours. Further prolongation of the crystallization time did not increase the yield much: after another three hours, so that the total duration of crystallization was seven hours, the yield was only increased 1.6%. Thus in seven hours a total of 85.4% was crystallized. This evidently does not represent a significant increase in comparison to four hours crystallization.

CONCLUSION

It is concluded from the experiments that the optimum conditions for obtaining high purity crystals of $AlF_3 . 3H_2O$ from supersaturated solutions by crystallization are as follows. A temperature of 101°C, at which the solution boils. Highly acid solution, pH ~ 1, which can be obtained by taking 5% less $Al(OH)_3$ than the stoichiometric quantity according to equation II. Before crystallization a relatively great quantity of vaccine crystals of $AlF_3 . 3H_2O$, about 27% of the expected yield of crystals, should be added to the solution. During crystallization the solution should be continuously mixed.

The filtrate obtained according to equation II, after removal of the SiO_2 precipitate, can be twice diluted with water from rinsing the precipitate without any untoward effect whatsoever on the rate of crystallization. A reasonable duration of crystallization is four hours, in which time about 84% of the total quantity of aluminum-III-fluoride crystallizes out.

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Original Scientific Paper

PHOSPHORUS IN CRUDE FLUOROSILICIC ACID*

by

SLOBODAN D. RADOSAVLJEVIĆ and VERA Č. ŠĆEPANOVIĆ

The fluorosilicic acid which is obtained as a by-product in the production of superphosphate or phosphoric acid from fluoroapatite has been used in recent years as a cheap source for obtaining various fluorine compounds(1, 2, 3). Because it is obtained by means of gas absorption, the crude fluorosilicic acid contains relatively little impurities. Impurities in the form of soluble compounds of phosphorus, iron, arsenic, titanium, and of solutions of the acids HF, HCl and H_2SO_4, are usually only present in very small quantities(4). Convenient methods of removal have been developed for the majority of these impurities(4, 5). The poorest results have been achieved with regard to the removal of phosphorus. Furthermore, phosphorus is particularly undesirable when fluorosilicic acid is used for obtaining the solvents aluminum-III-fluoride and cryolite, which must not contain more than 0.02% P_2O_5. In order to obtain solvents with such a small content of phosphorus, the fluorosilicic acid must not contain more than 0.2 to 0.3 *g* P_2O_5/*lit*(6). The phosphorus level in the crude fluorosilicic acid is often greater. The phosphorus concentration in the solutions of H_2SiF_6 varies from 0.1 to 25 *g* P_2O_5/*lit*, but most frequently is within the range from 0.1 to 6 *g* P_2O_5/*lit*(5).

TESTING THE QUALITY OF CRUDE FLUOROSILICIC ACID AND ATTEMPTS TO REMOVE PHOSPHORUS

In the present study we tested the quality of industrial H_2SiF_6 acid from two Yugoslav factories: the Superphosphate Factory in Prahovo and "Zorka" Chemical Industry in Šabac. There is considerable difference between these two crude acids as regards the concentration of both fluorosilicic acid and of the undesirable impurities phosphorus and iron. That from the Superphosphate Factory is more concentrated and also contains much more phosphorus and iron. Table 1 shows the concentrations and phosphorus and iron content in the two crude acids.

Considering that in the acid from Prahovo phosphorus was much above the permissible limit for solvent production, we made an attempt to remove the excess phosphorus. We assumed that all phosphorus is pre-

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* Reported at the II Congress for Pure and Applied Chemistry, June 1966, Belgrade.

TABLE 1

Phosphorus and iron in H_2SiF_6 solutions

Source of acid	H_2SiF_6 %	P_2O_5 *g/lit*	Fe_2O_3 *g/lit*
Superphosphate Factory, Prahovo	22	3.66	2.65
"Zorka" Chemical Industry, Šabac	23	0.2	0.11

sent in the form of phosphate ion, which was also the opinion of other authors(4, 5). Attempts at removing phosphorus by precipitation with Pb^{2+} ion, which forms poorly soluble phosphates with PO_4^{3-} ion, did not yield satisfactory results. We also attempted to remove phosphorus by running H_2SiF_6 through a column of active carbon. Almost all the phosphorus was removed, but at the same time the concentration of H_2SiF_6 was decreased from 27% to 16%.

These attempts indicated the possibility that the phosphorus was not only present in the form of PO_4^{3-} ion, but also in the form of some other ions, most likely of the complex type.

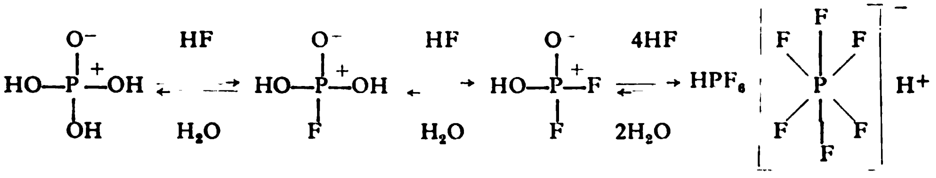
FLUORO-PHOSPHORIC ACIDS AND THEIR DETERMINATION

Forty years ago(7, 8, 9) three fluoro-phosphoric acids were studied and described:

H_2PO_3F	HPO_2F_2	$H(PF_6)$
Monofluoro-phosphoric acid	Difluoro-phosphoric acid	Hexafluoro-phosphoric acid

The first two acids have been isolated in the pure, anhydrous state, while the third, $H(PF_6)$, is known only in aqueous solutions. In a more detailed study of these compounds Lange and co-workers(9, 10) found that fluoro-phosphoric acids easily transform into each other, that they are susceptible to hydrolysis, and that the end product of their hydrolysis is ortho-phosphoric acid. However, although susceptible to hydrolysis, the fluoro-phosphoric acids can be formed even in the presence of considerable quantities of water.

The mechanism of formation of fluoro-phosphoric acid has not so far been adequately explained. It is explained on the basis of gradual substitution of fluoride ions for OH^- groups owing to the almost identical dimensions of these single-charge negative ions. The scheme of formation of fluoro-phosphoric acids from ortho-phosphoric and hydrofluoric acid, and of their hydrolytic decomposition to ortho-phosphoric acid, is:



H_3PO_4 Ortho-phosphoric acid — H_2PO_3F Monofluoro-phosphoric acid — HPO_2F_2 Difluoro-phosphoric acid — $H[PF_6]$ Hexafluoro-phosphoric acid

Hexafluoro-phosphoric acid is the most stable in aqueous solution, difluoro-phosphoric acid the least stable.

All the three fluoro-phosphoric acids Lange and co-workers(9, 10) obtained by one of the following ways:

a) reaction between P_2O_5 and 40% HF
b) hydrolysis of the gases POF_3 or PF_5
c) reaction between conc. H_3PO_4 and HF

The salts of the three acids show considerable differences. Salts of monofluoro-phosphoric acid are similar to sulfates, in the same way as pure mono-acid is similar to sulfuric acid — a heavy oily fluid. They differ from sulfates in hydrolysis; salts of monofluoro-phosphoric acid are very susceptible to hydrolysis. Salts of di- and hexafluoro-phosphoric acid are similar to perchlorates; this similarity is particularly marked with the salts of hexafluorophosphoric acid(9, 10).

Nitron (4,5-dihydro-1,4-diphenyl-3,5-phenylimino-1,24-tryazol), know as a reagent for the determination of nitrates and perchlorates, is recommended as the analytical reagent for difluoro-phosphoric and hexafluoro-phosphoric acid. With nitron both fluoro-phosphoric acids form poorly soluble precipitates of the following composition:

$$C_{20}H_{16}N_4 \,.\, HPO_2F_2 \quad \text{and} \quad C_{20}H_{16}N_4 \,.\, HPF_6$$

For the determination of monofluoro-phosphoric acid there is no known specific reagent. Its determination is made particularly difficult by the fact that it is usually present in a mixture with di- and hexafluoro-phosphoric acid, and orthophosphoric acid as well(9, 10).

DETERMINATION OF FLUORO-PHOSPHORIC ACID IN FLUOROSILICIC ACID

For the determination of di- and hexafluoro-phosphoric acid in the crude fluorosilicic acid we used nitron.

The solution of H_2SiF_6 (from Prahovo) was neutralized with ammonia while cooling. SiO_2 formed by hydrolysis of the previously formed $(NH_4)_2SiF_6$ precipitated. After removal of the SiO_2 precipitate, 10% acetate solution of nitron was added to the filtrate acidified with acetic acid. After prolonged standing colorless crystals appeared, which could have been a mixture of nitron-difluoro-phosphate and nitron-hexafluoro-phosphate.

The presence of hexafluoro-phosphate in these crystals was demonstrated in the following way:

The crystals obtained were first separated by filtration. After that they were dissolved by shaking in a separation funnel with a mixture of 25% NH_4OH and chloroform. During this the soluble NH_4-salts of di- and hexafluoro-phosphoric acid passed into the water layer, while nitron stayed in the chloroform layer. The presence of hexafluoro-phosphate ions in the water layer was demonstrated by means of the reaction with nickel-hexammine, which with $(PF_6)^-$ ions gives pale violet crystals of the composition $Ni(PF_6)_2.6NH_3$, of very low solubility in water (0.052 *g*/100 *ml*). Considering that identical crystals were also obtained with HPF_6-acid, which we synthesized by dissolving P_2O_5 in 40% hydrofluoric acid, we can claim that these experiments proved the presence of $(PF_6)^-$ ions in the crude fluorosilicic acid.

We were unable to quantitatively determine di- and hexafluoro-phosphoric acid in fluorosilicic acid by means of nitron, because with nitron it is not possible to obtain pure precipitates, and attempts to purify them by means of recrystallization involved great losses.

For that reason we decided to determine only the total phosphorus present in H_2SiF_6 in the form of fluoro-phosphate ion, on the assumption that all the phosphorus which is not present as PO_4^{3-} ion is present in the form of mono-, di- or hexafluoro-phosphate ion.

The total phosphorus was determined in the following way. By prolonged boiling and evaporation of the solution of H_2SiF_6 all the fluoro-phosphoric acids were hydrolyzed to orthophosphoric acid, so that all the phosphorus was transferred to $PO^3{}_4^-$ ions. After this treatment total phosphorus was determined by precipitation with ammonium molybdate.

Phosphorus present in the form of $PO^3{}_4^-$ ion was separated by precipitation with $Pb(CH_3COO)_2$. The solution of fluorosilicic acid was first neutralized with ammonia, and then the solution of $Pb(CH_3COO)_2$ was added. The precipitate, which also contained $Pb_3(PO_4)_2$, was filtered off, the filtrate acidified, and by introducing H_2S the excess Pb^{2+} was removed. After separation of the PbS precipitate the filtrate was boiled and then strongly acidified with nitric acid, evaporated to dryness, and phosphorus determined by means of ammonium molybdate. The quantity of phosphorus thus obtained corresponded to phosphorus present in the form of fluoro-phosphoric acids.

The results obtained with H_2SiF_6 from Prahovo showed that about 90% of the total phosphorus in this acid is in the form of phosphate ion, while the remaining 10% is most likely in the form of mono-, di- and hexa-fluoro-phosphoric acid.

THE POSSIBILITY OF FLUORO-PHOSPHORIC ACIDS FORMING IN THE PRODUCTION OF H_2Si_6F

Another interesting question with regard to the presence of fluoro-phosphoric acid in industrial fluorosilicic acid is the problem of their formation in the course of the process producing this acid.

Fluoro-phosphoric acids can also be obtained by hydrolysis of the gases POF_3 or PF_5. In 1927 Lucas and Ewing(11) reported that PF_5 is obtained by reaction of P_2O_5 (or H_3PO_4) with CaF_2. After that authors confirmed(12,13) that gaseous phospho-fluorides and phospho-oxifluorides are formed during the reaction between H_3PO_4 and CaF_2. Therefore, during the first phase of the production of phosphoric acid or superphosphate, when fluoro-apatite is exposed to the action of sulfuric acid, there is a possibility of obtaining gaseous phospho-fluorides and phospho-oxifluorides as well as gaseous SiF_4 and HF. On absorption of these gases in water SiF_4 gives a solution of H_2SiF_6, and phospho-V-fluoride and phospho-oxifluoride can undergo hydrolysis in the following way:

$$\underset{\substack{\text{Phospho-V-}\\\text{fluoride}}}{PF_5} \xrightarrow{HOH} \underset{\substack{\text{Phospho-}\\\text{oxi-}\\\text{flucride}}}{POF_3} \xrightarrow{HOH} \underset{\substack{\text{Difluoro-}\\\text{-phosphoric}\\\text{acid}}}{HPO_2F_2} \xrightarrow{HOH} \underset{\substack{\text{Monofluoro-}\\\text{-phosphoric}\\\text{acid}}}{HPO_3F} \xrightarrow{HOH} \underset{\substack{\text{Ortho-}\\\text{phosphoric}\\\text{acid}}}{H_3PO_4}$$

Apart from this, reactions are also possible between HF present in the waste gases and the phospho-fluorine gases or their hydrolysis products, as summarized in the following formulas:

$$\underset{\substack{\text{Difluoro-}\\\text{-phosphoric}\\\text{acid}}}{HPO_2F_2} \xrightarrow{HF} \underset{\substack{\text{Phospho-oxi-}\\\text{fluoride}}}{POF_3} \xrightarrow{2HF} \underset{\substack{\text{Phospho-}\\\text{penta-}\\\text{fluoride}}}{PF_5} \xrightarrow{HF} \underset{\substack{\text{Hexafluoro-}\\\text{-phosphoric}\\\text{acid}}}{HPF_6}$$

These reactions can explain the presence of both phosphoric acid and fluoro-phosphoric acids in the solution of crude fluorosilicic acid obtained during the production of superphosphate from fluoro-apatite.

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Original Scientific Paper

OSCILLOGRAPHIC-CHRONOPOTENTIOMETRIC TITRATION. III.

INFLUENCE OF THE A.C. CIRCUIT PARAMETERS AND THE ELECTRODES ON THE ACCURACY

by

ĐORĐE K. STEFANOVIĆ, VILIM J. VAJGAND and TIBOR A. KIŠ

In our earlier studies we have described the principles of oscillographic-chronopotentiometric titrations(1) and investigated the influence of direct current and of the composition of the titrated solution on the accuracy of the determination(2).

The aim of the present study was to investigate the influence of parameters of the alternating current circuit and of the electrodes on the accuracy of determination, using the titration of arsenic (III) as a model. The parameters studied were the type of oscillographic curve, the series resistance, the a.c. source voltage, the resistance of the galvanic cell, the rate of polarization of the electrodes, and the waveform of the driving oscillations.

In oscillographic-polarographic determination the distortion of the derivative curve is more marked than that of the $E = f(t)$ oscillogram. Ions also separate out on the electrode at the end-point, and it was possible to predict that the phenomena resulting from this separation would also cause more marked distortion of the derivative than of the $E = f(t)$ curve. In our experiments we found that the determinations were in fact better when the dE/dt curves were used (Table 1).

The resistance in the a.c. circuit (Fig. 1 of part I of the study(1)) is intended to ensure a constant alternating current even when the EMF of the galvanic cell, at the end-point of titration, suddenly changes. Since the capacitative current, which influences the shape of the oscillogram, depends on the value of this resistance, there is a range of resistances within which the oscillogram before the end-point will be a sine wave. Outside this interval the oscillograms would be irregular curves, so that the distortions which occur at the end-point would be less marked.

The voltage of the a.c. source and the series resistance should be chosen such that before the end-point the alternating voltage does not reach the separation potential of indicator ions. The a.c. voltage and the resistance were varied to find the optimum values.

In oscillographic-polarographic determinations the resistance of the galvanic cell should be as small as possible. Considering that similar phenomena take place at the end-point of oscillographic-chronopotentiometric titrations, we hypothesized that the distortion of the oscillogram would be greater if calomel electrodes of low resistance, i.e. with a large mercury surface area, were used.

By superimposing an alternating current of frequency lower than 50 *c/s*, the capacitive current is reduced in comparison with the faradic current, which should produce greater distortion of the oscillogram. This hypothesis was experimentally confirmed as well.

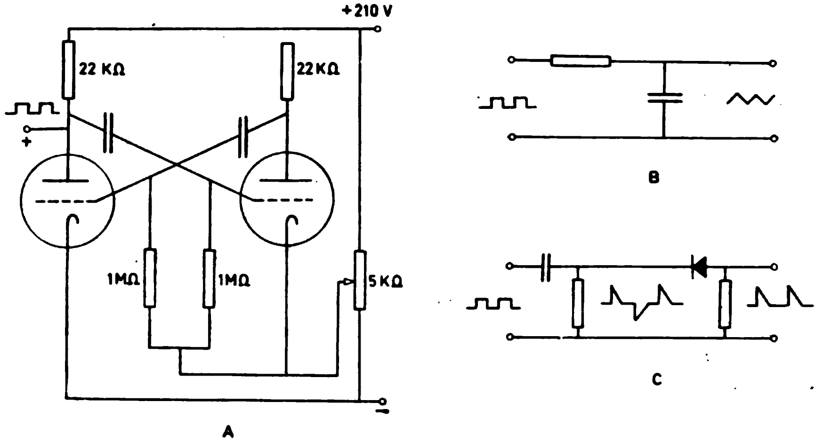

Figure 1

Circuit diagram of: *a* = multivibrator, *b* = integrating circuit, *c* = differentiating circui

If instead of sinusoidal oscillations we use sawtooth, square or pulse oscillations, the oscillographic distortion should be more marked. The results of the determinations in which toothed oscillations were used were in fact more accurate than those of the determinations done with sine waves (Table 2).

Considering that the processes during the depolarization of electrodes largely depend on the type, size, and quality of the surface and shape of the electrode at which the ions separated, we hypothesized that the shape and size of oscillographic distortion would also greatly depend on these factors. The experimental results confirmed this hypothesis (Table 3 and Fig 3).

EXPERIMENTAL

The preparation and standardization of 0.1 M solution of potassium bromate and arsenic trichloride, the determination procedure and the apparatus for the potentiometric titration and the oscillographic-chronopotentiometric titration have been described earlier⁽¹⁾.

Sinusoidal oscillations of a frequency below 50 *c/s* were produced by a Philips GM 2307 signal generator. Square waves were produced by means of a multivibrator (Fig. 1 *a*). By integrating these we obtained sawtooth oscillations (Fig. 1 *b*), and by differentiating them impulse oscillations (Fig. 1 *c*). By including a germanium diode (Fig. 1 *c*) negative pulses were eliminated.

TABLE 1

Comparison of results obtained by observation of E = f(t) and dE/dt = f(t)

Conditions of determination: As (III) in 5 M potassium bromide and 5 N hydrochloric acid is titrated with 0.1 N potassium bromate; spherical platinum electrode as indicator, SCE as reference electrode; sinusoidal a.c. (220 V, 50 c/s), 450 kΩ resistance, 0.33 μF capacitor (see fig. 1 and 3 of part I(1))

E – f(t)			dE/dt – f(t)		
mg arsenous oxide		relative error in %	*mg* arsenous oxide		relative error in %
taken	found		taken	found	
18.3	18.1	—1.0	19.2	19.3	0.5
21.4	21.6	1.1	20.3	20.5	0.7
24.6	24.4	—0.8	23.8	23.7	—0.6
98.6	99.5	0.9	45.2	45.0	—0.4
99.4	98.4	—1.0	46.8	47.0	0.4
100.2	101.4	1.2	104.3	104.9	0.6
108.2	107.3	—0.0	48.6	48.4	—0.5
118.3	119.3	1.0	115.2	114.7	—0.5
122.4	123.5	1.1	121.5	121.0	—0.4
Average deviations in %		1.0			0.5

1. INFLUENCE OF THE A.C. CIRCUIT PARAMETERS

Influence of the type of curve. Distortion of the dE/dt oscillograms was more marked and more sudden (Fig. 3 of part I of the study(1) than that of E = f(t) curves. The results obtained by means of the derivative oscillograms were better (Table 1), and for that reason subsequently only these were applied.

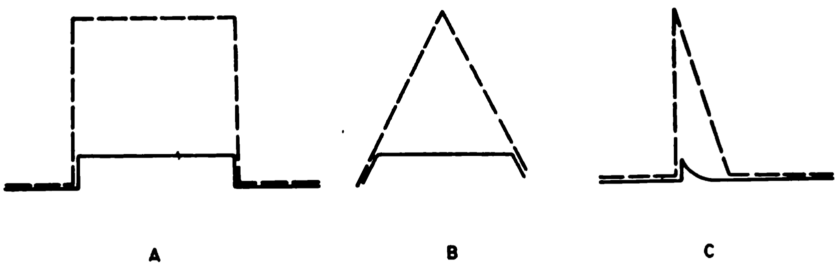

Figure 2

Oscillogram distortions in oscillographic-chronopotentiometric titrations with:

a — square wave, b — sawtooth, c — impulse oscillations

– – – – – – – = oscilogram before the end-point

———————— = oscillogram at the end-point.

Influence of the series resistance. A high resistance, 100 K Ω, gave a weak alternating current (0.1—1 *mA*) through the galvanic cell whose wave form was the same as that of the input voltage. The capacitative current is small and the charging time of the condenser (electrode with its differential capacity) is longer, the sinusoid thus being less steep. The distortions at the end-point are shown in Fig. 1 of part I⁽¹⁾.

With smaller resistances, from 35 K Ω to 45 K Ω, the sinusoid is steeper and slightly deformed because of the influence of the EMF of the galvanic cell. The distortion of the oscillogram at the end-point is less sudden and of a different shape from those obtained with greater resistances.

In the absence of the resistance there is no distortion of the oscillogram at the end-point.

Influence of the a.c. source voltage. With decreasing a.c. source voltage from 260 *V* to 40 *V* the distortion of the oscillogram increased. It was not possible to decrease the voltage further as the gain of the oscillograph was not sufficient.

Influence of the resistance of the galvanic cell. It was not possible to obtain distortion of the oscillograms at the end-point when using a Radiometer type K 100 calomel electrode as this electrode has a high resistance. With reduction of the resistance of the galvanic cell by increasing the area of mercury in the calomel electrode to 150 cm^2 and the diameter of the electrolytic bridge to 3 *cm*, the distortion was more marked and the results of the determinations better.

Influence of the alternating current frequency. When the indicator electrode was polarized slower (by using lower frequency sine waves, e.g. 2—10 *c/s*), the condenser current was decreased in comparison with the faradic current, so that the shape of the oscillogram was not changed but the distortion at the end-point was more sudden and greater.

Influence of the wave form. With sine waves the distortion was not as marked (Fig. 3 of part I⁽¹⁾ as with square (Fig. 2*a*), sawtooth (Fig. 2*b*) and impulse oscillations (Fig. 2*c*). The most marked distortions and the best determinations were obtained by superimposing these later.

2. INFLUENCE OF THE ELECTRODES

Platinum and saturated calomel electrode. Platinum electrodes with a very small surface area (about 0.05 mm^2) or a very large surface area (20 cm^2) were not suitable for determination of the end-point in oscillographic-chronopotentiometric titrations. Satisfactory results were obtained with a platinum electrode of 1 cm^2 (Radiometer type P101) and a platinum wire 5 *mm* long and 0.3 *mm* in diameter.

We found that distortion at the end-point was greater with a spherical platinum microelectrode of diameter 1 *mm* than with a platinum wire electrode of the same area (Table 2).

The platinum microelectrode was cleaned before use by successive cooking in a saturated solution of potassium cyanide, 30% solution of hydrogen peroxide, concentrated hydrochloric acid and distilled water. Sometimes the electrode became passivated and there were no distortions of the oscillogram at the end-point. However, after being cleaned, it again functioned properly.

TABLE 2

Influence of waveform on accuracy of oscillographic-chronopotentiometric titrations of arsenic (III) with 0.1 N potassium bromate in 5 N potassium bromide and 5 N hydrochloric acid, using a platinum microelectrode (indicator electrode) and SCE (see Fig. 1 and 2)

Waveform	Shape of the indicator electrode	Relative error in %	Average deviation in %
∿	|*)	—0.32	0.51
—‖—	● **)	+0.20	0.38
⎍⎍	●	—0.14	0.30
/\/\/	●	+0.03	0.25
_/_/_	●	0.00	0.18

* platinum wire 0.5 cm long.

** spherical platinum electrode (Ø = 1 *mm*)

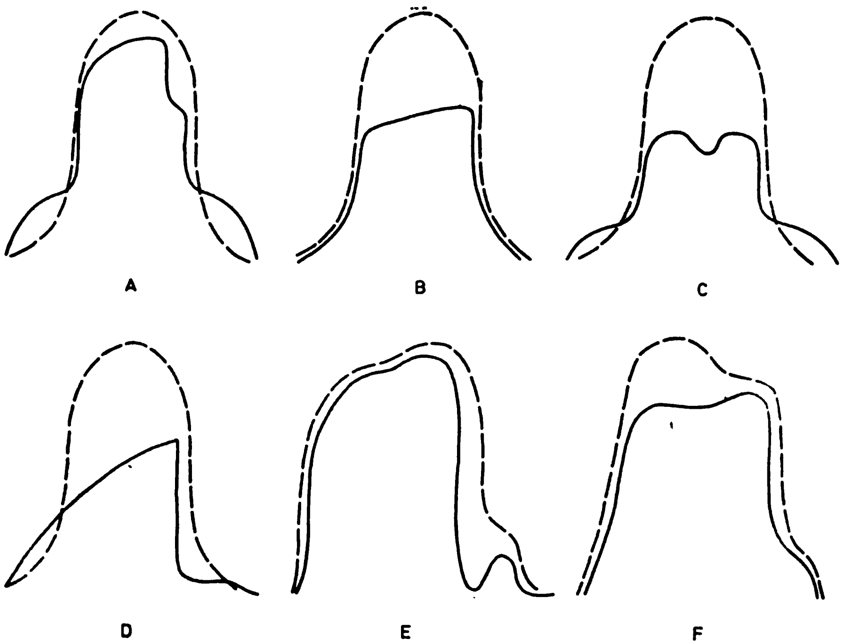

Figure 3

Oscillogram distortions in oscillographic-chronopotentiometric titrations using sinusoidal oscillations and two indicator electrodes

a was obtained with the electrodes described in Table 3 under experiment No. 1, *b* with the electrodes under 2, 3 and 4, *c* with the electrodes under 5, *d* with the electrodes under 6, and *f* with the electrodes 7, 8 and 9

Other indicator electrodes and the saturated calomel electrode. Instead of a platinum indicator electrode it is possible to use a gold electrode (Radiometer type P 201). Silver and mercury indicator electrodes did not yield satisfactory results of determinations.

Titrations by means of two indicator electrodes. By using two identical platinum microelectrodes with different areas (1 *cm*^{2} and a wire 0.5 *cm* long) distortions of the oscillogram at the end-point were obtained, but of a different shape (Fig. 3*a*) from those obtained using a saturated calomel electrode and a platinum microelectrode (Fig. 3 of part I(1)). The shape of the distortion also depends on which of the electrodes is floating and which grounded (Figs. 3*a* and 3*b*).

Two different microelectrodes (platinum-gold and platinum-mercury) or two identical electrode with different areas gave satisfactory distortions of the oscillograms.

TABLE 3

Effect of electrode shape on accuracy of oscillographic-chronopotentiometric titration of arsenic (III) with 0.1 N KBrO$_3$

Experiment No.	Electrodes		Circuit parameters *			Oscillogram as in fig.	Relat. error in % **	Average deviation in %
	Signal	Earth	V~	kΩ	μF			
1	□	│	260	100	0,33	3 a	+0.06	0.43
2	│	□	»	»	»	3 b	—0.15	0.42
3	│	│	»	»	»	3 b*	+0.12	0.82
4	△	□	»	»	47.000	»	+0.10	0.65
5	□	△	»	»	»	3 d**	—0.06	0.46
6	□	○	»	»	»	3d***	—0.02	0.32
7	□	▨	20	10	»	3 e	0.00	0.52
8	□	▮	»	»	»	»	+0.17	0.70
9	○	□	»	»	»	3 f	+0.20	0.59

* See Fig. 1, of part I(1)

* * The results are mean values of 8 determinations of 10—100 mg arsenic in 100 ml titrated solution

│ Platinum wire electrode of 0.5 *cm* length

□ Radiometer P 101 Platinum electrode

▨ Mercury precipitated on P 101 electrode

△ Radiometer gold electrode

▮ Mercury deposited on Pt wire electrode 0.5 cm long

○ Mercury (P – 10 cm^2) in the beacker

* Small oscillogram distortions

** Medium distortions

*** Great distortions

Data on the electrodes the experimental conditions and the results are shown in Table 3. The shape of distortions by means of which the end-point was detected is shown in Fig. 3.

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Original Scientific Paper

OSCILLOGRAPHIC-CHRONOPOTENTIOMETRIC TITRATION. IV.

REDOX AND PRECIPITATION TITRATIONS*

by

ĐORĐE K. STEFANOVIĆ, VILIM J. VAJGAND and TIBOR A. KIŠ

In earlier papers(1–3) we have described the basic principles of the new method of end-point determination, and on the example of titrating arsenic (II) with potassium bromate we have studied the influence of different factors on the accuracy of the method.

In the present report we shall describe results which show that this method of end-point determination can be successfully used not only for the titration of arsenic (III) with potassium bromate but also for other redox and precipitation titrations.

EXPERIMENTAL

REAGENTS

Preparation of 0.1 N standard solutions

Substances p.a. Merck were purified, their purity checked and the solutions prepared according to the usual methods: potassium bromate(5), antimony-trichloride(6), potassium stannochloride(7), ferrous ethylenediamine sulphate(8), potassium ferrocyanide(9), potassium iodide(10), hydrazine sulphate(11), 8-hydroxyquinoline(12), potasssium dichromate(13), potassium permanganate(13), iodine(14), sodium thiosulphate(13), silver nitrate(15) and sodium chloride(13).

Standardization of 0.1 N solution

The normality of the solution of potassium bromate was checked by means of titration with a solution of arsenic, visually(16) and potentiometrically(17). Against this solution the concentration of the following solutions was checked by potentiometry: antimony thichloride(17), ferrous ethylenediamine sulphate(18), potassium ferrocyanide(19), potassium iodide(20), hydrazine sulphate(21) and 8-hydroxyquinoline(22). The normality of the

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solution of ferrous ethylenediamine sulphate was checked by potentiometry against potassium dichromate(23), of sodium thiosulphate against iodine(24), of potassium permanganate against ferrous ethylenediamine sulphate(25) and of silver nitrate against sodium chloride(26) and potassium iodide(27)

EQUIPMENT

In potentiometric titrations we used a "Radiometer" type PHM 22p pH-meter, a TTA 1 type titration apparatus, a K 100 type calomel electrode, a K 601 type mercurous sulphate electrode and a P 101 platinum electrode.

The apparatus used in oscillographic-chronopotentiometric titrations has been described in a previous paper(1).

PROCEDURE

TITRATIONS WITH POTASSIUM BROMATE

General procedure

By means of a 2—25 *ml* burette 0.1 N solution of the substance to be determined was measured into a 250 *ml* beaker, 10 *ml* of concentrated hydrochloric acid and 0.5 *g* of potassium bromide is added, and this was diluted with distilled water to 50 *ml*. The Radiometer P 101 platinum indicator electrode was immersed into this solution which was then connected via an electrolytic bridge (filled with a solution of potassium nitrate) to a saturated calomel electrode with an area of about 10 cm^2, which was grounded. This galvanic cell was included into the apparatus whose scheme is shown in Fig. 1 of part I of this study(1). With continuous mixing the solution was titrated with a standard solution of 0.1 N potassium bromate. A sudden distortion of the oscillogram (Fig. 3, part I of the study(1)) indicates the end-point. The results of these determinations are shown in Table 1.

Special procedures

For the determination of antimony trichloride, any antimony (V) present was previously reduced with sulphur dioxide(28).

For the determination of potassium stannochloride 2 *g* of sodium carbonate was added to the acid titrated solution and the titration was done in a carbon dioxide atmosphere(29) at 90°C, at which the rate of reaction of stannochloride with potassium bromate was increased(31).

In order to accelerate the reaction of iron (II) with potassium bromate, ferrous ethylenediamine sulphate was titrated in the presence of 10 *ml* of the catalysts ammonium arsenate and cupric chloride(19, 31).

Potassium iodide was titrated in 0.7 N hydrochloric acid with and without the addition of potassium bromide(20). In the latter case the potential jump and the distortion of the oscillogram at the end-point were less.

Hydrazine sulphate was titrated in 20% hydrochloric acid in the presence and in the absence of potassium bromide(30). At 80°C the reaction rate was greater and at that temperature the titration can be done more rapidly.

Because of the low titration reaction rate 8-hydroxyquinoline had to be titrated slowly in 4.5 N hydrochloric acid at 50°C.

OTHER REDOX TITRATIONS

Titration of ferrous ethylenediamine sulphate with potassium dichromate

These determinations were done under the conditions already described for titrations with potassium bromate, the only differences being in that instead of the P 101 electrode around platinum microelectrode with

TABLE 1

Results of various oscillographic-chronopotentiometric redox and precipitateforming titrations. The results are mean values of 8 determination of 10—100 mg of titrated substance in 100 ml of titrated solution

Standard solution	Titrated substance	Relative error in %	Aver. dev. in %
Potassium bromate	Antimony trichloride	+0.15 +0.12*	0.51 0.45
	Ferrous ethylenediamine sulphate	+0.25 −0.03**	0.43 0.03
	Potassium stanous chloride	+0.15 −0.05*	0.48 0.48
	Potassium ferrocyanide	−0.19	0.59
	Potassium iodide	+0.13 −0.08***	0.25 0.33
	Hydrazine sulphate	+0.31 +0.03*	0.54 0.38
	8-hydroxiquinoline	+0.23	0.65
Ferrous ethylenediamine sulphate	Potassium dichromate	+0.25	0.43
Potassium dichromate	Ferrous ethylenediamine sulphate	+0.12	0.41
Potassium permanganate	„	+0.03	0.50
Sodium thiosulphate	Iodine	+0.25	0.43
Iodine	Sodium thiosulphate	50.13	0.40
Sodium chloride	Silver nitrate	±0.00	0.33
Silver nitrate	Potassium iodide	+0.04	0.36

* Titrated at 90°
** In presence of catalyst
*** With addition of potassium bromide

a diameter of 1 *mm* was used, and that the titrations were done in 2 N hydrochloric acid. Distortions of the oscillogram indicating the end-point are shown in Fig. 3 in part I of the study⁽¹⁾; the results are given in Table 1.

Titration of ferrous ethylenediamine sulphate with potassium permanganate

The titrations were done in 0.4 N sulphuric acid under the same conditions as the titrations with potassium dichromate, the only difference having been in the fact that instead of the saturated calomel electrode a saturated mercurous sulphate electrode was used, and that the a.c. source voltage was 110 *V*. Distortions of the oscillogram were shown in Fig. 3 of part I of this study⁽¹⁾; and the results are given in Table 1.

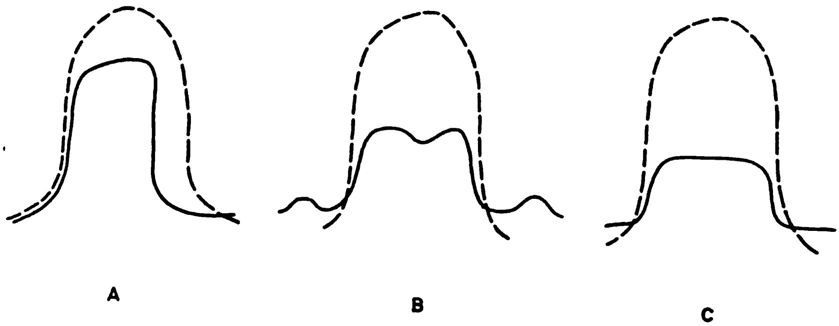

Figure 1

Oscillogram distortions in oscillographic-chronopotentiometric titration of iodine with a 0.1 N solution of sodium thiosulphate

Change *a* is observed under conditions given in Table II, experiments 1—4, *b* under the conditions of exp. No. 5, and *c* under those of exp. No. 6.

The form of the oscillogram:

– – – – – – = before the end-point
———————— = at the end-point

Titration of iodine with sodium thiosulphate

This determination was done in 5 N hydrochloric acid under different conditions which are shown in Table 2. Distortions occurring at the end-point are shown in Fig. 1, and the results of the determinations in Tables 1 and 2. Because of the low a.c. potential, the high resistance, 100 K Ω, and low vertical amplification of the Philips GM 5653 oscillograph, we were obliged to first step up the vertical gain by means of the vertical amplifier of an Avala type KO 701 oscillograph.

TABLE 2

Operating conditions for oscillographic-chronopotentiometric titrations of sodium thiosulphate with 0.1 N iodine solution

No. experiment	Electrodes		Values of the circuit†			Oscillogram figure	Relative error in % ††	Average deviations %††
	Signal	Earth	V~	KΩ	μF			
1	|	|	20	200	0.33	1a*	+0.60	0.52
2	|	□	„	„	„	„**	+0.32	0.39
3	|	○	„	„	„	„***	—0.08	0.25
4	|	SCE	260	100	„	„	—0.18	0.20
5	□	|	„	„	„	1b	+0.22	0.31
6	□	|	20	„	„	1c	+0.33	0.24

| Platinum wire 0.5 *cm* long

○ Platinum foil 20 *cm*²

SCE saturated calomel electrode

□ Radiometer P 101 platinum electrode

† See Fig. 1 of the previous paper(¹)

†† The results are mean values of 8 determinations of 10—100 *mg* sodium thiosulphate in 100 *ml* titrated solution

* small oscillogram distortions

** medium oscillogram distortions

*** large oscillogram distortions

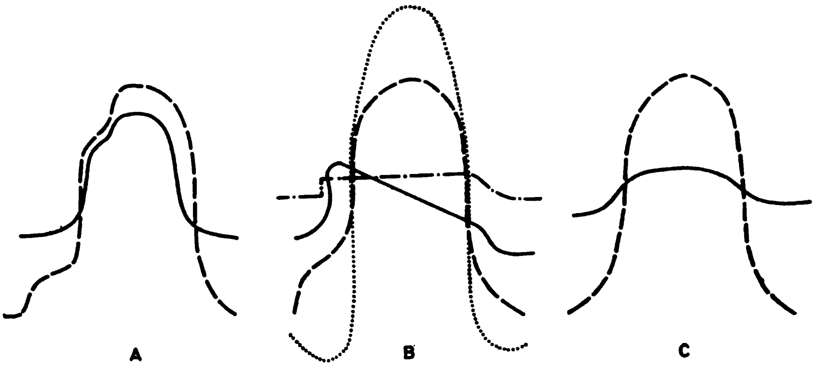

Figure 2

Oscillogram distortions in titrations of potassium iodide with 0.1 N silver nitrate in 2 N nitric acid using two platinum microelectrodes 0.5 *cm* long R = 450 *k*Ω, C = 0.33μF* A.C. source of: a) 260 *V*, b) 110 *V*, c) 20 *V*

Form of oscillogram: — — — — = before the end-point
. . . . . = just before the end-point
———— = at the end-point
.—.—.—.— = after the end-point

* See Fig. 1. in the previous paper(¹).

PRECIPITATION TITRATIONS

Titration of potassium iodide with silver nitrate

This titration was done in 2 N nitric acid with two platinum electrodes, each with a wire 0.5 *cm* long, using a vertical amplifier, a series resistance of 450 K Ω, condenser of 0.33 μF and a.c. source voltage of 260 *V* (Fig. 2 a), 110 *V* (Fig. 2 b) or 20 *V* (Fig. 2 c). The results of the determinations of potassium iodide with silver nitrate and of silver nitrate with potassium iodide are shown in Table 1.

With the use of a round platinum microelectrode and a saturated calomel electrode with a large surface area (10 cm^2), an a.c. voltage of 110 *V*, a resistance of 450 K Ω and a condenser of 0 33 μF, the usual distortions of the oscillogram were obtained (Fig. 3, part I(1)). The same distortion were also obtained when under the same conditions sodium chloride was titrated with silver nitrate and *vice versa*.

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CORRECTION

By mistake the title of the article by Zorka B. Vukmirović and Mirjana Matić, published in No. 2-3-4, 1968, was incorrectly translated. The correct title is as follows:

The Distribution of Hydrogen and Oxygen Isotopes in Some Natural Sites in Yugoslavia.

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Original Scientific Paper

SULFURIC ACID LEACHING OF ROASTED COPPER-CONTAINING GANGUE FOR RECOVERY OF COPPER

by

DUŠAN M. VUČUROVIĆ, ILIJA B. ILIĆ and RAJKO Ž. VRAČAR

A previous study(1) dealt with the leaching of copper gangue samples from the Bor mines with dilute sulfuric acid solutions by the agitation, aeration and percolation methods. The copper content of the gangue varies 0.12—1%, the average being considered as 0.34% Cu. Samples from two sites were investigated: Sample 1, old gangue containing 0.88% Cu; Sample 2, young gangue with 0.22% Cu. The maximum extraction percentages were 65—70% from Sample 1 and 75—95% from Sample 2. Since the results with Sample 2 were rather satisfactory compared with Sample 1, further investigations were confined to Sample 1. From the data made available by the Copper Institute at Bor it is seen that copper in the old gangue occurs predominantly as sulfate (50%), and the rest as sulfide and oxide. Most iron, however, occurs as sulfide and only a very small amount (up to 5%) as sulfate.

Recent investigations and certain new projects abroad concerning the processing of similar raw materials(2, 4) make use of previous roasting by sulfatization of low-copper ores and subsequent leaching of the roast either by water or by dilute sulfuric acid, achieving copper extraction percentages of 80—95%. Copper gangue from the Bor mines was investigated by a similar procedure.

EXPERIMENTAL

Laboratory roasting and subsequent leaching by dilute sulfuric acid were conducted on a relatively high-copper sample of the following chemical composition:

Cu	— 0.88%	CaO	— 2.05%
Cu sol. in H_2O	— 0.42%	SiO_2	— 42.10%
S	— 22.23%	Al_2O_3	— 10.14%
Fe	— 19.10%		

Copper minerals identified by mineralogical analysis were: covellin and chalcopyrite, followed by chalcosine, bornite, enargite, and cuprite. The dominant minerals apart from copper-minerals were pyrite and quartz.

Roasting was done in a laboratory tubular resistance furnace. After roasting, the material was leached with dilute sulfuric acid by the agitation method. The leaching solution was analyzed to establish the percentage of copper brought into solution. This was then compared with the amount of copper introduced with the test sample. The gangue particle size was mostly below 25 mesh.

The influence of a number of paremeters of roasting and leaching on copper extraction were investigated.

(a) *Roasting Conditions* — To find out the optimum roasting conditions, the influence of temperature, time and air flow rate were investigated. Roasting temperature tried were: 350, 400, 450, 500, 600, 700 and 800°C. The time of roasting at these temperatures was 2 h. The air flow rate for roasting a 50-g sample was 200 *ml/min*. The leaching conditions were kept constant: L : S ratio 4 : 1 (liquid to solid ratio), time 2 *h*, room temperature, 7% concentration of H_2SO_4 in the leaching solution. The influence of roasting temperature is shown in Table 1.

TABLE 1

The Influence of Roasting Temperature on Copper Extraction

Temperature (C)	350°	400°	450°	500°	600°	700°	800°
Copper extraction (%)	60.00	74.54	59.10	50.10	46.00	42.70	24.10

It may be seen from the results that the maximum copper extraction was achieved at 400°C. At this temperature the influence of roasting time was then investigated. The results are shown in Table 2.

TABLE 2

The Influence of Roasting Time on Copper Extraction

Roasting time (h)	0.5	1	2	3
Copper extraction (%)	69.09	74.54	74.50	63.63

From Tables 1 and 2 it may be seen that higher copper extraction was obtained at lower roasting temperatures (400°C) and shorter roasting time (1 h). Since the sample had a high content of silicon dioxide (42.10%) and iron (19.10%), the formation of ferrite and copper silicate was possible at higher temperatures and longer roasting. The silicate is only partly soluble in sulfuric acid and the ferrite is insoluble. For these reasons, a lower temperature and shorter roasting time are better. Also, at lower temperatures conditions for the formation of soluble copper sulfate are considerably more favorable.

TABLE 3

The Influence of Air Flow Rate during Roasting on Copper Extraction

Air flow rate (*ml/min*)	200	300	400	500	600
Copper extraction (%)	74.54	80.90	83.63	87.36	86.79

For the best conditions of roasting (400°C, 1 h), the influence of air flow was investigated (Table 3). The results show that an increase of air imput from 200 *ml/min* to 500 *ml/min* raised the percentage of copper extracted from 74.5 to 87.4%.

(b) *Leaching Conditions* — Investigations of the leaching conditions at optimum roasting covered the influence of: concentration of sulfuric acid solution, liquid to solid ratio, and time of leaching.

The results for H_2SO_4 concentration are shown in Table 4. Leaching time was 2 *h* and the L : S ratio 4 : 1. The results demonstrate that increasing the H_2SO_4 concentrations to 7% increased the copper extraction. Any further increase unfavorably affects the transfer of copper into solution.

The influence of liquid to solid ratio was then investigated at the optimum H_2SO_4 concentration of 7%. The results are presented in Table 5. The leaching time was 2 *h*, H_2SO_4 concentration 7%.

From the results it may be seen that an increase in the amount of solution to a 4 : 1 ratio increased the copper extraction. Further increase in the L : S ratio only negligibly increased the extraction.

TABLE 4

The Influence of H_2SO_4 Concentration in Solution on Copper Extraction

H_2SO_4 concentration (%)	2	5	7	10
Copper extraction (%)	66.36	79.00	87.36	62.70

TABLE 5

The Influence of L : S Ratio on Copper Extraction

L:S ratio	1:1	2:1	4:1	6:1
Copper extraction (%)	72.40	84.70	87.36	87.90

TABLE 6

The Effect of Time Leaching on Copper Extraction

Time (h)	0.5	1	2	3
Copper extraction (%)	70.72	76.30	87.36	88.70

From the data in Tables 4 and 5, the kinetics of leaching was investigated. The results for the dependence of copper extraction on leaching time are given in Table 6. H_2SO_4 concentration was 7%, and L : S ratio 4 : 1.

From the results it may be seen that most of the copper (76.30%) went into solution in 0.5—1 *h*. Extending the time of leaching to 2 *h* increased the extraction to 87.4%. Further extension to 3 *h* only increased it by 1.4%, which is practically negligible.

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Original Scientific Paper

AMMONIA LEACHING OF GANGUE FOR RECOVERY OF COPPER

by

DUŠAN M. VUČUROVIĆ, RAJKO Ž. VRAČAR and ILIJA B. ILIĆ

Flotation of sulfide copper ore at the Bor plant turns out a copper concentrate (maximum copper extraction 82—85%), and gangue containing 15—18% of the copper originally in the ore. The mineralogical forms of copper wasted in the gangue are: oxidic (cuprite, tenorite, chrysocolla, etc.), native copper (if present), and some of the sulfide minerals (covellin, chalcosine, chalcopyrite, etc.), which do not get floated out. Accordingly, the amount of copper in the gangue depends on the amount of oxide minerals and the efficiency of utilization of sulfide copper in flotation. Commensurately with the effects of these factors, the amount of copper in the Bor gangue varies 0.12—1.0% Cu.

Copper production trends today are dictated by the increasing demand for this metal, of which there is a deficit on the market. On the other hand, the deposits of high-copper ore are being worked out, so that there is a mounting interest in low-copper ores and other raw materials. This interest is accompanied by endeavors to develop a suitable technology, basically hydrometallurgical, to process such raw materials with reasonable economy(1, 4).

In the light of these facts, copper gangue is becoming increasingly interesting. For some time now the Department of Non Ferrous Metallurgy of the School of Technology and Metallurgy in Belgrade has been studying the possibilities of hydrometallurgical processing of copper gangue by direct leaching with certain reagents or leaching after pyrometallurgical preparation. The main difficulties in hydrometallurgical processing of gangue arise from the wide variety of copper minerals contained in it. A universal reagent which would convert all the minerals and native copper into soluble compounds is not yet known. With sulfuric acid, a reagent frequently used, a satisfactory degree of extraction may be achieved only if the gangue contains oxide copper (as CuO, Cu_2O and $Cu_2O.SiO_2$) and metallic copper, which sulfuric acid dissolves only in the presence of oxygen. Sulfide copper minerals and copper ferrites do not dissolve in H_2SO_4 unless other reagents (ferrisulfates, etc.) are present. From our previous study(5), it may be seen that the conventional leaching of the Bor gangue (containing 0.88% Cu) yields a maximum extraction of 65—68%, and that preparatory sulfatization of the gangue to convert sulfide copper into oxide copper might raise the extraction to 90%(6).

This paper describes experimental leaching of gangue with ammoniacal solution with a view to satisfactory copper extraction without pyrometallurgical pretreatment.

EXPERIMENTAL

The gangue contained 0.88% Cu, 42% of which was water-soluble $CuSO_4$. The high percentage of sulfate copper may be explained by the fact that sulfide copper had oxidized down to sulfate during its long exposure to atmospheric influences in the open. This circumstance favored the use of ammoniacal solution for leaching because most sulfide minerals (stable in ammoniacal solution in conventional leaching) had already been converted into soluble forms. The chemical composition of the gangue is given in Table 1.

TABLE 1

Chemical Analysis of Copper Gangue

Component	Cu	Cu soluble in H_2O	S	Fe	CaO	SiO_2	Al_2O_3
Content (%)	0.88	0.42	22.23	19.10	2.05	42.10	10.14

Leaching was done with aqueous solutions of $NH_3 + (NH_4)_2CO_3$, air being blown through the pulp. Standard laboratory apparatus was used, modified to facilitate air blowing and for mixing with an electric mixer.

Experiments were designed to examine the influence of the following parameters of leaching on the copper extraction:

— Liquid to solid ratio (L : S)
— Leaching time
— Solution concentration
— Gangue particle size
— Air flow rate through the pulp

RESULTS

(a) *Influence of L : S Ratio* — These tests were conducted at constant values of the other parameters: leaching time 2 *h*, solution concentrations 7% NH_3 and 5.9% CO_2, gangue particle size 100% — 24 mesh, air flow rate 250 *ml/min*, mixing rate 500 rpm.

TABLE 2

The Influence of L : S Ratio on Copper Extraction

L:S Ratio	2:1	4:1	6:1	8:1
Extracted Cu (%)	42.27	63.63	70.90	70.64

The results for the influence of L : S ratio are given in Table 2, showing that copper extraction markedly increases with decreasing pulp density down to an L : S ratio of 6 : 1. Whether this ratio or perhaps some other ratio, down to 4 : 1, can be considered as the optimum depends on economic factors. We kept it at 6 : 1 in our subsequent tests.

(b) *Influence of Leaching Time* — The other parameters, gangue particle size, solution concentration, and air flow rate, were the same as when investigating the influence of L : S ratio.

TABLE 3

The Influence of Leaching Time on Copper Extraction

Time (h)	1	2	3	5
Extracted Cu (%)	57.27	70.90	80.72	54.54

From the results in Table 3, it appears that the rate of copper extraction by ammoniacal solution is rather low. It is noteworthy that most of the copper finally extracted (60%) dissolves during the first hour, while the rest (approximately 20%) takes 2 more hours. This certainly results from the characteristic forms in which copper is present in the gangue, as explained above: 42% of the total copper is $CuSO_4$-bound. The decrease in leaching after 3 *h* is probably due to the instability of the dissolved copper-ammonia complex when the NH_3 concentration in the solution is reduced because of evaporation, and other factors causing the sedimentation of the already extracted copper.

(c) *Influence of Solution Concentrations* — To investigate the influence of solution concentration, leaching was done with solution of the composition given in Table 4.

TABLE 4

Dependence of Leaching on Concentration of Ammonia and Ammonium Carbonate in the Leaching Solution

Solution No.	Concentration of		Extracted Cu
	NH_3 %	CO_2 %	%
I	1.8	1.0	40.91
II	5.5	4.4	58.63
III	7.0	5.9	80.72
IV	10.3	7.9	66.81
V	14.8	11.9	59.99

A leaching time of 3 *h* was taken as the optimum, and the other parameters were kept the same as when investigating the influence of time. Table 4 shows that copper extraction increased with increasing NH_3 up to 7.0% and CO_2 up to 5.9%. These concentrations, with the given quantity of SO_4^{2-} ions from the $CuSO_4$, determine the solution concentration sufficient to form the complex $Cu(NH_3)_4^{2+}$ with the maximum of extracted copper. However, more important than this is to note that raising the solution concentration above this value cannot extract more than 80.72% Cu.

(d) *Influence of Gangue Particle Size and Air Flow Rate.* — Extraction of a useful component from an initial raw material depends on the area of contact between raw material and solution. In leaching copper from a material in which this metal occurs native or in sulfide form, the presence of oxygen may increase extraction. For this reason, the effect of these two parameters was also investigated, at the given optimum values of the other parameters (L : S = 6 : 1, leaching time 3 *h*, solution concentration 7.0% NH_3 and 5.9% CO_2). The results are given in Table 5 and 6.

TABLE 5

The Influence of Particle Size Distribution on Copper Extraction

Gangue particle size *(mesh)*	100%—24	100%—60	100%—100	100%—150	100%—200
Extracted Cu (%)	80.72	81.10	80.96	81.23	81.02

The results in Table 5 show that comminution of gangue below its natural grain size 100% — 24 mesh does not result in any gain. Accordingly, the particle size of copper minerals in the gangue, i.e. area of contact with the solution, does not constitute a factor limiting the copper extraction. What does limit it is the chemical stability of these minerals in the given solution and under the given circumstances.

Unlike the gangue particle size, the influence of air flow rate through the pulp is evident. Up to an air flow rate of 400 *ml/min*, copper extraction increases to 82.38%.

TABLE 6

The Influence of Rate of the Air Flow through the Pulp on Copper Extraction

Air flow rate (*ml/min*)	100	250	400	500
Extracted Cu (%)	69.54	80.72	82.38	81.65

This investigation of the influence of different parameters of the conventional ammonia leaching of copper gangue showed that the maximum copper extraction which can be achieved is 82%. This means that some, probably the sulfide minerals are sufficiently stable to prevent 18% of the copper from being extracted. For this reason the possibility of increasing extraction by pyrometallurgical pretreatment of the gangue was also explored. A series of tests were conducted with sulfatization of the gangue at up to 900°C to convert the sulfide minerals into sulfates or oxides, compounds readily soluble in ammoniacal solutions. However, the extraction was no higher. On the contrary, the amount of dissolved copper decreased, which means that the copper minerals in the gangue were bound by roasting with other minerals present into still more stable forms.

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Original Scientific Paper

EFFECT OF PHENYLHYDRAZINE ON THE CONCENTRATION OF NUCLEIC ACIDS IN THE WHITE RAT LIVER IN VITRO

by

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and JOVAN B. VUKOVIĆ

Phenylhydrazine, or some of its derivatives, have been used to investigate nucleic acids from various aspects. J. Webb and H. M. Levy(1) worked out a quantitative method for the determination of DNA in tissues and microorganisms using paranitrophenylhydrazine as a reagent. Particularly interesting is the recent research on cytotoxic and antitumor effects of methylhydrazine derivatives(2, 3, 4, 5), which has shown that 1-methyl-2-benzyl-hydrazine inhibits the growth of tumors by selectively decomposing DNA molecules. Direct action of hydrazine derivatives on tissue DNA has been studied by U. Zor *et al.*(6). They injected mebanazine (α-methyl-benzyl-hydrazine) into young rats and found a reduced amount and concentration of DNA in the liver. They suggested the mechanism of mebanazine's effect includes both the inhibition of DNA synthesis and the release of STH. RNA synthesis, according to their report, was not disturbed. The effect of phenylhydrazine on the growth of bacteria and on the amount and concentration of nucleic acids in them has been investigated by E. Levi-Jovanović *et al.*(7). In a nonpathogenic strain of *Staphylococcus albus* they noted both inhibition of growth and reduced RNA and DNA concentrations

The available literature led us to believe that it would be interesting to investigate the effect of phenylhydrazine on tissue nucleic acids in mammals. Since phenylhydrazine has hemolytic properties, we worked on isolated tissues.

EXPERIMENTAL

Male white rats weighing 200—230 *g* were decapitated and bled out, the livers taken out, weighed and homogenized in physiological saline (with citrate). To the test tissue phenylhydrazine chlorohydrate ($C_6N_5NH_2.HCl$) was added in a concentration of 300 *mg/kg* liver. All homogenates were thermostated at 38°C for 1 *h* with constant oxygenation and stirring. Instead of O_2, H_2O_2 was added to the homogenates of one group. Both test and control homogenates were incubated.

After incubation, nucleic acids were prepared from the homogenates by Schmidt-Theanhauser's or Schneider's method. First acid-soluble phosphorus compounds were removed with trichloracetic acid (10%, 7%, 5%). After the last centrifugation the residue was washed clean, once in water, three times in ethyl alcohol. All operations, from the sacrifice of the animals to the use of alcohol, were conducted cold. Delipidation was done after Bloor: three times in boiling ethyl alcohol and three times in boiling ether, followed by one or two washings in cold ether. The preparations were left to dry (either thermostated at 38—40°C, or at room temperature). The dry residue was weighed and an aliquot (150 *mg*, in our tests) was taken for alkaline hydrolysis.

Hydrolysis was conducted with N/2 NaOH for 17—24 *h*, after which the addition of perchloric acid ($HClO_4$) precipitated DNA and proteins, leaving acid-soluble ribonucleotides in the liquid phase.

DNA was extracted after Schneider, by heating at 80°C in 5% trichloracetic acid for 30 *min*. After DNA extraction, phosphorus was determined with diphenylamine by Burton's method(10).

RNA was determined by the orcinol test after Mejbaum(11).

As a check, both DNA and RNA were determined directly as phosphorus by Chen's method(12) with some modifications.

The viscosity of RNA and DNA solutions was determined on an Ubbelohde viscosimeter.

RESULTS

Incubation of liver homogenates with phenylhydrazine with constant oxygenation (O_2 was added to the controls too), yielded higher RNA and DNA values than in the control samples. RNA concentrations were up some 7% relative to the control, DNA concentrations about 5%. The RNA/DNA ratio was only about 2% greater than the control values (Table 1).

TABLE 1.

Incubation of Liver Homogenates with Phenylhydrazine and O_2

Nucleic acid concentratios in μg per *g* of dry residue			
Nucleic acid	Experimental group	Control group	% concentration difference
RNA	30.80	28.70	7
DNA	8.43	7.98	5
DNA/RNA	3.66	3.66	2

In the other experiments where H_2O_2 was added as well as phenylhydrazine (both to the test and control samples), the difference in concentrations was more marked, especially with RNA (12% higher than control); DNA was 6% above control. The RNA/DNA ratio was about 5% greater than in the control (Table 2).

TABLE 2.

Incubation of Liver Homogenates with Phenylhydrazine and H_2O

Nucleic acid concentrations in µg per g of dry residue			
Nucleic acid	Experimental group	Control group	% concentration difference
RNA	27.55	24.35	12
DNA	7.47	6.98	6
DNA/RNA	3.69	3.49	5

TABLE 3.

Differences in Nucleic Acid Concentrations in the Experiments with H_2O *and* O_2

Nucleic acid concentrations in µg per g of dry residue								
Nucleic acids + phenylhydrazine	RNA		DNA		% concentration decrease			
	exp.	contr.	exp.	contr.	ARN		ADN	
					exp.	contr.	exp.	contr.
O_2	30.8	28.70	8.43	7.98	—	—	—	—
H_2O_2	27.55	24.35	7.47	6.98	11	15	11	12

Addition of H_2O_2 reduced RNA and DNA concentrations compared, to the values in the first group of experiments, in both the test and control samples (Table 3). The RNA of test samples was about 11% lower and of control samples 15% lower. Respective differences for DNA were about 11% and 12%.

To assess the integrity of nucleic acid molecules in our samples, the viscosity of the preparation used for quantitative determination of RNA and DNA was measured. We did not find any differences between the test and control samples, either for RNA or for DNA (Table 4).

The occurrence of higher RNA and DNA concentrations when phenylhydrazine was added is attributed to the inhibitory effect of this reagent on autolytic processes taking place during liver homogenate incubation. The differences were less pronounced with DNA probably because

TABLE 4.

Viscosity of RNA and DNA Solutions during Incubation of Liver Homogenates with Phenylhydrazine + O_2 or Phenylhydrazine + H_2O

Nucleic acids	Viscosity in centistokes at +20°C			
	Phenylhydrazine + O_2		Phenylhydrazine + H_2O_2	
	Exp.	Contr.	Exp.	Contr.
RNA	0.197	0.197	0.198	0.200
DNA	0.215	0.214	0.214	0.212

TABLE 5.

Statistical Analysis

Nucleic acid	Mean		Stand. Dev.		T-test	Probability P
	Exp.	Contr.	Exp.	Contr.		
RNA + phenylhydr. + O_2	30.8	28.7	3.48	3.46	0.807	$p > 5\%$
RNA + phenylhydr. + H_2O_2	27.55	24.35	2.41	5.06	1.34	$p > 5\%$
DNA + phenylhydr. + O_2	8.43	7.98	0.72	0.62	0.86	$p > 5\%$
DNA + phenylhydr. + H_2O_2	7.21	6.98	1.03	0.044	0.35	$p > 5\%$
RNA/DNA + phenylhydr. + O_2	3.60	3.63	0.62	0.69	0.06	$p > 5\%$
RNA/DNA + phenylhydr. + H_2O_2	3.86	3.50	0.60	0.75	0.78	$p > 5\%$

of the presence of citrate in the incubation mixture. It follows that phenylhydrazine does not have a specific effect on nucleic acids under the conditions of our tests, as may also be seen from the statistical analysis of the results (Table 5).

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Original Scientific Paper

EXTRACTION OF PLUTONIUM BY NITROMETHANE

by

NIKOLA B. MILIĆ

The possibility of separating plutonium by extraction with some nitrocompounds, such as nitromethane, nitroethane, nitropropane, and nitrobenzene, is suggested by Seaborg (1), but no data is yet available either about the extraction capacity of these compounds or about the conditions under which they can extract plutonium. For this reason, we were interested in determining the conditions under which these or similar nitro compounds extract plutonium and also in investigating more closely the extraction of plutonium by nitromethane, the first member of the aliphatic nitrocompound series, because in a number of cases lower order homologous members proved to be better extraction agents.

EXPERIMENTAL

Reagents and Radioisotopes — All reagents were p.a. (BDH), and organic reagents were further redistilled twice before use.

Commercial ^{239}Pu was purified by ion exchange on Dowex 1, X4(2) and TTA extraction(3). Just before the experiment, the purified plutonium was treated with sodium nitrite once again for the conversion of any disproportionated plutonium into the tetravalent state.

Plutonium (VI) was prepared by treating a solution of plutonium (IV) with 0.1 *M* solution of potassium bromate in 1 *M* nitric acid at 93—95°C for several hours(4).

^{239}Np was obtained by irradiation of neutron-impoverished (down to 0.47% ^{235}U) native uranium. It was purified by lanthanum fluoride precipitation (reduction by ferrosulfate)(5) and ion exchange on Dowex 1, X4(6). Np (V) was converted to Np (VI) by oxidation with 0.01 *M* potassium bromate solution at room temperature(7).

^{234}Th was obtained by separation from uranyl nitrate solution using ethyl ether extraction and lanthanum fluoride precipitation(8), followed by purification on Dowex 1, X4(9).

Uranium (VI) solution was prepared from $UO_2(NO_3)_2 . 6H_2O$.

The amounts of radioisotopes in all tests were at labeling level.

Experimental Techniques — In all experiments, equal volumes of the organic and aqueous phases were kept in equilibrium by a mechanical mixer at constant temperature (25 ± 0.5°C).

The dependence of the distribution coefficient of Pu (IV) in extraction by nitromethane on the duration of mixing at constant nitric acid concentration (5 M) in the aqueous phase was investigated. It was found that equilibrium was approached very rapidly (Fig. 1), in the first three minutes. However, in all experiments the samples were mixed for 15 min to ensure constant temperature.

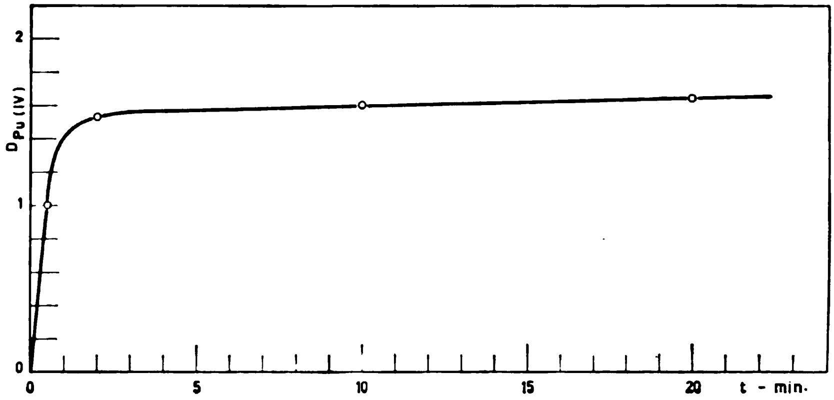


Figure 1.

Extraction of plutonium (IV) by nitromethane as a function of time.

After equilibration the phases were separated by centrifugation and in each of them the corresponding components were determined. For the samples which contained plutonium or other radioisotopes nitric acid and nitromethane were determined in non-radioactive dummy samples of the same composition and equilibration time.

Analytical Methods. — The distribution coefficient of plutonium and of other radioisotopes is defined as the ratio of the activities in the organic and in the aqueous phase:

$$D_{Pu} = \frac{\text{Pu concentration in org. phase [counts min}^{-1}\text{ ml}^{-1}]}{\text{Pu concentration in aq. phase [counts min}^{-1}\text{ ml}^{-1}]}$$

To determine plutonium, definite volumes of organic and aqueous phases were carefully put onto stainless steel disk and evaporated to dryness under an infrared lamp. The disks and solid residue were heated at 400—500°C, and then ^{239}Pu was determined by relative radiometry on a Tracerlab P-12 alpha scintillation counter. ^{234}Th was determined by measuring beta activity on a Geiger-Müller counter, and ^{239}Np by measuring gamma activity on a DS-5 Nuclear Chicago hollow-crystal scintillation counter.

The content of nitromethane in organic and aqueous phases was determined spectrophotometrically with vanillin(10) on a DK-1A Beckman spectrophotometer.

The concentration of nitric acid was determined by titration of aqueous phase with 0.1 M sodium hydroxide solution (indicator — methyl orange).

RESULTS

The dependence of the distribution coefficient of plutonium (IV) on nitric acid concentration in the aqueous phase was determined in extraction by nitromethane, nitroethane, 2-nitropropane, and nitrobenzene (Fig. 2).

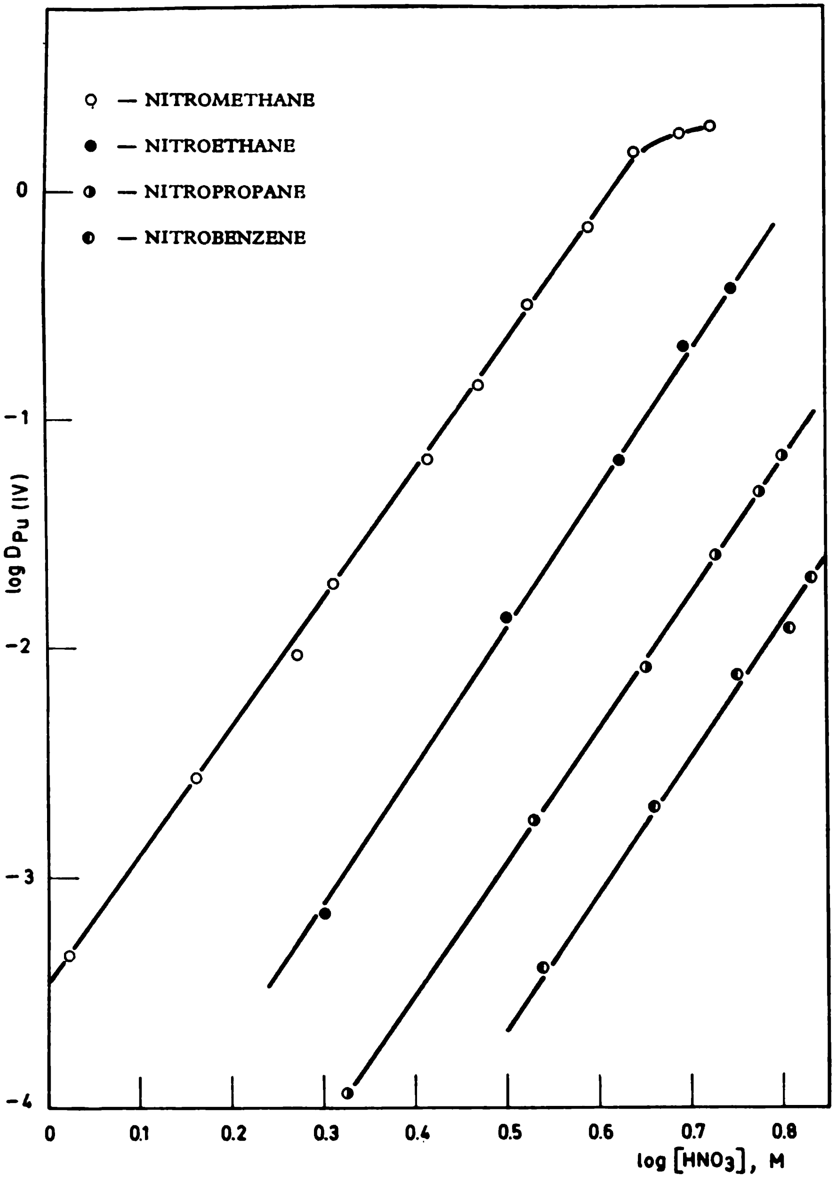


Figure 2

Dependence of the distribution coefficient of plutonium (IV) on nitric acid concentration in extraction by nitromethane, nitroethane, 2-nitropropane, and nitrobenzene

It was found that the distribution coefficient was considerably lower in extraction by nitrooctane than with these nitro compounds, viz. at 4 M NHO_3 in the aqueous phase it was less than 10^{-5}.)

From Fig. 2 it may be seen that the distribution coefficient of plutonium (IV) increases with increasing nitric acid concentration for all the nitrocompounds covered, but decreases with increasing number of carbon atoms in the compound. Table 1 gives the distribution coefficient of plutonium (IV) with the different nitro compounds at constant nitric acid con-

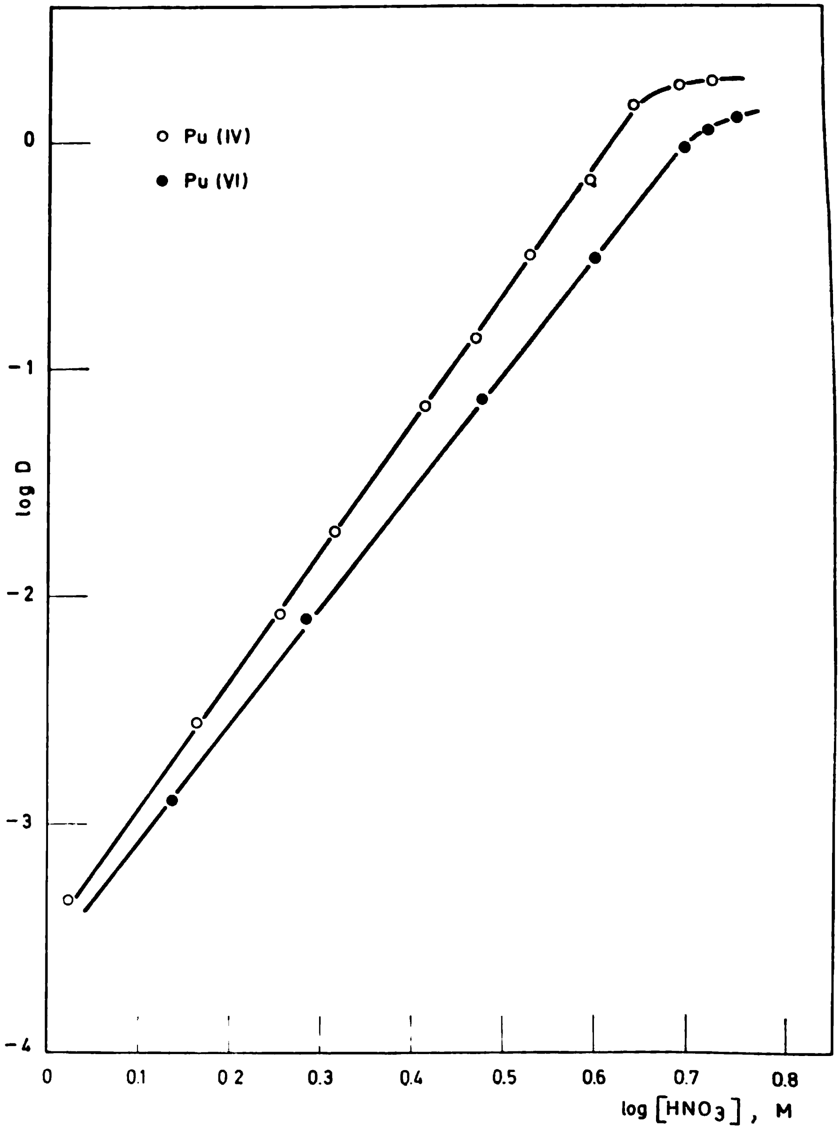


Figure 3

Dependence of the distribution coefficients of plutonium (IV) and (VI) on nitric acid concentration in extraction by nitromethane.

centration in the aqueous phase (4 M): an increase in the number of carbon atoms in the aliphatic nitro compound reduces the distribution coefficient by approximately an order of magnitude, while it is reduced by slightly more than two orders of magnitude when the methyl group is replaced by the phenyl group.

TABLE 1

Distribution Coefficient of Plutonium (IV) in Extraction by Different Nitro Compounds from 4 M Aqueous Nitric Acid Solution

Nitro compound	Formula	Distribution coefficient of Pu (IV)
Nitromethane	CH_3NO_2	$5.8 \cdot 10^{-1}$
Nitroethane	$CH_3CH_2NO_2$	$5.4 \cdot 10^{-2}$
2-Nitropropane	$CH_3CH(NO_2)CH_3$	$5.0 \cdot 10^{-3}$
Nitrooctane	$CH_3(CH_2)_7NO_2$	$<10^{-5}$
Nitrobenzene	$C_6H_5NO_2$	$1.4 \cdot 10^{-3}$

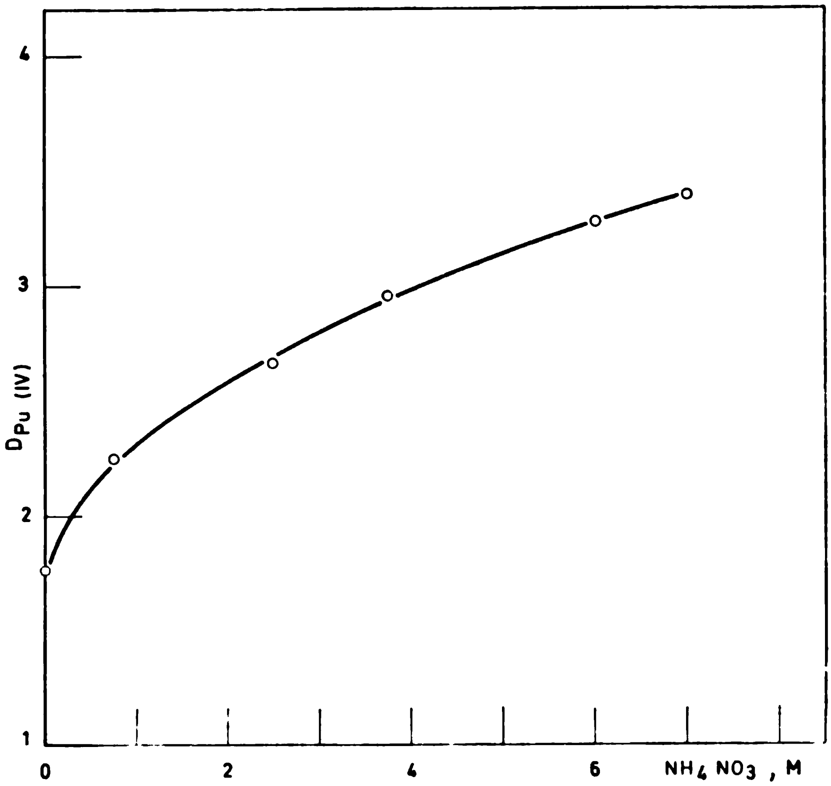


Figure 4

Dependence of the distribution coefficient of plutonium (IV) on ammonium nitrate concentration in extraction by nitromethane

The effect of aqueous phase nitric acid concentration on the extraction of plutonium (VI) is shown in Fig. 3, which for convenience of comparison also presents the data for plutonium (IV) from Fig. 2. Figure 3 shows that the distribution coefficient of plutonium (VI), like that of plutonium (IV), increases with nitric acid concentration but, in the given range of acidity, is less than that for plutonium (IV), which agrees with the general extractibility of the valency states of plutonium.

The effect of ammonium nitrate as a salting agent on the extraction of plutonium (IV) by nitromethane at constant nitric acid concentration (5 M) in the aqueous phase is presented in Fig. 4. Under the given experimental conditions, increasing ammonium nitrate concentration from 0.1 to 7.0 M increased the distribution coefficient of plutonium (IV) approximately by a factor of 2, which is not a significant effect.

The influence of nitromethane concentration in benzene on the extraction of plutonium (IV) and (VI) at constant nitric acid concentration (5 M) in the aqueous phase was investigated. Figures 5 and 6 show that increasing it considerably increased the distribution coefficients of both plutonium (IV) and (VI).

DISCUSSION

From Fig. 2 and Table 1 it may be concluded that the extraction power of the nitro compounds decreases in the following order: nitromethane > nitroethane > 2-nitropropane > nitrobenzene ≫ nitrooctane. This decrease with increasing number of carbon atoms is explained by the "dilution" of the extraction agent by the CH_2 or CH group, as an inert diluent since these groups do not have any substantial influence on the electronegative character of the functional group.

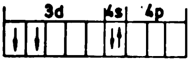
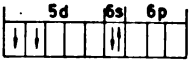
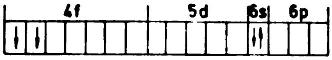
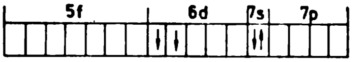
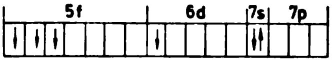
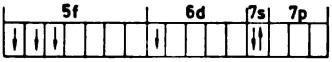
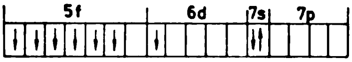
Considering that the dissociation constant of nitromethane is very small ($C_d = 10^{-11}$) and that the nitric acid concentration in the aqueous phase is high, it may be hypothesized that the extraction of plutonium by nitromethane proceeds via molecular compounds, i.e. by the formation of solvates with neutral molecules:

$$Pu(NO_3)_{4\,aq} + n\,CH_3NO_{2\,org} \rightleftarrows Pu(NO_3)_4 \cdot (CH_3NO_2)_{n\,org}$$

where the subscripts "aq" and "org" signify the aqueous and organic phases, and "n" denotes the solvate number of the extracted plutonium complex. The high slope of the curves of plutonium (IV) and (VI) distribution coefficients against nitromethane concentration in benzene (Figs. 5 and 6) suggest the hypothesis that plutonium is extracted by nitromethane in the form of a solvate with a high solvate number. This is supported by earlier research on plutonium(11–20) which shows plutonium, because of its large number of free orbitals, has a high coordination capacity (as may be seen from Table 2 which gives its electron structure) and a very marked tendency toward maximum coordinate saturation (under the given conditions). This tendency often results in coordinate unsaturation in compounds with few ligands, which results in a tendency to addition reactions. The addition of neutral molecules, i.e. the coordination of plutonium by neutral molecules, takes place at the expense of the free electron pair of the functional group of the ligand and of the free orbitals of plutonium. The number of

TABLE 2.

Electronic structures and coordination numbers of thorium and its chemical analogues(16)

Element	Electronic Structure	Coordination Number	
		Max. possible	Most. probable
TITANIUM		9	6
ZIRCONIUM		9	8
HAFNIUM		9	8
CERIUM		16	8 - 9
THORIUM		16	8 - 9
URANIUM		16	8 - 9
NEPTUNIUM		16	8 -9
PLUTONIUM		16	8 - 9

coordinate-bound ligands depends on their nature and on the conditions under which the interaction takes place, of which one of the most important is the ratio of the reacting components. Since in our experiments the concentration of nitromethane considerably exceeded that of plutonium nitrate, their ratio strongly favored the formation of solvates with high solvate numbers.

High solvate numbers were also obtained with some other oxygen extraction agents. Glueckauf and McKay(11) found that with extraction agents such as ethers and alcohols, uranyl nitrate builds hydrato-solvates of the type $UO_2(NO_3)_2 \cdot 4H_2O \cdot (4 \pm 2S)$, where S denotes extraction agent. By analogy with uranium (VI), these authors suggest similar solvates for plutonium (VI) and neptunium (VI). Bachelet(12), Kaizin(13) and Vdovenko(14) and their co-workers found that with diethyl ether uranyl nitrate builds complexes including those of the type $UO_2(NO_3)_2 \cdot 2H_2O \cdot 4(C_2H_5)_2O$. In studying the extraction of thorium by some cyclic ethers, Branica(15) established that thorium nitrate occurs as a solvate with 10 molecules of the extraction agent, $Th(NO_3)_4 \cdot 10\,S$, where S signifies a cyclic ether (tetrahydroxylan, tetrahydropyran, 2,5-dimethyltetrahydrofuran, or 2-ethyltetrahydrofuran). Knowing this and the fact that other actinides also have a high coordination capacity (Table 2), the dependence of distribution coefficients of thorium (IV) and neptunium (VI) on the concentration of nitromethane in benzene (Figs. 5 and 6) was determined under the same conditions as for plutonium. It was found that the curves for Th (IV) and Np (VI) are a very similar shape to those for Pu (IV) and Pu (VI), which is again consistent with the hypothesis that these actinides too are extracted by nitromethane in the form of solvates of high solvate number. However, to determine the precise composition of the solvates and their stability constants, many more experiments must be conducted.

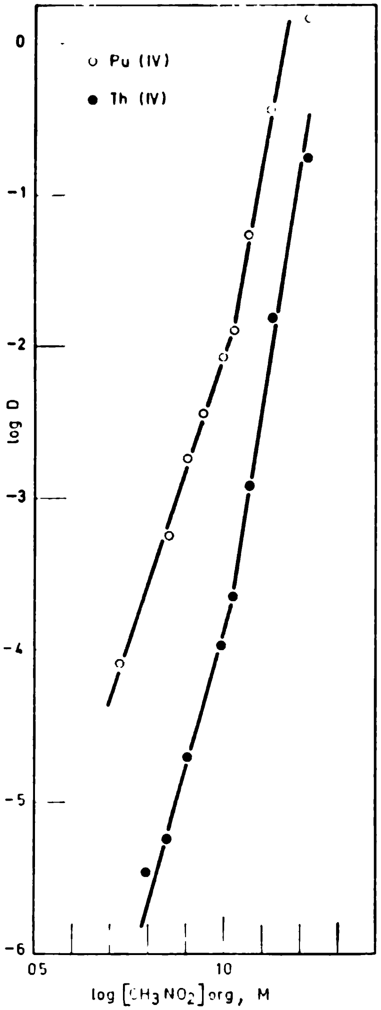


Figure 5.

Dependence of the distribution coefficients of plutonium (IV) and thorium (IV) on nitromethane concentration in benzene (equilibrium nitric acid concentration in the aqueous phase ... 5 M)

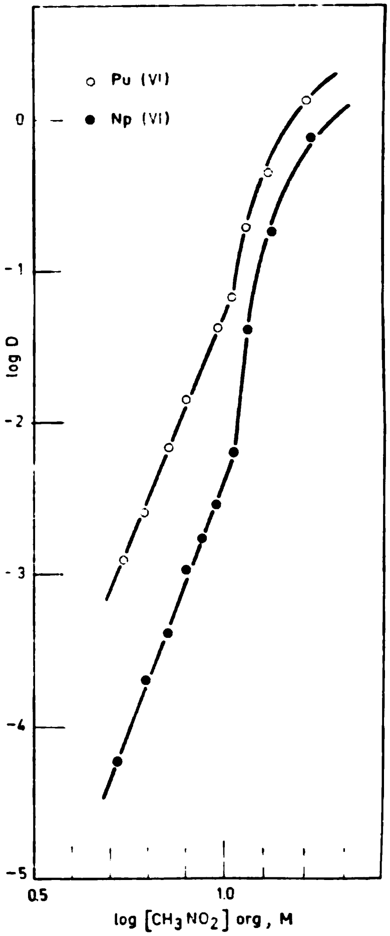


Figure 6.

Dependence of the distribution coefficients of plutonium (VI) and neptunium (VI) on nitromethane concentration in benzene (equilibrium nitric acid concentration in the aqueous phase ... 5 M)

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Original Scientific Paper

SACCHARIDES AND ORGANIC AND AMINO ACIDS IN WINES FROM THE VRŠAC VINEYARDS

by

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and VELJA M. VUČKOVIĆ

It is known that wine contains over 150 substances, on which its quality depends. Most of these substances occur in very small amounts, only about ten making up more than 1%(1).

The composition of wines produced in Yugoslavia has been studied(26), but insufficiently as yet. This refers especially to amino acids, both from the qualitative and quantitative aspects, and also to organic acids and sugars. As for organic acids, studies so far have mostly examined free acidity, and research in saccharides the total sugar. But the total amounts of sugar, organic acids, amino acids, or other constituents are not the only factors affecting the quality of wine. The qualitative composition of each of these groups of compounds and the amounts of their individual components greatly influence the quality, and together with other ingredients give the wine its specific character.

The composition of different sorts of wine from vineyards around Vršac has been investigated. Special attention was given in this work to amino acids, organic acids and saccharides, both from the qualitative and quantitative point of view.

EXPERIMENTAL

To elucidate the qualitative and quantitative changes of certain constituents which take place during fermentation and conversion of must into wine, samples of wine were prepared in the laboratory from must samples whose composition had been previously investigated(2).

The test samples were prepared out of the following grape varieties:

1963

Slankamenka from Radmilovac
1964 (all from Vršac)
Chasselas Rose
Gamay
Semillon
Prokupac
Muscat Ottonel
Traminer
Chasselas Dore
Kreaca
Silvaner
Pinot Noir
Muscat Hamburg
Dattier

Sauvignon Blanc Dinka White
Dinka White — falsification

The 1964 wines were obtained by fermentation of about 1 liter of must of which selected yeast (Vršački Breg, MO, Hladni Kvasac, Župa 1x, Breg 7, KP Breg) was added. After fermentation and natural clarification, the wine samples was decanted.

In 1963, bottled wines produced by Vršac or Radmilovac cellars were investigated, namely:

Italian Riesling (Italijanski rizling) — Vršac
Smederevka — Radmilovac
Kreaca (Banatski rizling) — Vršac.

Also studied was Vršac Italian Riesling produced from pasteurized must in the laboratory.

The samples were investigated and individual constituents determined either directly in the wine or after purification and separation of the constituents on ion exchangers(3, 4). The *pH*, and free, bound and total acidity were determined, and the saccharides, organic acids and amino acids were identified and determined by standard procedures described in a previous work(2). Sucrose was also identified by the sucrose identification method for wines(5). Alcohol, volatile acids and polyhydric alcohols were determined.

Polyhydric alcohols, like sugar contained in the same solution, were identified by paper chromatography(6). This procedure does not separate mannitol from glucose, but they differ in the way they react to a solution of silver nitrate and anilienhydrophthalate. Inositol was also demonstrated on the chromatogram by the color reaction after Fleury(7).

Polyhydric alcohols were determined, after chromatographic separation, in the corresponding aqueous eluates from the chromatogram. The determination was done by titrimetry(8), after the aqueous solution had been oxidized by periodic acid. Since mannitol cannot be separated from glucose by chromatography, these two constituents were first determined together by this procedure and then mannitol was computed from the difference of the value obtained and the value for glucose determined colorimetrically after Nelson-Somogy(9).

Alcohol was determined by densitometry in a distillate of the wine.

Total volatile acids were determined by titrimetry in the steam distillate of wine(10).

The chromatograms of sugars and polyhydric alcohols are shown in Figs. 1 and 2, those of organic acids in Fig. 3, and amino acids in Figs. 4 and 5. Figure 6 presents the elution chromatogram for organic acids on a silicic acid column*.

Tables 1 and 2 present the results of the determination of total reducing sugars, individual sugars, individual polyhydric alcohols, alcohols, and glucose-fructose ratio (G : F). Tables 3 and 4 show individual organic acids, *pH*, free, bound and total acidity, and volatile acids. Tables 5, 6 and 7 contain data on free amino acids, nitrogen of free amino acids, and decreases of certain amino acids (in percentage) compared with the initial must.

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* Figs. 1, 2, 3, 4, 5 and 6 only show the chromatograms of sugars, organic acids and amino acids for some wine samples. Similar chromatograms were obtained for the other sorts of wine.

DISCUSSION

The total amount of reducing sugars in the wine samples lies on the whole around 0.1 *g*/100 *ml*. A high value was found in Sauvignon Blanc, and in Semillon and Chasselas Rose. Their high sugar content shows that they had not fermented out. It is possible that the conditions under which the wines were prepared (laboratory, small amounts, etc.) either extend fermentation time or arrest fermentation too soon.

Of the saccharides, fructose is present in the largest amounts (0.012—0.053 *g*/100 *ml*). The wines Sauvignon Blanc, Semillon, Chasselas Rose and Silvaner have considerably more fructose than the others (Tables 1 and 2).

Glucose content varies between 0.001 and 0.130 *g*/100 *ml* (Tables 1 and 2).

Glucose-fructose ratio in the test samples was less than in the corresponding musts (0.03 up to 1.10). This figure also depends considerably on the content of total reducing sugars in the must(11). This confirms the conclusion that glucose ferments faster than fructose(12).

Data on the presence of galactose and sucrose in wine has not been found in the literature(12, 13, 14). However, in all wine samples other than Sauvignon Blanc, galactose was found in amounts varying between 0.001 and 0.009 *g*/100 *ml* (Fig. 2). Semillon, Chasselas Rose and Kreaca contained only traces of galactose. Sucrose was also found in all wine samples, but only in traces, except for the falsified Dinka White (Tables 1 and 2) which contained a somewhat larger amount.

Xylose was lower than galactose. The highest xylose content was found in Semillon, while Chasselas Rose and Sauvignon Blanc (Fig. 2) did not contain xylose even in traces (Tables 1 and 2). Since xylose is not contained in the initial musts(2), these results bear out the hypothesis(15) that it is created in wine via pentosan hydrolysis during fermentation.

In all wine samples arabinose was found in just detectable amounts. Traminer contained slightly more than the rest, but the methods applied could not determine it.

Mannitol was present in all wines except Gamay, Semillon, Prokupac and Traminer (0.12—1.58 *g*/*lit*). A very high mannitol content was found in Chasselas Rose (Tables 1 and 2). The occurence of mannitol is believed to depend mainly on the temperature of fermentation, and also on the presence of rotten and moldy berries, on the length of time the wine is left to stand on the lees, and on the free acidity(13). Even though sound wines are not known to contain mannitol, our results show that it may occur due to other factors, because the conditions of fermentation were identical for all samples and the grapes were fresh and sound.

Inositol ranges between 0.2 and 2.0 *g*/*lit* for different wines, except for Gamay and Dinka White which contain relatively large amounts. Falsifed Dinka White contains rather little of this alcohol (Tables 1 and 2). The great difference in inositol content between original and falsified wines might be used in wine analysis for discovering falsifications of this kind.

All test samples contained glycerol, which is of exceptional significance for wine quality(12). Most wines contain between 4.52 and 12.80 *g*/*lit*.

Alcohol ranges between 9 and 14 v % (Tables 1 and 2).

TABLE 1

SORT OF WINE*	Total reducing sugars	Galactose	Glucose	Fructose	Xylose	G/F	Inositol	Mannitol	Glucerol	Alcohol
	g/100 *ml* wine						*g*/*lit* wine			v %
Italian Riesling	0.107	0.006	0.001	0.053	0.001	0.03	1.05	2.58	8.46	12.70
Italian Riesling made from pasteurized must	0.087	0.004	0.005	0.013	0.002	0.44	0.69	2.18	4.55	11.74
Kreaca	0.068	traces	0.014	0.012	traces	1.10	1.67	0.44	5.83	12.26
Slankamenka	0.084	0.001	0.006	0.016	0.004	0.37	1.64	0.92	4.52	10.88
Smederevka from Radmilovac	0.125	0.004	0.040	0.039	0.003	1.02	1.50	0.85	7.55	11.13

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* All wines are from Vršac and Radmilovac cellars, except for Italian Riesling (made from pasteurized must in the laboratory).

TABLE 2

KIND OF WINE*	Total reducing sugars	Galactose	Glucose	Fructose	Xylose	Sucrose	G/F	Ino-sitol	Man-nitol	Gly-cerol	Alcohol
	g/100 *ml* wine							*g*/*l* wine			v%
Chasselas Rose	1.35	traces	0.610	0.880	—	traces	0.70	0.40	4.00	—	8.66
Gamay	0.12	0.004	0.050	0.014	0.007	traces	3.50	—	—	—	9.55
Semillon	2.56	traces	0.130	2.400	0.030	traces	0.05	2.00	—	—	12.50
Prokupac	0.09	0.008	0.020	0.030	0.005	traces	0.66	0.40	—	12.80	—
Muskat Ottonel	0.08	0.006	0.012	0.025	traces	traces	0.48	0.20	0.12	10.40	12.42
Traminer	0.09	0.004	0.050	0.050	traces	traces	1.00	0.57	—	7.40	—
Sauvignon Blanc	6.02	—	1.100	5.300	—	traces	0.20	1.70	—	12.80	9.30
Chasselas Dore	0.07	0.005	0.006	0.030	traces	traces	0.20	0.40	0.28	4.60	10.12
Kreaca	0.04	0.004	0.010	0.003	traces	traces	3.30	1.50	0.47	10.30	9.22
Silvaner	0.26	0.007	0.015	0.210	0.001	traces	0.07	1.00	0.37	12.30	9.71
Pinot Noir	0.13	0.005	0.028	0.032	0.003	traces	0.87	1.50	0.70	12.10	11.57
Muscat Hamburg	0.09	0.008	0.020	0.025	0.004	traces	0.80	0.40	1.50	10.20	—
Dattier	0.04	0.003	0.005	0.007	0.001	traces	0.71	0.45	0.20	7.30	7.43
Dinka White original	0.08	0.009	0.038	0.029	0.002	traces	0.97	—	0.86	7.40	11.01
Dinka White-falsification	0.02	traces	traces	traces	traces	0.005	—	0.30	1.00	5.00	10.14

* All wines made in the laboratory.

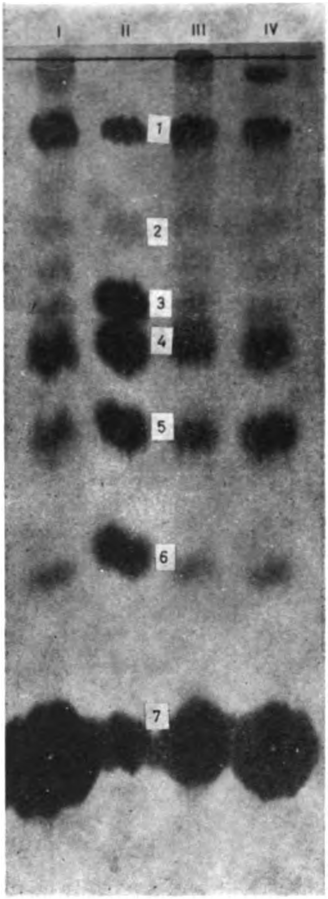

Figure 1

I — Dattier

II — Sugar mixture
  (1) inositol
  (2) sucrose
  (3) galactose
  (4) glucose + mannitol
  (5) fructose
  (6) xylose
  (7) glycerol

III — Pinot Noir

IV — Chasselas Blanc

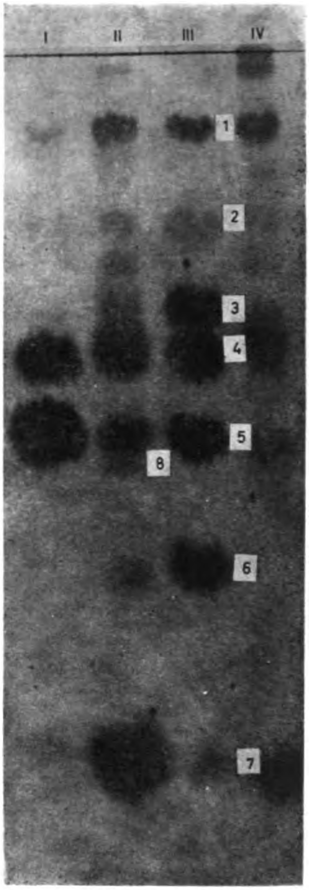

Figure 2

I — Sauvignon Blanc

II — Traminer

III — Sugar mixture
  (1) inositol
  (2) sucrose
  (3) galactose
  (4) glucose + mannitol
  (5) fructose
  (6) xylose
  (7) glycerol
  (8) arabinose

IV — Chasselas Rose

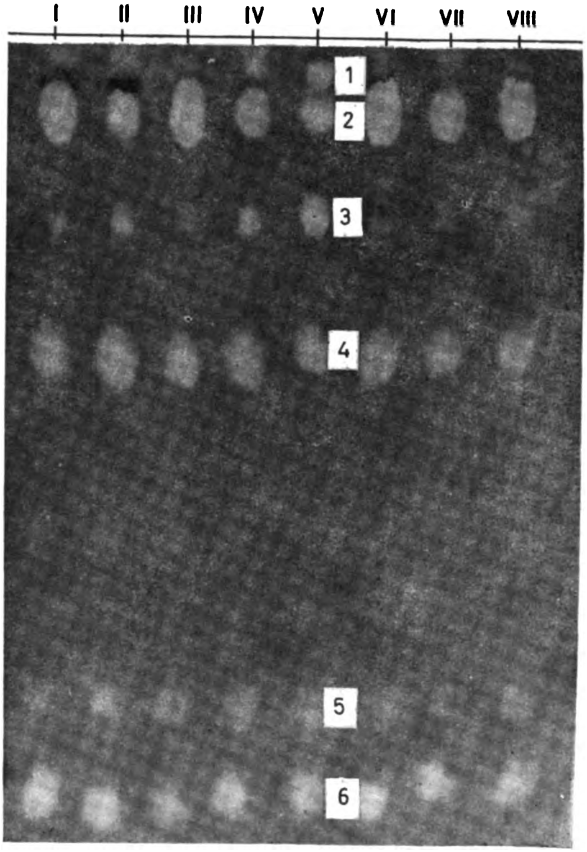

Figure 3

I — Muscat Ottonel

II — Muscat Hamburg

III — Kreaca

IV — Pinot Noir

V — Organic acid mixture

(1) glucuronic acid
(2) tartaric acid
(3) citric acid
(4) malic acid
(5) lactic acid
(6) succinic acid

VI — Gamay

VII — Semillon

VIII — Silvaner

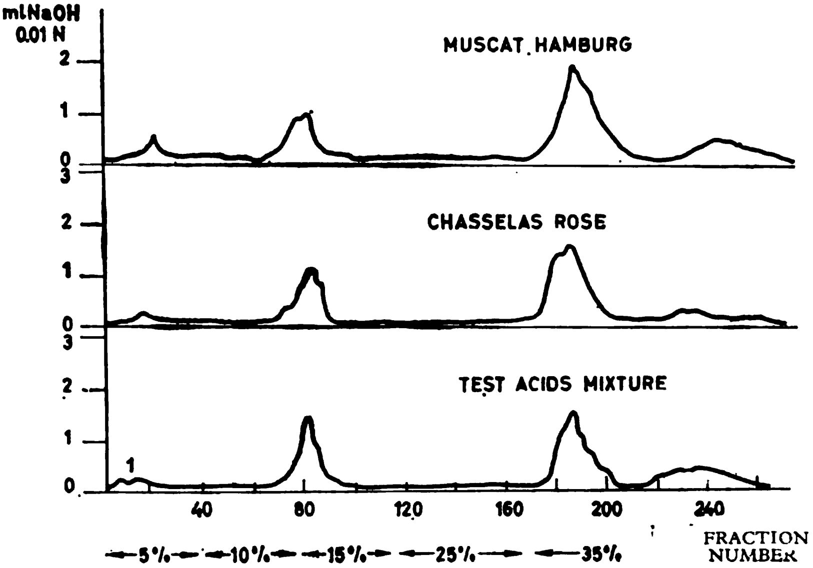

Figure 4

Elution curves of organic acids from some sorts of wine and test acid mixture on silicic acid column

The qualitative amino acid composition of the wine samples closely resembles that found by Bourdet and Herard(16), only in the wines we tested tryptophan was also identified (Figs. 5 and 6).

Qualitative and considerable quantitative differences in amino acids between musts and wines were established. Apart from the amino acids in the musts, aspartic acid and tryptophan were found in the wines. Some amino acids are believed to occur in wine due to the autolysis of yeast cells during fermentation(17).

The wine samples contained the most proline (160.00—4.02 *mg*/100 *ml*), followed by histidine (41.75—0.21 *mg*/100 *ml*) and arginine (22.50—0.10 *mg*/100 *ml*), and least tryptophan (only traces).

In glutamine, serine, γ-amino-n-butyric acid, tyrosine, methionine, valine and phenylalanine, the wine samples differed from one another only little. In these amino acids they differ little from those of the same varieties grown in other climates, but they differ substantially in having a low content of glutaminic acid(16, 18).

Compared with the initial must, the greatest decrease was in arginine, the acid particularly heavily consumed by yeasts(19). Proline decreased to some extent, but it remained the highest of all the amino acids because yeasts can hardly use as nutrition(20).

The difference in content of cystine, lysine, histidine, asparagine, glycine, tyrosine and valine between wines and their musts was highly non-uniform. In some samples decreases of about 99% were registered, in others there were even increases. The other amino acids showed rather great decreases, of between 90 and 99% (Table 7).

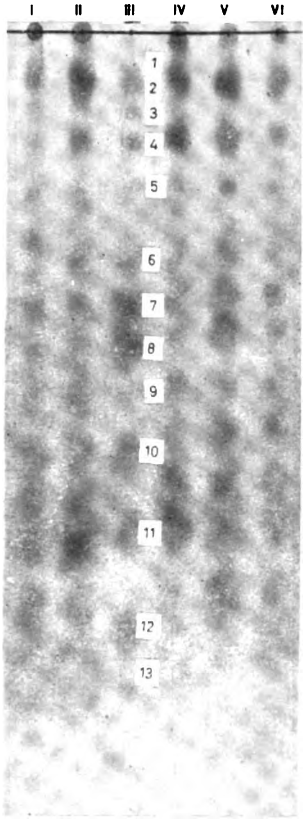

Figure 5

(The chromatogram was run for 60 h)

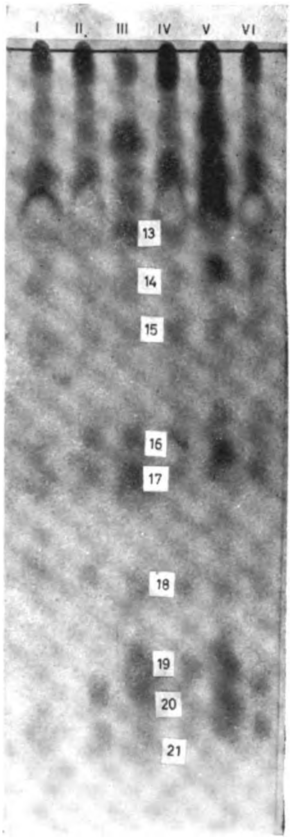

Figure 6

(The chromatogram was run for 40 h)

I Muscat Hamburg

II Muscat Ottonel

III — Amino acid mixture

(1) Cys-S-S-Cys
(2) Lys
(3) His
(4) Arg
(5) Asp-NH_2
(6) Glu-NH_2
(7) Ser
(8) Gly
(9) Asp
(10) Thre
(11) Glu
(12) Ala
(13) Pro
(14) Tyr
(15) γ-amino-n-butyric acid
(16) Meth
(17) Val
(18) Try
(19) Phe
(20) Ileu
(21) Leu

IV — Kreaca
V — Dattier
VI — Dinka White

TABLE 3

SORT OF WINE*	pH	Bound acids	Total acids	Free acids	Malic acid		Tartaric acid		Citric acid		Succinic acid		Volatile acids
		mE/100 *ml* of wine			*mE*/100 *ml* wine	%	*mE*/100 *ml* wine	%	*mE*/100 *ml* wine	%	*mE*/100 *ml* wine	%	*mE*/100 *ml* wine
Italian Riesling	3.50	6.49	10.16	3.65	1.41	13.7	6.38	62.2	0.22	2.2	1.56	15.0	1.44
Italian Riesling made from pasteurized must	3.20	8.25	11.32	3.07	1.50	13.2	8.51	75.2	0.09	0.7	0.91	8.0	0.15
Kreaca	3.60	5.53	9.26	3.73	0.54	5.8	6.94	74.9	0.29	3.1	1.36	14.7	0.65
Slankamenka	3.30	6.54	8.84	2.30	2.40	26.4	5.51	60.7	0.38	4.2	0.65	7.1	0.17
Smederevka from Radmilovac	3.30	8.09	11.90	3.81	0.48	4.0	9.60	80.6	0.24	2.0	0.77	6.4	0.90

* All wines are from Vršac and Radmilovac cellars, except for Italian Riesling (made from pasteurized must in the laboratory).

TABLE 4

SORT OF WINE*	pH	Free acids	Total acids	Bound acids	Malic acid		Tartaric acid		Citric acid		Succinic acid		Volatile acids
		mE/100 *ml* wine			*mE*/100 *ml* wine	%	*mE*/100 *ml* wine	%	*mE*/100 *ml* wine	%	*mE*/100 *ml* wine	%	*mE*/100 *ml* wine
Chasselas Rose	3.05	6.41	10.48	4.07	2.52	23.9	5.66	53.6	0.20	1.9	1.26	12.0	0.44
Gamay	3.20	10.49	13.86	3.37	4.07	29.2	7.16	51.3	0.44	3.2	1.76	12.6	0.19
Semillon	3.20	8.44	10.38	1.94	2.66	25.4	5.18	49.3	0.41	4.0	0.81	17.2	0.36
Prokupac	3.55	11.74	14.69	2.95	5.28	35.9	7.32	49.7	0.96	6.5	0.98	6.7	0.92
Muscat Ottonel	3.25	7.28	10.34	3.06	2.50	23.9	5.79	55.4	traces	traces	1.41	13.6	0.11
Traminer	3.00	7.04	9.75	2.71	2.08	21.3	4.01	41.1	0.43	4.4	1.74	17.8	0.08
Sauvignon Blanc	2.90	9.86	12.34	2.48	2.51	20.2	7.63	61.3	0.38	3.1	1.52	12.2	0.71
Chasselas Dore	3.15	8.14	10.11	1.97	2.28	22.6	5.84	57.7	0.38	3.7	1.19	11.7	0.29
Kreaca	2.95	10.17	12.34	2.17	3.81	30.6	5.78	46.5	0.80	6.4	1.09	8.7	0.27
Silvaner	3.40	8.04	10.38	2.34	3.30	31.5	3.86	36.8	0.68	6.5	1.04	9.9	0.11
Pinot Noir	4.00	7.94	11.51	3.57	4.50	38.8	3.52	30.3	0.91	7.8	1.86	16.0	0.14
Muscat Hamburg	3.25	7.90	11.67	3.77	4.88	39.6	4.02	37.5	0.46	3.9	1.38	11.2	0.90
Dattier	3.15	9.36	11.28	1.92	3.20	28.1	5.52	48.6	1.07	9.4	0.84	7.4	0.18
Dinka White original	3.65	4.70	7.40	2.70	0.50	6.6	3.94	52.9	0.32	4.3	2.27	30.5	0.19
Dinka White falsification	3.95	4.22	7.23	3.01	1.45	20.0	4.91	67.5	0.63	8.7	0.08	1.1	0.63

* All wines made in the laboratory.

TABLE 5

SORT OF WINE*	Nitrogen of free amino acids	His	Arg	Asp-NH_2	Glu-NH_2	Ser	Gly	Asp	Thre	Glu	Ala	Pro	γ-Amino-n-butyric acid	Tyr	Meth	Val	Try	Phe	Leu + Ileu
	mg/100 *ml* wine																		
Italian Riesling	35.00	24.20	22.50	1.82	1.60	1.90	4.90	0.66	1.10	4.70	11.75	130.3	0.75	5.00	0.65	1.60	traces	3.15	1.10
Italian Riesling made from pasteurized must	12.03	9.00	2.37	traces	0.40	0.95	0.70	0.62	0.43	0.50	1.20	66.00	0.30	0.67	0.28	0.80	„	1.16	1.50
Kreaca	25.73	20.25	6.87	0.62	1.40	1.55	4.60	1.33	2.10	3.15	11.75	109.00	0.96	1.72	0.57	1.23	„	3.57	2.00
Slankamenka	9.97	8.00	1.75	traces	0.46	0.31	1.40	0.80	1.09	1.18	3.95	46.25	0.60	0.45	0.20	0.67	„	1.08	1.00
Smederevka from Radmilovac	46.19	41.75	22.50	3.60	3.40	5.50	5.50	3.00	2.90	6.10	16.61	160.00	1.03	0.40	1.10	4.30	„	3.70	8.50

* All wines from Vršac and Radmilovac cellars, except for Italian Riesling (made from pasteurized must in the laboratory).

SORT OF WINE*	Tyr	Meth	Val	Try	Phe	Leu + Ileu
Chasselas Rose	38	0.09	traces	traces	0.06	0.09
Gamay	36	0.04	„	„	traces	0.03
Semillon	11	0.01	„	„	„	0.05
Prokupac	ces	traces	„	„	„	traces
Muscat Ottonel	79	0.23	„	„	0.13	0.17
Traminer	79	0.68	„	„	0.35	0.75
Sauvignon Blanc	ces	traces	„	„	traces	traces
Chasselas Dore	„	„	„	„	„	„
Kreaca	19	0.01	0.01	„	„	„
Silvaner	39	0.31	0.27	„	0.25	0.42
Pinot Noir	18	traces	0.07	„	traces	0.14
Muscat Hamburg	36	0.04	0.08	„	0.03	traces
Dattier	12	0.09	0.12	„	traces	0.17
Dinka White original	37	0.21	0.20	„	0.17	0.09
Dinka White falsification	80	0.06	0.10	„	0.14	0.01

* All wines made in the

SORT OF WINE*	tyric acid	Tyr	Meth	Val	Try*	Phe	Leu + Ileu
Chasselas Rose		61.7	97.8	99.9		8.90	98.3
Gamay		increase	99.2	the same		99.9	99.1
Semillon		»	99.2	»		99.9	95.9
Prokupac		99.9	99.9	»		99.9	99.9
Muscat Ottonel		39.0	91.6	99.9		88.1	91.7
Traminer		increase	45.1	99.9		91.9	83.4
Sauvignon Blanc		99.9	99.9	the same		99.9	99.9
Chasselas Dore		99.9	99.9	the same		99.9	99.9
Kreaca		increase	99.5	increase		99.9	99.9
Silvaner		82.3	96.4	83.9		97.8	96.1
Pinot Noir		92.5	99.9	increase		99.9	97.1
Dattier		increase	32.2	88.7		99.9	97.8
Dinka White falsification		increase	66.5	50.0	the same	14.7	88.9
Italian Riesling made from pasteurized must		86.6	58.2	50.0	the same		increase

* Not present in the must.

Nitrogen of free amino acids in the wine samples decreased with respect to the corresponding musts by 89—94%. The total nitrogen content is believed(21, 22) to fall by 40—70% during fermentation, the bulk from free amino acid nitrogen, that mostly consumed by the activity of wine yeasts(23). The utilization of amino acids by yeast is also affected by *pH* of the must, which results in the different changes of amino acid content in different wines.

The least free amino acid nitrogen was found in Sauvignon Blanc, whose must also contained the smallest amount(2); it may be taken that there was insufficient for wine yeast nutrition so that this wine did not ferment out entirely.

The amounts of different organic acids in different wines vary considerably. Tartaric acid contributes the largest share, 3.5—9.6 mE/100 *ml*, or 40—50% of the total acid content of the wine (Tables 3 and 4).

The content of malic acid is 0.5—5.3 mE/100 *ml*. That of citric acid is the least, most frequently 0.20—1.07 mE/100 *ml*. In Muscat Ottonel, citric acid was found only in traces (Tables 3 and 4).

The content of malic acid did differ widely between must and wine samples. However, the content of tartaric acid was considerably reduced because of the formation of cream of tartar and citric acid was increased because this acid forms from sugar and glutaminic acid during fermentation(14, 25).

The content of succinic acid, which is not present in grape and is produced from sugar during fermentation, was also different (0.7—1.9 mE/100 *ml*). It is noteworthy that the largest amount of this acid was found in Dinka White (2.27 mE/100 *ml*) and the smallest in the Dinka White falsification (0.008 mE/100 *ml*). Since the content of glutaminic acid in the musts was very low, the succinic acid in the wine samples originated principally from sugar.

It was found that free and bound acidity varied considerably depending on the sort of wine. Free acidity was higher and bound acidity lower than in the musts, because during fermentation some mineral matter and acids settle and some acids are created from sugars.

The content of volatile acids and the *pH* values lie within regulation standards.

The results show differences between Kreaca made in 1963 and the same wine made in 1964. Glycerol, free and bound acidity, and malic acid were higher in the 1964 wine. Also, the glucose-fructose ratio in this wine was about three times higher. On the other hand, alcohol and nitrogen of free amino acids were lower than in the 1963 wine.

On the basis of these results alone no general conclusion can be drawn on the effect of different weather conditions on the content of individual constituents of grapes and wine, nevertheless the results suggest the existence of such differences.

It was also established that Italian Riesling made from pasteurized must differed in composition from the same wine made from nonpasteurized must: it had less glycerol, reducing sugars and nitrogen of free amino acids (some amino acids were down 50—99%) and more total and bound acidity. Stronger acidity and less reducing sugars in the wine made from pasteurized must indicate a more regular and complete fermentation(13), while the fermentation of nonpasteurized must is also affected by the microorganisms found on the grapes.

The falsified Dinka White differs from its original counterpart in containing very little sugar, much less inositol and slightly less nitrogen of free amino acids, and more mannitol. It also exhibits a very low proline content. These differences are due to the different composition of the fleshy part of the berry compared with the skins, pips and stalks of grapes contained in the marc on which sugar is fermented into a falsified wine.

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Original Scientific Paper

DEPENDENCE OF FOLIAR PHOSPHORUS CONTENT ON EXCHANGEABLE HYDROGEN OF SOIL (I)

by

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PRELIMINARY COMMUNICATION

The plant is only able to absorb phosphorus from the soil in the ionic state. However as the phosphorus is for the most part inactivated because of forming only weakly soluble compounds(2, 5, 6), the soil solution as a rule lacks phosphate ions so much that it cannot meet the plant's requirements for this element(1, 4).

However, the phosphate ion, together with other nutrient ions, also occurs in the soil adsorbed to the micelle of the soil colloid. Through the close contact between its root and the micelle, the plant is able to absorb these phosphate ions(7).

The ions on the micelle always include some adsorbed hydrogen ions (exchangeable hydrogen), which play an important role in many soil processes. Also important for our further discussion are those hydrogen ions which occur free in the soil solution and whose concentration is measured by the *pH* of the soil.

This preliminary report present evidence for an active role of hydrogen ions in the soil regarding the plant's uptake of phosphorus. The findings will be discussed theoretically in future papers.

EXPERIMENTAL

Material for analysis was collected during two vegetation periods. The plants had very different soil and climatic conditions (specimens from various parts of Yugoslavia). Phosphorus content was determined exclusively in the leaf. The plants were: corn, rye, wheat, barley, sunflower, soybean, cabbage, beans, potato, tomato, lavender, and grazing grass. A total of 73 samples was investigated.

For the determination of phosphorus(3) the material was washed clean in double-distilled water and dried at 105°C. The value was expressed in *mg* P per 100 *g* dried foliage.

Soil samples were taken from right below the plant at depths of 15 and 50 cm. After drying in air, exchangeable hydrogen was determined(8), and expressed as *me* H_s^+ per 100 *g* soil (mean value of the two depths). For all soil samples *pH* was also determined(9).

DISCUSSION

By plotting phosphorus content on the ordinate against exchangeable hydrogen (H_s^+) on the abscissa the graph in Fig. 1 was obtained.

It may be seen that irrespective of plant species or external growth-influencing factors at the time of sampling, leaf phosphorus content directly depends on the exchangeable hydrogen content of the soil. The correlation evidenced by Fig. 1 was previously unknown.

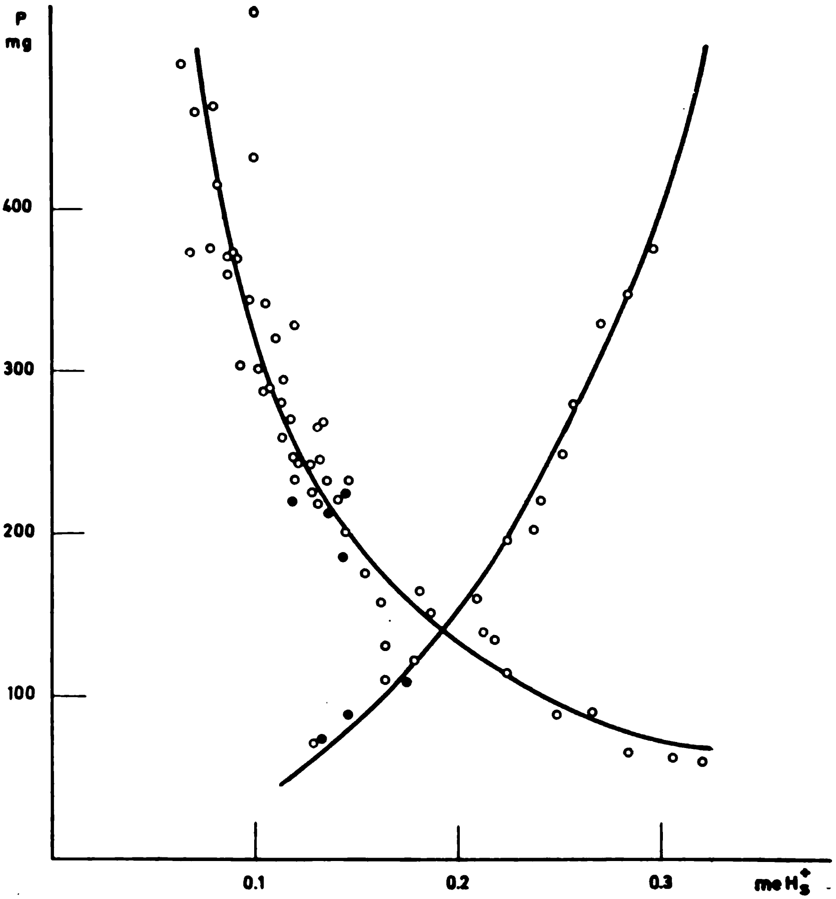

Figure 1
Dependence of leaf P content on H_s^+ of soil

The relationship is manifested by two curves, probably resulting from two different processes of phosphorus uptake. The equations of these curves may be written

$$P = 31 \times \frac{1 - H_s}{H_s - 0.0155} \qquad P = 31 \times 10^2 \frac{H_s^2}{1 - H_s}$$

Left curve Right curve

It is from the theoretical aspect noteworthy that the constant 31 which appears in both expression is the atomic weight of phosphorus.

In a 1-year field experiment (Kosijerić) we verified the influence of exchangeable hydrogen ions on the phosphorus content of grazing grass. Seven test plots were treated by various commercial fertilizers. Phosphorus in the test samples and the exchangeable hydrogen in the corresponding soil are shown in Table 1.

TABLE 1.

P in grass and me H_s^+ *of the soil*

No.	Treated with	P *mg*	H_s^+ *me*
1	control	109.1	0.175
2	Ca	89.3	0.146
3	N	73.5	0.132
4	P	212.0	0.137
5	NPK I	224.4	0.146
6	NPK II	185.5	0.144
7	K	219.7	0.119

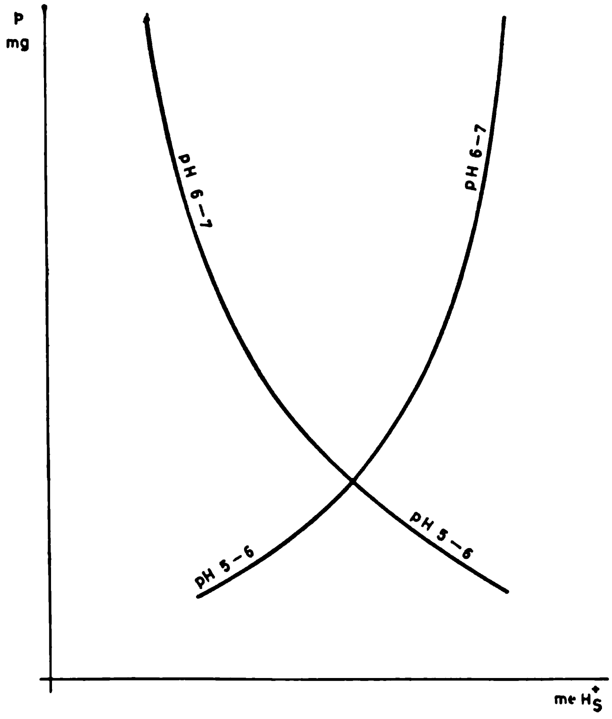

Figure 2
Influence of H_s^+ and pH on leaf P content

Theoretically, the phosphorus content of the test samples could have any value (50—500 *mg*, Fig. 1). However, the position of these samples on the correlation curves (full circles in Fig. 1) shows that their phosphorus content precisely agrees with what could have been predicted on the basis of the previously determined exchangeable hydrogen content of the soil.

If the hydrogen ions adsorbed to the micelle of the soil colloid play some role in the process of phosphorus uptake, it might be expected the free hydrogen ions (*p*H of the soil) also have some influence. (The *p*H of the soil samples ranged between 5 and 7.65.) This was confirmed by parallel study of the influence of H_s^+ and *p*H values on the position of the samples on the curves (Fig. 1). This effect is schematically represented by Fig. 2. Samples whose soil *p*H lies between 5 and 6 lie below the intersection of the two curves, those between 6 and 7 above it.

Figure 2 does not show the position of the samples taken from basic soils, which without exception, are found on the left-hand curve, together with the acid samples.

Thus, as might have been expected, the hydrogen ions of the soil solution (pH) take part in plant phosphorus uptake as well as the exchangeable hydrogen ions (H_s^+).

From the experimental findings above, it may be concluded that phosphorus content of plants can be predicted on the basis of experimental curves (Fig. 1), if the exchangeable hydrogen value and pH of the soil are known.

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THE HYDROLYSIS OF CHLORODIMETHYL ETHER AND RELATED COMPOUNDS. I.

by

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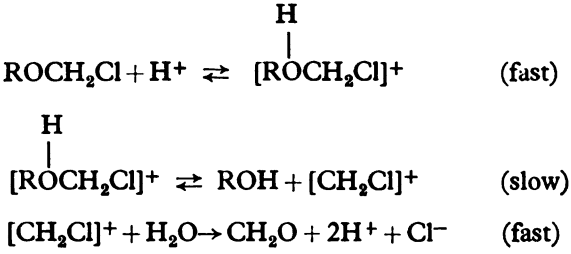
INTRODUCTION

The rate of hydrolysis of chlorodimethyl ether and some of its homologues was first investigated by Böhme(1) and co-workers. They observed hydrolysis in a dioxane-water mixture by determining the hydrochloric acid generated, and concluded that this was a reaction of the first order and that hydrolysis was autocatalyzed by the hydrochloric acid produced. They suggested the following mechanism:



$$ROCH_2Cl + H^+ \rightleftarrows [R\overset{\overset{\displaystyle H}{|}}{O}CH_2Cl]^+ \qquad \text{(fast)}$$

$$[R\overset{\overset{\displaystyle H}{|}}{O}CH_2Cl]^+ \rightleftarrows ROH + [CH_2Cl]^+ \qquad \text{(slow)}$$

$$[CH_2Cl]^+ + H_2O \rightarrow CH_2O + 2H^+ + Cl^- \qquad \text{(fast)}$$

Leimu and Solomaa(2) investigated the alcoholysis of these compounds in dioxane in the presence of small amounts of ethanol. They also found the reaction was catalyzed by the hydrochloric acid and agreed with the mechanism Böhme suggested. Later Salomaa(3) concluded that not a catalytic but a primary salt effect was involved. Ballinger *et al.*(3) studied this reaction in ethanol and in an ethanol-diethyl ether mixture, with and without some salts added. They found the reaction proceeded according to mechanism S_N1 (Hughes and Ingold's terminology)(4), but that in the presence of ethoxide ion it also contained a bimolecular component.

This report gives the results on the rate of hydrolysis of chlorodimethyl ether and the ethoxy-, n-propoxy-, n-butoxy- and sec-butoxy- homologues in an acetone-water mixture.

EXPERIMENTAL

Chlorodimethyl ether and its homologues were prepared through reaction between trioxane, the corresponding alcohol and hydrogen chloride, and then purified by fractional distillation(5). The boiling points were 58.3—58.5°C for chlorodimethyl ether, 81.2—81.6°C ethoxymethyl chloride, 108.5—108.8°C n-propoxymethyl chloride, and 121.5—121.8°C sec-butoxymethyl chloride, at 710 *mm Hg*. Acetone of p.a. purity was purified by cooking and distillation in the presence of potassium permanganate and finally by column distillation. The inorganic salts (of *p.a.* purity) were dried before use.

Kinetic measurement were made in the following manner. The solvent (95 volume parts of acetone and 5 parts water) in a volumetric flask was thermostated to a constant temperature (±0.05°C with 0°C, and ±0.2°C with cca —20°C). Next the corresponding chloride was added to the solvent and, at different intervals, 5-*ml* aliquots were transferred to cca 200-*ml* neutralized acetone previously cooled below —40°C. The solution was then quickly titrated with cca 0.005 N sodium hydroxide using a lacmoid indicator.

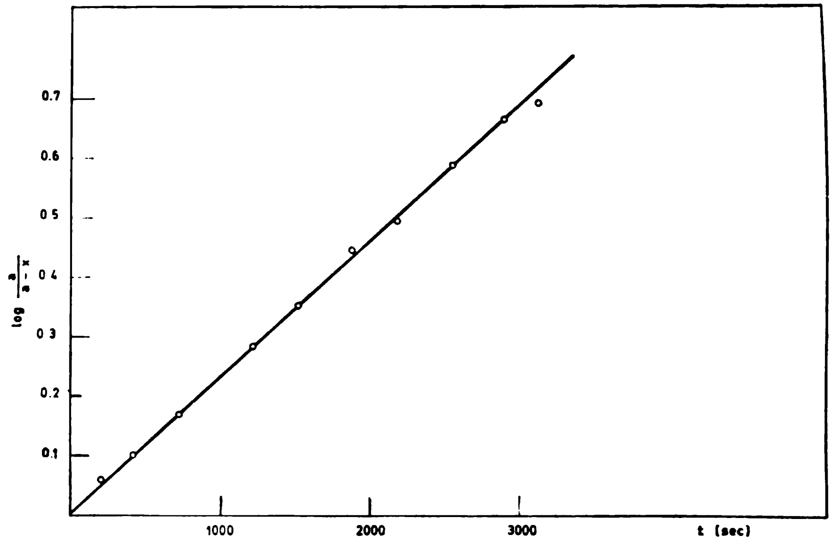


Figure 1

Hydrolysis of Chlorodimethyl ether in 95% acetone at 0.0°C

Figure 1 shows a typical experimental curve proving a first-order reaction.

Rate constants were computed from the integrated form of equation for a first order rate. The values in Table 1 are mean values of at least three separate measurements.

TABLE I

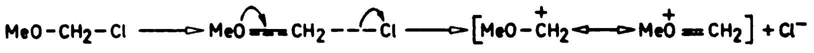
Rate Constants for the Hydrolysis of $ROCH_2Cl$ in 95% Acetone at 0.0°C

Compound	Added salt *mol/lit*	$k_{273°K} \cdot 10^4$ *sec*$^{-1}$
$CH_3 \cdot O \cdot CH_2Cl$	—	5.38±0.10
„	$2.50 \cdot 10^{-2}$ LiCl	9.82±0.13
„	$5.00 \cdot 10^{-2}$ $LiNO_3$	7.58±0.09
„	$4.0 \cdot 10^{-3}$ HCl	6.68±0.21
„	$5.40 \cdot 10^{-2}$ HCl	7.82±0.16
„	—	1.45±0.30 at —20°C
„	$3.2 \cdot 10^{-3}$ LiBr	10.3 (falling)
„	$2.0 \cdot 10^{-3}$ LiBr	7.17 (falling)
$C_2H_5 \cdot O \cdot CH_2Cl$	—	19.5±0.9
$n\text{-}C_3H_7 \cdot O \cdot CH_2Cl$	—	13.7±0.7
$n\text{-}C_4H_9 \cdot O \cdot CH_2Cl$	—	12.1±0.7
„	$5.2 \cdot 10^{-3}$ LiCl	20.3±1.1
„	$3.3 \cdot 10^{-3}$ LiBr	38.6 (slightly falling)
sec-$C_4H_9 \cdot O \cdot CH_2Cl$	—	60.9±1.4
„	$4.7 \cdot 10^{-3}$ LiCl	73.3±1.2
„	$2.1 \cdot 10^{-3}$ LiBr	80.6±1.5
„	$2.6 \cdot 10^{-3}$ LiBr	81.9±1.4

DISCUSSION

Chlorodimethyl ether and its homologues very readily undergo reactions in which the chloride ion is substituted by some nucleophilic reactant. It is generally considered that this reaction takes place according to mechanism S_N1⁽⁶⁾. The replacement of the hydrogen atom in the methoxy group by methyl, ethyl or propyl group could be expected to gradually step up hydrolysis, the maximum effect presumably be produced by substitution of the methyl group. Our results do in fact show that the substitution of the methyl group increases the rate constant by about four times compared with chlorodimethyl ether. Further extension of the chain, however, reduced the rate constant compared with the previous member of the homologous sequence. With sec-butoxymethyl chloride the rate constant goes up again. This behavior can be explained if hydrolysis is assumed to proceed not only according to mechanism S_N1 alone but also with an S_N2 component.

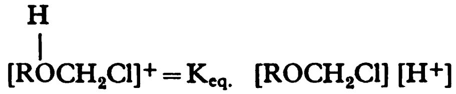
The high rate of hydrolysis of chlorodimethyl ether by mechanism S_N1 is interpreted by mesomery which facilitates the formation of carbon ion. It may be hypothesized that



The substitution of methyl group for hydrogen atom in the methoxy group by induction affects the free electron pair in the oxygen making for further stabilization of the activated complex according to mechanism S_N1. With extension of the chain the induction effect increases only negligibly. However, if the reaction also proceeds according to mechanism S_N2, the extension of the chain reduces reactivity. This means that there are two opposing effects: extension of the chain accelerates the reaction according to mechanism S_N1 and slows it down according to S_N2. With sec-butoxymethyl chloride, probably because of the ramification of the chain, the induction effect overwhelms the steric effect, so that the rate again goes up.

Studying the effect of the addition of salts, it was found that lithium bromide increased the reaction rate of chlorodimethyl ether by about six times, while the other salts, even if added in ten times higher concentrations, produced much less effect. This is explainable in terms of mechanism S_N2, because a shift to more nucleophilic reactants favors mechanism S_N2. Apart from this, the variation of lithium bromide concentration also suggests a reaction of this character. With -n-butoxymethyl chloride, lithium bromide speeds up the reaction by some three times, while the acceleration with sec-butoxymethyl chloride is only 30%, which agrees with the conclusions above about simultaneous operation of reaction mechanisms S_N1 and S_N2. Preliminary experiments with strongly nucleophilic reagents also suggest simultaneous action of mechanisms S_N1 and S_N2.

The results do not comply with Böhme's finding that the hydrolysis was autocatalyzed by the hydrogen ions generated, because throughout the reaction the same values were obtained for the rate constant. According to Böhme's mechanism, the rate should be proportional to the concentration of oxonium ions, which in turn depends on the concentration of hydrogen ions:



$$[R\overset{\overset{\textstyle H}{|}}{O}CH_2Cl]^+ = K_{eq.}\ [ROCH_2Cl]\,[H^+]$$

Since the concentration of hydrogen ions increases during the reaction, the rate should not fit the equation for a first-order reaction. Furthermore, the addition of hydrochloric acid does not step up the reaction any more than the other salts.

Böhme's results may be explained perhaps in terms of a primary salt effect, because starting from a fairly high initial concentration of reactant, the ionic strength of the solution increases more and more during reaction, resulting in higher rates of reaction. In dilute solution this effect lies within the limits of experimental error.

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HYDRATION OF BIIONIC (Ca, K)-MONTMORILLONITES. I.

DIFFERENTIAL HEATS AND ENTROPY CHANGES OF WATER ADSORPTION ON (Ca, K)-MONTMORILLONITE*

by

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In a study of the montmorillonite-water system, adsorption isotherms for (Ca, K)-montmorillonite were determined by the isopiezometric method at temperatures of 5 and 18° C. The experimentally obtained isotherms were analyzed thermodynamically to determine the differential heats and entropy changes of water adsorption on (Ca, K)-montmorillonite. Isoelectronic calcium and potassium ions were chosen as the complementary cations because of the theoretical and practical significance of knowledge of the behavior of (Ca, K)-montmorillonite in studies of the genesis and diagenesis of clay minerals, in the technology of clays and in soil science. Earlier works on the hydration of montmorillonite have dealt mainly with the hydration of homoionic forms. No systematic study of precisely defined biionic forms has yet been undertaken. In addition, investigations of the properties and hydration of biionic forms of montmorillonite open up another approach to the understanding of the mechanism of montmorillonite hydration.

For the boundary surface of a phase which is developed to A one can write$^{(1)}$.

$$dE_s = TdS_s - pdV_s - \gamma\, dA + \mu_s dn_s \qquad (1)$$

where

$$\gamma = -\left(\frac{\partial E_s}{\partial A}\right)_{S_s,\ V_s,\ n_s}; \qquad \mu_s = \left(\frac{\partial E_s}{\partial n_s}\right)_{S_s,\ V_s,\ A}$$

E = internal energy of the phase in the boundary surface
γ = surface tension
A = fraction of boundary surface free for adsorption
μ = chemical potential

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* Reported at the 11th Conference of Chemists, SR of Serbia January, 1965.

The Gibbs free energy for the boundary surface, G_s, is defined as

$$G_s = E_s + pV_s - TS_s$$

or

$$dG_s = dE_s + d(pV_s) + d(TS_s)$$

By substituting for dE_3 from Eq. (1), differentiating and simplifying, we obtain

$$dG_s = -S_s dT + V_s dp - \gamma dA + \mu_s dn_s$$

Taking the area of the surface as a constant, the expression for the change of chemical potential becomes

$$d\mu_s = -S_s dT + \bar{V}_s dp + \left(\frac{\partial \mu_s}{\partial n_s}\right)_{T,p} dn_s \tag{2}$$

$\bar{S}_s$ and $\bar{V}_s$ = partial molar entropy and volume of the phase in the boundary surface.

It will be noted that

$$\mu_s = \frac{dG_s}{dn_s} \quad \text{and} \quad \bar{S}_s = \frac{dS_s}{dn_s}$$

The change in chemical potential for a gaseous phase is

$$d\mu_g = -\bar{S}_g dT + \bar{V}_g dp \tag{3}$$

In equilibrium $d\mu_g = d\mu_s$. Taking the gas as ideal and $V_g \gg V_s$, equating (2) and (3) gives

$$\frac{d\ln p}{dT} = \frac{\bar{H}_g - \bar{H}_s}{RT^2} + \frac{1}{RT}\left(\frac{\partial \mu_s}{\partial n_s}\right)_{T,p} \cdot \frac{dn_s}{dT} \tag{4}$$

A single-component, biphasic system is monovariant, but for isothermal, conditions it becomes invariant. Hence, for isothermal conditions the second term on the right of Eq. (4) disappears, because $d\mu_s = 0$. For isothermal, conditions Eq. is normally written

$$\frac{d\ln p}{dT} = \frac{\Delta H_{st}}{RT^2} \tag{5}$$

Equation (5) is analogous to the Clausius-Clapeyron equation. The value ΔH_{st} represents the isosteric heat of desorption. The isosteric heat of adsorption is equivalent to the differential heat of adsorption at constant pressure. The final values of the isosteric heats of adsorption can be computed if the partial pressures of the adsorbed phase for two different temperatures are known, from the equation

$$\Delta H_{st} = \frac{RT_1T_2}{T_1 - T_2} \ln \frac{p_1}{p_2} \tag{6}$$

Eq. (6) may be used to analyze adsorption isotherms at two temperatures, provided they are roughly parallel. This was done in our experiments.

From the adsorption isotherms it is further possible to calculate the changes in free energy, enthalpy and entropy involved in the process. The change in free energy is given by

$$\Delta \overline{G} = \Delta \overline{H} - T \Delta \overline{S} \tag{7}$$

The change in partial entropy for the same process may be obtained by application of the thermodynamic relation which follows from Eq. (7):

$$\Delta S = \frac{\Delta H - \Delta G}{T}$$

When the process takes place in equilibrium ($\Delta G = 0$, i.e. adsorption proceeds under conditions differing infinitesimally from equilibrium conditions), the change in entropy may be computed from the equation

$$\Delta S = \frac{\Delta H}{T} \tag{8}$$

We also used Eq. (8) for the thermodynamical analysis of the data obtained in experiments.

According to Kitchener(2) the differential free energy, entropy and enthalpy yield more direct information than the corresponding integral quantities of adsorption processes. The differential thermodynamic quantities show the dependence of the thermodynamic state of the adsorped phase on the saturation of the adsorbent.

EXPERIMENTAL

Material. — The initial material was a fraction of the standard mineral, Wyoming bentonite, with grain size below 2 microns. It was separated by multistage sedimentation.

The cation exchange capacity, CEC, of the fraction was determined by the standard method using ammonium acetate. It was found to be 86 *mg*/100 *g* montmorillonite.

A 2% suspension of montmorillonite was converted into the hydrogenous form on an exchanger column(3) of Dowex-50 in H form.

Homoionic K-form, Ca-form and biionic (Ca, K)-forms of montmorillonite were produced by direct neutralization of H-montmorillonite suspension with KOH and $Ca(OH)_2$, or mixtures of them. To produce biionic forms, the potassium-calcium hydroxide ratio was changed as necessary for the desired form.

The results of analytical determination of exchangeable cations of the montmorillonites are shown in Table 1. The symbols in column 3 of Table 1 are used hereafter to denote the samples and present results.

TABLE 1

Exchangeable Ca^{++} and K^{+} of the Homoionic and Biionic (Ca,K)-Montmorillonites

Ca fraction % of capacity	K fraction % of capacity	Symbol
100	—	Ca-montmorillonite
28.2	71.8	Ca-2-K-8
46.2	53.8	Ca-4-K-6
70.3	29.7	Ca-6-K-4
86.4	13.6	Ca-8-K-2
—	100	K-montmorillonite

Method. — Montmorillonite samples were hydrated by the isopiezometric method, with exciccators containing a definite concentration of sulfuric acid. The samples were equilibrated with H_2O at different constant pressures and at temperatures of 5 to 18°C. The difference between 5 and 18° is small enough to permit the thermodynamic analysis of the results.

Later, from a perusal of the literature it was noted that the method had already been used and experimentally verified[4, 5]. It was shown that the results obtained by the standard determination of hydration on a McBain-Baker balance agree very well with those obtained by the isopiezometric method, which is much simpler.

According to Eirich[6], the isopiezometric methods enables the adsorption of water vapor at any relative pressure; the time required to establish equilibrium is around a week. Dickel *et al.*[4] assert that 6—8 weeks is necessary to reach equilibrium. In our experiments we took the hydration time as 5 weeks. The results for adsorption after two months fully agreed with those after 5 weeks.

To determine any adsorption of water vapor by the measuring cylinders, these were weighed after drying at a temperature of 110°C and after storage in exciccators of certain humidity for a week. Weighing showed that the amount of water adsorbed was negligible.

The weight of samples was in all cases between 2 and 3 *g* dry montmorillonite. The amount of water adsorbed was computed in milligrams per gram of dry sample.

RESULTS AND DISCUSSION

Adsorption Isotherms. — The measurements of hydration at 5 and 18° and the corresponding adsorption isotherms are shown graphically in Figs. 1 and 2. The adsorbed H_2O expressed as *mg* H_2O per *g* montmorillonite is plotted against the relative pressure of H_2O at which adsorption took place.

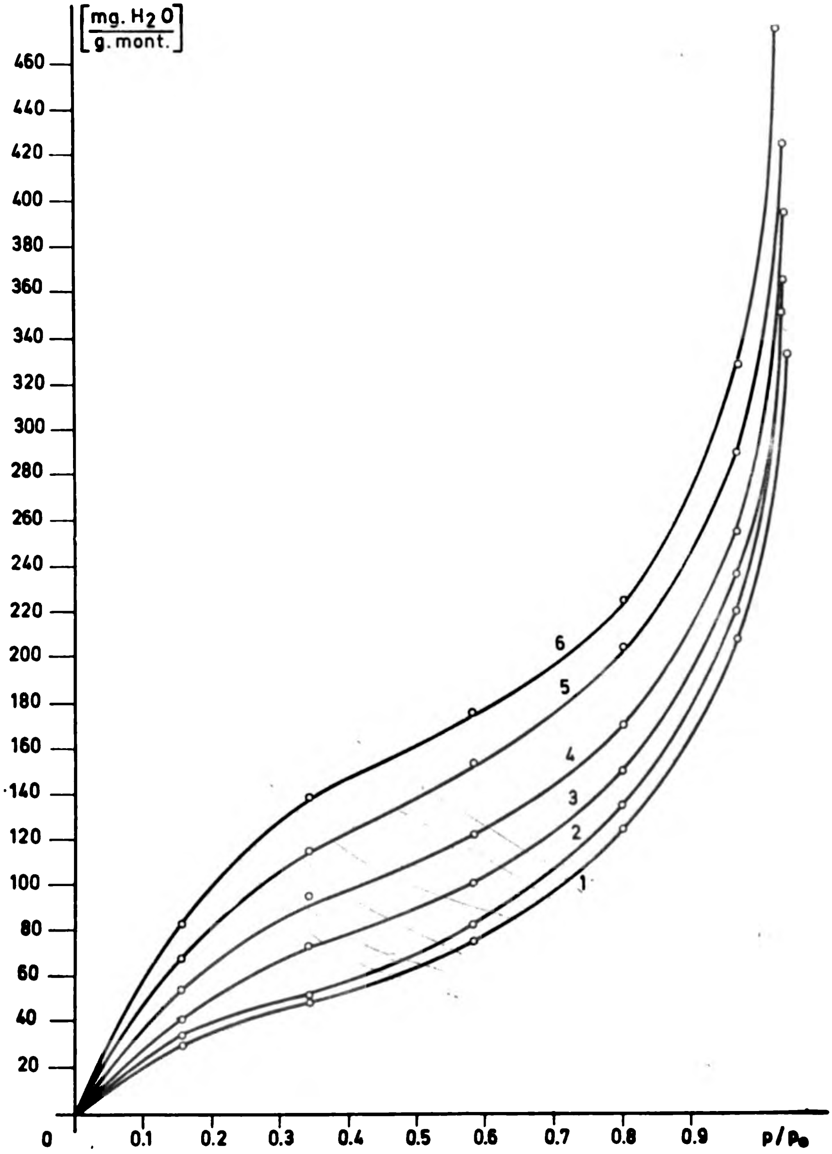

Figure 1

Water vapor adsorption isotherms at 18°C for (*Ca, K*)-montmorillonite

isotherm 1 — K-montmorilonite	isotherm 4 — (Ca-6-K-4)
isotherm 2 — (Ca-2-K-8)	isotherm 5 — (Ca-8-K-2)
isotherm 3 —(Ca-4-K-6)	isotherm 6 — Ca-montmorillonite

From Figs. 1 and 2 it appears that the isotherms do not conform in shape to any standard isotherm. For nearly all montmorillonite forms tested they are S-shaped. At low relative pressure of H_2O they are convex relative to the relative pressure axis, and after a saddle point they become concave. Presumably, this tendency of the isotherms to straighten out is due to the formation of a monomolecular H_2O layer in the inter-layer region of the montmorillonite.

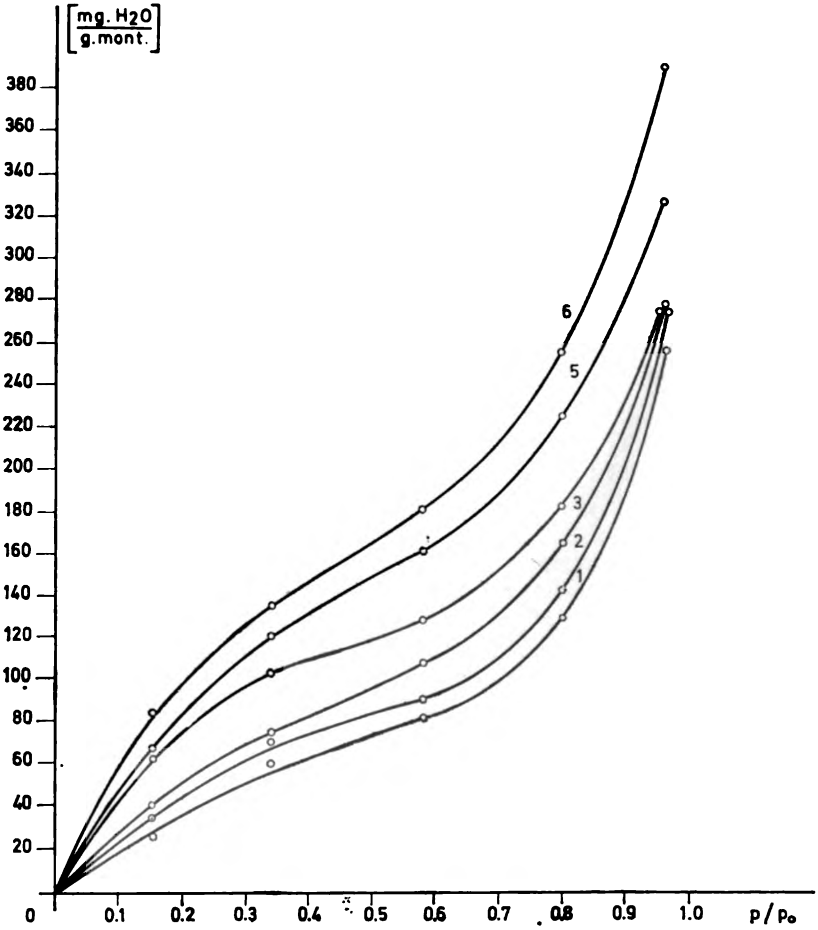

Figure 2

Water vapor adsorption isotherms at 5°C for (Ca, K)-montmorillonite

isotherm 1 — K-montmorillonite
isotherm 2 — (Ca-2-K-8)
isotherm 3 — (Ca-4-K-6)

isotherm 4 — (Ca-6-K-4)
isotherm 5 — (Ca-8-K-2)
isotherm 6 — Ca-montmorillonite

The results show that the hydration of biionic (Ca, K) forms of montmorillonite is a function of the proportion of calcium and potassium as exchangeable cations. The hydration capacity rises with the proportion of calcium, but analysis of the experimental results shows that the dependence is not linear. This is discussed in our paper "Hydration of Biionic (Ca, K)-Montmorillonites. III. Specific Effect of Potassium as Exchangeable Ion"(6).

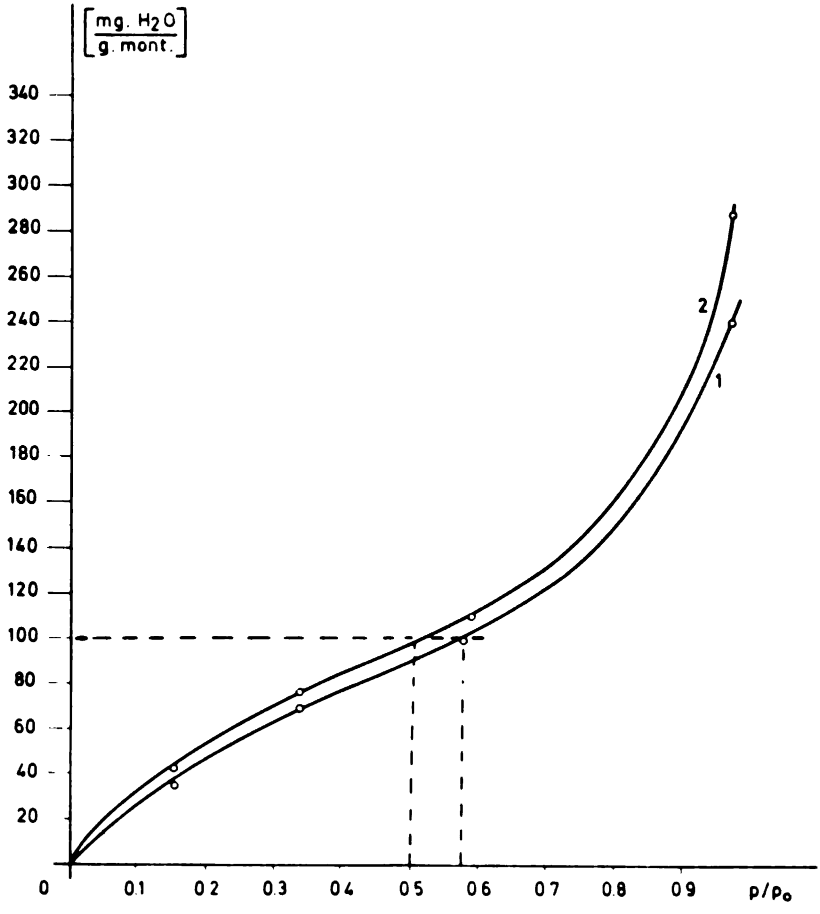

Figure 3

Water vapor adsorption isotherms for (Ca-4-K-6)-montmorillonite at different temperatures

Isotherm 1 — at $t_1 = 18^\circ C$ Isotherm 2 — at $t_2 = 5^\circ C$

Dashed line shows how to read off partial pressure for a given saturation in order to calculate differential heat of adsorption

Thermodynamic Analysis of Results. — From the adsorption isotherms at two different temperatures, it is possible to compute the quantitative changes in enthalpy and entropy (accompanying the process) by using Eqs. (6) and (8). To illustrate, Fig. 3 shows a pair of isotherms for the (Ca-4-K-6)-form at two different temperatures. The pressures P_1 and P_2 needed to calculate the differential heat from Eq. (6) are determined graphically from isotherms for the chosen saturation of the montmorillonite, as shown by the dashed line in Fig. 3. The differential heat and differential entropy changes accompanying the process are presented in Tables 2 and 3 respectively.

The differential heat of adsorption varies within the interval of 8—10 *kcal/mol*, which suggests physical adsorption and a mechanism of hydrogen bond formation. With increasing available surface area the heat of adsorption falls towards about 8.05 *kcal/mol* in all cases. The heat of condensation of water at 18°C is 8.7 *kcal/mol*, and the heat of sublimation of ice 12.2 *kcal/mol*. The adsorption heats of 8—10 *kcal/mol* indicate that the thermodynamic state of the adsorbed water is comparable with the liquid state.

TABLE 2

Differential Heat, ΔH kcal/mol, of Water Adsorption on (Ca, K)-Montmorillonite as a Function of Exchangeable Ca and K Fractions ($T_1 = 291°K$, $T_2 = 278°K$)

mg H_2O per *g.* mont.	(Ca, K) — forms of montmorillonite					
	(K)	(Ca-2-K-8)	(Ca-4-K-6)	(Ca-4-K-4)	(Ca-8-K-2)	(Ca)
	Δ H *kcal/mol*					
40	—	9.3	—	—	—	—
60	8.78	8.55	8.60	—	—	—
80	8.40	8.51	8.55	9.49	—	—
100	8.15	8.20	8.45	9.37	9.53	9.71
120	8.09	—	8.20	8.65	8.90	9.27
140	—	8.05	8.11	8.30	8.62	—
160	8.09	—	8.00	8.11	8.30	—
180	—	7.96	—	8.09	—	—
200	7.96	—	8.00	—	8.20	8.3
220	—	7.94	—	8.09	—	8.12
240	7.90	—	7.94	—	8.09	8.11
260	—	—	—	7.96	—	8.12
280	—	—	—	—	8.05	—
300	—	—	—	—	—	8.05

The values obtained for the entropy change bear out the hypothesis on the basis of the adsorption heat. The entropy change for the evaporation of liquid water at 18°C is 30 *cal/mol*°K, and at 0°C it is 42.8 *cal/mol*°K. The entropy change at adsorption are again comparable to the entropy of condensation of liquid water at 18°C; it ranges 27—34 *cal/mol*°K (Table 3).

TABLE 3

Differential Enthropy Change, ΔS_1 cal/mol °K, of Water Adsorption on (Ca, K)-Montmorillonite as a Function of Exchangeable Ca and K Fractions ($T = 291'°K$)

mg H_2O per *g* mont.	(Ca, K)- forms of montmorillonite					
	(K)	(Ca-2-K-8	(Ca-4-K-6)	(Ca-6-K-4)	(Ca-8-K-2)	(Ca)
	ΔS_1 *kcal/mol* °K					
40	—	31.9	—	—	—	—
60	30.2	29.4	29.5	—	—	—
80	28.8	29.2	29.3	31.7	—	—
100	28.0	28.2	29.0	32.2	32.7	33.4
120	27.8	—	28.2	29.7	30.5	31.8
140	—	27.7	27.9	28.5	29.6	—
160	27.7	—	27.5	27.9	28.5	—
180	—	27.4	—	27.8	—	—
200	27.4	—	27.5	—	28.2	28.5
220	—	27.3	—	27.8	—	27.9
240	27.0	—	27.3	—	27.8	27.9
260	—	—	—	27.4	—	27.9
280	—	—	—	—	27.5	—
300	—	—	—	—	—	27.7

It may be seen that the entropy change of adsorption increases with decreasing available surface area. It can be inferred that reducing the available surface increases the ordering of the adsorbed water. The entropy change is between 27 and 34 *cal/mol°K*, which, compared with the entropy change of evaporation of water (30 *cal/mol°K* at 18 C), suggests that the adsorbed water is close to the state of liquid water in structure, and as the available surface area decreases, the structure becomes more ordered.

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Original Scientific Paper

DILATOMETRIC INVESTIGATION OF THE INFLUENCE OF CARBON CONTENT ON TEMPERING STAGE TEMPERATURES IN CARBON STEELS

by

NADA P. VIDOJEVIĆ and NADA M. NOVOVIĆ-SIMOVIĆ

Steel quenched from the homogeneous γ-region at room temperature has a martensite structure with a certain amount of residual austenite. As a result of nondiffusive transformation, the martensite represents a super saturated solid solution of carbon in α-iron with ordering of the carbon atoms which results in tetragonal lattice symmetry. In the range of temperatures at which carbon atoms are sufficiently mobile, diffusion begins to separate carbon out of the supersaturated solution in the form of ε-carbide (the first tempering stage). At higher tempering temperatures the residual austenite decomposes into a mixture of supersaturated ferrite and carbide (the second tempering stage), and carbon continues to separate out of the solid solution, accompained by changes in the carbide phase (the third tempering stage).

Different opinions are found in the literature concerning the effect of steel composition on the position of temperature intervals of tempering stages in carbon steels. Kurdiumov(7) considers that carbon content affects the temperature of initiation of the first stage, i.e. the greater the carbon content the earlier the beginning of martensite breakdown. On the other hand, carbon concentration does not affect the temperature of the end of the first tempering stage, because at temperatures above ~150°C the solid solution contains a constant quantity of carbon, irrespective of the carbon content of the steel. In other words, the amount of carbon in the solid solution then depends on nothing else but the tempering temperature.

Kenneford(2) used the dilatometric method to study the tempering of the carbon steels containing different amounts of carbon. He found out that the temperature at which martensite breakdown begins was lower the higher the carbon content, up to 0.18%, while a further increase made it rise again. The temperature of termination of the first tempering stage increases with increasing in carbon content, but with steels containing 0.49—0.70% C it levels out at 177—178°C. The temperature of initiation of the third stage rises with carbon content up to 0.70%, and then drops, levelling out at approximately 250°C. The temperature of the end of the third stage increases with increasing C up to 0.81% C; with further increase it remains approximately the same.

The temperature interval of the tempering stages at constant carbon content also depend on the nature and quantity of the alloying elements. Kenneford(2) established that the presence of silicon and manganese in a steel containing 0.32% C caused some shifting of the temperature intervals of the first and second stages (decomposition of the residual austenite was prevented by secondary cooling of the steel after quenching down to below 0°C). His experimental results show that an increase in silicon from 0.26% to 0.48% does not affect the temperature of the beginning of martensite breakdown, while the temperature of termination of the first stage rises from 132 to 163°C. Temperatures of the initiation and termination of the third stage are increased by 40 and 30°C, respectively. Manganese has a somewhat different effect from silicon. Increasing Mn from 0.48 to 9.95% moves the beginning of martensite decomposition down in temperature, but raises the termination temperature from 132 to 165°C. Manganese does not affect the beginning of the third tempering stage, but it moves the end of it to a high temperature.

From these studies it may be inferred that silicon and manganese in the steel in quantities which make them alloying elements cannot be disregarded because they influence the temperature intervals of the stages of tempering.

According to Guliaev(1), the carbon content of the steel and the amount of residual austenite do not affect the temperature range of the second stage. Nazarenko(3), however, established that the amount of residual austenite in steel with 1.2% C influenced the temperature dependence of magnetic saturation; in the presence of 10% residual austenite (steel with 1.2% C cooled to —196°C after quenching in oil) the magnetic saturation of the tempered steel began to this at 125°C; in the presence of 30% austenite (steel with 1.2%C quenched in oil) the increase began at 100°C. In both cases, however, the saturation reach its maximum at 275°C. Krishtal(4) attributes the maximum of inner friction during the tempering of carbon steels in the temperature interval 200—260°C to the diffusion of carbon in austenite, i.e. to the decomposition of residual austenite. From his experimental results Krishtal(4) concludes that the magnitude of the inner friction maximum and the temperature at which it occurs increase linearly with increasing carbon content of the steel, and with increasing residual austenite in the quenched steel.

The reviewed literature data is not consistent on how the temperature intervals of the various tempering stages depend on carbon content and the amount of residual austenite. One reason for this is certainly the different methods used in the investigations. Methods of different sensitivity register different initiations of the processes which characterize a given tempering stage. However, the various methods although often giving different data, certainly help fill in the overall picture of the process of tempering.

It is from this aspect that we undertook a study of the effect of carbon content on the temperature intervals on the 1st, 2nd and 3rd tempering stages and of the volume changes during tempering by dilatometry.

MATERIAL

Tests were conducted on carbon building steels (for reinforsement) Č. 1330, Č. 1430, Č. 1530, St. 7011, and Č. 1730, and carbon tool steels Č. 1840, Č. 1940, and Č. 1943, in the form of dilatometry specimens Ø 3.3 *mm* and 50 *mm* long. For examine tempered hardness specimens of Ø 5 *mm* and 4 *mm* long were used, and to measure hardness after tempering, samples of Ø 3.3 *mm* 4 *mm* long, cut out of the dilatometry specimens. The chemical composition of the steels tested is shown in Table 1.

TABLE 1

Chemical Composition of the Steels (%)

Quality, JUS*	C	Si	Mn	P	S
Č. 1330	0.21	0.31	0.52	0.007	0.035
Č. 1430	0.36	0.33	0.78	0.025	0.047
Č. 1530	0.45	0.33	0.61	0.036	0.017
St. 7011 (DIN)	0.52	0.31	0.72	0.017	0.040
Č. 1730	0.63	0.26	0.68	0.013	0.042
Č. 1840	0.80	0.31	0.28	0.006	0.020
Č. 1940	1.03	0.24	0.17	—	0.019
Č. 1943	1.23	0.32	0.34	0.006	0.020

* Yugoslav standards

THERMAL TREATMENT

Dilatometry specimens and samples were quenched in water after austenitization by heating in a melt of salt SŽ 700. The time of heating at the austenitization temperature was 5 *min*. Quenching temperatures were chosen according to catalog data, except for steel Č. 1943 for which two different temperatures were used to investigate the effect of the residual austenite on tempering.

Steel was tempered in a dilatometer furnace in an air atmosphere. Since 2—3 dilatometry specimens of each steel were treated under the same conditions, one specimen was tempered at once, while the others were left in a refrigerator to prevent tempering at room temperature.

In the dilatometer, the specimens were tempered during heating up to 620°C at a rate of ~5°/*min* (5—5.9). The heating rate was regulated by a transformer. Cooling after tempering was in the furnace, at an average rate of 4°/*min*.

TESTING METHODS

To study the tempering process the absolute dilatometric method (Leitz dilatometer) was used. The dilatometric curves reveal volume changes caused by transformations at different stages of tempering. It is well known that martensite, because of its stressed lattice, has a larger specific volume than the finely dispersed mixture of ferrite and cementite. Therefore martensite decomposition is followed by a decrease in volume, i.e. contraction of the dilatometric specimen, in the lst and 3rd tempering stages. During the 2nd stage the volume increases, i.e. the specimen elongates, because of the transformation of austenite with the least specific volume. The 4th tempering stage is not registered on the dilatometric curve, because it does not produce transformations accompanied by volume changes.

The volume changes registered on the dilatometric curves and the temperature intervals of the tempering stages were determined. The manner of determination was standardized as much as possible to avoid errors. Temperatures of the beginning and end of the 1st, 2nd and 3rd tempering stages were determined as the projection on the abscissa of the first common point of the curved segment corresponding to transformation and the extended straight line segment before the beginning or end the completion of transformation.

A hardness check was made by measuring after quenching, and also after tempering up to 620°C. The methods of Rockwell (C) or Vickers with a loading of 30 kp were used, three impressions on each sample. The mean of six impressions was taken as the final result, because pains of samples were treated under equal conditions.

RESULTS AND DISCUSSION

The results of hardness checks are shown in Table 2 and 3. Table 2 shows the hardness after quenching, and Table 3 after continuous tempering to 620°C. As was expected, the hardness after quenching increases with increasing carbon content. The difference between the steels Č. 1330 to Č. 1530 is particularly marked after which it is less. With steel Č. 1943 it was observed that the hardness decreased with the increasing quenching temperature because of a rather large amount of residual austenite after quenching.

TABLE 2

Hardness after quenching

Quality	Temperature quenching °C	Hardness (HRC)
Č.1330	880	48
Č.1430	860	52
Č.1530	840	63
St.7011	830	63
Č.1730	830	63
Č.1840	795	65
Č.1940	770	67
Č.1943	780	66
	960	64

The hardness after tempering to 620°C shows 50—60% lower values for all steels than after quenching, but it is higher the higher the carbon content. This is related to the nature of the resulting structure, a ferrite-cementite mixture in which the proportion of cementite is the greater the higher the carbon content of the steel.

TABLE 3

Hardness after Tempering by Continuous Heating to 620°

Quality	Hardness (HV 30)
Č.1330	232
Č.1430	260
Č.1530	275
St.7011	288
Č.1730	297
Č.1840	313
Č.1940	348
Č.1943 quenched from: 780°	350
960°	347

Dilatometric curves of tempering are shown in Figs. 1, 2, 3, 4, 5, 6, 7, 8, and 9, the temperature intervals of tempering stages and changes in length of the specimens given in Tables 4 and 5 respectively.

Figure 1 shows the dilatometric curve of tempering Č. 1330. At first the specimen elongates at an even rate, as shown by the straight line segment of the curve. With rising temperature the slope decreases, because the decomposition of martensite begins (1st tempering stage). The relatively high temperature at the beginning of martensite decomposition in this case can be related to the high M_s point of the steel (partial tempering can take place

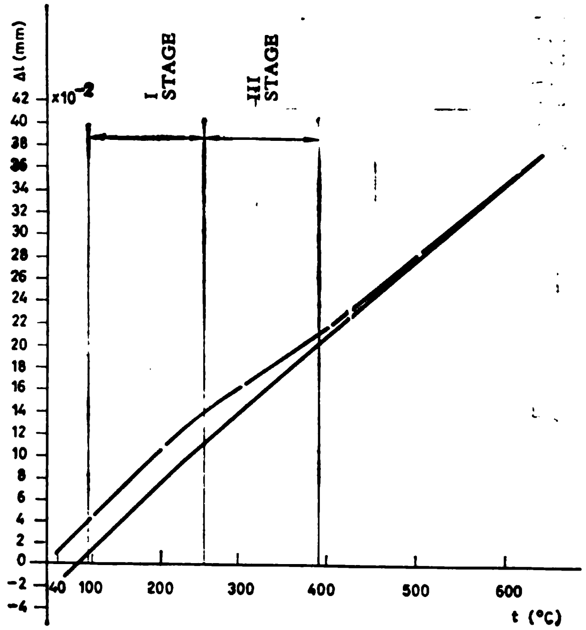


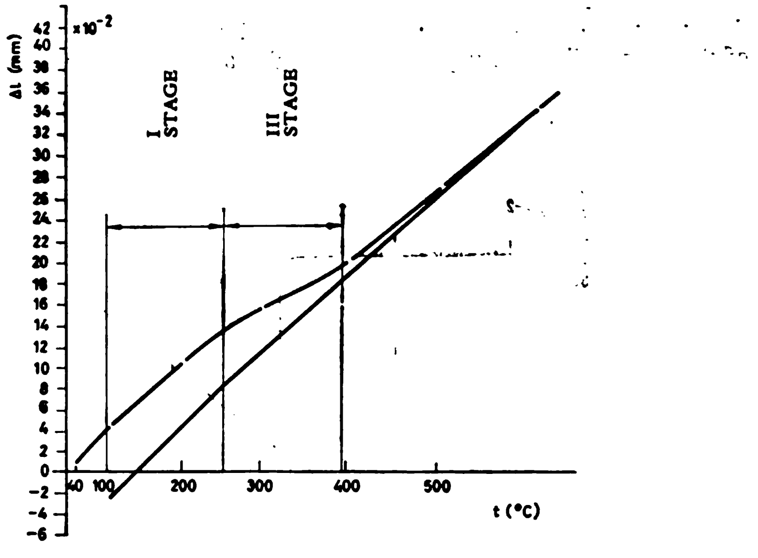
Figure 1

Dilatometric curve of tempering of steel Č. 1330 during quenching) and to the small amount of carbon in the solid solution being absorbed by the martensite lattice defects and only at higher temperatures precipitating as submicroscopic carbide particles.

The process of tempering intensifies with temperature, and at 250°C cementite precipitates, manifested on the dilatometric curve as another change in slope. This temperature is therefore taken as the beginning of the 3rd tempering stage.

Since steels with less than 0.4% C cannot have a measurable quantity of residual austenite after quenching, the 2nd tempering stage cannot be registered by dilatometry.

Figure 2 shows the dilatometric curve for Č. 1430. It can be seen that this and the preceding curves are very much alike. With this steel however, the slowing down of elongation at the 1st and 3rd tempering stages is more marked due to the somewhat greater amount of carbon which precipitates from the supersaturated solid solution.



Слика 2. Figure

Dilatometric curve of tempering of steel Č.1430

Figure 3 shows the dilatometric curve of Č. 1530. The slope changes at only 85°C, initiating the 1st tempering stage. The somewhat lower temperature of the beginning of the 1st stage and slower elongation of the specimen than with the previous steels is attributed to the higher carbon content, or to the specific mechanism of martensite breakdown in this case. It is known(5, 6, 7) that in the 1st tempering stage, steels having over 0.4% C exhibit biphasic decomposition of α'-martensite into a less supersaturated solid solution, α''-martensite, and ε-carbide. α''-martensite contains ~0.25% C and has a tetragonal lattice with a smaller ratio of lattice parameters c/a

than α′-martensite. ε-carbide precipitates at the subgrain boundaries of α′-martensite forming a ~200 Å thick network around the subgrains. Its amount is the greater the more carbon there is in the steel. The specific mechanism of martensite breakdown in steels containing more than 0.4% C influences the volume change during tempering, the more so the greater the carbon content of the steel.

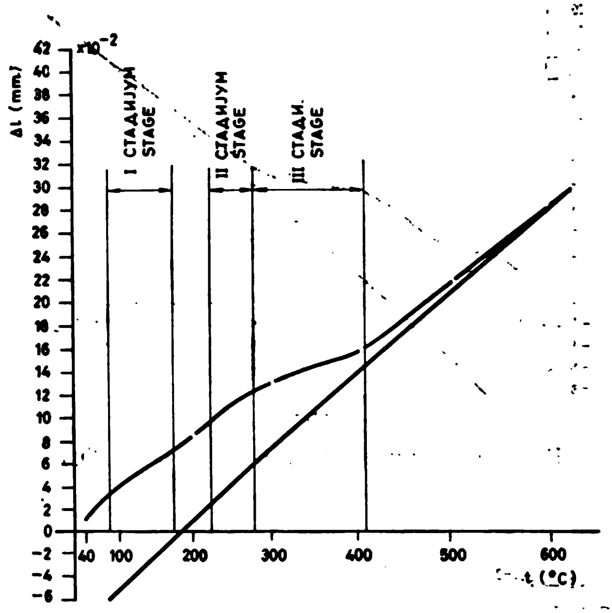


Figure 3

Dilatometric curve of tempering of steel Č.1530

The curve further reveals that after the end of the 1st stage the specimen elongates uniformly up to a temperature of ~225°C, when the slope changes again. This temperature marks the beginning of the 2nd stage, during which the specimen elongates somewhat faster.

In the 3rd stage the elongation of the specimen is less rapid, since there is contraction due to the further precipitation of carbon from martensite recovery of the ferrite matrix, and occurrence of cementite.

Figure 4 shows the dilatometric curve of St. 7011. Unlike the previous curve, this one shows a nearly horizontal segment for the 1st tempering stage, which means that contraction due to transformation is so great that it offsets the elongation of the specimen over a certain temperature interval. This is also noticed at the 3rd stage.

Figure 5 shows the dilatometric curve for tempering of Č. 1730. It reveals well-defined volume changes at different stages of tempering. The beginning of the 1st stage is moved to 80°C, because of the heavily supersaturated solid solution, which proves to be unstable.

Figure 6 shows the dilatometric curve for Č. 1840. The three tempering stages are evident. Contraction due to martensite breakdown in the

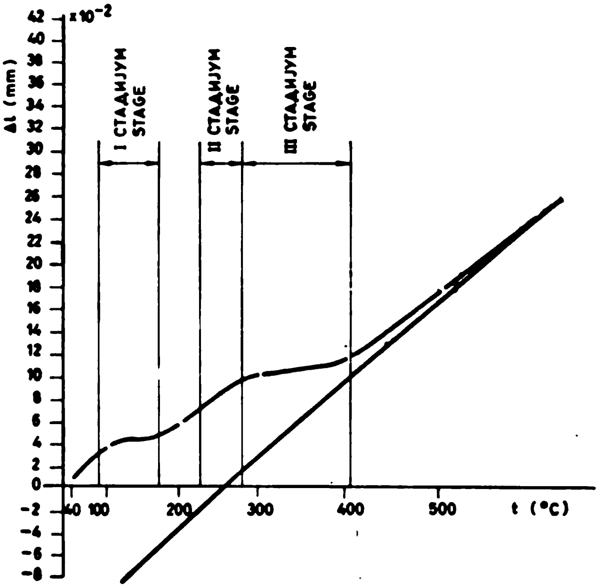


Figure 4

Dilatometric curve of tempering of steel St.7011

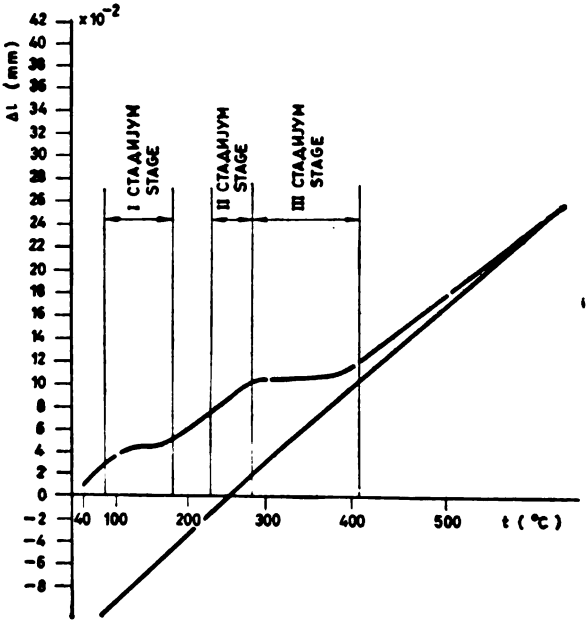


Figure 5

Dilatometric curve of tempering of steel Č.1730

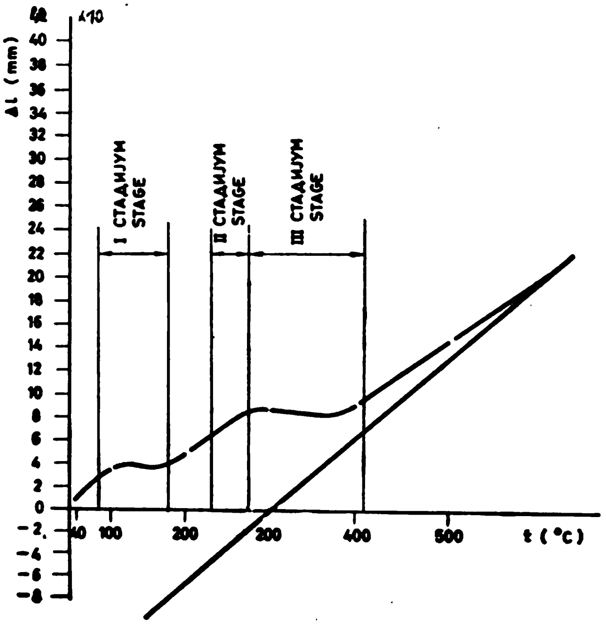


Figure 6

Dilatometric curve of tempering of steel Č.1840

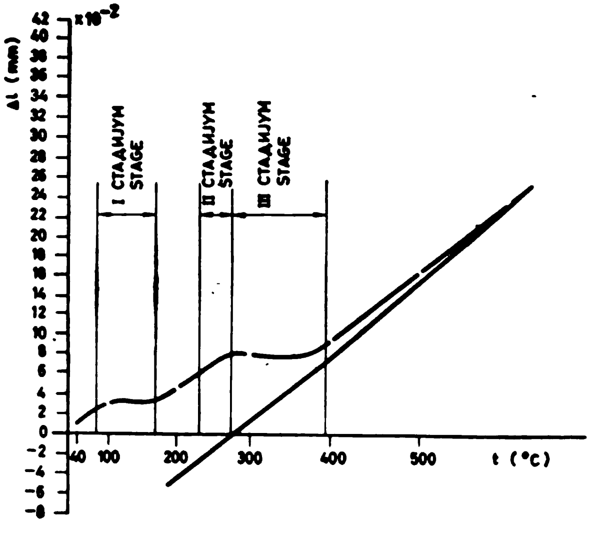


Figure 7

Dilatometric curve of tempering of steeel Č.1940

1st stage and the further precipitation of carbon from martensite, the transformation of carbide and complete stress removal in the 3rd stage, almost entirely compensate the thermal expansion of the specimen, as manifested in the two horizontal segments of the curve.

Figure 7 shows the dilatometric curve for Č. 1940. The three tempering stages are distinctly visible.

Figure 8 shows the dilatometric tempering curve of Č. 1943. Here the 1st tempering stage begins at a temperature of only ~74°C. With this steel too, the 1st and 2nd stage transformations are accompanied by considerable contraction because of the relatively great amount of carbon retained in solid solution. As with the other steels, the transformation of residual austenite at the 2nd stage is accompanied by an increase in specific volume.

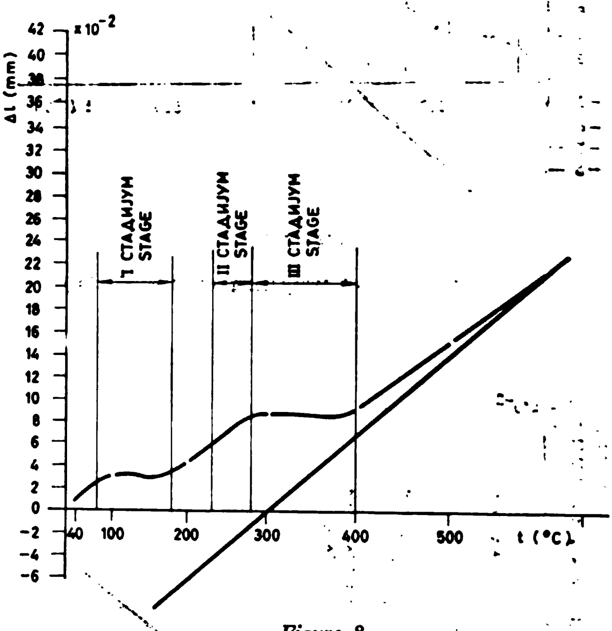


Figure 8

Dilatometric curve of tempering of steel Č 1943.

Figure 9 shows the dilatometric tempering curve of Č. 1943, previously quenched at 960°C. Its shape indicates that raising the temperature of quenching emphasizes the tempering stages. The start of martensite breakdown is here down to ~67°C, attributable to the larger amount of carbon dissolved in martensite than in the same steel quenched from 780°C (Fig. 8). For the same reason, contraction at the 1st and 3rd stages is somewhat more pronounced. It can also be seen from the curve that the temperature interval of the 2nd stage is ~24°C wider than for the same steel quenched from the optimum temperature. Here the temperature at which residual austenite begins to decompose is 223°C instead of 232.3°C, while the temperature at the end of its decomposition is up to 293.5°C, from 278.6°C. Elongation in the 2nd stage is very marked, ~8 × 10^{-2} *mm*.

To verify how the quenching of Č. 1943 from the homogeneous γ-region affects the temperature interval of the 2nd tempering stage, the investigations were extended to cover another above-eutectoid steel. The steel Č. 1940 was quenched from 920°C, i.e. within the homogeneous γ-region, to try and augment the amount of residual austenite relative to the same steel quenched from the optimum temperature (Fig. 7), along with raising the content of carbon in the austenite. Comparing the results reveals that the temperature interval of the 2nd stage of steel Č. 1940 quenched from 920°C is expanded by 13°C, to 220—278°C. (With the steel quenched from the optimum temperature, the range of residual austenite decomposition is 231—274°C.) Elongation was also greater — 6.5 × 10^{-2} *mm* as against 2.3 × 10^{-2} *mm*.

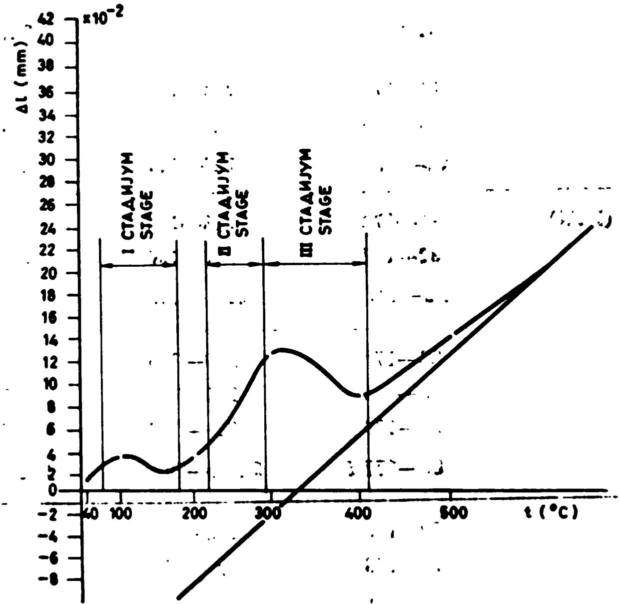


Figure 9

Dilatometric curve of tempering of steel Č. 1943, quenched from 960°

Tables 4 and 5 present numerical data for temperature intervals of individual tempering stages and changes in the elongation of specimens during tempering for different carbon contents.

CONCLUSION

From the results obtained, the following conclusions are drawn:

Increasing the carbon content of steel lowers the beginning of the 1st tempering stage. Here all the dilatometric curves of a given steel agree

TABLE 4

The Effect of Carbon Content on the Temperatures of the Tempering Stages

Quality (JUS)	Temperature range °C		
	1st stage	2nd stage	3rd stage
Č.1330	95		257—393
	94		258—396
	94.5		**257.5—394.5**
Č.1430	92		248—394
	91		252—392
	91		253—392
	91.3		**251—392.6**
Č.1530	85—173	224—270	270—409
	84—173	228—272	272—409
	84.5—173	**226—271**	**271—409**
St.7011 (DIN)	81—172	228—280	280—406
	82—172	231—280	280—407
	81.5—172	**229,5—280**	**280—406.5**
Č.1730	80—178	229—283	283—406
	80—176	231—282	282—407
	80—179	229—283	283—407
	80—177.6	**229.6—282.6**	**282.6—406.6**
Č.1840	78—178	230—276	276—409
	77—178	227—277	277—406
	77.5—178	**228.5—276.5**	**276.5—407.5**
Č.1940	77—181	231—274	274—393
Č.1943 (780°)	74—181	233—279	279—400
	72—181	234—281	281—400
	75—181	230—276	276—397
	73.6—181	**232.3—278.6**	**278.6—399**
Č.1943 (960°)	64—171	221—293	293—411
	69—183	225—294	294—411.2
	66.5—182	**223—293.5**	**293.5—411**

TABLE 5

The Effect of Carbon Content on the Length Changes of Dilatometric Specimens at Tempering Stages

Quality (JUS)	Elongation, $10^2 \cdot \Delta$ l, *mm*		
	1st stage	2nd stage	3rd stage
Č.1330	9.8		7.4
	10.0		7.3
	9.90		**7.35**
Č.1430	9.2		5.9
	9.3		5.9
	9.2		5.9
	9.23		**5.90**
Č.1530	4.0	3.0	3.8
	3.9	2.7	4.0
	3.95	**2.85**	**3.90**
St.7011 (DIN)	1.8	2.8	2.3
	1.8	2.4	2.3
	1.80	**2.60**	**2.30**
Č.1730	2.3	2.8	2.0
	2.1	2.7	2.0
	2.0	2.8	2,3
	2.13	**2.76**	**2.10**
Č.1840	1.4	2.4	0.8
	1.7	2.5	1.0
	1.55	**2.45**	**0.90**
Č.1940	0.8	2.3	0.8
Č.1943 (780°)	0.8	2.7	0.5
	0.8	2.8	0.3
	1.2	2.5	0.5
	0.93	**2.66**	**0.43**
Č.1943 (960°)	0	7.8	—3.0
	0.3	8.0	—3.2
	0	8.0	—3.5
	0.10	**7.93**	**—3.23**

very well. Minor changes in carbon content do not affect the position of the beginning of the 1st stage to any important degree, as confirmed by the small temperature differences (1–6°C) between low- and high-carbon steels. The maximum difference in temperature of initiation of the 1st stage is between the 0.2% C steel Č. 1330 and the 1.2% C steel Č. 1943, amounting to 21°C or 28°C depending on the quenching temperature of Č. 1943.

This phenomenon might be interpreted thus: the more carbon in the steel, the more carbon in the martensite, the more tetragonal the martensite lattice, accompanied by stronger interval stresses. The stress state is relaxed as soon as the atoms become sufficiently mobile and the surplus carbon segregates as ε-carbide. The higher the lattice stress, the earlier the beginning of martensite breakdown.

The temperature of termination of the 1st tempering stage shows a mild upward trend starting from the steel Č. 1530. In view of the fact that at tempering temperatures above 150°C the carbon content of α″-martensite is equal for all steels containing more than 0.4% C, it would be logical to expect that the temperature of termination of the 1st stage should stay the same.

Since there is no residual austenite after quenching Č. 1330 and Č. 1430, in this case the 1st tempering stage is directly followed by the 3rd stage, as already discussed above.

The elongation in the 1st tempering stage, irrespective of certain deviations, decreases with increasing percentage of carbon in the steel. This can be associated with the fact that more carbon in the steel means more carbon in the martensite, which leads to more precipitation of carbide, i.e. higher contraction.

With the exception of Č. 1943 quenched from 960°C and Č. 1940 quenched from 920°C, the temperatures of the beginning and end of the decomposition of residual austenite change only slightly with increasing carbon content (maximum differences are 6 and 12°C respectively) and in an irregular fashion.

It can be inferred from the results that the small variations in the temperature of the 2nd stage are more likely attributable differences in heating rate during tempering and a non-uniform content of alloying elements than to differing carbon content.

The fact that the temperature of the 2nd tempering stage practically does not depend on carbon content can be explained as follows: austenite with less carbon is exposed to less stress, for it is surrounded by low-carbon martensite, and also is less stable. Austenite with more carbon is more stable than low-carbon austenite, but the coefficient of carbon diffusion in it is higher, which makes for its relatively easy decomposition, similar to that of low-carbon austenite.

However, an explanation for the lowering of 2nd stage initiation in the above-eutectoid steels containing 1.0 and 1.2% C should perhaps be sought in an abrupt increase of the carbon diffusion coefficient in austenite with an increase of carbon content of the steel above 0.8% (or 3.6 at. %), which facilitates the decomposition of residual austenite. The upward shift of the temperature of termination of the 2nd stage in this case would appear to be associated with an appreciable increase in the amount of residual austenite in the structure of quenched steels when carbon is increased above ~0.9% C. This means that there must be some critical amount of residual austenite in quenched steel, above which the termination temperature of the 2nd stage rises.

The elongation of the specimens in the 2nd tempering stage, beginning with steel Č. 1530, is approximately the same. It can be assumed that because of the reduced thermal expansion due to increasing carbon content of the austenite, and the simultaneously greater elongation of the specimen due to the increasing amount of austenite which is being transformed, these two effects practically cancel out. However, with Č. 1943 quenched from 960°C and Č. 1940 quenched from 920°C, an abrupt elongation of the specimens was observed, which is explained by predominance of the influence of the increased amount of residual austenite in this case (due to the complete dissolution of the carbide), over thermal expansion, which decreases as the carbon content of the steel increases.

The width of the temperature interval of the 3rd stage shows a decreasing trend with increasing carbon in the steel, despite certain deviations. For the steels Č. 1330 and Č. 1430 it is noted that the 3rd stage ends at a lower temperature owing to the low supersaturation of martensite. With Č. 1530, St. 7011, Č. 1730 and Č. 1840, the 3rd tempering stage ends at 406—409°C. With a further increase in carbon content of the steel this temperature falls off, but then rises again to 411°C with Č. 1943 quenched from 960°C.

For Č. 1943 quenched from 780 the termination temperature of the 3rd stage is higher when quenched from 960°C, which would mean that a higher carbon content of the solid solution is responsible for this change. No corresponding influence is observed with change of the carbon content of the steel from 0.45% C(Č. 1530) to ~0.9% C, which is how much Č. 1943 is reckoned to contain in solid solution after quenching from 780°C.

With increasing carbon in the steel, the contraction of the dilatometric specimen in the 3rd tempering stage increases. The magnitude of this volume change directly depends on the degree of phase deformation of the α-solid solution, which increases together with increasing carbon in the steel, i.e. with increasing changes in volume in the previous tempering stages. It is noted that the change in the form of carbide which takes place at this stage of tempering does not have any major effect on the volume.

Observing the results as a whole, it can be concluded that a satisfactory reproducibility was achieved on the dilatometric specimens of one and the same steel. The maximum deviations in the temperature bounds of the tempering stages were 4—5°C, and in volume changes 0.4×10^{-2} *mm*.

It is further important to note that certain deviations with some steels from the general trend of temperature intervals of tempering stages with increasing carbon content, can be attributed to a non-uniform amount of alloying elements in the steels, and to the technical impossibility of an absolutely constant heating rate(2, 9) during tempering. It may be added that the deviations noticed with some steels could be due to difficulties in diagrammatically determining the volume changes and temperature intervals of the tempering stages in cases without pronounced tempering effects.

It is certain that automatic control of the heating rate and the application of greater magnifications in registering dilatometric curves will allow us to make further improvements.

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Original Scientific Paper

METHOD OF PREPARING SPECIMEN SURFACE FOR ELECTRON MICROSCOPY OF CATALYSTS WITH LOW MECHANICAL STRENGTH*

by

PAULA S. PUTANOV, DRAGOMIR B. KARAULIĆ and ŽARKO D. JOVANOVIĆ

For the interpretation of catalytic effects and for the investigation of conditions under which a catalyst is applied, it is of particular significance to know the form, dispersion, pore structure, size and relief of the specific surface, and the number and distribution of active centers. These data are obtained by various methods based on direct observation of the surface or on indirect investigation through phenomena taking place on the surface.

Electron microscopy is a direct method. Its advantages are: direct observation of pore patterns on a submicroscopic scale, applicability in detailed studies of surface relief of very different macro and micro structures, and in following the changes through the life of the catalyst (1, 2). The scope and accuracy of the method depend above all on the technical specification of the microscope and on the methods for statistical processing of the data(7). The basic experimental problem is preparing the specimens.

The complex chemical composition, heterogeneous structure and diverse mechanical properties of catalysts restrict the possibility of applying simple methods for the preparation and direct observation of samples. The best results in catalyst surface investigation are obtained by the two-step replica method, allowing a relatively large number of combinations with the replica materials now available, although the procedure involves many problems concerning the choice of combination and the conditions of its application(3).

The problem of maximum fidelity in the reproduction of a surface with minimum damage to the structure becomes especially acute with catalysts of low mechanical strength, and when their changes during use are investigated, for which purpose several successive replicas of the surface of one specimen must be obtained. Replication with collodion or other organic membranes which are deposited from solution does not give satisfactory results with these catalysts, because on removal they take away some material(5). The standard oriented pressure method, e. g. with polystyrol in its standard form(4), is not satisfactory either, because the pressure to which

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the replica and matrix materials are exposed deforms both the internal pore structure and the surface relief.

For the investigation of catalysts of low mechanical strength, the standard two-step polystyrol-carbon replica method was modified. The modified method was tested on a vanadium catalyst for sulfur dioxide oxidation, and on iron-chromium gas shift catalysts for the conversion of carbon monoxide.

The standard method was modified by changing the form of the reproduction material and the mode of deposition and formation of replicas. Instead of the standard solution, granulated polystyrol, we used a 0.3—0.6 *mm* stressed foil. The mechanical pressure oriented in one direction was replaced by a pressure equally distributed over the surface, caused by dilatation of the foil under specific thermal conditions. In this way the relief of the surface is not disturbed and multiple reproduction is made possible.

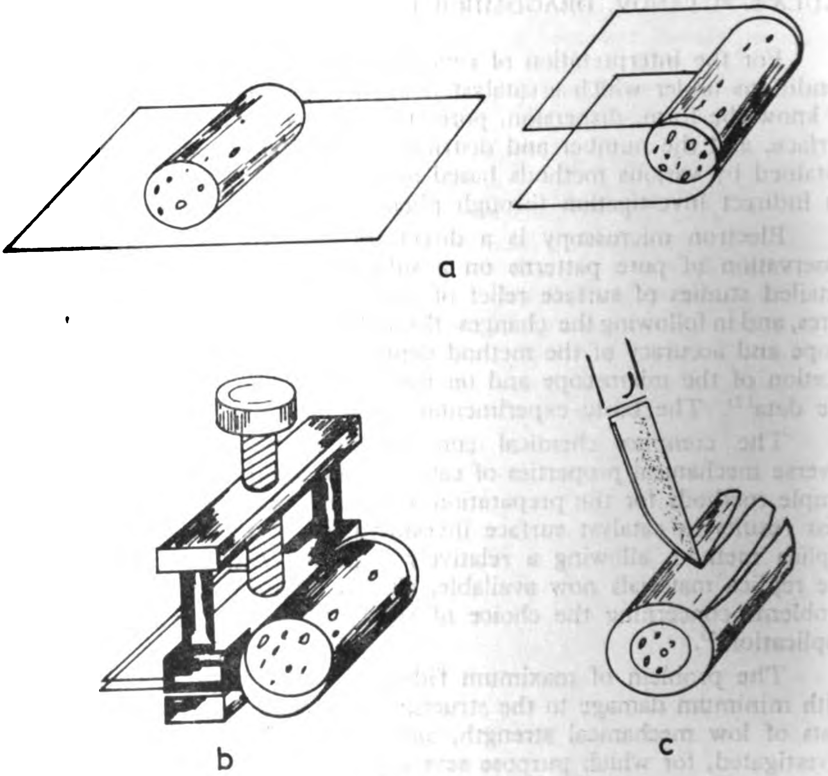

Figure 1
Application of polystyrol foil to catalyst partic'e

Experimental procedure includes the following: the surface of the catalyst, because of its low mechanical strength, is not worked mechanically, but the damaged portions are taken away and the dust is removed from the surface and pores by vacuum suction. On the cleaned surface the first replica is formed: instead of granulated polystyrol strips of stressed polystyrol foil 0.3—0.6 *mm* thick are used. The foil must be wider than the length of a cylindrical particle of the catalyst (Fig. 1, a). The foil is folded around the cylindrical part of the particle and its ends are lightly stretched and clipped to ensure the pressure required during the formation of the replica (Fig. 1, b). It is then exposed to heat. The polystyrol softens, and during cooling the foil contracts in the direction of prestressing. The pressure caused by this contraction is uniformly distributed over the surface and impresses the softened polystyrol into the relief. The cooling procedure is also important: cooling must be abrupt for the outer parts of the foil to cool off more rapidly and thus, by their contraction, to impress the soft parts (lying directly on the heated particle which cools off slowly) into the relief of the catalyst. After cooling has been completed, the particle has to be released from the membrane. The clip is removed and the membrane is cut into smaller parts, which are separated from the surface mechanically (Fig. 1, c).

The polystyrol replicas obtained in this way are further treated according to standard procedures: a secondary replica is created by evaporating carbon in vacuum and shading with an alloy of 60% Pd and 40% Au. The carbon replica is removed from the polystyrol with gelatin solution, picked up on a grid and viewed under the microscope.

Figure 2

Surface of polystyrol foil overheated to 170°C. (48 000 ×)

The effect of temperature was studied in the range 100—180°C. A temperature of 140°C proved to be most suitable; the entire surface of the foil reproduced the particle relief and the minimum dimension of clearly detectable details was around 50 Å, which is close to the limit of resolution of the microscope used.

At temperatures below 140°C, the replicas reproduce the relief structure only in rough outlines. At temperatures higher than 150°C, the polystyrol melts and breaks, and the dilatation effect does not take place. Between 170 and 180°C, the structure of polystyrol itself changes, and the electron microscopic photos show the disordered structure of the polystyrol instead of the relief of the catalyst. One such replica is shown in Fig. 2.

The time of replica formation was varied in the range 5—40 *min*, and the optimum time established at 20 *min*. Time less than 15 *min* did not result in satisfactorily reproducible replicas. If heating was longer than 25 *min*, the foil broke down and the result was the same as with heating over 150°C.

A detail of the surface of fresh vanadium catalyst for sulfur dioxide oxidation, obtained by the described method under the optimum conditions, is shown in Fig. 3.

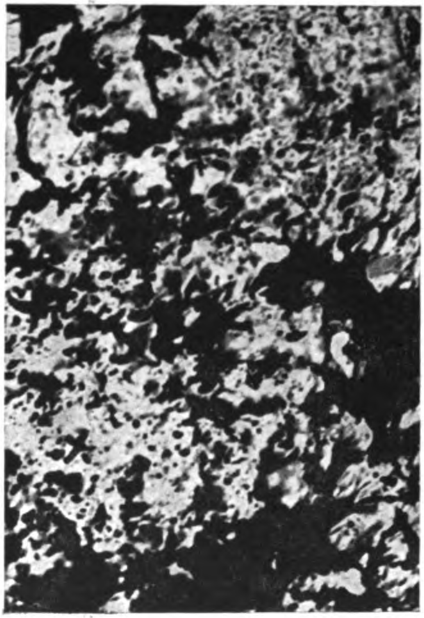

Figure 3

Surface of the vanadium catalyst (detail) (48 000 ×)

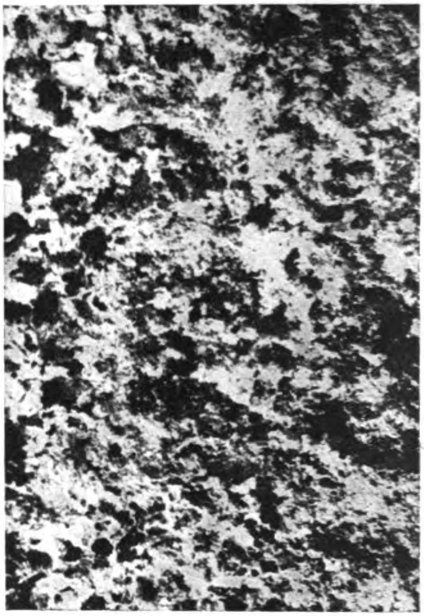

Figure 4

Surface of the iron-chromium-based gas shift catalyst (detail). (24 000 ×)

Figure 4 shows the surface of an iron-chromium-based gas shift catalyst for the oxidation of carbon monoxide synthesized in our laboratory.

A photo of a detail of the vanadium catalyst surface reproduced under the optimum conditions as established in this study (formation time of the polystyrol replica 20 *min*, temperature 140°C) is shown in Fig. 5. It can be seen from the photo that the heterogeneous pore structure was well reproduced, with distinct details within the range of $1.5 \,.\, 10^{-7}$ to 10^{-4} *cm*.

Between successive replicas of parts of the surface of the same particles, very good agreement in the character of the pore structure was found.

This indicates that the method could be used to observe changes of the catalyst surface during utilization.

It may be concluded that the reproducibility of the surface by our method is satisfactory, being as good as in the other methods applied in electron microscopy (Fig. 5).

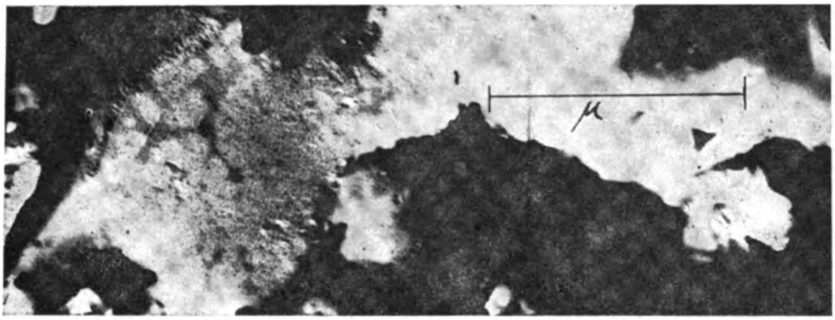

Figure 5
Surface of the vanadium catalyst for sulfur dioxide oxidation. (48000 ×)

Replicas were photographed on a Carl Zeiss Jena ELMI-D2 electron microscope, with a direct magnifying power of 30,000 × and a maximum resolving power of 20 Å.

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Original Scientific Paper

DETERMINATION OF UNSATURATION OF ALEKSINAC OIL SHALE KEROGEN BY MODIFICATIONS OF THE IODINE NUMBER METHOD. I.

EFFECT OF TEMPERATURE AND TIME OF BROMINATION

by

DRAGOMIR K. VITOROVIĆ and PETAR A. PFENDT

On the basis of the effect of selenium oxichloride, sulfuryl chloride, and chlorine on California, Colorado, Nevada, and Elko oil shales, McKee and Goodwin(1) conclude that the kerogens of these shales are highly unsaturated. Kogerman(2) holds that the organic substance of Estonian kukersite is a highly polymeric resin with a large number of double bonds. Many researchers(3–7) who studied the structure of kerogen by degradation arrived at similar conclusions, i. e. that kerogen includes double olefin bonds.

A large number of studies indicate the unsaturated nature of kerogens, but quantitative data on unsaturation are scant. Brower and Graham(8), applying the same reagents and similar procedures as McKee and Goodwin(1), found that the organic substance of Colorado shale behaves as a typical unsaturated substance, and on the basis of the amount of bound H Br conclude that there is one double bond to every 16 carbon atoms. They believe that this value is not entirely exact, because the exact kerogen content of the concentrate is not known, and also because it is very difficult to complete the reaction in a heterogeneous system like this.

Our opinion was that same quantitative information about the unsaturation of kerogen could be obtained by applying some of the reagents otherwise used for the determination of iodine number to native or to minimally altered kerogen. As it has not yet been possible to obtain the native and unaltered kerogen in the pure state, we decided to take as the initial material the kerogen concentrate resulting from a relatively simple treatment of the shale.

A great many methods are available to determine unsaturation(9). A universal method for the iodine number is not known as yet. For each type of substance it is necessary to verify the existing methods, to make modifications or to develop new methods. Our attention was attracted particularly by the bromine reagents, irrespective of the fact that secondary reactions are more frequent with them than with other reagents, because of their higher reactivity, and which is very important in view of the inhomogeneous nature and insolubility of the oil shale kerogens. On the other hand, a tendency to substitution, the effect of peroxide and other functional groups, and various other adverse properties, are characteristic in a certain measure of all reagents used for the determination of iodine number, being more or less expressed depending on the substance whose unsaturation is to be determined(9).

Thus we held that bromine reagents for determining iodine number should be tested in the investigation of kerogen unsaturation, bearing in mind both the properties of the individual reagents and the features of kerogen concentrate as a whole, i. e. the presence of various functional groups, pyrite, etc. Because of the specific properties of kerogen, we expected that the results would be affected by experimental conditions (temperature, time, etc.), which also had to be investigated.

Three bromine reagents in relatively frequent use were selected: (1) bromine solution in carbon tetrachloride after McIlhiney(10); (2) bromine solution in chloroform after Hal'pern and Vinogradova(11); (3) bromine solution in methanol saturated with sodium bromide after Kaufmann(12). Advantages and disadvantages of these methods are treated fairly extensively in the literature(13–23).

EFFECT OF TEMPERATURE AND TIME OF BROMINATION

In determining the iodine number or unsaturation, many authors restrict themselves to working at unspecified "room" temperature for an empirically chosen time. The effect of temperature has been given particularly little attention, although some authors concluded that the maintenance of a specified temperature was essential to obtain reproducible results. In the determination of iodine number for soybean oil by Kaufmann's method, Earle and Milner(19) noted that minor temperature changes did not affect the results. They also found that a half-hour bromination, as prescribed by the standards, was insufficient for soybean oil, and two hours was required. Casimir and Dimitriu(9) maintain that the McIlhiney reagent for petroleum products can yield good results provided, among other conditions, the temperature is low and the time of bromination 15—30 *min.*

Working with bromine solution in carbon tetrachloride and chloroform, Williams and James(24) established that the addition rate of bromine in nonaqueous solvents depends on several factors: position of the ethyle bond, presence of certain substituents, kind of solvent, and presence of catalyst. They divide the substances into three groups: (a) substances which combine quickly with bromine releasing hydrogen bromide as a substitution product; (b) substances which combine slowly at first but after the initial inhibition period their addition rate grows rapidly; (c) substances which do not combine with bromine under the given conditions. On the basis of their results they were not able to set up a general classification capable of predicting the behavior of a compound towards bromine. Likewise, working with the Kaufmann reagent, Petrova(25) arrived at the conclusion that different unsaturated compounds with carbonyl or carboxyl group required different times, from a few minutes to 24 hours. Also, in compounds with a conjugated double bond, addition is incomplete, particularly after a short time.

Some researchers, e. g. Peters(10), maintain that at low temperatures addition is at first faster than substitution. It is on this Peters' modification of McIlhiney's method is based: the iodine number is determined by plotting iodine number as a function of time and extrapolating to zero time. The value obtained should be very close to the theoretical value or slightly below it.

Buckwalter and Wagner(15) brominated a fairly large number of compounds with McIlhiney's reagent at different temperatures and for different times. Although the experiments were not systematic, the authors concluded that different conditions, temparatures and times were necessary for different compounds. Aside from this, they observed that the amount of hydrogen bromide was greater at higher temperatures and ascribed this fact to substitution.

OUR RESEARCH

Kerogen concentrate contains two entirely different substances which are capable of reacting with a bromine reagent — kerogen and pyrite. Kerogen itself, as has been stressed, is not homogeneous and in addition to double bonds it has various other functional groups. In view of these facts, and the experience of the authors cited above, one can hardly expect to find optimum conditions for the kerogen concentrate (temperature and time of bromination) under which all double bonds react quantitatively with bromine without any secondary reaction taking place at the same time. In spite of this, by conducting bromination at several different temperatures and extending the time until a maximum constant value is reached, while keeping all the other conditions constant, we were able to establish the magnitude of the effect of changing temperature and time of bromination. As we knew the composition of the concentrate, the resulting "iodine numbers" were corrected on the basis of separate determinations with pure pyrite. By applying the three methods referred to above, we arrived at a fairly good estimate of the unsaturation of Aleksinac shale kerogen. For each method the conditions were chosen for simplicity of procedure and convenient analysis of results.

EXPERIMENTAL

Preparation of Samples

Aleksinac oil shale was ground in a ball mill to a particle size of —60 DIN. The powder was treated with 6N HCl (10 *ml/g*), washed till negative for chlorides, and the product extracted with benzene (Soxhlet, 20 h). The kerogen concentrate was then graded by standard sifting.

Kerogen content of the concentrate was determined by the method of Jovanović and Vitorović(26). The sample contained 27.33% kerogen and 18.90 pyrite (elementary analysis of kerogen: 74.52 C, 10.75% H, 2.56% N).

Pyrite for determining the correction was obtained from the Bor mines. It was first ground in an agate mortar, treated with concentrated hydrochloric acid and heated to boiling, then washed in distilled water till negative for chlorides, and dried at 80°C. After another comminution in an agate mortar, it was sifted through standard sieves. As in the case of kerogen concentrate, the fraction —110 +130 DIN was taken for the tests.

All reagents used were of p. a. purity, except methanol which was refluxed with quicklime for 6 h and distilled: the distillate was condensed at 64—65°C.

Determination of Iodine Number

About 0.1000 *g* dried kerogen concentrate or pyrite samples were weighed out into 300 *ml* Erlenmeyer flasks with ground glass stoppers. Determinations by different methods were done as follows.

(a) *Bromine Solution in Carbon Tetrachloride* (*McIlhiney*)

Reagent — 5.5 *ml* bromine dissolved in 1 liter of carbon tetrachloride.

Procedure — 15 *ml* carbon tetrachloride was added to the samples in the Erlenmeyer flasks and the mixture was cooled in ice for 10 min. The flasks were wrapped in fabric, 15.00 *ml* reagent was added from a burette and the stoppered flasks were kept in darkness for the required time at a specified temperature. For 0°C, an ice bath was used, and for 20°C a temperature controlled chamber (19—22°C). After the set time, 15 *ml* 20% potassium iodide solution and about 100 *ml* distilled water were added to the mixture, which was immediately titrated with 0.1 N solution of sodium thiosulfate, using starch as indicator. The end point was taken to have been reached when the color of the iodine-starch complex did not recur in 2 min. Control tests were carried out for each experimental series.

(b) *Bromine Solution in Chloroform* (*Hal'pern-Vinogradova*)

Reagent — 5.5 *ml* bromine dissolved in 1 liter of chloroform and left for at least 48 h.

Procedure — First, 10 *ml* chloroform and then 15.00 *ml* reagent were added to the samples. The Erlenmeyer flasks were left at a definite temperature in the dark as described above. For the tests at 30°C and 40°C, the flasks were thermostated in water: the temperature ranges were 29—31°C and 39—40°C. After a specified time, 15 *ml* 10% potassium iodide solution and about 100 *ml* water were added to the mixtures, and the iodine liberated was titrated as above. Parallel controls were run.

(c) *Solution of Bromine in Methanol Solution of Sodium Bromide* (*Kaufmann*)

Reagent — 500 *ml* of dry methanol was saturated with dry sodium bromide, and 5.2 *ml* bromine added from a burette. (According to Kaufmann, the bromine concentration should be half as much.)

Procedure — 11 *ml* reagent was added to the samples, which were then left to stand in darkness at specified temperature. After the specified time, 15 *ml* 10% solution of sodium iodide and about 50 *ml* distilled water were added and iodine liberated was titrated as described above. Each time two parallel controls were run to check the reagent concentration. In computing iodine numbers, the mean values were taken.

EXPERIMENTAL RESULTS

Mean values of the iodine number of the kerogen concentrate and pyrite, obtained under differing conditions (temperature and time) and by the three methods are given in Figs. 1 and 2.

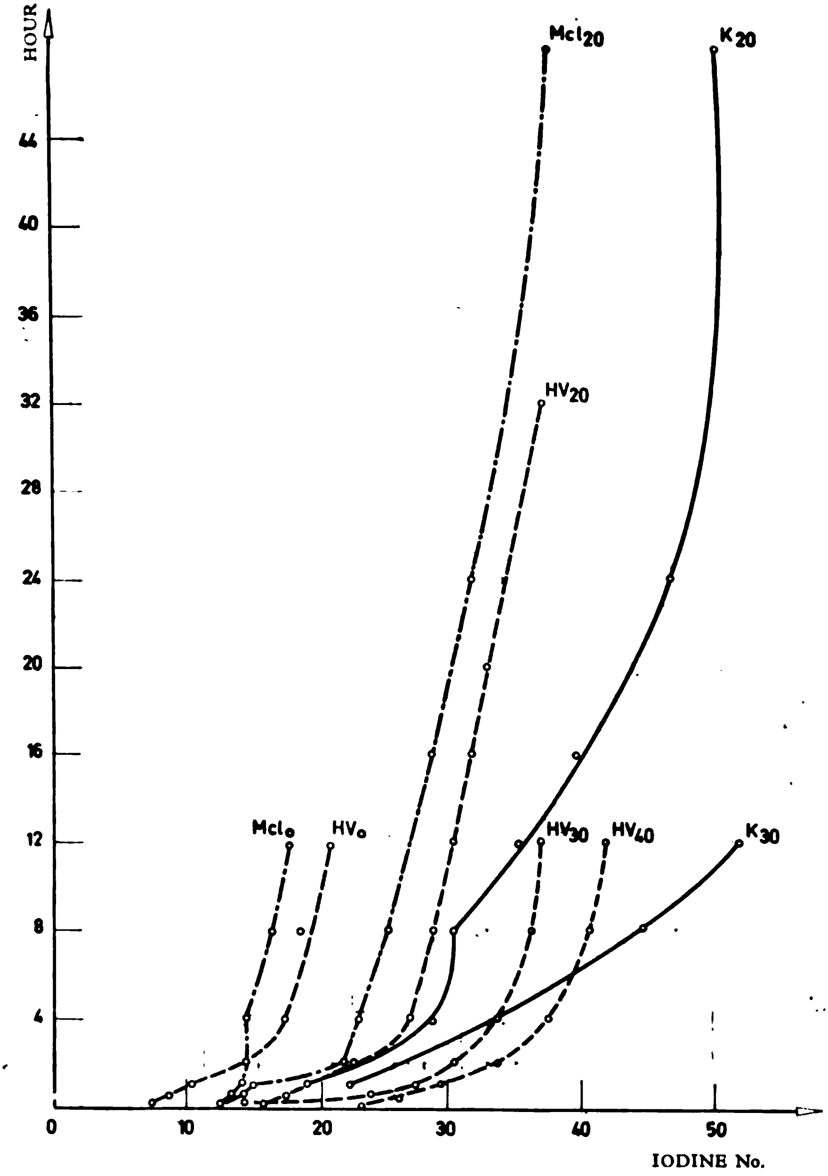

Figure 1

Iodine number against bromination time and temperature for Aleksinac kerogen (suffisces denote T°C)

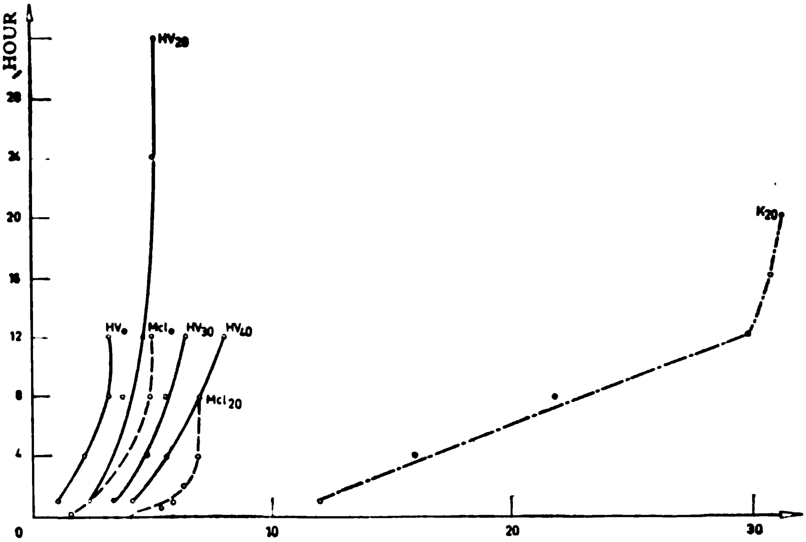

Figure 2

Iodine number against bromination time and temperature for pyrite (suffisces denote bromination time)

DISCUSSION

The iodine numbers of the kerogen concentrate and pyrite show without exception that the amount of bromine which enters into reaction increases with increasing temperature of bromination (Figs. 1 and 2). The values for kerogen concentrate rise quickly at first, up to 2 h bromination at low temperature, and up to 4 h or more at higher temperatures, after which the rate of increase is less.

The dependence of iodine numbers of kerogen concentrate and pyrite on temperature at constant time of treatment by the Hal'pern-Vinogradova method is shown in Figs. 3 and 4. As a measure of the rate at which bromine

TABLE 1

Tangents of Angles Made with the Abscissa by Straight Lines between Two Temperature

Substance	Temperature range	Zeit (Min)		(Time h)				
		10	30	1	2	4	8	12
Concentrate	0—20°	1.11	1.13	1.05	1.20	1.01	1.00	1.03
	20—30°	0.91	0.75	0.67	0.66	0.74	0.69	0.74
	30—40°	2.30	2.25	2.37	1.41	1.20	1.33	1.08
Pyrite	0—20°	—	—	3.00	—	—	3.65	2.14
	20—30°	—	—	1.93	—	—	1.08	1.20
	30—40°	—	—	2.43	—	2.43	1.44	1.23

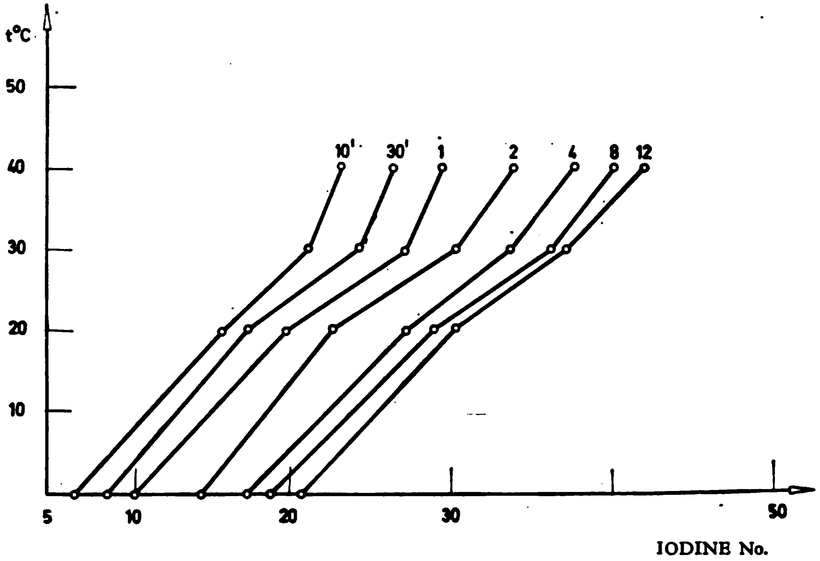

Figure 3

Iodine number of kerogen concentrate against temperature for constant bromination time by Gal'pern and Vinogradova's method. Number are bromination times

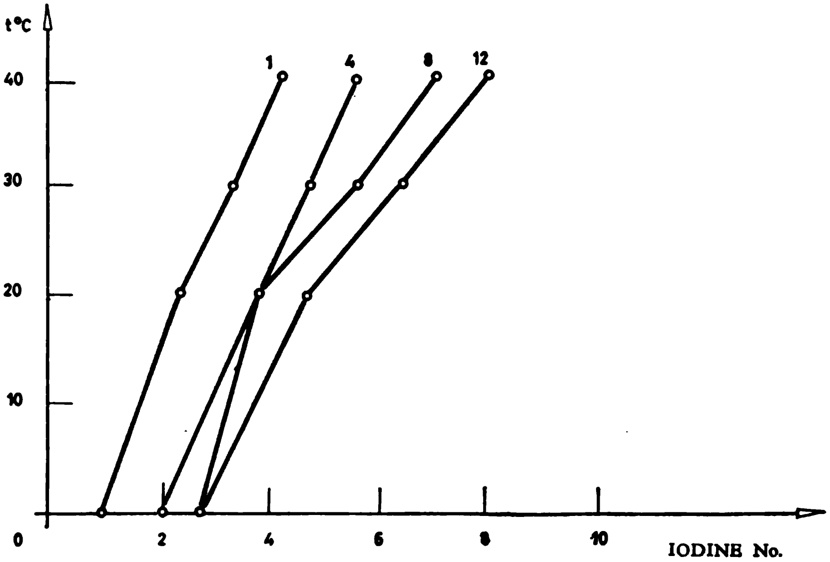

Figure 4

Iodine number of pyrite against temperature for constant bromination time by Gal'pern and Vinogradova's method. Number are bromination times.

reacts with increasing temperature, the tangents of the angles made by the straight lines between two tempereture points with the abscissa (Figs. 3 and 4), is presented in Table 1. Since the rate of reaction of bromine is higher the smaller the tangent, it can be concluded that the largest amount of bromine reacts with the kerogen concentrate in the temperature range of 20—30°C (tan $\alpha \sim 0.7$), and the least at 30—40°C (tan α = 1—2.4). With pyrite, the greatest increase is also at 20—30°C (tan α = 1—2), but the least increase is in the 0—20°C range (tanα = 2.1—3.6). The relative amount of reacting bromine is in all temperature intervals greater for concentrate than for pyrite. Hence the rate of reaction of kerogen with bromine is faster that of pyrite.

The reasons for the obvious dependence of iodine numbers of kerogen concentrate and pyrite on the time of bromination can be various. In the first place, since the reaction takes place in a heterogeneous system, it takes time for bromine to diffuse to all possible reaction sites. Secondly, it has been proved that the substances with conjugated olefin bonds react with some of the bromine relatively quickly, and with the rest very slowly, so that the theoretical value is sometimes only achieved after several days of bromination(14, 17). However, the olefin bonds of Aleksinac kerogen thought to be isolated(6, 7): Brower and Graham(8) did not find conjugated bonds in Colorado kerogen tested with maleic acid anhydride. Also possibly influential is the catalytic action of hydrogen bromide which is only created in large amounts by secondary reactions after some time. This is connected with the selection of the optimum temperature of bromination, because the secondary reactions also depend on temperature.

The dependence of the iodine number of two entirely different substances, kerogen concentrate and pyrite, on the time of bromination (Figs. 1 and 2), may suggest that this is a common characteristic of insoluble substances. However, in spite of this similarity, the bromination of these two substances is essentially different. Bromine can only react with pyrite on the surface of particles, and since a nonaqueous medium is involved, the reaction rate falls off relatively quickly. With the kerogen concentrate, however, the organic substance becomes more or less soaked with bromine solution in a short time, so that the reaction does not occur only on the particle surface but also within the particles. Hence it could be concluded that the particle size of the sample also plays a significant role in bromination.

The iodine numbers of both kerogen concentrate and pyrite obtained by different methods are different even when the experimental conditions were not changed (temperature, time, amount and concentration of reagents, etc.). The differences result from different reactivities of the reagents; this phenomenon will be investigated in a future study.

Unsaturated of Kerogen

The appearance of the curves in Fig. 1 allows the conclusion that the reaction of kerogen concentrate with bromine at 0°C ends after 12 h, and at 20°C after 36—48 h, irrespective of the method applied. The curves for reaction at higher temperatures (HV_{40} and K_{30}) show a continuous upward trend even after 12 h of bromination, and the reaction cannot be regarded as completed. The end value of the iodine number of kerogen concentrate, for 0°C or 20°C, corrected by the corresponding maximum

TABLE 2

Iodine Number and Unsaturation of Aleksinac Kerogen Determined at Two Temperatures Reaction

	Method	Temperature	
		0° C	20° C
Iodine number of concentrate	McI HV K	17.9 20.9 —	37.5 35.5 50.2
Iodine number of kerogen	McI HV K	61.8 70.0 —	130.4 125.2 149.0
No. of C atoms per $>C=C<$ bond	McI HV K	25 22 —	12 12 10
meq $>C=C<$ to 1 g kerogen	McI HV K	4.9 5.5 —	10.3 9.9 11.7

value for pyrite, gives the iodine number and unsaturation of kerogen can be computed, given the kerogen and pyrite content. The values computed are given in Table 2.

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Original Scientific Paper

SOLUBILITY OF THE ORGANIC SUBSTANCE IN ALEKSINAC OIL SHALE. II.

SOLVENTS BOILING BETWEEN 100° AND 207°

by

DRAGOMIR K. VITOROVIĆ and MIRJANA M. ŠABAN

A previous study(1) established that the solubility of the organic substance in Aleksinac oil shale does not depend on extraction temperatures up to 100°C. It was also established that the solubility in 14 solvents (of dissimilar boiling points, chemical properties, polarity, and capacity to build hydrogen bonds) did not exceed 5%, except for dioxane (11%) and diethylamine (12%). Therefore the organic substance of the Aleksinac oil shale does not differ substantially from those of other oil shales of different geographic origin in its low solubility in organic solvents.

The literature gives data on a considerably higher solubility of the organic substance in oil shales at increased temperatures. Dulhunty(2, 3) found that benzene, under pressure, dissolves 4—14% of torbanite organic substance at 300—340°C in 40 h, and 90% at 360—400°C on prolonged heating. At the US Bureau of Mines(4) experiments were conducted involving parallel extraction of Colorado shale in a Soxhlet apparatus (24 h) and under pressure at 200°C (30 min) with the following solvents: benzene, tetralin, phenanthrene, methanol, *n*-heptane, acetone, dipropylene-glycol, and Dow polyglycol P-400. Tetralin dissolved the most (28% of the organic substance) and acetone the least (5%). However, irrespective of the conditions, applied, the solvents dissolved approximately the same amounts of organic substance both in the Soxhlet extraction apparatus and under pressure. When this shale(5) is heated in the presence of tetralin, first for 30 min and then four times for 24 h, a total of 86% of organic substance dissolves. On the other hand, 90% organic substance of Estonian shale can be dissolved in ether or benzene if the shale is heat pretreated at 175°C(6).

The literature also contains contradictory data. Robinson and Hubbard(7) assert that the organic substance in Colorado shale does not extract much at temperatures below 320°C. On dissolving kukersite in benzene at about 250°C under pressure, Kogerman(8) found less than 1% of organic substance dissolved.

Nevertheless, most scientists working on the solubility of the organic substance of oil shale agree that extraction increases with the duration of solvent action and with temperature. The much greater solubility at higher temperatures and pressures is attributed by most authors to decomposition of the macromolecular organic substance of the shale into fractions of lower molecular weight which are more soluble. In other words, extraction at higher temperatures is accompanied by thermal degradation.

Our objective in the present and in previous(1) studies was to determine the solubility in organic solvents of the organic substance in Aleksinac oil shale under conditions which do not allow it to decompose. We were guided by the fact that the isolation of pure native organic substance would be of value for structural investigations by physical and chemical methods. In selecting solvents and extraction conditions account was taken of the factors which might affect the solubility of the organic substance, as in the previous study(1). Keeping in view the fact that the solubility is low at temperatures below 100°C, and that the organic substance begins to undergo rather great changes above 250—300°C(9), we chose solvents boiling between 100 and 207°C.

The solvents used were: nitromethane, pyridine, n-butyl alcohol ethoxyethanol, amyl acetate, cyclohexanol, petrol (140-150°), tetralin, and acetic acid. Two of these are non-polar solvents: petrol and tetralin. The others are more or less polar.

In Ewell's classification of solvents by their capacity to build H-bonds, acetic acid, cyclohexanol, n-butyl alcohol, ethoxyethanol, and nitromethane belong to group 2, amyl acetate and pyridine to group 3, and tetralin and petrol to group 5.

Four of these solvents were here used for the first time to dissolve the organic substance out of oil shales: nitromethane, n-butyl alcohol, ethoxyethanol, and amyl acetate.

The products obtained were investigated: (a) determining elementary composition of all dissolved fractions of organic substance; (b) determining average molecular weights of some extracts, after Rast; (c) analysis of infrared spectra.

EXPERIMENTAL

Aleksinåc oil shale, was comminuted in a ball mill (—100 mesh, 0.149 *mm*, Tyler).

The organic substance content, determined after Jovanović and Vitorović(10), was 21.36% in raw shale and 29.84% in shale enriched by treatment at 60°C with hydrochloric acid (1 : 1).

Extraction was done in a Soxhlet apparatus for 100 h with 20—30 *g* samples.

The solvents were purified, unless already of *p.a.* purity, and redistilled before use.

After extraction, most of the solvent was removed by distillation at atmospheric pressure, and the residue was removed in vacuum to constant weight.

The solubility of the organic substance was expressed as weight percentage relative to the total organic content (Table 1). The solvents are ordered according to boiling point.

TABLE 1

Solubility of Organic Substance from Raw and Enriched Aleksinac Oil Shale

Solvent	Boiling point C°	% of total organic substance dissolved from	
		Raw shale	Enriched shale
Nitromethane	101	1.21	3.67
Pyridine	115	8.78	15.74
n-Butyl alcohol	117	6.69	9.47
Acetic acid	118	35.90	10.13
2-Ethoxyethanol	135	11.52	26.51
Amyl acetate	149	5.10	10.70
Petrol, Gasoline	140—150	5.62	5.05
Cyclohexanol	161	38.66	80.98
Tetralin	207	32.10	74.56

The extracts were light brown to brown pasty substances, except a few which were brown powders. Their melting points, lying within the range 64—95°C, were in most cases sharply defined.

Elementary microanalysis of all extracts was performed. Frequent difficulties were encountered as regards the reproducibility of results, because of in homogeneity of the materials. In most products, nitrogen and sulfur were demonstrated by qualitative microreactions. Nitrogen was also determined quantitatively by the micro-Dumas method.

Most extracts left some ash after combustion. The amount of ash was weighed during elementary analysis.

Table 2 gives data on C/H, C/N, and C/O + S ratios extracts and ash after combustion.

TABLE 2

Weight Ratios of Elements and Ash Content

Solvent	C/H		C/N		C/O + S		Ash (%)	
	R	E	R	E	R	E	R	E
Nitromethane	7.34	6.65	13.56	27.00	4.26	4.53	4.25	2.70
Pyridine	7.19	8.49	27.37	15.63	7.62	3.26	1.45	6.89
n-Butyl alcohol	6.54	6.84	74.12	62.81	7.99	5.34	11.58	10.48
Acetic acid	6.43	7.20	112.65	77.80	1.23	2.78	26.76	12.64
2-Ethoxyethanol	6.68	6.17	33.07	35.71	2.75	2.01	2.30	2.75
Amyl acetate	6.57	7.06	74.21	43.52	9.48	5.12	0.76	0.76
Petrol gasolin	6.89	6.56	112.65	25.24	10.21	11.62	0.67	0.90
Cyclohexanol	7.27	7.44	28.45	54.86	3.42	3.35	2.78	15.78
Tetralin	10.76	10.78			12.92	10.05	0.00	0.00

R = Raw shale extract E = Enriched shale extract

Average molecular weights of extracts obtained with petrol, amyl acetate, and n-butyl alcohol were determined by a semimicro modification of the Rast method(11), using camphor as solvent. Since most extracts did not dissolve in camphor, other solvents were tried: carbamide, β-naphthol, and phenanthrene. However, carbamide and β-naphthol also did not dissolve well the extracts insoluble in camphor. Phenanthrene dissolved some, but the depression of the melting point was so small ($K = 12$) that reproducible results could not obtained.

Table 3 presents average molecular weights of petrol, amyl acetate and n-butyl alcohol extracts, the rations of carbon, hydrogen, oxygen and nitrogen atoms computed from the elementary analysis (oxygen from the difference), and formulas which correspond to the experimental average molecular weights.

TABLE 3

Average Molecular Weight and Corresponding Formula of n-Butyl Alcohol, Amyl Acetate and Petrol Extracts

Solvent		Average molecular weight by Rast method	Ratio of number of atoms in extract	Formula corresponding to average molecular weight
n-Butyl alcohol	R	350	$C_{6\cdot45}H_{11\cdot83}O_{0\cdot60}N_{0\cdot07}$	$C_{22}H_{38}O_{2}$
	E	385	$C_{6\cdot17}H_{11\cdot84}O_{0\cdot86}N_{0\cdot08}$	$C_{22}H_{42}O_{3}$
Amyl acetate	R	372	$C_{6\cdot55}H_{11\cdot97}O_{0\cdot52}N_{0\cdot07}$	$C_{25}H_{46}O_{2}$
	E	319	$C_{6\cdot13}H_{10\cdot41}O_{0\cdot86}N_{0\cdot12}$	$C_{21}H_{36}O_{3}$
Petrol, Gasoline	R	506	$C_{6\cdot65}H_{11\cdot60}O_{0\cdot48}N_{0\cdot05}$	$C_{42}H_{74}O_{3}$
	E	662	$C_{6\cdot52}H_{11\cdot93}O_{0\cdot42}N_{0\cdot22}$	$C_{48}H_{84}O_{3}$

R – Raw shale extract E – Enriched shale extract

Further information was obtained on the nature of the extracts from their infrared spectra (Perkin Elmer 337, Grating Infrared). It is noted that spectra of different extracts are similar. They are also similar to the spectra of the native organic substance of the oil shale. All spectra show mainly only the characteristic absorption bands corresponding to CH_2, C—CH_3, and CO groups. Apart from this, the spectrum of the tetralin extract of enriched shale, and of cyclohexanol, 2-ethoxyethanol, and acetic acid extracts of both raw and enrished shale, contain certain bands which correspond to the functional groups of the solvents themselves, and thus presumably indicate incomplete removal of the solvent.

DISCUSSION

Since solubility depends on intermolecular forces, above all on the capability of both the solvent and the solute to build hydrogen bonds, the results should be examined relative to factors affecting these forces and the constants which give a measure of them.

We analyzed the ratio of solubility of the organic substance of the raw and enriched oil shale, and: (a) extraction temperature, i.e. the boiling point of the solvent; (b) solvent polarity, i.e. the dipole moment and the dielectric constant; (c) capacity of the solvent to build hydrogen bonds; (d) chemical character of the solvent. From this the following conclusions are drawn:

(a) With solvents boiling at over 100°C solubility begins to change with temperature, unlike solvents boiling below 100°C. Table 1 shows that the most efficient solvents are cyclohexanol and tetralin. As their boiling points fall within the range 161—207°C, the markedly greater solubility of the shale's organic substance in these solvents may be attributed in some measure to a certain change in the substance itself. The dependence of the solubility on temperature is also evident from a comparison with solvents of a similar nature but different boiling points. For example, petroleum ether (40—70°C) dissolves only 0.5% of the organic substance of raw shale and 0.9% of enriched shale(1), but petrol (140—150°C) dissolves 5.6% and 5.1% respectively, or about ten times more. Methyl and ethyl alcohols respectively dissolve 3.1% and 3.8% organic substance of the raw shale, and 4.8% and 4.7% of the enriched shale(1), while n-butyl alcohol dissolves 6.7% and 9.5% from raw and enriched shale respectively, or about double the amount. Finally, amyl acetate, which boils 70°C above ethyl acetate, dissolves about twice as much organic substance of the raw and about three times more of the enriched shale.

The data for solvents boiling at over 100°C also show that solubility increases with the boiling point of the solvent, but not as a linear function, most probably due to the effects of other factors on extraction.

(b) With these solvents, no regularily of solubility of the organic substance of the oil shale in dependence on the solvent polarity or on the constants which measure this property was established (Tables 4 and 5).

TABLE 4

Dipole Moment of Solvent and Solubility of the Organic Substance of Raw and Enriched Aleksinac shale

Solvent	Dipole moment	% of total organic substance dissolved from	
		Raw shale	Enriched shale
Acetic acid	0.83	35.90	10.13
n-Butyl alcohol	1.68	6.99	9.47
Cyclohexanol	1.90	38.66	80.98
Amyl acetate	1.91	5.10	10.70
2-Ethoxyethanol	2.08	11.52	26.51
Pyridine	2.20	8.78	15.74
Nitromethane	3.17	1.21	3.65

Since intermolecular forces resulting from the dipole-dipole attraction, Kessom's forces, depend on temperature, and the power of attraction falls to zero at high temperatures, it can be presumed that when the organic substance is dissolved by solvents boiling at over 100°C these forces are weak, and hence solubility does not depend on the dipole moment. London's intermolecular forces do not depend on temperature, and it can be assumed that they are more important in extraction at temperatures higher than 100°C. Since the refraction index is directly related to polarizability, Table 6 classifies the solvents according in order of increasing refractive index measured at 20—25°C intervals, along with the extraction percentage. Except for raw shale in pyridine and acetic acid, and enriched shale in pyridine and cyclohexanol, the solubility of the organic substance increases relatively regularly with the refractive index, it may held that London intermolecular forces are dominant here.

TABLE 5

Dielectric Constant of Solvent and Solubility the Organic Substance of Raw and Enriched Shale

Solvent	Dielectric constant	% of total organic substance dissolved from	
		Raw shale	Enriched shale
Tetralin	2.757	32.10	74.56
Amyl acetate	4.75	5.10	10.70
Acetic acid	6.15	35.90	10.13
Pyridine	12.3	8.78	15.74
Cyclohexanol	15.0	38.66	80.98
n-Butyl alcohol	17.1	6.09	9.47
Nitromethane	35.87	1.21	3.65

(c) The higher solubility of the organic substance in these solvents can be ascribed to the building of hydrogen bonds, in addition to the higher temperatures and chemical effects. The solvents which boil relatively low, and are rather inert chemically, like ethoxyethanol or n-butyl alcohol, dissolve the organic substance perhaps mostly by forming H-bonds with active hydrogen or with an electronegative atom from the kerogen molecule.

(d) In acid solvents, such as acetic acid, or very weakly acid solvents like alcohols, the solubility is higher than in solvents boiling at approximately the same or even higher temperatures but which are chemically inert.

TABLE 6

Refractive Index of Solvent and Solubility of the Organic Substance from Raw and Enriched Shale

Solvent	Dielectric constant	% of total organic substance dissolved from	
		Raw shale	Enriched shale
Acetic acid	1.36995	35.90	10.13
Nitromethane	1.37947	1.21	3.65
n-Butyl alcohol	1.39922	6.69	9.47
Amyl acetate	1.40228	5.10	10.70
2-Ethoxyethanol	1.40751	11.52	26.51
Cyclohexanol	1.46055	38.66	80.98
Pyridine	1.5067	8.78	15.74
Tetralin	1.53919	32.10	74.56

As it might have been expected, the solubility of the organic substance of enriched shale exceeds (by about 1.5 times) that of the raw shale, except with petrol and acetic acid. The low solubility of the shale's organic substance can, therefore, be partly attributed to some kind of protective effect of the inorganic substance.

Table 2 shows that the C/H ratios of extracts of raw shale (6.43—7.34) and enriched shale (6.17—7.44) are below those of native kerogen (7.36)(1), with the exception of the tetralin extracts and the pyridine extract of enriched shale. The C/H ratios of extracts from enriched shale in most cases exceed those from raw shale.

The C/N ratio of the extracts from the raw shale extends over a wide range (6.28—112, nitrogen content 0.45% to 2.80%). The range for enriched shale is somewhat narrower (6.67—77.80, nitrogen content 0.85%—3.10%). Since the C/N ratio of native kerogen is 99.40(1), it can be said that all the extracts except those of petrol, tetralin and acetic acid, have a smaller C/N ratio, or are richer in nitrogen than kerogen itself.

The C/O + S ratio of the extracts differs both for raw and enriched shale (1.23—24.88 and 2.78—11.62 respectively). The C/O+S ratio of kerogen is around 3(1), so that most of the extracts are poorer in oxygen and sulphur than kerogen itself.

Ash (Table 2) after combustion of the extracts of low dielectric constant solvents, such as petrol, tetralin and amyl acetate, does not exceed 1%. Extracts of solvents with higher dielectric constants, notably nitromethane, n-butyl alcohol, cyclohexanol, pyridine, and acetic acid, leave more ash. The acetic acid extract of raw shale leaves most ash, 26.76%, as is expected, because the acid dissolves a considerable portion of the shale's inorganic substance (carbonates). Half the amount of ash is left by enriched shale acetic acid extract (12.64%).

The average molecular weights of extracts obtained with solvents of higher polarity are of the same order of magnitude, while that of the extracts obtained with non-polar petrol is higher. In solvents with higher polarity the number of hetero-atoms relative to carbon is higher in exctracts of enriched shale, while it is about the same in petrol extract.

It can be concluded from the study as a whole that the greater solubility of the organic substance of Aleksinac oil shale at temperatures higher than 100°C, and especially at over 160°C, than below 100°C, indicates that at these temperatures and in the presence of solvents the organic substance is partially degraded into products of lower molecular weight, which are more soluble. The determinations of elementary composition and average molecular weight of the extracts bear out this conclusion.

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Original Scientific Paper

SOLUBILITY OF ALEKSINAC OIL SHALE KEROGEN. III.

SOLUBILITY OF PREHEATED KEROGEN

by

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Although investigations of oil shales are often connected with obtaining crude oil or liquid fuels by pyrolysis, there is relatively little explanation of the changes of kerogen during heating and of intermediary products which occur before crude oil. We have investigated the changes of shale during pyrolysis both because of this and also to try and explain the chemical structure of kerogen.

The mechanism of pyrolysis was investigated in the past mainly through controlled heating of dry shale(1–7), and recently also by heating in the presence of solvents(8–11). In tests with dry shale, it was concluded that changes in kerogen were measurable only above 300°C, or between 300° and 400°C, and that they took place in clearly defined stages. During the first stage, by losing carbon dioxide and hydrogen sulfide, the kerogen transforms into insoluble bitumen, in the second stage the bitumen becomes soluble and more hydrogen sulfide and carbon dioxide are given off. In the third stage, soluble bitumen turns into a liquid product, and the fourth represents cracking of this oil. Cane(5, 6, 7) and other authors do not give full data on the products of individual stages, nor details of the nature of each transformation. However, they believe that in the first stage some depolymerization of the kerogen takes place, while the reactions in the other stages are of the thermal decomposition type. Cane(6) gives a scheme of torbanite kerogen decomposition:

He calls the conversion of kerogen to kerogen I a partial depolymerization during which kerogen decomposes into simpler fragments, and holds that the fragments crack during further heating.

The increased solubility of kerogen at temperatures about 200°C encouraged many authors to apply "thermal extraction" in pyrolytic studies at low temperatures. On heating shale in the presence of solvent, the changed kerogen can be separated immediately and secondary reactions which otherwise take place when dry shale is heated are avoided. Schnackenberg and Prien(10) hypothesized that in this way the products of first stage decomposition of kerogen could be extracted, i.e. before cracking. They applied solvents of various physical and chemical properties to the Colorado shale at temperatures of 200—300°C. They succeeded in obtaining different kerogen fragments with different amounts of nitrogen and sulphur and proved that these temperatures were sufficient to cause changes in the organic matter of the kerogen. Thompson and Prien(11) gave further details on the decomposition of kerogen in the presence of solvent. They calculated the enthalpies of pyrolysis, of dissolution and solvatization, and the enthalpy of the solute, on the basis of which they discuss the nature of bonds in kerogen, and the effect of the organic-inorganic ratio in the shale on pyrolytic decomposition.

Investigations have shown that in the presence of solvent, kerogen begins to change at considerably lower temperatures than was earlier thought.

In this study we investigated the pyrolytic changes of the organic substance of Aleksinac oil shale by determining the solubility (in some organic solvents) of the organic matter in the preheated dryshale. The shale was kept at 200°, 250°, 300° and 350°C for 10 hours, because it is known that the organic substance usually changes within this interval. This increased the solubility in organic solvents. The solubility of preheated shale is a function of temperature for the same time of preheating. Under the experimental conditions we judged that an equilibrium for changes in the organic matter was reached. After heating, the shale was Soxhlet-extracted and changes in solubility with temperature of preheating were investigated. The solvents used were benzene, acetone and methanol. From the changes in the solubility of organic substance with preheating temperature we calculated the order of magnitude of the heat of fragmentation during heating.

EXPERIMENTAL

Two samples were used: raw Aleksinac oil shale (—100 mesh, Tyler) (I) and enriched oil shale (II). Sample (II) was obtained by elimination of carbonates with hydrochloric acid (1 : 1). Organic matter determined after Jovanović and Vitorović(12) was 25.01% (I) and 35.89% (II).

A 500 *ml* stoppered flack, a condenser and a thermometer were placed in an eletric furnace with a rheostat for adjusting temperature. The apparatus is shown in Fig. 1. 200 *g* shale samples were heated for 10 h, counting from the moment one the specified temperature (200°, 250°, 300° or 350°C) was reached. Temperature was measured in the shale bed and in the oven. A difference between the temperature of the shale and the oven could not be avoided; the former was always about 10°C below the latter. The oven temperature was adjusted so as to maintain the required temperature in the shale.

During the heating a certain amount of distillate was obtained. The yield of distillate and the organic matter content of the residue are given in Table 1.

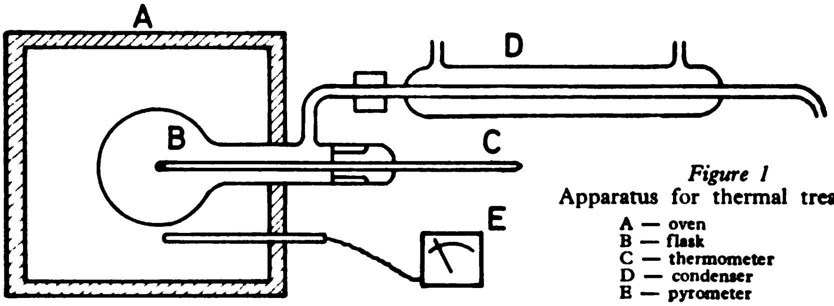

Figure 1
Apparatus for thermal treatment
A — oven
B — flask
C — thermometer
D — condenser
E — pyrometer

TABLE 1

Organic Matter Content of Thermally Treated Oil Shale Samples

Sample	Temperature (C°)	Distillate (%)*	Organic matter content of the residue
I_{200}	200	—	25.01
I_{250}	250	2.0	23.01
I_{300}	300	8.0	17.01
I_{350}	350	6.0	19.01
II_{200}	200	—	35.89
II_{250}	250	5.0	30.89
II_{300}	300	5.1	30.79
II_{350}	350	4.5	31.39

* Calculated relative to starting material

After heating, 25—35 *g* samples of residue were extracted in benzene, acetone or methanol in a Soxhlet apparatus for 70 h. The solvent was then removed by distillation and the residue weighed. Data on solubility are given in Fig. 2. Solubility was calculated with respect to initial organic substance.

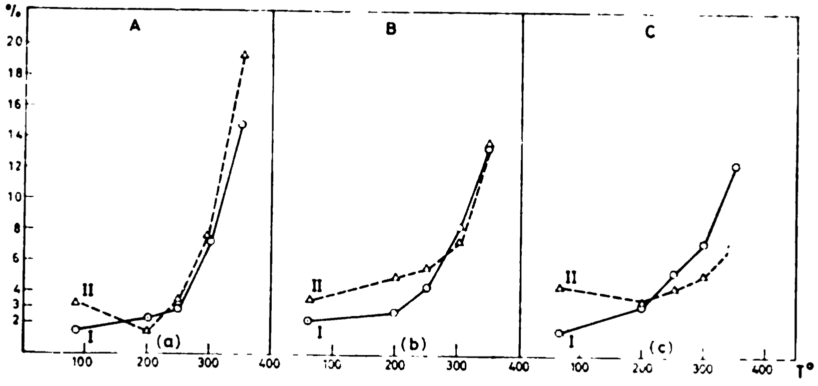

Figure 2
Solubility of the oil shale organic matter as a function of preheating temperature
A — benzene solvent, B — acetone solvent, C — methanol solvent
—⊙— (I) — raw shale
—△— (II) — enriched shale

DISCUSSION

From the curves in Fig. 2 it can be seen that the extraction yield in nearly all the solvents increases with preheating temperature, both for raw and enriched shale. During the heating of kerogen, fragments of different chemical nature occur, as may be presumed by the different yields of extraction with different solvents. Changes on heating depend on the amount of organic matter, as can be seen from the difference between the curves for the raw and enriched shale.

By analyzing the results for each solvent separately, the following may be ascertained:

(1) Solubility of the organic substance of the preheated shale is highest in benzene. With the raw shale sample, a big jump was registered in the 250—300°C range, and with enriched shale in the range 300—350°C. It is noteworthy that the amount of organic substance extracted from the enriched shale at 200°C is less in this case. The yield begins to increase at 300°C, and at 350°C more extract is obtained from the enriched sample.

(2) The solubility in acetone increases with temperature. At 200°C it increases little, but after 250°C it rises abruptly. A marked change in solubility was produced by treating raw shale at 300°C, which means that fairly appreciable decomposition of kerogen took place in the 250—300°C range. With the enriched shale the increase in solubility appears in the 300—350°C range. Extracts from samples I_{350} and II_{350} show that yields at this temperature do not depend on the amount of organic substance in the shale, because the same yields were obtained from both samples.

(3) Solubility in methanol shows the least increase with temperature of pretreatment. In this case, unlike the two previous cases, an abrupt increase in yield was not registered. A certain rise occurs at 300—350°C, more with raw than with enriched shale. Here again, the solubility of enriched shale preheated at 200°C was reduced.

It can be concluded from the results that the greatest change in solubility of raw shale occurs within the 250—300°C range. With the enriched shale some regularities appear up to 250°C, and the main solubility increase occurs above 300°C. It is inferred that heating the shale at lower temperatures causes changes depending on the inorganic content, which agrees with the studies of Prien and Thompson(11). They explain the phenomenon by the existence of a large number of "weak" bonds in poor shale (i.e. the binding energy of bonds between the organic and inorganic components is of a lower order than that of the bonds in the organic part); these bonds can be broken more easily and allow higher yields. The phenomenon in our case can be explained thus: during enriching, unlike in naturally rich shales, some kind of "stabilization" of the organic substance takes place, which is then less soluble when preheated at lower temperatures. This stabilization could be the reason for the "inversion" on solubility.

In Table 2, solubility is given as the ratio between dissolved and undissolved organic substance (apparent equilibrium constant). On the basis of these values change of solubility with preheating temperature was studied. It can be seen that two types of change take place on heating: changes up to 300°C and those above 300°C. The changes at lower temperatures are

TABLE 2

Ratio between Dissolved and Undissolved Organic Matter of Thermally Treated Raw and Enriched Oil Shale

Temperature C°	Raw shale	Enriched shale
	Solvent: *benzene*	
—	$1.57 \cdot 10^{-2}$	$3.32 \cdot 10^{-2}$
200	$2.25 \cdot 10^{-2}$	$1.53 \cdot 10^{-2}$
250	$3.10 \cdot 10^{-2}$	$3.63 \cdot 10^{-2}$
300	$8.04 \cdot 10^{-2}$	$8.06 \cdot 10^{-2}$
350	$17.60 \cdot 10^{-2}$	$23.75 \cdot 10^{-2}$
	Solvent: *acetone*	
—	$2.41 \cdot 10^{-2}$	$3.89 \cdot 10^{-2}$
200	$2.97 \cdot 10^{-2}$	$5.71 \cdot 10^{-2}$
250	$4.47 \cdot 10^{-2}$	$6.04 \cdot 10^{-2}$
300	$9.06 \cdot 10^{-2}$	$7.85 \cdot 10^{-2}$
350	$15.90 \cdot 10^{-2}$	$16.08 \cdot 10^{-2}$
	Solvent: *Methanol*	
—	$1.69 \cdot 10^{-2}$	$4.68 \cdot 10^{-2}$
200	$3.40 \cdot 10^{-2}$	$3.96 \cdot 10^{-2}$
250	$6.18 \cdot 10^{-2}$	$4.94 \cdot 10^{-2}$
300	$8.11 \cdot 10^{-2}$	$5.40 \cdot 10^{-2}$
350	$14.29 \cdot 10^{-2}$	$8.31 \cdot 10^{-2}$

different in raw and enriched shale, while those at higher temperatures are similar. Then we found the order of magnitude of the heat of fragmentation during heating. For all the solvents used, it ranges within 4—8 *kcal/mole*. From this it can be maintained that the fragments do not originate by cleavage of the main valency bonds for which much more energy would be necessary, but that the cleavage of secondary bonds is involved.

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COULOMETRIC DETERMINATION OF SOME QUINOLINE COMPOUNDS

by

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A previous study(1) reviewed the coulometric determination of some pyridine bases in acetonitrile, based on Streuli's method(2). Continuing our study on the possible coulometric titration of heterocyclic bases we have attempted to quantitatively determine the following compounds: quinoline, 2-, 4-, 6-, 7- and 8-methylquinoline, 6- and 8-methoxyquinoline, 8-hydroxyquinoline, 8-hydroxyquinaldine 6- and 8-nitroquinoline, and 5,6-benzoquinoline. All these compounds are weak bases. Coulometric titration was conducted in acetonitrile solution, by Streuli's procedure(2) to avoid solvolysis, because these compounds are more basic in acetonitrile than in water.

Previous investigations showed that the presence of quinoline compounds in acetonitrile does not interfere with the electrochemical generation of hydrogen ions, which takes place at 100% current efficiency. Under the given conditions of coulometric titration, the quinoline compounds and their neutralized products do not react electrochemically, nor were any other interfering reactions detected.

EXPERIMENTAL

The reagents and other chemicals and their purification and the apparatus were the same as described in a previous paper on the coulometric titration of pyridine.

6-, 7- and 8-methylquinoline were obtained by synthesis, 6- and 8-methoxyquinoline from Bayer, Leverkusen, and the other compounds from BDH. The synthesized compounds had the specified physical constants.

Procedure. — The end point of titration was determined coulometrically on a potentiometer, by titrating the solution up to the definite potential. The selected potential was within the range of the biggest potential changes registered during coulometric titration of pure anolyte. This range was 300—350 *mV*, and 305—315 *mV* was taken as the end point.

TABLE 1

Titrated substance	(Taken *mg*)	No. of titrations	Found
2-Methylquinoline	10.00	6	10.05±0.013*)
4-Methylquinoline	10.00	6	10.08±0.018
6-Methylquinoline	10.00	6	10.08±0.022
7-Methylquinoline	10.00	6	10.07±0.023
8-Methylquinoline	10.00	6	10.08±0.025
6-Methoxyquinoline	10.00	6	10.06±0.052
8-Methoxyquinoline	10.00	6	9.96±0.042
8-Hydroxyquinoline	10.00	6	10.09±0.022
8-Hydroxyquinaldine	10.00	6	10.09±0.033
6-Nitroquinoline	10.00	6	10.08±0.014
8-Nitroquinoline	10.00	6	10.08±0.023
5,6-Benzoquinoline	10.00	6	10.03±0.014
Quinoline	10.00	6	9.99±0.021

*) Standard deviation of the mean.

For the coulometric determination, 0.1 *ml* 10% solution of the quinoline compound in acetonitrile was made up immediately before use. Before the investigated substance was added to anolyte, current was passed through the latter until a potential in the range 305—315 *mV* was reached. After the addition of 0.1 *ml* solution of the substance, the potential fell, and was then restored by passing a current of 30 *mV*. As the end point potential is approached the current must be passed in short bursts, so as to come up to the desired potential accurately. Because of the slow establishment of potential, the current should be stopped from time to time to allow it to steady and then continued in short bursts.

From the duration and strength of the current, the amount of the quinoline compound can be calculated by Faraday's laws.

DISCUSSION

The results of determinations by the coulometric procedure are shown in Table 1. They show that this method is satisfactorily accurate. The results are reproducible and deviations small. Satisfactory results were not obtained with 2-chloroquinoline and 6-methoxy-4-cyanoquinoline. The presence of chlorine or the cyanogen group reduces the basicity of the quinoline ring, thus preventing the determination of these compounds in an acetonitrile solution. The addition of these substances to the anolyte caused only small changes in potential, which affected the accuracy of determination.

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