SRPSKO HEMIJSKO DRUŠTVO (BEOGRAD)

BULLETIN OF THE CHEMICAL SOCIETY
Belgrade

(Glasnik Hemijskog društva — Beograd)
Vol. 29, No. 1-2, 1964

Editor:
MILOŠ MLADENOVIĆ

Published by
SRPSKO HEMIJSKO DRUŠTVO (BEOGRAD)
1965.

Translated and published for U. S. Department of Commerce and
the National Science Foundation Washington, D. C., by
the NOLIT Publishing House, Terazije 27/II, Belgrade, Yugoslavia
1965

Translated by
DANICA LADJEVAC and ALEKSANDRA STOJILJKOVIĆ

Edited by
PAUL PIGNON

Printed in Beogradski Grafički Zavod, Belgrade

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CONTRIBUTION TO THE COULOMETRIC DETERMINATION OF SULFONAMIDES

by

RADOMIR M. POPOVIĆ, KOSTA J. NIKOLIĆ and ZORA T. BLAGOJEVIĆ

The literature describes numerous methods for the determination of sulfonamides using the characteristics of the benzene nucleus, and the presence of the — SO_2, SO_2NH_2 and NH_2 groups.

The pharmacopoeial procedures for the determination of sulfonamides and their salts mainly refer to the reactions of diazotizing, bromizing, neutralization and titration in an anhydrous medium.

In selecting a method for determining sulfonamides we decided on coulometry because it has certain advantages over the conventional volumetric titration.

Coulometry is a precise and reliable method especially for determinig small quantities. It does not require the preparation of titrimetric solutions. The reaction rate may be changed and therefore it requires more accuracy in adding the reagents. The apparatus used is simple and the procedure is economical of time the reagents.

Sykut(1) performed the coulometric titration of solfonamides with a solution of potassium bromide in hydrochloric acid at pH 2 — 2.5.

Sulfonamides, as weak organic acids, dissociate in aqueous solutions giving an H^+ ion which can be neutralized with a base. We made use of this in our experiments.

The mechanism of the reaction is as follows:

$$H_2N—C_6H_4—SO_2NHR \rightleftarrows (H_2N—C_6H_4—SO_2\overline{N}R)H^+ \qquad (1)$$

$$H_2N—C_6H_4—SO_2\overline{N}R/H^+ + NaOH \rightleftarrows (H_2N—C_6H_4SO_2—\overline{N}R)Na^+ + + H_2O \qquad (2)$$

The reaction of the salts obtained is alkaline in aqueous solution, except for sodium salts of sulfathiourea whose reaction is neutral.

Since the characteristics of the sodium salts of sulfonamides allow them to be determined acidimetrically we applied coulometric titration to them too.

The reaction that proceeds in the solution can be expressed as follows:

$$2(H_2N—C_6H_4—SO_2\overline{N}R)Na^+ + 2H^+ + SO_4^{=} \rightleftarrows 2(H_2N—C_6H_4— —SO_2NR)H^+ + Na_2SO_4 \qquad (3)$$

EXPERIMENTAL

Reagents

— Ethanol $96^{0}/_{0}$

— Solution of sodium sulfate 1 M (322.21 g sodium sulfate + + $10H_2O$ dissolved in water and made up to one 1000 ml with water).

— Thymolphthalein (i):(0.3 g dissolved in 100 ml of $96^{0}/_{0}$ ethanol).

—m-Nitrophenol (i):(0.3 g dissolved in 100 ml of water).

— Methyl-red (i):(0.1 g dissolved in 100 ml of $70^{0}/_{0}$ ethanol).

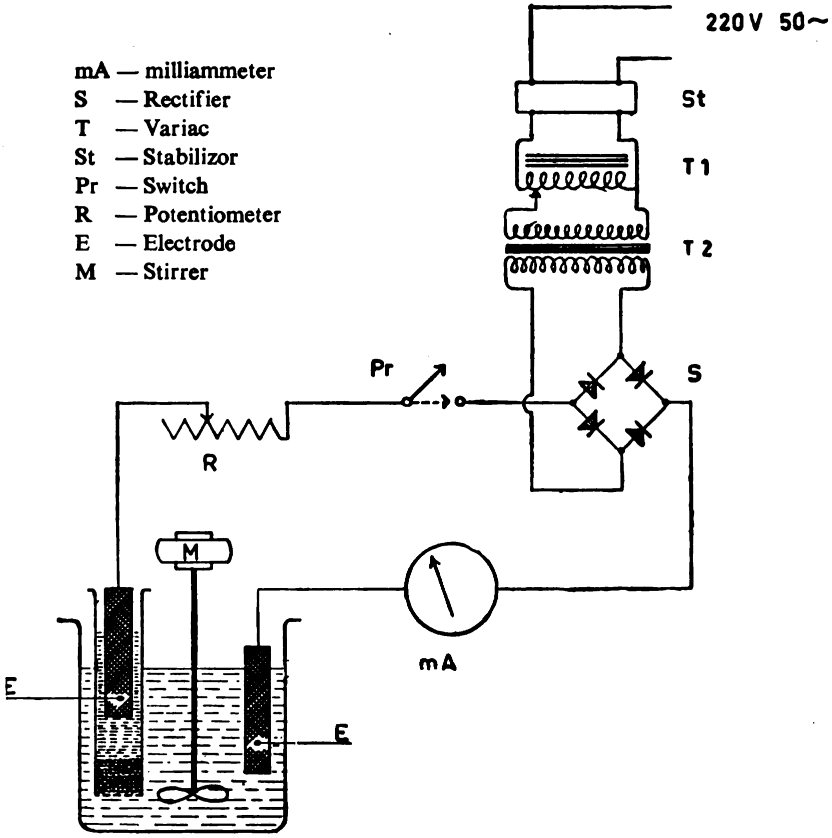
— 0.01 N sodium hydroxide solution

— 0.01 N hydrochloric acid solution.

For determining sulfonamides we used pure substances which are used as raw materials for the production of galenic sulfonamide drugs.

Apparatus

The apparatus is shown in Fig. 1.



mA — milliammeter
S — Rectifier
T — Variac
St — Stabilizor
Pr — Switch
R — Potentiometer
E — Electrode
M — Stirrer

Fig. 1.

The d.c. was obtained from a selenium pile rectifier, regulation transformer and stabilizer, connected to the 220 V network. The regulation transformer and a variable resistor were used to adjust the voltage and the current. The current range was 1—100 mA.

A Chavin Arnoux milliammeter measured the current. The electrodes were of platinum. The cathodic and anodic spaces were connected via a small flask with a porous bottom covered with a thin layer of agar-agar and potassium nitrate.

The current flow time was measured with a chronometer to an accuracy of 0.2".

Procedure

(a) *Determination of sulfonamides*

A solution of 10 mg of sulfonamide is pipetted into the cathodic space of the flask and 10 ml 1 M sodium sulfate an 2 drops of the corresponding indicator are added. The solution is stirred and a constant current is passed until color change of the indicator.

A blank run is also made simultaneously (ethanol, sodium sulfate solution and the indicator).

The quantity of sulfonamide is calculated from the equation

$$g = \frac{E i t}{96.500} \tag{4}$$

where

$g =$ quantity of sulfonamide

$E =$ chemical equivalent

$i =$ current

$t =$ current flow time

b) *Determination of sodium salts of sulfonamides*

A volume of solution of the sodium salts containing 10 mg of the salt is pipetted into the anodic space and 10 ml 1 M sodium sulfate and 2 drops of a corresponding indicator are added. A constant current is passed through the solution until the indicator changes in color.

In parallel with the coulometric titrations we determined the sulfonamides volumetrically with 0.01 N sodium hydroxide. The sodium salts were titrated with 0.01 N hydrochloric acid. The indicators used were the same as in the coulumetric titrationis. The results are shown in tables 1,2,3,4,5,6,7,8 and 9.

TABLE 1

2 — (sulfanilamine)—4,6—dimethylpyrimidine (sulfamethazine) 0.5 g dissolved in 100 ml $96^{0}/_{0}$ *ethanol. Indicator — thymolphthalein*

Pipetted mg	Found by coulometry, mg	Found by volumetric method, mg
10	10.02	10.02
10	10.02	10.02
10	10.05	10.03
10	10.05	10.03
10	10.02	10.02
10	10.02	10.02
10	10.05	10.03
12	12.01	12.03
12	12.01	12.03
12	12.01	12.03

TABLE 2

2 — (sulfanilamine)—4—methylpyrimidine (sulfamerazine) 0.200 g dissolved in 100 ml of $96^{0}/_{0}$ *ethanol. Indicator — thymolphthalein.*

Pipetted mg	Found by coulometry, mg	Found by volumetric method, mg
10	10.02	10.03
10	10.02	10.03
10	9.99	9.99
10	10.02	10.03
10	10.02	10.03
10	10.02	9.99
10	9.99	9.99
12	10.03	12.03
12	12.03	12.01
12	11.95	12,01

TABLE 3

2 — (sulfanilamine)—thiazol (sulfathyiazol) 1 g dissolved in 100 ml $96^{0}/_{0}$ ethanol.
Indicator — thymolphthalein

Pipetted mg	Found by coulometry, mg	Found by volumetric method, mg
10	9.99	10.00
10	9.99	10.00
10	10.03	10.05
10	10.03	10.05
10	9.99	10·00
10	10.03	10.05
10	9.99	10.00
15	15.15	15.08
15	15.15	15.08
15	15.12	15.08

TABLE 4

2 — (sulfanilamine thioured (sulfathiourea) 0.5 g dissolved in 100 ml $96^{0}/_{0}$ ethanol
Indicator — m—nitrophenol

Pipeted mg	Found by coulometry, mg	Found by volumetric method, mg
10	10.08	10.10
10	10.05	10.03
10	10.08	10.10
10	10.08	10.10
10	10.08	10.10
10	10 08	10.03
10	10.08	10,03
12	12.07	12.07
12	12.07	12.07
12	12.07	12.03

TABLE 5

2 — (sulfanilamine)—methylthiazol (sulfazol) 1 g dissolved in 100 ml 96% ethanol. Indicator — thymolphthalein

Pipetted mg	Found by coulometry, mg	Found by volumetric method, mg
10	10.00	9.99
10	10.00	9.99
10	9.97	9.96
10	10.00	9.99
10	9.97	9.96
10	9.97	9.99
10	10.00	9.99
12	11.97	11.96
12	11.97	11.96
12	11.97	11.90

TABLE 6

3 — (sulfanilamine)—2—phenylpyrazol (sulfaphenazol, Plisulphan) 0.5 g dissolved in 100 ml 96% ethanol. Indicator — thymolphthalein

Pipetted mg	Found by coulometry, mg	Found by volumetric method, mg
10	9.87	9.87
10	9.89	9.90
10	9.89	9.90
10	9.87	9.87
10	9.89	9.90
10	9.89	9.87
12	11.86	11.83
12	11.86	11.87
12	11.86	11.83
10	9.89	9.87

TABLE 7

Sulfanilacetamide—sodium (sulfacetamide sodium) 1 g dissolved in 100 ml distilled water. Indicator — methyl red

Pipetted mg	Found by coulometry, mg	Found by volumetric method, mg
10	10.02	9.97
10	10.02	9.97
10	10.05	10.02
10	10.02	9.97
10	10.05	10.02
10	10.05	10.02
10	10.02	9.97
12	12.01	12.00
12	12.01	12.00
12	12.01	12.05

TABLE 8

2 — (sulfanilamine—) pyrimidine sodium (sulfadiazine sodium) 1 g dissolved in 100 ml of water. Indicator — methyl red

Pipetted mg	Found by coulometry, mg	Found by volumetric method, mg
10	10.01	10.07
10	10.01	10.07
10	9.98	10.01
10	9.98	10.01
10	9.98	10.01
10	9.95	10.01
10	9.95	10.01
12	12.01	12.08
12	12.01	12.08
12	11.98	12.11

TABLE 9

2 — (sulfanilamine) — thiazol sodium (sulfathiazol sodium) 1g dissolved in 100 ml of water. Indicator — methyl red

Pipetted mg	Found by coulometry, mg	Found by volumetric method, mg
10	10.50	10.48
10	10.50	10.48
10	10.50	10.48
10	10.47	10.45
10	10.47	10.45
10	10.47	10.45
10	10.47	10.48
15	15.75	15.72
15	15.72	15.72
15	15.72	15.70

DISCUSSION

The tables show good agreement between the coulometric and volumetric results. Hence, we may conclude that the presence of the sulfonamide and its neutralization products does not influence the electrochemical reactions, and hydrogen and hydroxyl ions are produced with 100 percent current efficiency.

Since the sulfonamides investigated have different dissociation constants different indicators were used. The indicator was chosen so that the end-point should be as close to the equivalence point as possible. The influence of ethanol on dissociation of the indicator was negligible so that no corrections were necessary.

The results of the coulometric determinations are within the errors permitted by the Yugoslav Pharmacopeia, so the method may be recommended for quick precise determination of small quantities of sulfonamides.

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GLASNIK HEMIJSKOG DRUŠTVA, Vol. 29, No. 1—2, 1964, pp. 11—15.

AMPEROMETRIC DETERMINATION OF HYDROCHLORIC ACID USING THE BISMUTH-BISMUTH BIMETALLIC PAIR

by

MOMIR S. JOVANOVIĆ and RADOSLAV V. BABIĆ

In addition to the glass electrodes which is mainly used in pH-determinations, antimony and bismuth electrodes are also often used as indicator electrodes. The amperometric technique with two identical or two different electrodes, on account of its simplicity and because it does not require constructing titration curves, is now acquiring increasing application. Therefore, it is not surprising that bismuth and antimony have been used in attempts to perform neutralization titrations using bimetallic pairs of these metals with other metals. Thus in 1928, Fuoss$^{(1)}$ studied the applicability of bismuth paired with silver as a bimetallic indicator pair in titrations of hydrochloric acid with sodium hydroxide. In the same year, Franke and Willaman$^{(2)}$ investigated the dependence of the EMF of an antimony-amalgam copper pair on the pH of the solution. A significant contribution to the knowledge of the behavior of bimetallic systems in neutralization titrations was recently made by Stock and Purdy$^{(3)}$, who for the first time applied the system of identical indicator electrodes (antimony-antimony pair) in alkalimetric titrations of some strong and weak acids.

Since there are no reports in the literature on the application of the bismuth-bismuth bimetallic pair to the neutralization systems, we have started investigations attempting to use this as the end-point detecting system in the titration of hydrochloric acid with sodium hydroxide.

EXPERIMENTAL

Solutions. The titrations were carried out with n/10 solution of hydrochloric acid, made from concentrated acid (p.a. C. Erba). It was standardized in the usual way by titrating a weighed amount of anhydrous sodium carbonate (p.a., E. Merck). Thus it was found that

$$T_{HCl} = 3.601 \text{ mg/ml}.$$

The standardized acid was used to standardize an n/10 sodium hydroxide (p.a. Chemapol) solution which was to be used as the titrant. It was found that

$$T_{NaOH} = 4.034 \text{ mg/ml}.$$

Apparatus. The indicator electrodes were made by inserting two rods of metallic bismuth into glass tubes which were as narrow as possible, so that lmm of the metal protruded out of the tube. The electrodes were fixed to the glass tube by means of glue resistent to water, dilute acids and bases. The bismuth was connected to the electrical circuit by means of a few drops of mercury.

The elements of the electric circuit were connected as shown in Fig. 1. By means of a potentiometrically connected resistor, the voltage from an accumulator battery was adjusted so that the current between the bismuth electrodes in the solution was 15 μA.

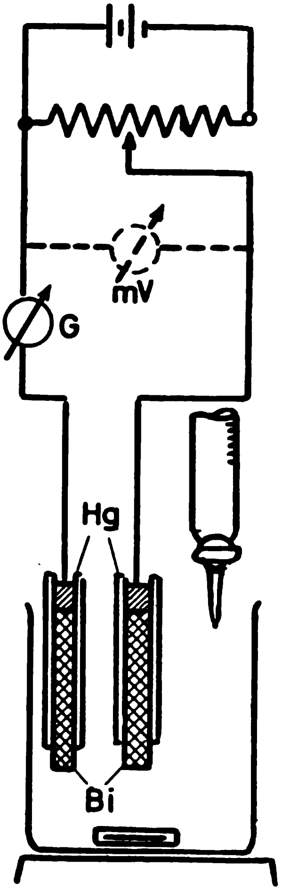

Fig. 1

The titrations were carried out at room temperature in a 100 ml beaker. The solutions were stirred with a magnetic stirrer.

Method. To obtain a current of 15 μA between the electrodes of the bimetallic pair it is necessary to apply an external voltage of some hundreds of mV to the electrodes. This voltage depends on the surface area of the electrodes and the dilution of the solution, and therefore it need not necessarily be measured. The essential point is that the electrodes cannot be polarized equally by such a small voltage between them. The electrode which is more polarized will behave as an indicator electrode and the other as a standard electrode(4).

Bismuth electrode is known to be a redox electrode and its responsiveness to changes of the pH of the solution is based on the reduction of the oxide coating to metallic bismuth in acid media:

$$Bi(OH)_3 + 3\,H^+ + 3\,e = Bi^\circ + 3\,HOH$$

In the titration of acids, with decreasing acidity of the solution, the possibility of reduction to metallic bismuth decreases so the current at the electrode falls (cathode). The current drop for a given increment of the titrant will be greatest just before the titration end-point. When the end-point is reached, the other electrode will start functioning as an indicator. With increasing alkalinity of the solution the anodic oxidation of bismuth to the ionic state will occur, and this will result in an increase of the anodic current. A qualitative graph of the titration curve is shown in Fig. 2.

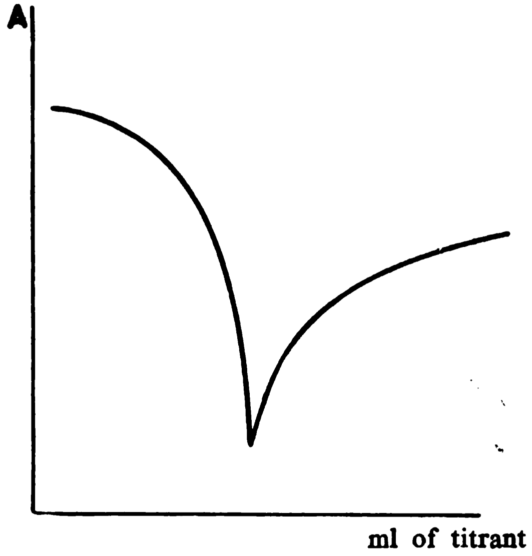

Fig. 2

Accordingly, the titration end-point is reached when the galvanometer deflexion is maximal.

Table 1 shows some results of a series of determinations of n/10 hydrochloric acid by titrating it with n/10 sodium hydroxide.

TABLE 1

No.	Taken mg HCl	Consumed ml NaOH	Found mg HCl	Difference in mg	Error %
1.	3.601	0.970	3.565	— 0.036	— 1.0
2.	3.601	0.978	3.597	— 0.004	— 0.1
3.	10.803	2.950	10.849	+ 0.046	+ 0.42
4.	10.803	2.920	10.741	— 0.062	— 0.56
5.	18.005	4.940	18.170	+ 0.165	— 0.9
6.	18.005	4.851	17.839	— 0.166	— 0.9

Only maximal deviations are shown

School of Chemical Engineering
Institute of Analytical Chemistry
Beograd

Received, May 21st, 1964

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GLASNIK HEMIJSKOG DRUŠTVA, Vol. 29, No. 1—2, 1964, pp. 17—22.

CALIBRATION CURVES FOR THE QUANTITATIVE X—RAY DIFFRACTION ANALYSIS OF Sb_2O_3, Sb_2O_4 AND Sb BY THE INTERNAL STANDARD METHOD

by

VERA RAJKOVIĆ

In 1895 Röntgen discovered X-rays, and in 1919 Hull(1) pointed out the simplicity and advantage of X-ray analysis over the chemical analysis of powders. However, it was not until 1936 that Clark and Reynolds(2) adapted the internal standard method, previously used in optical spectroscopy, for X-ray determination of quartz in mine dust.

At first a film technique was used. In 1945 the Norelco X-ray diffraction spectrometer appeared(3), allowing more precise quantitative analysis of powder mixtures. Soon after, H. P. Klug, L. E. Alexander and E. Kummer published a series of papers on the use of this spectrometer, preparing specimens and the theory of the method(4—9).

The purpose of the present work was to investigate whether quantitative X-ray diffraction analysis of antimony compounds is possible and to plot calibration curves for their determination.

EXPERIMENTAL

Apparatus. — All X-ray measurements were made on an Isodebyreflex I apparatus, product of R. Seifert, Hamburg, with a Berthold goniometer and an automatic recorder. The apparatus worked under the following conditions:

X-ray tube with two Lindeman windows and a Cu anode.

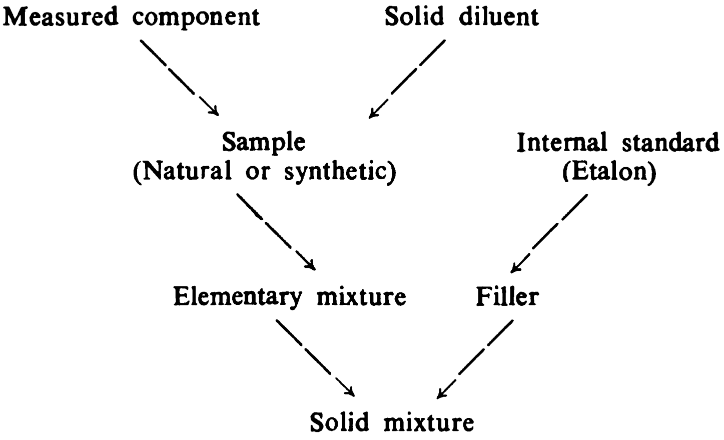
Voltage 4 OkV, current 20mA.

GM counter type IZ = 10, scanning speed 1° O/min

Maximum strength height 1000 counts/sec

Preparation of specimens. The specimens were made by Kay's method(10) modified to be suitable for most of powdered materials(11). The method consists in dispersing 0.4 g of solid mixture in a certain quantity of a dispersion medium and spreading a some of this suspension over a 4 cm^2 slide. 0.4 g of solid mixture was dispersed in 2 ml of the dispersion medium, and 0.08 ml of the suspension was put on each slide.

Solid mixtures of all three measured components were prepared as shown schematically below:



In the solid mixtures, the same substance amorphous silica dioxide, was used as the diluent and filler for all three measured component. The ratio of the filler to the elementary mixture was 1 : 1. The ratio of the specimen to the internal standard (etalon) varied with each measured component. It was determined experimentally by X-rays, and had to be such that the line intensity of the measured component was at least twice that of the internal standard.

The components were mixed and the mixture homogenized by stirring three times with ether until complete evaporation in an agate mortar with a ball pestle.

Dispersion medium. — Microscopic(12) and visual observation of the sedimentation(13, 14, 15) and the quality of the specimens showed that a mixture of 8 volumes of iso-amyl acetate, 4 volumes of ethyl alcohol and 3 volumes of 4% colodium in ether is most suitable for mixtures containing Sb_2O_3. Usually a large quantity of this dispersion medium is made and kept in a bottle tightly stoppered with a rubber bung.

Determination of I/I_s *and plotting the calibration curve.* — In the internal standard method the calibration curve is a plot of I/I_s against the percentage concentration of the measured component, where:

I = maximum intensity diffracted by the measured component
I_s = maximum intensity diffracted by the internal standard.

These two values were determined for each specimen and each concentration of the measured component.

For each measured component I/I_s was determined for five concentrations, 20 — 100%, of the measured component. Three specimens were taken from each mixture and three recordings were made for each specimen, each on a different place on the specimen. Hence each I/I_s value represents an average of mine measurements.

RESULTS AND DISCUSSION

In the solid mixtures from which specimens were made for plotting calibration curves for Sb_2O_3, Sb_2O_4 and Sb, the three substances were combined as measured components and as internal standards. This was practicable because the main lines of their diffraction series are close but do not coincide:

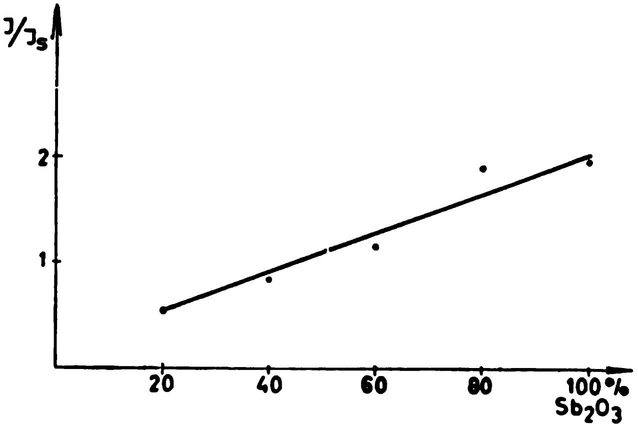


Fig. 1 — Calibration curve for quantitative determination of Sb_2O_3

Main line for Sb_2O_3 $\Theta_{Cu} = 13.84°$
„ „ „ Sb_2O_4 $\Theta_{Cu} = 14.54°$
„ „ „ Sb $\Theta_{Cu} = 14.38°$.

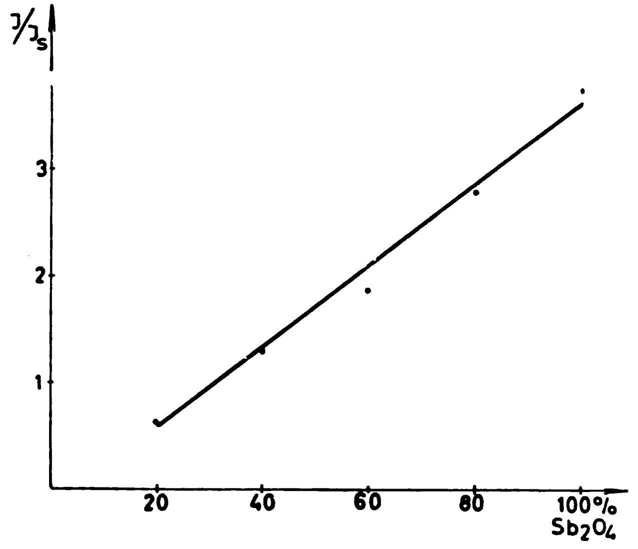


Fig. 2 — Calibration curve for quantitative determination of Sb_2O_4

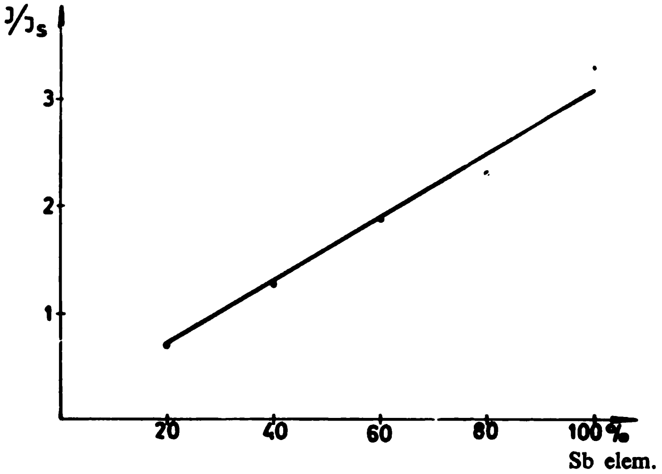


Fig. 3 — Calibration curve for quantitative determination of Sb

To specimens in which Sb_2O_3 was the measured component elementary antimony was added as the internal standard, in the following proportion:

$$(Sb_2O_3 + SiO_2) : Sb = 1 : 1.$$

To specimens in which Sb_2O_4 was the measured component, Sb_2O_3 was added as the internal standard in the proportion

$$(Sb_2O_4 + SiO_2) : Sb_2O_3 = 12 : 1.$$

To specimens in which Sb was the measured component, Sb_2O_3 was added as the internal standard in the proportion

$$(Sb + SiO_2) : Sb_2O_3 = 8 : 1.$$

The three calibration curves obtained for the solid mixtures are shown in Fig. 1, 2, and 3. All the curves are linear and can be used for the quantitative determination of Sb_2O_3, Sb_2O_4 and Sb in powdered material when the concentration of the measured component is between 20—100%.

The scattering of the points is smallest for Sb_2O_3. For Sb_2O_4 and Sb it is slightly greater does not exceed that for quartz obtained by other authors.

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GLASNIK HEMIJSKOG DRUŠTVA, Vol. 29, No. 1—2, 1964, pp. 23—28.

SEDIMENTATION INFLUENCE ON CALIBRATION CURVES FOR X-RAY DIFFRACTION ANALYSIS OF SOME ANTIMONY COMPOUNDS.

Part I. — INFLUENCE OF QUANTITY QF SUSPENSION PER SPECIMEN ON THE I/I_s RATIO

by

VERA RAJKOVIĆ

Many authors[1-4] have investigated the possibility of precise determination of quartz in mine dust by quantitative X-ray diffraction analysis. The results have been interpreted in different ways. H. P. Klug and co-authors[5,6] classified the prevailing methods in three groups according to the composition and absorption properties of the tested material:

1. If the tested material contains n components whose absorption coefficients are equal, direct analysis, i.e. direct determination of the concentration of one of its components, is possible. In such cases the concentration is proportional to the diffracted intensity I. The calibration curve is a straight line.

2. If the mixture contains two components (binary system) whose absorption coefficients are different, the concentration of the determined component is not proportional to the diffracted intensity. Here, calibration curves must be plotted of the dependence of the ratio $I/(I)_0$ on the % concentration of the component determined. I is the X-ray intensity diffracted by the determined component in the tested material, $(I)_0$ is the intensity diffracted by the pure determined component.

3. If the mixture contains n components whose absorption coefficients are different, a given quantity of an internal standard or etalon substance is added to a sample. Direct analysis is not possible in this case either, so calibration curves must be plotted of the dependence of I/I_s on the % concentration of the determined compound. Here I is the intensity diffracted by the determined compound and I_s that diffracted by the internal standard in the same specimen.

The plotting of calibration curves for quantitative X-ray analysis of some antimony compounds in powdered material required extensive and varied investigations because a slight change in one of the conditions in making specimens often caused a change in the shape and position of the calibration curve.

The purpose of this work was to find out the optimal conditions for plotting calibration curves for the quantitative determination of antimony trioxide by the internal standard method. To determine these conditions we made suspensions containing different volumes of the dispersion medium per 0.4 g of the powdered material, applied different volumes of the suspension to slides of the same area, and then observed the changes in I/I_s ratio and the shape of the calibration curves.

EXPERIMENTAL

The technique for making synthetic samples, mixtures of suspensions and specimens is presented in another paper(7). It is the same throughout this series of investigations dealing with the problem of obtaining good calibration curves for the quantitative determination some antimony compounds in a powdered material by X-ray diffraction analysis.

X-ray measurements were made with an Isodebyeflex I apparatus produced by R. Seifert, Hamburg.

Solid powder mixtures had the following composition:

$$(Sb_2O_3 + SiO_2) : Sb = 1 : 1 \text{ (without filler).}$$

Dispersion medium for making the suspension was obtained by mixing 8 volumes of isomylacetate, 4 volumes of ethyl alcohol and 3 volumes of 4% colodium in ether. Usually a large quantity of the dispersion medium was made and kept in a bottle tightly stoppered with a rubber bung.

Dilution of suspension: 0.4 g of powdered material per 1—2.5 ml of the dispersion medium.

Quantity of suspension per slide, was the amount of suspension needed to cover a 4 cm² slide, made by cutting a microscope slide in three equal pieces.

Results of X-ray measurements

All investigations were performed with mixtures of the composition

$$(Sb_2O_3 + SiO_2) : Sb = 1 : 1$$

and concentrations of 20—100% Sb_2O_3. Four suspensions were made from each mixture by dispersing 0.4 g of the powdered material in 1—2.5 ml of the dispersion medium. Three specimens were made of each suspension with 0.08 ml and 0.16 ml of the suspension per slide. Each specimen was X-rayed in three positions on the holder of a goniometer, so that the I/I_s ratios (are averages) of 9 measurements of 3 specimens.

DISCUSSION

The calibration curves in Fig. 1 show the dependence of I/I_s on the % concentration of Sb_2O_3 when the dilution of the suspension is 0.4 g of powdered material per 1.5 ml of the dispersion medium and when the specimens are made of 0.08 ml and 0.16 ml of

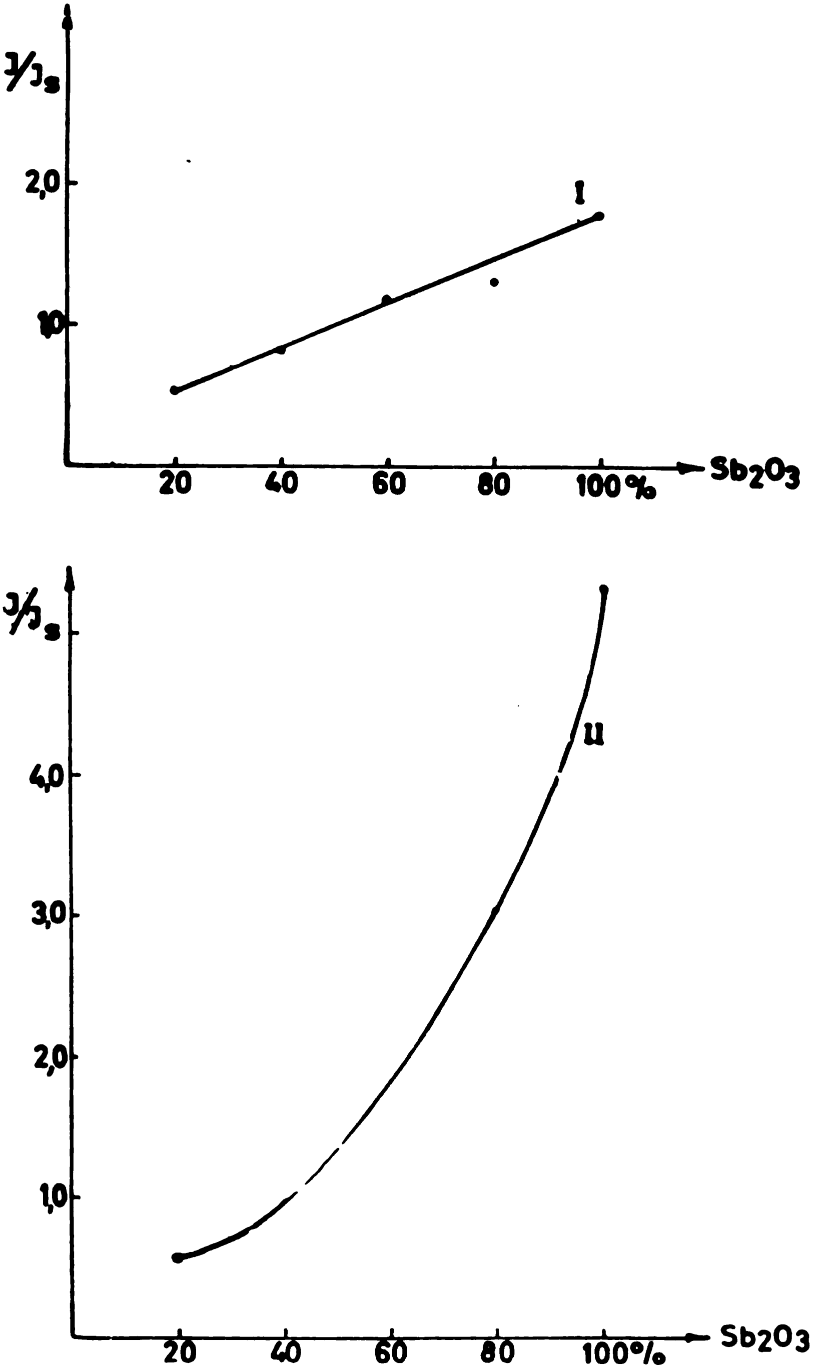

Fig. 1 — Intensity ratio—concentration calibration curves for the determination of Sb_2O_3

suspension. Curve I was plotted for the 0.08 ml specimens and curve II for the 0.16 ml specimens. Curve I is linear course and curve II is exponential. The curves obtained for the other dilutions were very similar.

An attempt was made to interpret the I/I_s changes with change in the quantity of suspension per slide by the "absorption theory" of L. E. Alexander and H. P. Klug. According to this theory, if the mixture contains *n* components with different absorption coefficients, the line of the component that absorbs weakest will be weaker and, vice versa, the line of the component that absorbs strongest will be stronger(8).

The mass absorption coefficients of the components of the tested mixtures are given in Table 1. According to the absorption theory, the line for Sb, whose mass absorption coefficient is higher would be the stronger, while the Sb_2O_3 line would be the weaker. However, for specimens made from mixtures in which Sb_2O_3 and Sb were equal in weight, the I/I_s, i.e. $I_{Sb_2O_3}$ I_{Sb} ratios show that the intensity of the antimony trioxide is the stronger. We hypothesized that the changes of the I/I_s ratio were due to selective sedimentation of the components in the suspensions during drying. If the particle size distribution of all components is the same in all, the test, Sb_2O_3 particles of the same dimensions, having a lower specific gravity, will move slower than the Sb particles in the same suspension. The specific gravities and the absorption coefficients of the components are given in Table 1.

TABLE 1

Compound	Mass absorption coefficient	Specific gravity
Sb_2O_3	239.32	5.67
Sb	284	6.684

This selective sedimentation could only increase the Sb_2O_3 concentration and decrease the Sb concentration in the surface layer of the specimen, i.e. increase the ratio of their surface layer concentrations. This change would depend on the duration and the conditions of sedimentation. Since this accords with the X-ray measurements of I/I_s presented in Fig. 1 as calibration curves I and II, the above hypothesis appeas to be correct.

A more detailed check of this hypothesis and study of different effects on the I/I_s ratio will be presented in further papers.

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GLASNIK HEMIJSKOG DRUŠTVA, Vol. 29, No. 1—2, 1964, pp. 29—34.

SEDIMENTATION INFLUENCE ON CALIBRATION CURVES FOR X-RAY DIFFRACTION ANALYSIS OF SOME ANTIMONY COMPOUNDS

Part II. — INFLUENCE OF CONCENTRATION OF COMPONENTS WHOSE INTENSITIES ARE NOT MEASURED, ON THE I/I_s RATIO

by

VERA RAJKOVIĆ

K. Kay developed a method for making specimens for the X-ray diffraction analysis of quartz. He noticed that some calibration curves deviate from linearity at high quartz concentrations, increasing with this concentration. The reason for this deviation is not known.

In the investigation of minerals from Zajača mine(2,3) we wanted get calibration curves for the quantitative analysis of some mineralogical forms of antimony. It was shown that the shape of the calibration curves for Sb_2O_3 and Sb depends considerably on the structure of the mineral, i. e. the nature and concentration of the accompanying gangue components.

In this work we investigated the possibilities of eliminating these effects by adding to the tested mixtures some solid substances whose their diffracted intensities would not have any direct influence on the intensity of the determined compound and the internal standard (etalon).

EXPERIMENTAL

The technique for making synthetic samples, mixtures, suspensions and specimens(4), and the conditions of the X-ray measurements were the same as those used in the other experiments of this series(5,6).

Solid powder mixtures had the following composition:

1. $(Sb_2O_3 + SiO_2) : Sb = 1 : 1$
   a) Initial mixture without filler
   b) Initial mixture : $SiO_2 = 1 : 1$
   c) Initial mixture : $SiO_2 = 1 : 9$
2. $(Sb + SiO_2) : Sb_2O_3 = 8 : 1$
   a) Initial mixture without filler
   b) Initial mixture : $SiO_2 = 1 : 1$
   c) Initial mixture : $SiO_2 = 1 : 9$

Dispersion medium was obtained by mixing 8 volumes of isoamylacetate, 4 volumes of ethyl alcohol and 3 volumes of 4% colodium in ether. The dilution of the suspension was 1—2.5 ml of the dispersion medium per 0.4 g of the powdered mixture.

Quantity of suspension per slide was 0.08 ml or 0.16 ml of the suspension per 4 cm^2.

RESULTS AND DISCUSSION

Selective sedimentation of the measured components in the specimens was observed. It was observed that sedimentation was greater in specimens of mixtures with higher concentrations of the tested compound. The calibration curves for such specimens were exponential instead of linear. This is illustrated by the calibration curve for 20—100% of Sb_2O_3 and the mixture composition under 1a, and the curve for 20—100% of Sb and the mixture composition under 2a.

Assuming that these deviations were due to differing conditions of sedimentation of Sb_2O_3 and Sb particles in mixtures of a given series, we made a more detailed analysis of the sedimentation of suspensions of solid powder mixtures in graduated 10 ml cylinders(7,8). It was possible to visually observe the selective sedimentation because of the different colors of the components: Sb_2O_3 is white and Sb dark grey. The composition of the dispersion medium and its volume per unit mass of powdered material were the same as for making specimens.

The experiments were made with $Sb_2O_3 + Sb$ and $Sb_2O_3 + Sb + SiO_2$ mixtures. It was found that an increased concentration of amorphous SiO_2 in a solid mixture, i.e. in the corresponding suspension, retards selective sedimentation of the measured components Sb_2O_3 and Sb in a time period which corresponds to the specimen drying time.

These experiments lead to the conclusion that if the sedimentation of Sb_2O_3 and Sb in all suspensions of a given series took place under the same conditions, the calibration curves for Sb_2O_3 and Sb would be linear. To obtain at least similar sedimentation conditions in a given series without changing the ratio of the tested compound and the internal standard (etalon), we added the same quantity of silica dioxide to all solid mixtures with 20—100% of Sb_2O_3 and 20—100% of Sb, i.e. the weight ratios were 1 : 1 and 1 : 9. Suspensions and specimens of these mixtures and of the initial mixtures were made under identical conditions. The corresponding calibration curves in Fig. 1b and 1c for Sb_2O_3 and 2b and 2c for Sb show that our assumption, that changes of the I/I_s values were caused by selective sedimentation of Sb_2O_3 and Sb in specimens is correct because they do not occur if the sedimentation is retarded by the addition of silica dioxide.

The role of the amorphous silica dioxide appears to be the same as that of a spectrochemical buffer, a substance which is added to the specimen to minimize the dependence of excitation emission on the general composition of the specimen apart from the concentrations of the elements being directly determined(9).

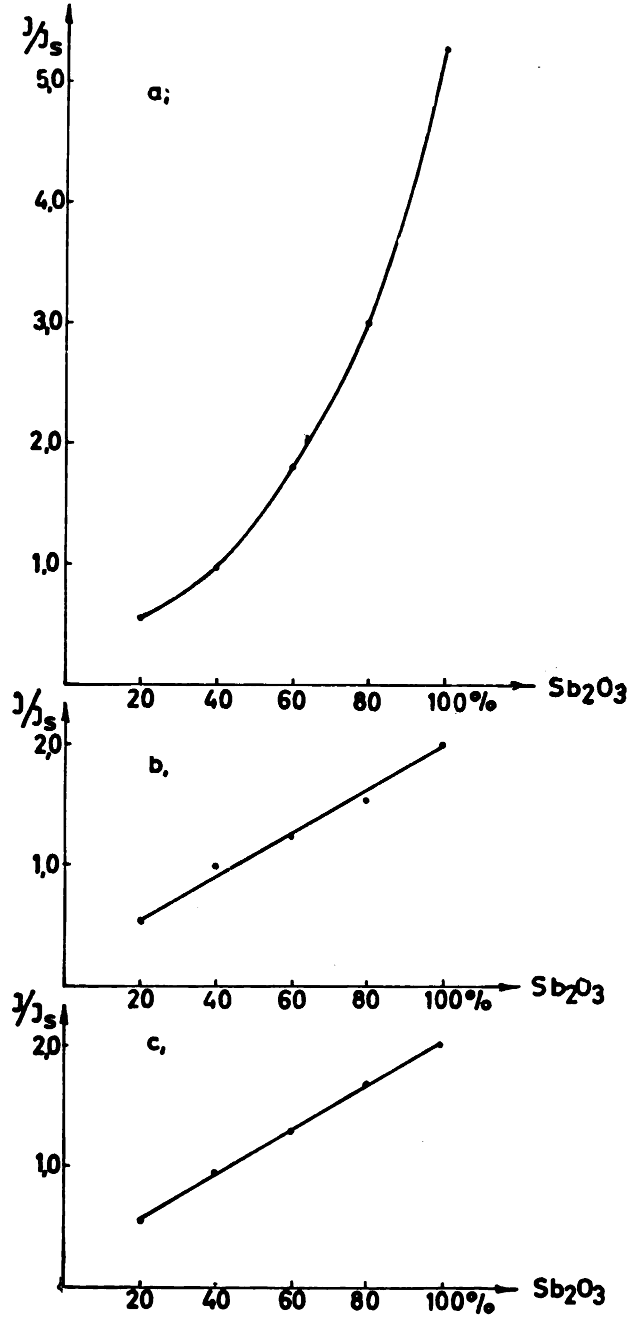

Fig. 1 — Calibration curves for determination of Sb_2O_3

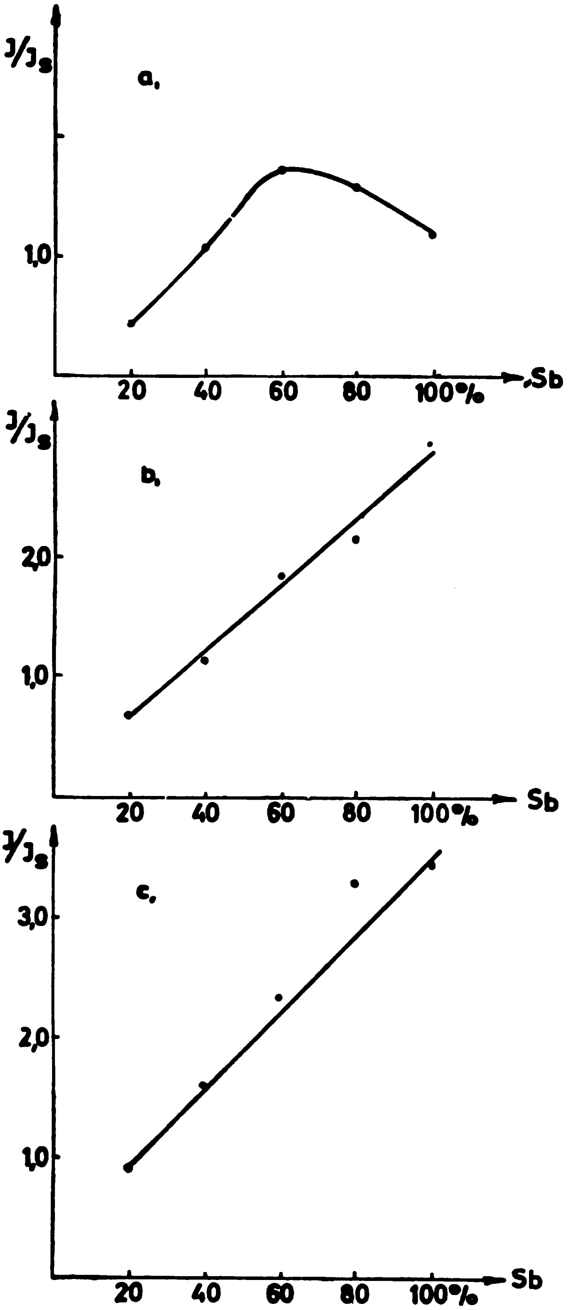

Fig. 2 — Calibration curve for determination of Sb

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SEDIMENTATION INFLUENCE ON CALIBRATION CURVES FOR X-RAY DIFFRACTION ANALYSIS OF SOME ANTIMONY COMPOUNDS

Part III. — DIRECT ANALYSIS

by

VERA D. RAJKOVIĆ

According to the classification of L. E. Alexander and H. P. Klug, direct analysis by measuring the diffracted intensity of a specific compound in a mixture, is possible only if the mixture contains *n* components whose absorption coefficients are the same. If the mixture contains components with different absorption coefficients direct analysis is not possible. In this case the internal standard method is applied (1,2).

Experiments to find out the most suitable calibration curves for the quantitative analysis of some antimony compounds by the internal standard method, lead to the following statements: 1) the I/I_s ratio is proportional to the ratio of the concentration of the determined compound and the internal standard (etalon) in the surface layer of the specimen but not to the ratio of their concentrations in the mixture from which the specimen is made, and 2) deviations of the calibration curves from linearity are due to selective sedimentation in the specimens (3,4).

The latter statement was checked by visual observation of selective sedimentation of Sb_2O_3 and Sb particles in suspensions of their mixtures in 10 ml graduated glass cylinders. From the change of the color distribution in separated sediments and suspensions during sedimentation we concluded that our statement was tenable (5,6).

A more reliable check was made in the present work, by X-ray measurement of the intensity of one component of three-component systems.

EXPERIMENTAL

The technique for making the mixtures, suspensions and specimens (7) and the conditions for X-ray measurements are the same as in the other papers of this series of investigations dealing with the problem of obtaining good calibration curves for the quantitative determination of antimony compounds in powdered material (1,2).

Solid powdered mixtures in this work contained antimony trioxide, elementary antimony and amorphous silicon dioxide. They were divided into three groups according to the content of elementary antimony. Mixtures of group I contained 60%, group II 25% and of group III 5% of Sb. The concentrations of antimony trioxide and silicon dioxide were changed as shown in Table 1.

TABLE 1

Number	Group I 50% Sb		Group II 25% Sb		Group III 5% Sb	
	% Sb_2O_3	% SiO_2	% Sb_2O_3	% SiO_2	% Sb_2O_3	% SiO_2
1	50	—	25	50	5	90
2	40	10	20	55	4	91
3	30	20	15	60	3	92
4	20	30	10	65	2	93
5	10	40	5	70	1	94

The Dispersion medium was obtained by mixing 8 volumes of isoamyl-acetate, 4 volumes of ethyl alcohol and 3 volumes of 4% colodium in ether.

Dilution of suspensions: 1—2.5ml of the dispersion medium per 0.4 g of powdered material.

Quantity of suspension per slide: 0.08 ml or 0.16 ml of suspension per 4 cm^2.

RESULTS AND DISCUSSION

There were 2 phases in this study of the influence of sedimentation in specimens for X-ray diffraction analysis of powders on the measured intensity of one component of the mixture:

1. investigation of the possiblity of direct analysis for the determination of the content of one component in the mixture;
2. observation of the change of the maximum diffracted intensity of a component of fixed concentration in a series of tested mixtures with change of the concentrations of the other components whose intensities are not measured.

Investigation of the possibility of determining Sb_2O_3 content by direct analysis

The calibration curves in Fig. la for the dependence of the intensity of diffracted radiation of Sb_2O_3 on % concentration of Sb_2O_3 were obtained by X-ray measurements of specimens made from mixtures from group I in Table 1. The curves in Fig. 2a, were obtained on specimens made from mixtures from group II, and those in Fig. 3a for specimens made from mixtures from group III in Table I.

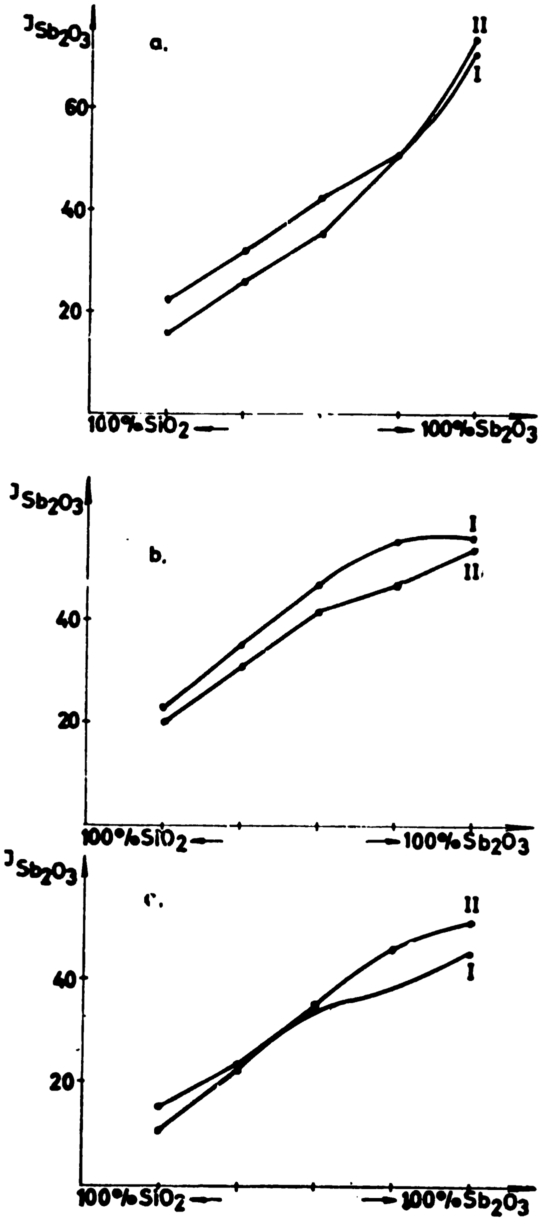

Fig. 1 — Calibration curves for direct analysis of Sb_2O_3

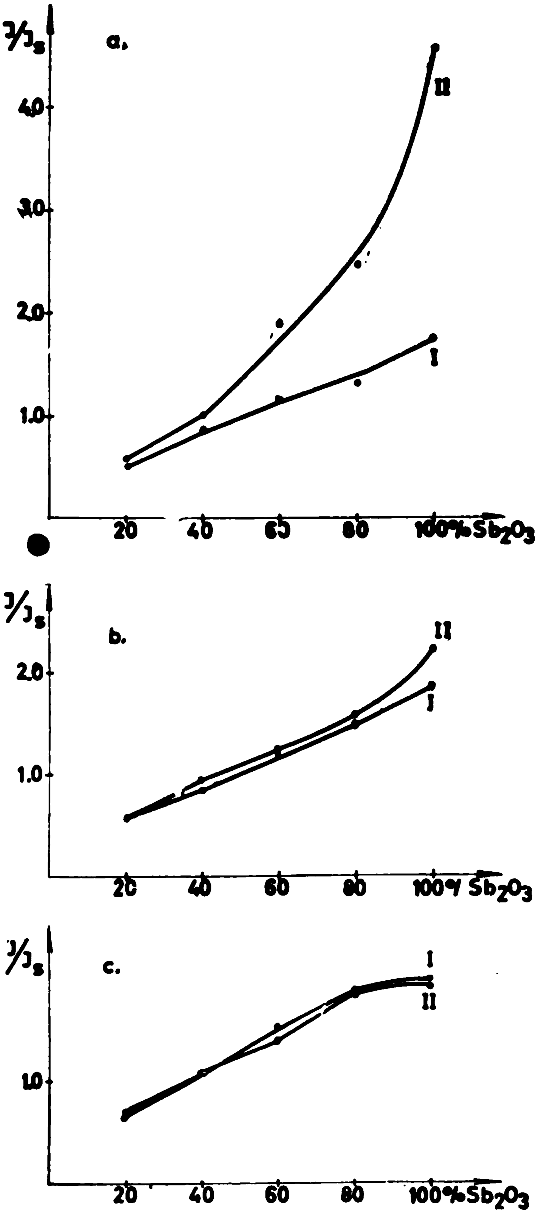

Fig. 2 — Calibration curves for determination of Sb_2O_3 by internal standard method

TABLE 2

$I_{Sb_2O_3}$ in mm

Suspension for specimen	Dilution	Group I % Sb_2O_3					Group II % Sb_2O_3					Group III % Sb_2O_3				
		50	40	30	20	10	25	20	15	10	5	5	4	3	2	1
0.08 ml	1.0 ml	73.59	64.83	61.55	46.90	27.66	64.06	58.58	50.42	40.06	28.07	47.83	41.89	32.28	24.39	14.06
	1.5 ml	72.39	55.22	49.28	31.92	22.78	66.52	60.43	43.09	36.30	26.46	45.33	33.29	29.22	20.00	12.50
	2.0 ml	70.72	51.30	42.52	32.75	22.38	56.08	55.61	46.70	35.00	22.33	45.11	36.72	35.11	23.06	15.42
	2.5 ml	64.47	56.58	54.11	34.83	24.11	69.28	65.72	50.89	58.64	26.03	43.23	39.08	31.19	22.64	15.69
0,16 ml	1.0 ml	56.81	35.77	28.26	19.80	13.44	77.11	66.13	55.28	49.39	28.72	56.28	47.64	39.41	32.24	19.28
	1.5 ml	82.47	66.52	43.67	27.55	17.45	76.17	68.22	56.00	46.44	26.56	48.67	37.83	31.48	19.28	11.94
	2.0 ml	73.86	50.88	35.34	26.03	15.94	53.93	46.42	41.69	31.00	20.00	51.28	46.31	34.56	22.67	14.83
	2.5 ml	74.02	49.22	40.65	26.56	19.17	73.00	69.72	60.69	44.02	39.49	40.30	37.5	30.95	20.17	13.86

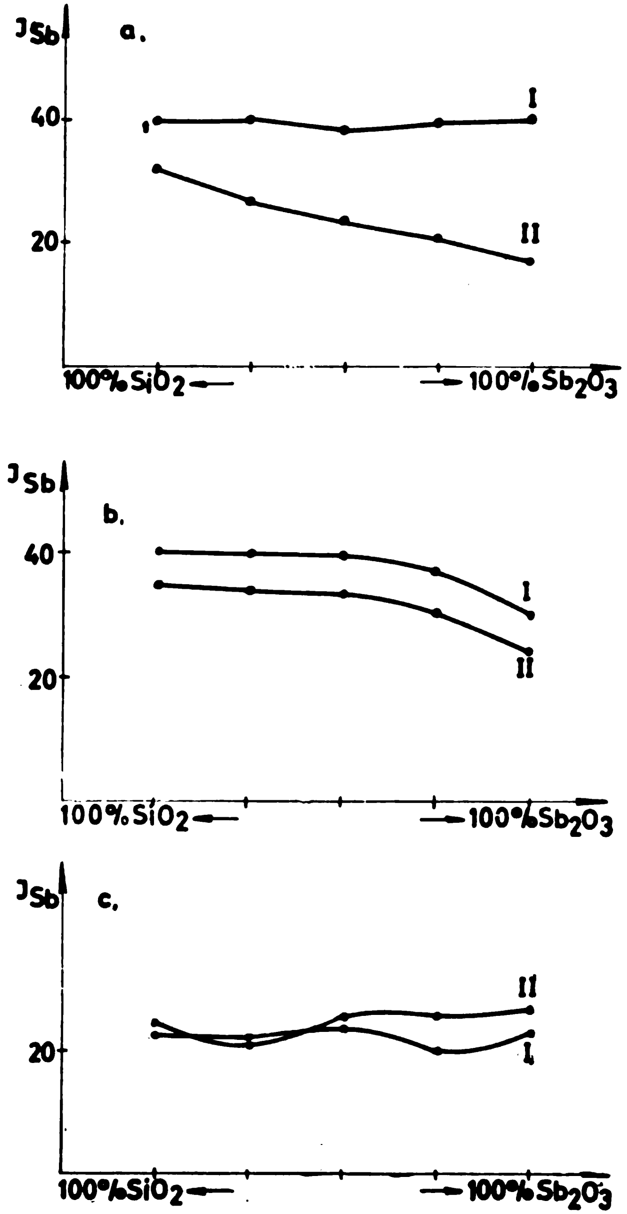

Fig. 3 — The dependence of I_{Sb} on the concentration of other substances i the mixtures

TABLE 3

I_{Sb} in mm

Suspension for specimen	Dilution	Group I % Sb_2O_3					Group II % Sb_2O_3					Group III % Sb_2O_3				
		50	40	30	20	10	25	20	15	10	5	5	4	3	2	1
0.08 ml	1.0 ml	50.85	48.67	54.19	53.37	67.11	32.83	37.25	41.81	45.64	50.33	25.89	27.94	26.78	28.33	32.0
	1.5 ml	40.75	42.30	41.64	39.42	41.92	34.81	38.83	43.50	42.39	43.92	20.89	18.00	18.30	17.91	22.67
	2.0 ml	40.02	39.50	37.42	40.22	39.89	30.03	37.33	39.89	39.44	40.11	23.11	19.92	23.20	21.50	22.86
	2.5 ml	36.86	34.67	36.27	37.86	38.69	31.31	42.97	39.03	43.17	39.29	21.56	18.89	21.17	18.42	19.86
0.16 ml	1.0 ml	12.33	15.28	19.25	21.75	23.56	31.42	37.39	42.17	48.75	52.44	25.08	25.44	27.40	29.94	30.22
	1.5 ml	16.19	20.03	23.75	28.03	33.17	37.83	43.61	47.83	47.64	49.08	23.06	22.89	24.69	20.67	21.94
	2.0 ml	17.28	21.13	23.17	26.50	31.92	24.94	30.22	33.94	33.67	35.00	26.94	25.11	25.39	20.69	24.28
	2.5 ml	19.14	24.69	26.39	27.33	28.33	36.39	46.22	51.67	49.94	47.39	19.03	20.97	20.08	17.61	22.90

All suspension were diluted with 2 ml of the dispersion medium per 0.4 g of the powdered material. Curves marked with I were obtained by measuring specimens made with 0.08 ml and those marked with II with 0.16 ml of suspension per slide.

The maximum intensities of diffracted radiation for Sb_2O_3 in Table 2 show that very similar curves are obtained for other dilutions as well. Figures 1 b, 2 b, and 3 b present the respective calibration curves for the determination of Sb_2O_3 by the internal standard method.

It is clearly seen that the shapes of the calibration curves obtained by direct analysis and the internal standard method are quite similar. However, deviations of the direct analysis curves are smaller than those for the internal standard method. This can only be ascribed to the fact that in the direct analysis method the diffracted intensity maximum is proportional to the Sb_2O_3 concentration in the surface layer of the specimen. With the internal standard method the I/I_s ratio is proportional to the concentration ratio of the Sb_2O_3 and Sb components in the surface layer, and thus depends the surface layer concentrations of both, so that greater deviations from the values which would be obtained if there was no sedimentation are possible.

This is confirmed by the following results.

Investigation of the change of the maximum intensity for Sb for a series of mixtures with a fixed Sb concentration

The same specimens made from mixtures given in Table 1, were used in this experiment.

The X-ray intensities are given in Table 3. The curves for the dependence of intensity I for Sb in mm on the concentration increase of Sb_2O_3 and decrease of SiO_2 in the mixtures are shown in 1 *c*, 2 *c*, and 3 *c*. The suspensions employed were also diluted with 2 ml of the dispersion medium per. 0.4 g of powdered material. Curves for the other dilutions are not shown because they are very similar in shape apart from random errors.

These curves indubitably prove that deviation from linearity of the calibration curves for X-ray diffraction analysis of powder is due to selective sedimentation in specimens during their making and drying.

These results also show that the absorption theory or L. E. Alexander and H. P. Klug is not satisfactory in case of the analysis of antimony trioxide. If deviations in direct analysis were due to different mass absorption coefficients of the components, they would not occur in the internal standard method. Hower, for antimony trioxide they become greater. This accords with the hypothesis of selective sedimentation in specimens and confirms that the diffracted intensity of a component in a mixture is proportional to its concentration in the surface of the specimen.

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GLASNIK HEMIJSKOG DRUŠTVA, Vol. 29, No. 1—2, 1964, pp. 45—49.

DETERMINATION OF SMALL AMOUNTS OF COPPER IN CADMIUM[1]

by

SRETEN N. MLADENOVIĆ and BOŽIDAR FILIPOVIĆ

Among the methods for the determination of copper in electrolytic cadmium of 99.99% purity the colorimetric method with sodium diethyldithiocarbamate, cupral, has been found to be the most sensitive. Copper diethyldithiocarbamate, formed by the reaction of copper with sodium diethyldithiocarbamate, is extracted with carbon tetrachloride(1) from an aqueous solution of pH 4.5 to 5.0. The amount of copper is determined by measuring the intensity of the yellow color of the solution. Because the copper complex is only formed, in a narrow pH-range, the method is of limited value.

By investigating the effect of the pH on complex formation and on the extraction of copper carbamate we have established that the pH-range for complex formation and extraction with carbon tetrachloride is considerably wider (Table 1).

TABLE 1

8.10^{-6} g Cu in 1 g Cd; extraction with carbon tetrachloride

Experiment	pH of aqueous solution	Absorption
1	0.6	10.0
2	1.7	10.0
3	2.4	10.0
4	4.9	10.0
5	8.5*	bad separation of layers
6	9.6*	10.0
7	10.0*	10.0

*) ammonia solution

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[1] Communicated at the XXXIVth International Congress of Industrial Chemistry, September 1963, Belgrade.

In acid media of pH 0.6 to 4.9 and in alkaline ammonia solutions of pH > 9 the intensity of the yellow extract is the same. These findings show that copper in cadmium can be determined within these pH-ranges without determining the actual pH. In the pH-range 5.0 to 9.0 the extraction is not easy to do, especially in the presence of a precipitate. This difficulty may be ascribed to the form in which the copper is present; copper is not easily extracted from the precipitate and therefore only a small fraction of it goes into the carbon tetrachloride solution. Moreover, the separation of the organic and aqueous layer is very bad.

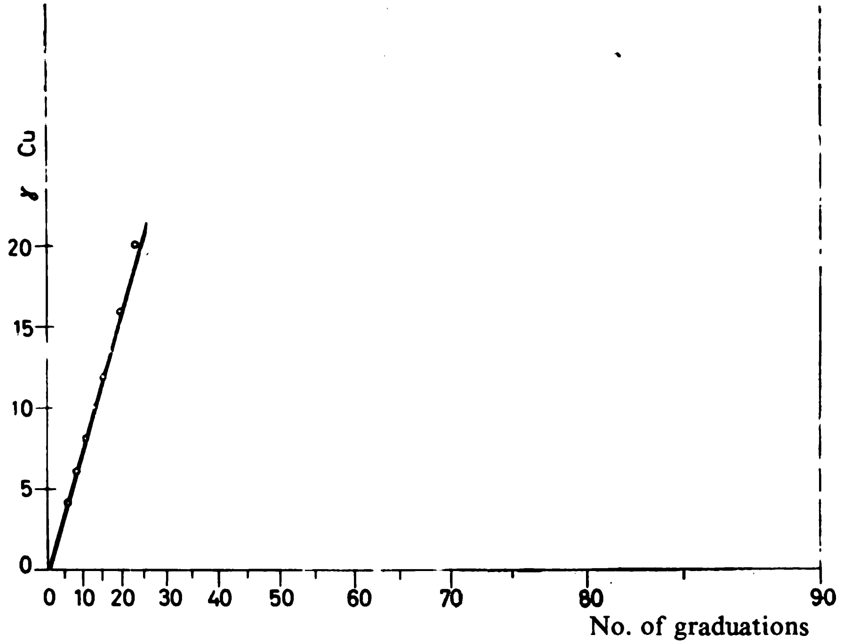

Fig. 1

We also used toluene as an extraction solvent and got results similar to those with carbon tetrachloride. Experiments with different amounts of copper in cadmium and with toluene as the solvent showed that all the copper diethyldithiocarbamate was extracted in one operation and that there is a relation between the concentration and the extinction (Table 2 and Fig. 1).

The results for the effect on the determination of copper using toluene were the same as with carbon tetrachloride (Table 3).

The same absorption was obtained for identical copper concentrations in acid aqueous solutions of pH from 0.8 to 4.6 and in alkaline ammonia solutions of pH > 9, indicating that the determination can be carried out in these pH-ranges. The extraction

TABLE 2

Copper in cadmium

Experiment	Cu γ	Absorption %
1	0	0.0
2	4	6.0
3	6	8.0
4	8	10.5
5	10	12.2
6	12	15.0
7	16	19.0
8	20	23.0

TABLE 3

8.10^{-6} Cu in 1 g Cd; extraction with toluene

Experiment	pH of aqueous solution	Absorption %
1	0.8	10.0
2	1.6	10.0
3	4.6	10.0
4	7.2*	9.2
5	7.7*	9.0
6	9.0*	10.0
7	10.0*	10.0

*) Ammonia solution

of copper from acid and slightly alkaline ammonia solutions goes better with toluene than with carbon tetrachloride. The separation of layers is also very good. However, the extraction of copper complex with toluene it not complete.

Using the possibility of extracting copper diethyldithiocarbamate complex with toluene we have developed a method for the determination of copper in cadmium. The results obtained with the two extraction solvents were in good agreement.

Procedure. 25 ml of water is added to ten grams of cathodic cadmium and then concentrated nitric acid (a total of 25 ml) is added slowly till the cadmium is completely dissolved. The cadmium solution is transferred to a 100 ml volumetric flask which is then filled up to the mark.

To an aliquot of the solution (10 ml; 1 g cadmium) 10.0 ml of distilled water and 1 ml of 0.3% sodium diethyldithiocarbamate solution is added. The solution is transferred to a separatory funnel and 10 ml of toluene is added. After vigorous shaking for two minutes the toluene extract is put in a cuvette and the color intensity of copper diethyldithiocarbamate is determined with a blue light filter.

The results show that copper in cadmium can be determined with cupral in a considerably wider pH-range by using toluene as the extraction solvent.

School of Technology
Institute for Physical Chemistry
and Electrochemistry

Received, Sept. 16th, 1964

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GLASNIK HEMIJSKOG DRUŠTVA, Vol. 29, No. 1—2, 1964, pp. 51—56.

THE OXIDATIVE SPLITTING OF SOME FLUORENONE DERIVATIVES BY MEANS OF LEAD TETRAACETATE

by

BOJAN D. PODOLEŠOV

As a continuation of our work on the condensation and properties of polyoxo compounds (1,2) we have carried out the condensation of 2-acetylfluorene with diethyl oxalate in the presence of sodium ethylate. From earlier investigations made by Wislicenus(3) and Jančulev and Podolešov(1), and on the basis of the experimental conditions employed in this condensation, we expected it to take place at the active methylene group in the 9-position and at the acetyl group in the 2-position of the fluorene nuclei.

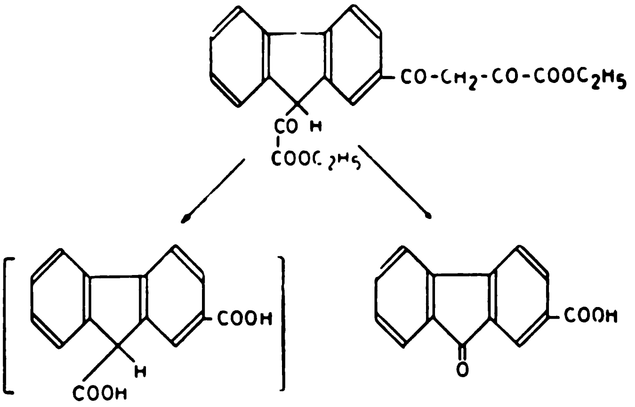
In this condensation two compounds were isolated. The main product melted at 114—117°C and its elementary analysis corresponded to 9-oxalo-fluorenoyl-2-pyruvate. The other product, which was isolated in a smaller amount, melted at 173°C and its elementary analysis corresponded to the formula $C_{40}H_{30}O_{1}6$. The structure of this compound will be reported in a forthcoming paper.

According to the works of E. Bear(4) the oxidative splitting of aroylcarboxylic acids by means of lead tetraacetate gives arylcarboxylic acids. Similarly, according to Jančulev and Podolešov(2), the splitting of ethyl aroylpyruvates also gives arylcarboxylic acids.

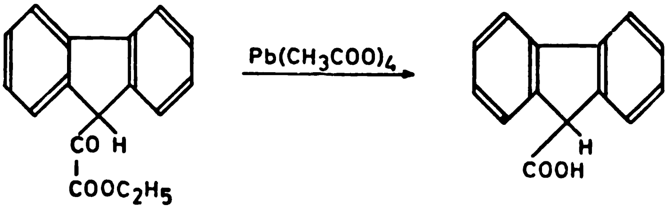
On the basis of these works we assumed that the oxidative splitting of ethyl 9-oxalo-fluorenoyl-2-pyruvate wauld give the hitherto little described fluorene-2,9-dicarboxylic acid. However, the oxidative splitting of ethyl 9-oxalo-fluorenoyl-2-pyruvate (I) did not give rise to the expected fluorene-2,9-dicaroxylic acid (II) but to the well-known 9-fluorenone-2-carboxylic acid (IIa) which was determined by the preparation of its methyl ester.

From these results it follows that in the oxidative splitting of ethyl 9-oxalo-fluorenoyl-2 pyruvate the $—CO—CH_2—CO——COOC_2H_5$ group in the 2-position is oxidized to the carboxylic group, and the $—CO—COOC_2H_5$ group in the 9-position to the keto group.

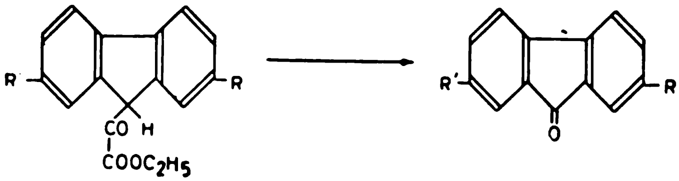
In order to explain the unexpected oxidative splitting of the $—CO—COOC_2H_5$ group in the 9-position we have studied the oxidative splitting of ethyl fluorenyl-9-gyoxalate (III).



On the basis of the results obtained in the oxidative splitting of ethyl 9-oxalo-fluorenoyl-2-pyruvate, the oxidative splitting of ethyl fluorenyl-9-glyoxalate should give rise to already known fluorenone. However, we were unable to isolate fluorenone from the reaction mixture and we obtained only small amounts of fluorene-9-carboxylic acid.



The oxidative splitting of substituted derivatives of ethyl fluorenyl-9-glyoxalate gave different results. The splitting of ethyl 2-nitrofluorenyl-9-glyoxalate resulted in the formation of 2-nitrofluorenone, and in the oxidation of ethyl 2,7-dibromofluorenyl-9-glyoxalate gave 2,7-dibromofluorenone.



From these results it may be concluded that the $CO-COOC_2H_5$ group in the 9-position is oxidized with lead tetra-acetate to the keto group only in case of substituted derivatives of ethyl fluorenyl-9-glyoxalate.

The results of the oxidative splitting with lead tetraacetate of the compound melting at 114—117°C and of the other substituted derivatives of ethyl fluorenyl-9-glyoxalate prove that the structure ascribed to ethyl 9-oxalo-fluorenoyl-2-pyruvate is correct.

The mechanism of the oxidative splitting of the —CO—$-COOC_2H_5$ grouping in the 9-position encountered in substituted derivatives of ethyl fluorenyl-9-glyoxalate will be published later.

EXPERIMENTAL

Condensation of 2-acetylfluorene with diethyl oxalate (ratio 1 : 2) *in the presence of sodium ethylate* (ethyl 9-oxalo-fluorenoyl-2-pyruvate)

In a 200 ml round-bottomed flask with a condeser and a $CaCl_2$-tube, sodium ethylate was prepared from 0.69 g of sodium (0.03 mole) and 1.38 g (0.03 mole) of absolute alcohol after N. Lund and J. Bjerrum (5): Anhydrous ether was added to the reaction mixture until all the sodium was covered. After one hour heating on a water-bath, the reaction mixture was left to stand overnight. To the obtained sodium ethylate solution, with constant stirring, were added first 3: 12 g(0.015 mole) of 2-acetylfluorene, and then, 4.38 g (0.03 mole) of freshly distilled diethyl oxalate, slowly and with cooling so that no overheating of the reaction mixture occurred. After standing for three days, the reaction mixture was orange colored.

The reaction product was filtered off, washed with ether and dried in air. The obtained 7.7 g of orange colored sodium derivative was treated with ice cold hydrochloric acid (1 : 1). 6.6 g of brown-red condensation product was obtained after drying in air. It was readily soluble in alcohol, acetone, glacial acetic acid and ethyl acetate. It was then treated with 200 ml of benzene whereby a dark red colored deposit was left undissolved. The benzene solution was filtered and left to crystallize.

After standing two days the benzene solution yielded about 1.5 g of a dark red precipitate which melted at 100°C. After some time the concentrated filtrate gave an additional 3 g of a yellow precipitate which melted at 110°C. Further standing of the filtrate resulted in the formation of a yellow deposit which melted at 150°C. The crystals melting at 100—110°C, after two further crystallizations, gave yellov needles of m. p. 114°C (Kofler block m. p. 117°C). The results of the elementary analysis corresponded to ethyl 9-oxalo-fluorenoyl-2-pyruvate (Ia).

Analysis

Found :C 67.45%; H 4.90%
Calculated for $C_{23}H_{70}O_7$:C 67.74%; H 4.94%.

The recrystallization of the yellow needles melting at 150°C from benzene or acetone gave crystalline plates melting at 168—169°C (Ib).

Analysis:

Found :C 71.10%; H 4.34%
Calculated for $C_{40}H_{30}O_{10}$: C 71.63%; H 4.51%.

Oxidative splitting of ethyl 9-oxalo-fluorenoyl-2-pyruvate with lead tetraacetate (9-Fluorenone-2-carboxylic acid) (IIa).

To a suspension of 1 g of ethyl 9-oxalo-fluorenoyl-2-pyruvate (m. p. 114—117°C) in 48 ml of 98% acetic acid, 8 g of powdered lead tetraacetate was added. In the course of 30 minutes the suspension turned to a yellow colored solution and its temperature rose about 6°C. The reaction mixture was stirred for a further 6 hours and a yellow precipitate separated. The stirring was continued for 15 hour whereby lead tetraacetate completely disappeared from the solution. To remove any traces of unreacted lead tetraacetate a few ml of ethylene glycol were added to the reaction mixture. The separated yellow reaction product was filtered off and dried. The yield was about 0.25 g. By adding water to the filtrate an additional 2 g of the reaction product was obtained. Recrystallization from glacial acetic acid gave yellow needles melting at 333°. The mixed melting point determination with an authenti. sample of 9-fluorenone-2-carboxylic acid showed no depressionc

Analysis:
Found :C 74.78%; H 3.85%;
Calculated for $C_{14}H_8O_3$: C 74.99%; H 3.60%.

Methyl ester of 9-fluorenone-2-carboxylic (IIb)

The product of the oxidative splitting of 9-oxalo-fluorenoyl--2-pyruvate was determined by the preparation of its methyl ester in the following way:

By heating 0.15 g of the oxidation product (IIa), m. p. 333°C, with 5 ml of thionyl chloride on a water bath for 90 minutes a clear solution was obtained. The excess thionyl chloride was removed in vacuo and the solid residue was heated on a water-bath with 30 ml of methanol for 90 minutes. Then active charcoal was added to the solution, the mixture was boiled for 5 minutes and filtered hot. On cooling the methanolic solution yielded long shiny needles melting at 182°C. Repeated recrystallization yielded crystals of m. p. 182—184°C. The mixed melting point with an authentic specimen of 9-fluorenone-2-carboxylic acid (m. p. 180—185°C, prepared according to Fortner(8)) gave no depression.

Analysis:
Found :C 75.38%; H 4.30%;
Calculated for $C_{15}H_{10}O_3$: C 75.62% H 4.23%

From the elementary analysis of the oxidation product (IIa) and its melting point and from the melting point of the corresponding methyl ester, it may be concluded that its structure corresponds to 9-fluorenone-2-carboxylic acid.

Oxidative splitting of ethyl fluorenyl-9-glyoxalate (III) with lead tetraacetate

Ten grams of ethyl fluorenyl-9-gluoxalate prepared by the method of Wislicenus⁽⁸⁾ was dissolved in 100 ml of 99% acetic acid with an addition of 2—3 ml of water. 30 g of lead tetraacetate was added to the solution and the reaction mixture was kept at 60°C with warming and constant stirring for about 30 hours. Then a small amount of ethylene glycol was added in order to remove the unreacted lead tetraacetate. The reaction mixture was diluted with water, the separated flaky precipitate was collected and the filtrate was extracted with ether. The sticky yellow precipitate was dissolved in benzene and from the cooled solution an almost white product was deposited. It was recrystallized from benzene-petroleum ether, yielding about 0.1 g of a substance melting at 210—230°C. Recrystallization from a mixture of glacial acetic acid and water yielded white needles melting at 321°C (lit. 325°C⁽⁹⁾). The mixed melting point with fluorene-9-carboxylic acid remained unchanged.

On removal of the solvents, etherial extract and the benzene solution gave a yellow-red residue from which fluorene was obtained.

Distillation of the residue furnished no fluorenone but only fluorene, which was probably formed by the decomposition of ethyl fluorenyl-9-carboxylic acid.

The oxidative splitting of ethyl 2-nitrofluorenyl-9-glyoxalate (IV) with lead tetraacetate

To a solution of 0.84 g of powdered ethyl 2-nitrofluorenyl--9-glyoxylate (m. p. 140—144°C)⁽¹⁰⁾ in 70 ml of acetic acid, 4 g of powdered lead tetraacetate were added. The reaction mixture was heated at 50—60°C with constant stirring for about 20 hours. After some time a yellow crystalline precipitate appeared. Some ml of ethylene glycol were added in order to remove the unreacted lead tetraacetate, and the separated product was filtered off, giving 0.35 g of compound melting at 210°C. Recrystallization from glacial acetic acid with the addition of active charcoal gave long shiny needles of m. p. 216—217° (lit. 218.5°C)⁽¹¹⁾.

Analysis:

Found :C 69.15%; H 3.20%;
Calculated for $C_{13}H_7NO_3$:C 69.33%; H 3.13%.

The mixed melting point with 2-nitrofluorenone obtained by the oxidation of 2-nitrofluorene with dichromate showed no depression. All thes data show that the obtained product is 2-nitrofluorenone.

Oxidative splitting of ethyl 2-7-dibromofluorenyl-9-glyoxalate (V) with lead tetraacetate

To a mixture of 0.8 g of ethyl 2.7-dibromofluorenyl-9-glyoxalate(12) and 50 ml of 98% acetic acid 5 g of powdered lead tetraacetate was added. The reaction mixture was kept at 55—60°C with constant stirring for 20 hours. Then some ml of ethylene glycol were added in order to remove the unreacted lead tetraacetate, and the reaction mixture was diluted with water. The separated precipitate was recrystallized from 96% alcohol, yielding about 0.25g of a crystalline product in the form of yellow needles which melted at 202° (lit 202°C)(13).

Analysis:

Found :C 46.30%; H 1.95%;
Calculated for $C_{13}H_6OBr_2$:C 46.19%; H 1.95%.

The mixed melting point with 2,7-dibromofluorenone prepared by the oxidation of 2,7-dibromofluorene showed no depression.

The obtained oxidation product was determined in the form of its oxime which crystallized as light yellow needles of m. p. 236—237° (lit. 235°C)(13).

From the above data it is evident that the obtained product is 2,7-dibromofluorenone-9.

Institute of Chemistry
School of Sciences
University of Skoplje

Received, May 25th, 1964

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GLASNIK HEMIJSKOG DRUŠTVA, Vol. 29, No. 1—2, 1964, pp. 57—71.

REACTION OF PHENYLMAGNESIUM BROMIDE WITH SIX- AND FIVE-MEMBERED STEROID LACTONES*

by

MILORAD M. ROGIĆ

It is welll known that five-membered lactones in reaction with an excess of a Grignard reagent give a tertiary alcohol(1) which can be subjected to Barbier-Wieland degradation. In the literature there is not much data concerning the reaction of a Grignard reagent with six-membered lactones. However, it was recently found that the lactone of 4,5-seco-4-nor-androstane-5,11,17-trihydroxy-3-oic acid reacts with an excess of phenylmagnesium bromide in an unexpected manner, giving 3,5-seco-4-nor-3-phenyl-3,11,17-trihydroxy-androstane-5-one as the main product, and a small quantity of 3,5-seco-4-nor-3,3-diphenyl-11,17-dihydroxy-2-androsten-5-one(2). This may be explained by assuming that the intermediate formed after the attack of the phenyl ion on the lactone carbonyl can undergo an intramolecular hydride ion transfer.

This paper describes another abnormal Grignard reaction of a six-membered lactone.

1 Ozonolysis(3) of progesterone at —70° in ethyl acetate-methylene chloride gave about 70% yield of 3,5-seco-4-nor-pregnane-b,5-dione-3-oic acid(4) (II). This compound was reduced with sodium borohydride in an alkaline alcoholic solution, and then heated with hydrochloric acid, whereby the corresponding six-membered lactone (bII) of the above acid was obtained; its infrared spectrum had bands at 3490, 1725, 1255, 1110, 1075, 1055, and 965 cm^{-1}. The oxidation of the C_{20}-hydroxyl group with chromic acid gave the keto-lactone (IV) whose infrared spectrum did not show the hydroxyl band at 3490 cm^{-1}, but had a band at 1705 cm^{-1}, characteristic for open-chain ketones. The nuclear magnetic resonance spectrum of this keto-lactone had a resonance signal for the C_5 proton at 6.14 τ, which is in good agreement with an axial proton resonance, which

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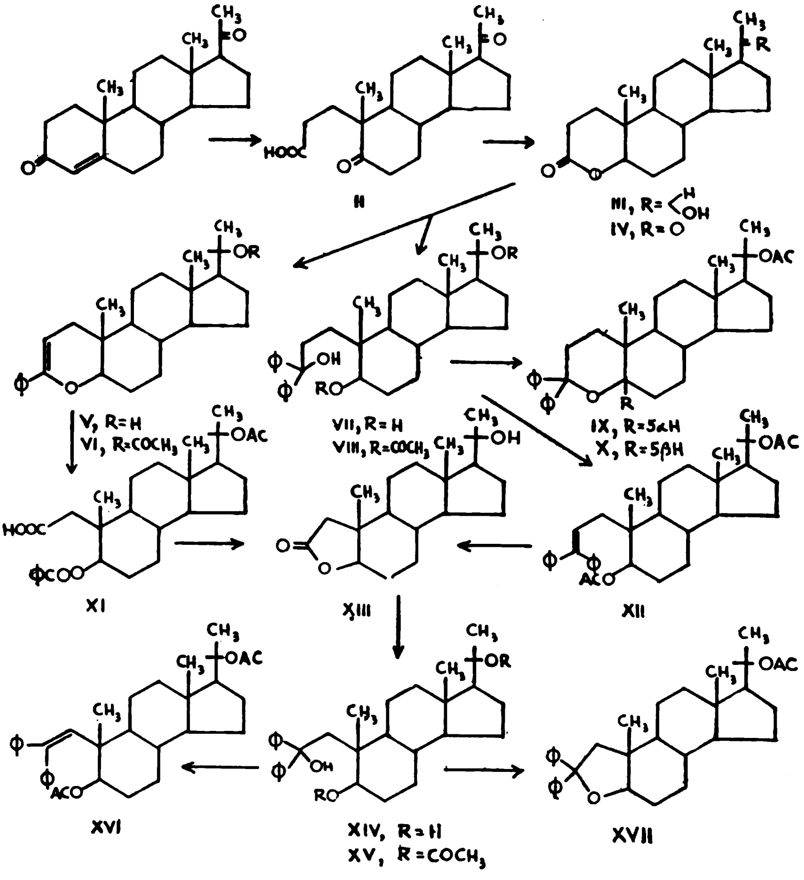
*) This work was done at the *Worcester Foundation for Experimental Biology in Srewsbury*, Mass., USA, where the author, at that time on leave of absence from School of Sciences in Beograd, was postdoctoral research fellow during 1961—1962. The author expresses his thanks to Dr. Marcel Gut for financial support.

usually appears between 6.05 and 6.48 $\tau^{(2,7)}$. Hence, the C_5-hydroxyl group of the intermediate 5-hydroxy acid must be equatorial. From the filtrate obtained after crystallization of the hydroxy-lactone III, a small quantity of a substance melting at 185° was isolated. This substance is probably the C_5-isomeric lactone with lactone III since its infrared spectrum was very similar to that of the lactone III. However, this compound was not further investigated.



When the hydroxy-lactone III was treated with an excess of phenylmagnesium bromid a mixture of two compounds, compound V, m. p. 156—158° and compound VII, m. p. 110—112°, was obtained. These compounds were easily separated on a silica gel column. The compound V, m. p. 156—158°, was isolated in a 56% yield and it had an analysis for $C_{26}H_{36}O_2$. It absorbed ultraviolet light at λ_{max}^{MeOH} 224mμ and 264mμ, and its infrared spectrum had bands at 3580 and 4000 cm^{-1}, showed no absorption in the carbonyl group region, had characteristic bands for a phenyl-conjugated double bond (1650, 1600, 1580, 1480), and a very strong band at 1075 cm^{-1}. The NMR spectrum of the corresponding acetate (VI), m.p. 120°, showed only one proton on a double bond at 4.68τ, a doublet at 6.33 and 6.52τ which was assigned to a C_5 axial proton, and a resonance signal at 5.14τ of an *H*—C_{20}—OAc proton. Ozonolysis of acetate VI gave an acid XI, m. p. 237—239°, with an analysis for a $C_{28}H_{38}O_6$ compound. The acid XI absorbed ultraviolet at λ_{max}^{MeOH} 229, 273 and 280mμ, characsteristic of benzoic acid esters⁽⁸⁾. The infrared spectrum of the same acid indicated the presence of the carboxyl (3050, 2650, 1650, 950 cm^{-1}), acetate (1725, 1250 cm^{-1}) and benzoate groups (1720, 1275, 1100 cm^{-1}). These data are consistent with the structure V assigned to the compound melting at 156—158°.

The product VII, m. p. 110—122°, isolated in 36% yield, had an analysis for $C_{32}H_{44}O_3$ and did not absorb ultraviolet light. Its infrared spectrum had a very intense band at 3330 cm^{-1} but it did not show a band for a carbonyl group. Bands at 3010, 1600, 1585, and 705 cm^{-1} are characteristic of aromatic moeties, but there is not indication of the presence of a phenyl-conjugated double bond. There were also very intense bands at 1080 and 1035 cm^{-1}. In the NMR spectrum the band centered an 6.45τ indicated an axial proton at C_5. When compound VII was treated with acetic acid containing 10% acetic anhydride, the acetate X, m. p. 201—202° was obtained. This acetate had the analysis of a $C_{34}H_{44}O_3$ substance, and showed weak UV absorptions at λ_{max}^{MeOH} 242, 248, 254 and 260 mμ. Its infrared spectrum did not show a band for a hydroxyl group or any bands which would indicate the presence of a phenyl-conjugated double bond. Bands at 1725 and 1250 cm^{-1} are those of an acetate group, bands at 1600 and 1480 cm^{-1} those of an aromatic ring, and three relatively intense bands at 1090, 1060, and 1050 cm^{-1} indicated the presence of C—O—C grouping. The absence of a hydroxyl group and a phenyl-conjugated double bond suggested that this substance is a cyclic six-membered ether, 3,3-diphenyl-20-acetoxy-4-oxa-pregnane IX. The axial configuration of the C_5-proton was deduced from the NMR spectrum (6.96τ). These results suggest that the product melting at 110—112° has the structure VII, i.e., it is 3,5-seco-4-nor-3,3-diphenyl-3,5,20-trihydroxy-pregnane. When 3,5-seco-4-nor-3,3- diphenyl-3, 5,20-tri-hydroxy-pregnane, obtained from the crude lactone III, was treated with acetic acid containing 10% acetic-anhydride, in addition to compound IX the product X, m. p. 192—194°, was obtained. The analysis of this compound and its ultraviolet spectrum were the same as those of product IX, and their infrared spectra differed only in the region of C—O vibrations. In accordance with the accepted generalization that an equatorial bond absorbs at higher frequencies than an axial⁽⁹⁾, compound IX exhibited a band for a C—O bond at 1050 cm^{-1} whereas product X, m. p. 192—194°, showed the same band at 1030 cm^{-1}. Further proofs that the latter compound is a *cis*-isomer of 3,3-diphenyl-20-acetoxy-4-oxa-pregnane with the equatorial proton at C_5 were obtained by nuclear magnetic spetroscopy. The resonance signal for 5ρ-proton of this compound appeared at 6.77τ and for protons of the C_{19} methyl group at 8.93τ, while the resonance of the protons the C_{19} methyl group of compound IX appeared at 9.27.

When compound VII was treated with acetic anhydride in boiling pyridine and then boiled in an acetic acid solution an oil which contained no hydroxyl group was obtained. The infrared spectrum of this compound had bands at 1725 and 1250 cm^{-1} (acetate), and a band at 1370 cm^{-1} (CH_3—C)[6], which was stronger then the same band of 3,3-diphenyl-20-acetoxy-4-oxa-pregnane IX, indicating the presence of two acetate groups. Bands at 1700, 1650, 1600 and 1575 cm^{-1} showed the presence of a phenyl--conjugated double bond. In addition the ultraviolet spectrum of this compound was typical for a conjugated $Ph_2C=CH$— system(1e,10). These recults suggest that the diacetate product is 3,5-seco-4-nor--3,3-diphenyl-5,20-diacetoxy-pregn-2-ene XII.

The benzaote of the hydroxy acid XI, m. p. 237-239°, obtained by ozonolysis of compound V, on hydrolysis with 20% alcoholic potassium hydroxide followed by boiling with hydrochloric acid, gave the lactone of 2,5-seco-3,4-nor-20-hydroxy-pregnane-2-oic acid XIII, m. p. 237-239°. This compound had an analysis of $C_{19}H_{30}O_3$, and did not absorb ultraviolet light. Its infrared spectrum showed bands at 3500, 1780 (characteristic of five-membered lactones(11)), 1280, 1225, 1190 and 1110 cm^{-1}. The NMR spectrum showed a resonance signal at 6.25τ, which is in good agreement with an axial C_5 proton. The same compound XIII was obtained by ozonization of 3,5-seco-4-nor-3,3-diphenyl-5,20-diacetoxy-pregn-2-ene XII. The acid obtained had an infrared spectrum typical of an acid(6), and after treatment with alcoholic potassium hydroxide and boiling with hydrochloric acid it was converted to a crystalline substance whose properties were identical with those of the five--membered lactone XIII.

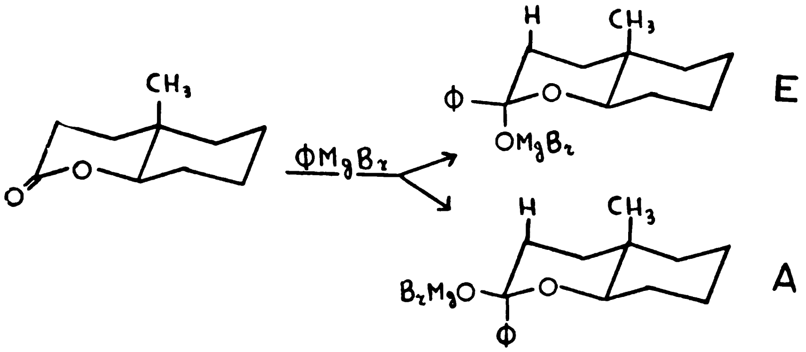
The five-membered lactone XIII treated with an excess of phenulmagnesium bromide gave only one product-2,5-seco-3,4-bis-nor--2,2-diphenyl-2,5,20-trihydroxy-pregnane XIV, m. p. 190°. This had an analysis of $C_{31}H_{42}O_3$. It did not absorb ultraviolet light and its infrared spectrum was consistent with the spectrum of an alcohol containing no phenyl-conjugated double bond. The NMR indicated the presence of an axial proton at C_5 (6.27τ). When 2,5-seco-3,4--bis-nor-2,2-diphenyl-2,5,20-trihydroxypregnane XIV was treated with acetic anhydride at room temperature, followed by boiling in an acetic acid solution, an oily product was obtained. This product was chromatographed on a silica gel column furnishing a crystalline substance m.p. 203-204°, and a small amount of an oil. The product m.p. 203-204° had an analysis of $C_{33}H_{42}O_3$ and its ultraviolet spectrum was the same as for the six-membered cyclic ethers IX and X. The infrared spectrum showed neither the presence of a hydroxyl group nor a phenyl-conjugated double bond. The NMR spectrum suggests that she C_5 proton has an axial configuration. These results are consistent with the assigned structure XVII, i.e., the compound is 2,2-diphenyl-3-nor-20-acetoxy-4-oxa-pregnane.

When product XIV was treated with acetic anhydride in boiling pyridine, 2,5-seco-3,4-bis-nor-2,2-diphenyl-2-hydroxy-5,20-diacetoxy-pregnane XV, m.p. 238-240° was obtained. It had the analysis of a $C_{35}H_{46}O_5$ compound and did not absorb ultraviolet light. The IR spectrum showed bands at 3400 cm^{-1} (hydroxyl group) and at 1725 and 1705 cm^{-1}. The band at 1705 cm^{-1} is that of acetate carbonyl at C_5 shifted to lower frequency due to the formation of a hydrogen bond with the C_2 hydroxyl group. In this case, as in the case of compounds VIII and IX, the band at 1375 cm^{-1} (CH_3—C) is more intense than the corresponding band of the cyclic ether XVII.

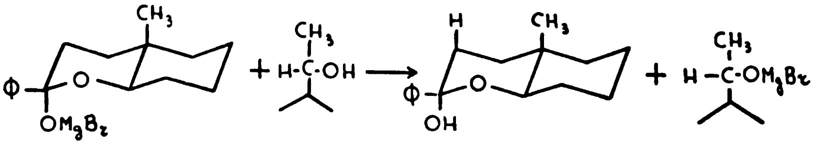
By boiling diacetate XV with acetic acid, 2,5-seco-3,4-bis-nor-2,2-diphenyl-5,20-diacetoxy-pregn-1-ene XVI, an oily substance was obtained. According to the UV (λ_{max}^{MeOH} $251_{m\mu}$) and IR spectra this substance has the structure XVI. Ozonolysis of 2,5-seco-3,4-bis-nor-2,2-diphenyl-5,20-diacetoxy-pregn-1-ene, followed by reductive decomposition and treatment with hydrazine hydrate gave a complex reaction mixture, which was chromatographed, giving several oily products. The structures of these products were not determined but on the basis of their infrared spectra they are obviously mixtures of the following: hydrazone of 1,5-seco-2,3,4-tris-nor-5,20-diacetoxy-pregnane-1-aldehyde, a mixed hydrazone of this aldehyde and benzophenone, and hydrazone of benzophenone.

The addition of a Grignard reagent to the carbonyl group of the steroid molecule gives a mixture of equatorial and axial carbinols(12a). The ratio of the carbinols depends on the position of the keto group in the steroid molecule. 3-keto-steroids with two axial hydrogens in the "meta"-position to the keto group react with methylmagnesium iodide and give a mixture containing 57-60% of a product with an equatorial methyl group(12). 17-keto-D-homosteroids which have three axial hydrogens in the "meta"-position to the carbonyl group give only a product with a methyl group in the equatorial position. This result may be ascribed to the presence of three axial hydrogens(13). As has been mentioned before, there is not much data in the literature about Grignard reactions of six-membered lactones, which from the stereochemical point of view, would be similar to the corresponding ketone. However, it is known that coumarin, the lactone of hydroxycinnamic acid, reacts with Grignard reagents and gives 4-(*o*-hydroxyphenyl)-2-alkyl or aryl-3-butane-2-ols or the corresponding substituted 2,2-dialkyl or 2,2-diaryl-1,2-benzopyrane(15). In this case it is not possible to make a comparison because of the different stereochemical structures of coumarin and similar lactones on the one hand and steroid lactones on the other. In addition, the presence of the aromatic ring gives coumarin different electronic properties.

Due to the steric effect of the axial hydrogens at C_1 and C_5 in the molecule of the lactone III, phenylmagnesium bromide adds to the carbonyl group more easily from the equatorial than from the axial side. Since the ratio of products V and VII does not depend on the reaction time (in other words, products V and VII are the result of a kinetically controlled reaction), and since the same ratio of products was obtained using different rations of reagents, this means that the formation of product V is also independent of the concentration of phenylmagnesium bromide. Therefore, in the reaction of phenylmagnesium bromide with the lactone III, two intermediate products, E and A, may be formed:

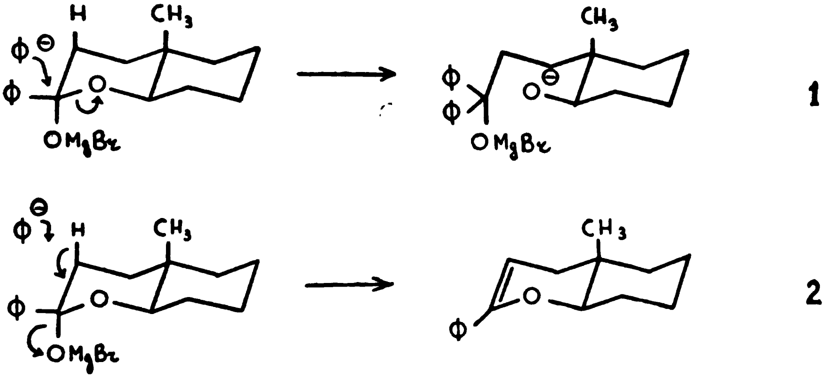


Since there is a free hydroxyl group at C_{20}, it must be assumed that this reacts too. However, since there is a large excess of phenylmagnesium bromide, it is less probable that the other possible reaction, disproportionation of the following type, could occur to any extent.



However, if it does, the formation of the unsaturated cyclic ether V would be easily explained by trans-diaxial elimination (16) of water. Another possible explanation is that in the next step of reaction the second molecule of phenylmagnesium bromide may act on the intermediate complex in two ways. In the first case, like in the reaction of esters (17) with an excess of a Grignard reagent, the nucleophilic phenyl ion displaces the $^{-}O—C$ group. This explains the formation of the tertiary carbinol. Howeve, instead of acting on the initial carbonyl carbon atom (reaction 1), the nucleophilic phenyl ion may attack the axial hydrogen of the neighboring CH_2 group of the intermediate E, thus causing trans-diaxial elimination (reaction 2):

Thus, the intermediate E, once formed, can react further, yielding either tertiary carbinol or cyclic olefin. However, because of the presence of the phenyl group and oxygen on the same carbon atom, reaction 2 probably proceeds faster than reaction 1, and it may be assumed that most of the molecules of the lactone III which react via the intermediate E yield the unsaturated product V. In case of the intermediate A, the stereochemical configuration



required for trans-diaxial elimination does not exist, and further reaction occurs as in reaction 1, yielding tertiary carbinol VII. The fact that under identical conditions the reaction of five-membered lactone XIII and phenylmagnesium bromide only gave tertiary carbinol clearly shows that for the formation of unsaturated product V it is necessary to have a hydrogen trans-diaxially oriented with the $^{-}$OMgBr group. Nevertheless, it should be pointed out that the explanation given for this „abnormal" Grignard reaction does not exclude other mechanisms. Consequently, to establish the course of this reaction with certainty, further investigations are needed.

EXPRIMENTAL*

(3,5-Seco-4-nor-pregnane-5,20-dione-3-oic acid II[4]*).* — A solution of progesterone I, 5 g in 100 ml methylene chloride, 100 ml ethyl acetate and 2 ml of acetic acid, was cooled at —70° and treated with a stream of ozone-enriched oxygen. After ozonization was complet, 3.5 ml 30% hydrogen peroxide was added to the solution. The reaction mixture was left overnight at room tempera-

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* Melting points are not corrected. Ultraviolet absorption spectra were determined on a Cary 11 MS spectrophotometer on methanolic solutions. Infrared spectra were taken on solid material incorporated into potassium bromide pellets. NMR spectra were taken at 60 Mc/s in deuterated chloroform containing tetramethyl silane as the internal standard on a Varian V 4300 B High Resolution Spectrometer. The results are expressed in τ units(18).

ture and then concentrated to a small volume. The residue was dissolved in ether and extracted with 1N sodium carbonate solution. The acid II was precipitated with 3N hydrochloric acid and filtered off. The yield of the crude acid II vas 60—70%. It was crystallized from methanol to m. p. 174—176°. IR spectrum: 3100, 1735, 1695, 1675, 1185, 950 cm^{-1}.

20-Hydroxy-4-oxa-pregnane-3-one, (III). — To a solution of acid II, 2.5 g in 30 ml 1N sodium hydroxide and 8 ml 95% ethanol, 1 g of sodium borohydride was added, and the mixture was refluxed for 2 hr. The excess of sodium borohydride was destroyed with a few drops of acetic acid, then 20 ml of 2N hydrochloric acid was added and boiled for 30 min. The separated solid was filtered off and crystallized from methanol, yielding 1.67 g (70%) of hydroxylactone III, m. p. 252—254°. IR spectrum: 3490, 1725, 1255, 1110 cm^{-1}.

Analysis for $C_{20}H_{32}O_3$:

Calcd.: C, 74.96; H, 10.06
Found : C, 75.16; H, 9.93

From the mother liquor of crystallization of crude hydroxylactone III an additional 600 mg of oily material was obtained. It solidified from methanol-ether solution, m. p. 185°. The IR spectrum of this substance was very similar to that of hydroxylactone III, but it was not investigated further.

4-Oxa-pregnane-3,20-dione (IV). — The hydroxyactone III, 65 mg, was dissolved in ether, 5 ml, and sodium dichromate solution, 2 ml, containing a few drops of sulfuric acid. The reaction mixture was stirred at room temperature for 2 hr and the ether solution separated. The water solution was extracted a few times with 5 ml portions of ether. The combined etheral solutions were washed with brine, dried over magnesium sulfate and evaporated. The residue was crystallized from methanol, giving 53 mg of ketone IV, m.p. 152-154°. IR spectrum: 1725, 1705, 1080, 1060, cm^{-1}. NMR: 6.14τ.

Analysis for $C_{20}H_{30}O_3$:

Calcd.: C, 75.43; H, 9.49
Found.: C, 75.37; H, 9.54

Reaction of phenylmagnesium bromide with the six-membered lactone III. — To a solution of phenylmagnesium bromide prepared from 2.6 g of activated magnesium and 10.6 ml of bromobenzene in dry ether, a solution of the lactone III, 2.5 g in tetrahydrofurane, 150 ml, was added dropwise through 2 hr. The mixture was kept under reflux for 4 hr. Then a saturated solution of ammonium chloride was added and the precipitated solid was filtered. The water solution was extracted several times with ether. The combined etheral solutions were washed with brine, dried over magnesium sulfate and concentrated. The oily residue was dissolved in benzene and chromatographed on a silica gel column. Eluates of 2% ethyl acetate in benzene gave 1.67 g (56%)of crustalline material, m. p. 156—158° (from methanol). Eluates with 20% ethyl acetate in benzene gave 1.30 g (36%) of solid m. p. 110—112°. Using 50% ethyl acetate in benzene an additional 2—4% of oily material was eluted whose infrared spectra shows the presence of hydroxyl and carbonyl groups, but it was not investigated further. The substance m. p. 156—158° (V), shows the following bands in the IR spectrum: 3580, 3400, 3010, 1650 (very strong), 1600, 1580, 1480, 1075 cm^{-1}. UV spectrum: λ_{max}^{MeOH} 264mμ, $\varepsilon = 16700$, 224μm, $\varepsilon = 13700$. NMR: 6.14τ.

Analysis for $C_{26}H_{36}O_2$:

Calcd.: C. 82.06; H, 9.54
Found : C, 82.17; H. 9.54

The compound VII, m. p. 110—112° does not absorb ultraviolet light. IR spectrum: 3330, 3010, 1600, 1485, 1085, 1035, 705 cm^{-1}. NMR: 6.45τ.

Analysis for $C_{32}H_{44}O_3$:

Calcd.: C, 80.63; H, 9.30
Found: C, 82.44; H, 9.39

Ozonolysis of 3-phenyl-20-acetoxy-4-oxa-pregn-2-ene (VI). — When compound V, m. p. 156-158°, was treated with acetic anhydride in pyridine, the corresponding acetate VI, m. p. 120°, was obtained. Its infrared spectrum does not show a band for a hydroxyl group. A solution of this acetate, 2 g in 30 ml of acetic acid and 30 ml of ethyl acetate, was cooled to 0° and treated with a stream of ozone-enriched oxygen. When the reaction had stopped 30 ml water was added to the solution and the reaction mixture left overnight at room temperature. The solution was concentrated and the residue dissolved in aceti acid, 90 ml. To this solution 1 g of chromic acid dissolved in 4 ml of water was added and heated for 30 min at 40-50°. The excess chromic acid was reduced with methanol and the reaction mixture concentrated to small volume, diluted with water and extracted with ether. The etheral solutions were combined, washed with brine and extracted with 0.25N sodium hydroxide solution. The alkaline solution was acidified with 3N hydrochloric acid and extracted with ether. This etheral solution was washed with brine, dried over magnesium sulfate and evaporated *in vacuo*. The yield of the acid XI, m. p. 237-238°, was 1.80 g (73%). IR spectrum: 3050, 2650, 1725, 1650, 1275, 1250, 1100, 950 cm^{-1}. UV spectrum: λ_{max}^{MeOH} 229mμ, $\varepsilon = 11180$, 273 mμ, $\varepsilon = 1040$, 280mμ, $\varepsilon = 1000$.

Analysis for $C_{28}H_{38}O_6$:

Calcd. ; C, 71.46; H, 8.14
Found : C, 71.64; H, 8.15

20-Hydroxy-3-nor-4-oxa-pregnane-2-one (*XIII*). — The acid XI, 1.25 g, was dissolved in 20% potassium xydroxide solution in 80% ethanol, 20 ml, and boiled for 2 hr. The reaction mixture was acidified with concentrated hydrochloric acid, diluted with water, 15 ml, and boiled for 30 min. The resulting solution was poured into cold water, extracted with ether, the ether evaporated and the residue dissolved in methylene chloride. This solution was washed at 0° with a concentrated sodium bicarbonate solution, dried over magnesium sulfate and concentrated to yield 667 mg (87) of the crude lactone XIII. The lactone XIII was crystallized from methanol, m. p. 237-239°. IR spectrum: 3500, 1775, 1205, 1180, 1100, 980 cm^{-1}. NMR: 6.25 τ.

Analysis for $C_{19}H_{30}O_3$:

Calcd.: C, 74.47; H, 9.87
Found: C, 74.68; H. 9.94.

Dehydration of 3,5-seco-4-nor-3,3-diphenyl-3, 5, 20-trihydroxy pregnane (VII).—a) A solution of diphenylcarbinol VII, 1.6 g, in 30 ml of acetic acid and 3 ml of acetic anhydride, was boiled for 4 hr. After removing acetic acid, the resulting oil was chromatographed on a silica gel column. Eluates obtained with benzene were combined and crystallized from methanol to give 1,49 g of product IX, m.p. 201-202°. IR spectrum: 1725, 1600 1485, 1250, 1090, 1060, 1050 cm^{-1}. UV spectrum: λ_{max}^{MeOH} 242 mμ, $\varepsilon = 857$, 248 mμ, $\varepsilon = 1400$, 254 mμ, $\varepsilon = 1870$, 260 mμ, $\varepsilon = 1430$. NMR: 6.96 τ.

Analysis for $C_{34}H_{44}O_3$:

Calcd.: C, 80.56; H, 8.86
Found: C, 81.31; H, 8.76

Eluates of 2% ethyl acetate in benzene gave 186 mg of only substance XII. IR Spectrum: 1725, 1700 1650, 1600, 1575, 1485. 1245, 1075, 1030 cm^{-1}. UV spectrum: λ_{max}^{MeOH} 251 mμ, $\varepsilon = 13000$,

b) A solution of diphenylcarbinol VII, 3 g in 45 ml of pyridine and 4 ml of acetic anhydride, was boiled for 2.5 hr. The excess of anhydride was destroyed with water and then acetic acid evaporated to dryness. The oily residue was dissolved in acetic acidi 45 ml, water, 0.5 ml, was added and boiled for 16 hr. After removing acetic acid the resulting oil was dissolved in ether and the ethereal solution washed first with water, then with saturated sodium bicarbonate solution and finaly with brine. After drying over magnesium sulfate, ether was evaporated and the residue dissolved in benzene and chromatographed on a silica gel column. Eluates of of 2% ethyl acetate in benzene gave only one product, identical with compound XII from the preceeding experiment.

c) When crude hydroxy-lactone III was used for the reaction with phenylmagnesium bromide, the isolated diphenylcarbinol VII in reaction with acetic acid gave a mixture of compounds IX and **X**. The resulting oil was chromatographed on a silica gel column.

Eluates of pure benzene gave in about 18% yield a substance m.p. 192-194°, followed by product IX, m.p. 201-202°. The compound X, m. p. 192-194°, had the same UV spectrum as product IX. IR spectrum: 1725, 1685, 1600, 1580, 1485, 1245, 1075, 1030 cm^{-1}. NMR: 6.78 τ.

Analysis for $C_{34}H_{44}O_3$:

Calcd.: C, 81.56; 8.86
Found: C, 81.70; 8.91

Ozonolysis of diphenylethylene-diacetate XII. — Ozonolysis and hydrolysis were performed as for the reaction VI→XI. From 2.8 g of XII, 1.24 g of the lactone XIII was obtained. This product was identical with the lactone obtained from XI as described above.

Reaction of phenylmagnesium bromide with five-membered lactone XIII.— To a phenylmagnesium bromide solution prepared from 1 g of activated magnesium and 4 ml of bromobenzene in dry ether, a solution of the lactone XIII, 900 mg in 25 ml of tetrahydrofurane, was added dropwise. The mixture was kept under reflux for 6 hr and worked up as described for the reaction of six-membered lactone III. Chromatography on a silica gel column, using 5% ethyl acetate in benzene gave only one product, XIV, 1.24 g. This compound was crystallized from a methylene chloride—hexane solution and had m. p 190°. IR spectrum: 3300, 3010, 1600, 1485, 1180, 1085, 1045, 1010 cm^{-1}. NMR: 6.27 τ.

Analysis for $C_{31}H_{42}O_3$:

Calcd.: C, 80.47; H, 9.15
Found: C, 80.71; H, 9.32

2,2 Diphenyl-3-nor-4-oxa-20-acetoxy-pregnane- (XVII).— A solution of diphenylcarbinol XIV, 800mg in 20 ml of pyridine and 2 ml of acetic anhydride, was left at room temperature overnight. After removing pyridine *in vacuo*, the residue was dissolved in acetic acid, 30 ml, 0.5 ml of water was added and boiled for 6 hr. Acetic acid was distilled *in vacuo*, the residue dissolved in benzene and chromatographed on a silica gel column. Eluates of 2% ethyl acetate in benzene gave 580 mg of compound XVII, mp. 203-204° (from methanol). IR spectrum: 1725, 1600 1485, 1375 1250 1050, cm^{-1}. UV spectrum: λ_{max}^{MeOH} 242 mμ,$\varepsilon = 850$; 248mμ,$\varepsilon = 1360$; 254 mμ,$\varepsilon = 1845$; 260 mμ, $\varepsilon = 1400$.

Analysis for $C_{33}H_{42}O_3$:

Calcd.: C, 81.44; H, 8.70
Found: C, 81.70; H, 8.81

Eluates of 5% ethyl acetate in benzene gave 120 mg of oily substance XVI which had the following bands in IR spectrum: 1725, 1685, 1600, 1575, 1245, 1075, 1030 cm^{-1}. UV spectrum: $\lambda_{max}^{MeOH} = 251$ mμ, $\varepsilon = 13500$.

2,5seco-3,4-bis-nor-2,2-diphenyl-2-hidroxy-5,20-diacetoxy-pregnane (XV).— A solution of diphenylcarbinol XIV, 1.8 g in 40 ml of pyridine and 4 ml of acetic anhydride, was boiled for 2.5 hr. Pyridine was evaporated *in vacuo* and to the residue 150 ml of cold water was added. The resulting solid (2.03 g) was filtered and crystallized from methylene chloride-methanol to givg XV, m. p. 238-240°. IR spectrum: 3400, 3010, 1725, 1705, 1600, 1485, 1375, 1255, 1245, 1060, 1035 cm^{-1}.

Analysis for $C_{35}H_{46}O_5$:

Calcd.: C, 76.89; H, 8.50
Found: C, 76.99; H, 8,33

2,5-Seco-3,4-bis-nor-2,2-diphenyl-5,-20-diacetoxy-pregn-1-ene (XVI). — A solution of compound XV, 1.5 g in 50 ml of acetic acid and 0.5 ml of water, was boiled for 6 hr. The acid was removed *in vacuo*. The remaining oil had IR and UV spectrums identical with product XVI described above.

A solution of this crude olefin XVI, 1 g in 50 ml of methylene chloride and 50 ml of ethyl acetate was cooled at 0° and treated with a stream of ozone-enriched oxygen. After reductive decomposition of ozonide, treatment with hydrazine hydrate and the usual work up, by chromatography on a silica gel column several oily products were isolated in small yields. According to their IR spectra these are probably hydrazone of 1,5-seco-2,3,4-tris-nor-5,20-diacetoxy-preganne-1-aldehyde, a mixed hydrazone of this aldehyde and benzophenone, and a hydrazone of benzophenone.

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GLASNIK HEMIJSKOG DRUŠTVA, Vol. 29, No. 1—2, 1964, pp. 73—78.

PHYTIN CONTENT OF WHEAT

by

V. D. CANIĆ and T. T. STOJSAVLJEVIĆ

Phytin is a mixed calcium-magnesium salt of inositol hexaphosphoric acid. Phytin was synthesized from inositol, phosphoric acid and phosphorus pentoxide by Posternak(1). Its structure is still a subject of interest. Phytic acid is thought to be mesoinositol hexaphosphate $C_6H_6\,[OPO\,(OH)_2]_6$. This accords with the fact that it forms salts with twelve equivalents of a metal. Since phytic acid is associated with three molecules of water it is ascribed the formula $C_6H_6\,[OPO\,(OH)_2]_6 \cdot 3H_2O$.

Phytin is present everywhere in plants and is especially accumulated in seeds, where it stores phosphorus. In cereals phytin is usually accumulated in the bran and the aleurone layer. With a phosphotase, probably a phytase, phytin is gradually converted to lower phosphoric esters and finally to mesoinositol. This process proceeds especially in the course of germination, in which case phosphorus is liberated from phytin(2).

The literature data on the phytin content of wheat grain differs quite a lot, from 160 mg% to 485 mg% calculated as phytic phosphorus(3—11),which amounts to 52%—94%(12) of the total phosphorus content of the wheat grain. If the variations due to the use of different methods of determination are excluded, the above differences can be attributed to differences in type of wheat and conditions of cultivation (climate, soil, fertilizer, etc).

The purpose of this work was to determine the content of phytin in various groups of wheat and its relation to phosphorus, calcium, magnesium and the total mineral substances (ash) in them.

MATERIALS AND METHODS

All the wheat samples were taken from the 1961 harvest from different places in Yugoslavia. One hundred samples were investigated, mostly of high-yield varieties. Five different groups of wheat were investigated: 59 samples of 13 high-yield earl-ripening Italian varieties (San Pastore, Leonardo, Leone, Mara, Menrimp, Abbondanza, Generoso, Autonomia, Argelato, Produttore, S-15, Fortunato, Funo), 21 samples of 6 high-yield late-ripening varieties (Etoile de Choisy, Magdalena, Primus, Rival, Elia, Funone) 4 samples of 3 new domestic intensive late-ripening varieties (Vitka, Bosa, Zlata), 9 samples of 8 extensive varieties (U_1, Bankut 1205, Novosadska 1446, Novosadska 1993, Rumska crvenka, Mala ruska, Helkorn, Triumph), and 3 samples of 3 *Triticum durum*, maccaroni wheat varieties (Senatore Cappelli, Patrizio-6, Garigliano). One sample was a mixture of San Pastore and Leone (50: 50) and we grouped it among the high-yield early-ripening Italian wheats.

The grain was ground to 60 mesh. The results were calculated for a moisture content of 12%.

For calcium, magnesium, total phosphorus and ash we used the results obtained earlier(12). In determining the total content of phosphorus we did not separate silicic acid(13).

For the determination of phytin we used the method of separating it in the form of the hardly water-soluble ferric phytate which is then decomposed with sulphuric and nitric acid (3, 5, 14). This was done in the following way: 10 grams of ground wheat was weighed and extracted with 100 ml 0.4 N hydrochloric acid for three hours on a shaker at thirty-five rotations per minute. The extract was centrifuged and then filtered through fluted Scheicher u. Schuell 595 1/2 filter paper. Twenty-five ml of the clear filtrate was measured into a 50 ml volumetric flask and the solution neutralized with 25% sodium hydroxide with phenolphthalein as the indicator, acidified with several drops of 5.5 N hydrochloric acid and the flask filled up to the mark with distilled water. Twenty milliliters of this solution was measured off into a 50 ml centrifuge tube and 4 ml of ferric chloride added (1 gram Fe per liter 1 N HCl solution). Overnight ferric phytate precipitated. The gelatinous precipitate was then separated by centrifugation and the liquid decanted. The residue was washed with 5 ml 0.5 N hydrochloric acid, centrifuged and the liquid decanted. The precipitated ferric phytate was then dissolved in a Kjeldahl flask with concentrated sulphuric acid to vhich, after brief heating a few drops of concentrated nitric acid were added. Phytic phosphorus was determined potentiometrically by measuring the intensity of the blue color obtained with ammonium molybdate(15).

TABLE 1

Phytic acid content		Number of samples	Percentage of all samples
in mg$^0/_0$	in mvals		
up to 850	up to 15.5	14	14
850 — 950	15.5 — 17.3	23	23
950 — 1050	17.3 — 19.1	42	42
1050 — 1150	19.1 — 20.9	16	17
over 1150	over 20.9	4	4
	Total	100	100

To calculate the content of phytic acid the formula of meso-inositol hexaphosphate was used in the anhydrous form with a molecular weight of 660 and equivalent weight 55.

RESULTS AND DISCUSSION

The content of phytic acid in the samples varied from 627.8 to 1245.4 mg%. This is shown in Table 1.

The mean value (M), the standard deviation (δ) and the variation coefficient for the tested samples are:

$M = 976.5$ mg%

$\delta = 111.4$ mg%

$CV\% = 11.4$

The phytic acid content expressed in milliequivalents (millivals) varied from 11.2 to 22.6, with a mean value 17.8 mvals.

The contents of ash, calcium, magnesium, total and phytic phosphorus, and the percentage of phytic phosphorus of total phosphorus, are shown in Table 2.

TABLE 2

	Italian high-yield early--ripening	High--yield late--ripening	New Yugoslav intensive late--ripening	Extensive varieties	Maccaroni wheats (Triticum durum)
Number of varieties (samples)	13 (59)	6 (21)	3 (4)	8 (9)	3 (3)
Ash in %	1.62	1.62	1.62	1.79	1.77
Calcium in mg% (mval)	36.8 (1.8)	37.4 (1.9)	35.6 (1.8)	42.9 (2.1)	41.5 (2.1)
Magnesium in mg% (mval)	121.7 (10.0)	122.2 (10.1)	133.5 (11.0)	138.5 (11.4)	124.6 (10.2)
Phosphorus as P_2O_5 in mg% (phytic)	843.8 (630.2)	853.2 (608.7)	838.2 (604.5)	950.9 (691.2)	887.1 (647.4)
% of phytic in total P_2O_6	74.7	71.3	72.1	72.7	72.9
Phytic acid in mg% (mval)	976.2 (17.7)	942.8 (17.2)	936.3 (17.0)	1070.8 (18.2)	1004.8 (18.2)

The phytic acid content decreased in the following order: extensive varieties, maccaroni wheats (*Triticum durum*), Italian high--yield early-ripening, high-yield late-ripening, new Yugoslav intensive late-ripening varieties. There is an obvious difference in the phytic acid content of the extensive and maccaroni varieties and the early and late-ripening high-yield varieties.

In some samples the percentage of total phosphorus as phytic phosphorus varies from 50.3 to 96.1%. Varieties containing more phosphorus had more phytic acid too, but while usually with a lower percentage of phytic in total phosphorus. The highest percentage of total phosphorus as phytic was found the Italian high-yield early-ripening varieties — 74.7%.

The ratio of phytic acid to calcium and magnesium is interesting because phytin is the calcium magnesium salt of phytic acid. The total millivals of calcium and magnesium was about 12.1. This indicates that 5.7 mvals (the difference up to 17.8 mvals) of phytic acid could be neutralized with other metals(16).

Table 2 shows that groups of wheats with a larger ash content also have a larger content of calcium, magnesium, phosphorus and phytic acid. The total millivals of calcium and magnesium from 11.8 to 13.5 corresponds to the ash content, i.e., varieties with a larger ash content also have a higher millivals total of calcium and magnesium. The ratio between the millivals of calcium and magnesium is 1 : 5 and 1 : 6, i. e. fairly constant. Assuming that calcium and magnesium are quantitatively associated with phytic acid it may be said that two thirds of phytic acid in wheat is neutralized with calcium and magnesium and their millival ratio is between 1 : 5 and 1 : 6, as was already shown recently(16).

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SRPSKO HEMIJSKO DRUŠTVO (BEOGRAD)

BULLETIN OF THE CHEMICAL SOCIETY
Belgrade

(Glasnik Hemijskog društva — Beograd)
Vol. 29, No. 3-4, 1964.

Published by
SRPSKO HEMIJSKO DRUŠTVO (BEOGRAD)
1966.

Translated and published for U.S. Department of Commerce and
the National Science Foundation, Washington. D. C., by
the NOLIT Publishing House, Terazije 27/II, Belgrade, Yugoslavia
1966.

Translated by
DANICA LADJEVAC and ALEKSANDRA STOJILJKOVIĆ

Edited by
PAUL PIGNON

Printed in Beogradski Grafički Zavod, Belgrade

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GLASNIK HEMIJSKOG DRUŠTVA, Vol. 29, No. 3—4, 1964, pp. 81—93.

OXIDATION AND HYDROLYSIS KINETICS OF OXIDIZED IRON IN AQUEOUS SOLUTIONS AT ELEVATED TEMPERATURE AND PRESSURE IN AN AUTOCLAVE

by

DUŠAN VUČUROVIĆ, RAJKO VRAČAR and ILIJA ILIĆ

The oxidation of bivalent iron by gaseous oxygen from aqueous solutions has been studied by several authors(1, 2, 3). Their results show that it in a number of phases: 1) dissolution of oxygen, 2) adsorption of its molecules on the surface of bivalent salt, 3) transformation of molecular to atomic oxygen, 4) oxidation by atomic oxygen.

This multiphase process considerably retards the rate of oxidation at room pressure and temperature. Phase 1) has a particularly great retarding influence. At room temperature and pressure this heterogeneous-homogeneous process provides maximum solubility of 7 mg/l of water. With increasing temperature in an open vessel the solubility decreases, becoming negligible at 100°C.

According to some authors(4) the presence of copper ions in the aqueous solution accelerates the oxidation. It is reported that with a fine spray of oxygen and the presence of copper ions oxidation proceeds to completion. However, investigations done so far, and our results as well(5), show that quantitative oxidation of Fe^{2+} under normal conditions is hardly possible in a reasonable time.

On the other hand, in oxidation of Fe^{2+} by gaseous oxygen in a closed vessel at elevated temperatures, the solubility of oxygen in the solution is higher. The increased solubility and the increased rates of the other phases with higher temperature greatly accelerate oxidation.

Iron oxidation in a closed vessel at a given solution pH is accompanied by simultaneous hydrolysis of the oxidized iron. According to the literature(3, 6) the chemism of oxidation and hydrolysis depends on the presence of free acid in the solution. In acidified aqueous solutions, with an excess of free sulphuric acid, it can be expressed as follows:

$$4\,FeSO_4+0_2+2H_2SO_4=2Fe_2(SO_4)_3+2H_2O \qquad (1)$$

$$Fe_2(SO_4)_3+nH_2O=3H_2SO_4+Fe_2O_3\,.\,nH_2O \qquad (2)$$

and in solutions without an excess of free acid:

$$6\,FeSO_4+1\ ^1/_2O_2+nH_2O=Fe_2(SO_4)_3+Fe_2O_3\,.\,nH_2O \qquad (3)$$

$$Fe_2(SO_4)_3+(3+n)H_2O=Fe_2O_3\,.\,nH_2O+3\,H_2SO_4 \qquad (4)$$

Obviously, the difference is that in Eq. (1) sulphuric acid directly participates in the oxidation reaction and in Eq.(3) some of the iron oxidizes to hydrated oxide which precipitates. However, the above differences are not constant. Later in the process the sulphuric acid extracted by hydrolysis according to Eq.(4) will participate in oxidation. After a time this leads to transformation of the process in Eq.(3) to that in Eq.(1).

The precipitation of iron and the extraction of H_2SO_4 by hydrolysis represent an important characteristic of the autoclave oxidation process.

Oxidation of Fe^{2+} by oxygen in an autoclave and simultaneous hydrolysis of oxidized iron are very important from the practical point of view. The formation of ferric hydroxide or other hardly soluble salts of trivalent iron is accompanied by a greater change of the isobar potential than in the formation of the same compounds of bivalent iron, nickel, cobalt and some other metals. Hence Fe^{3+} precipitates by hydrolysis at considerably lower pH than the other metals, so it can be separated from them to.

If iron is in bivalent form in the solution it must first be oxidized. It has been pointed out that oxidation by gaseous oxygen, the most suitable oxidizing agent, at room pressure and temperature is a slow process. Therefore it is reasonable to try oxidation in an autoclave with simultaneous hydrolysis of Fe^{3+} to separate it from other metals.

It is well known that iron is always present in sulphide nickel-containing cobalt minerals. In the processing of these minerals by acid leaching in an autoclave with the presence of oxygen Fe^{3+} hydrolyzes. If the initial iron has a sulphide form before hydrolysis it must first be oxidized. This behavior of the iron and knowledge of this behavior is an important prerequisite for successful extraction of cobalt and nickel.

In this work we wished to contribute to the study of the kinetics of ferrous sulphate autoclave oxidation and hydrolysis of the ferric sulphate formed. It is of practical interest to find what conditions of autoclave oxidation produce quantitative oxidation of iron and how much of it can be separated by hydrolysis, i. e. what are the optimal conditions to get maximum purification of iron from the solution.

To this end the influence of the following factors was investigated: a) temperature, b) oxidation time, c) initial Fe^{2+} concentration in the solution, d) acidity of the solution, e) partial pressure of oxygen.

EXPERIMENTAL

An aqueous solution of chemically pure $FeSO_4 . 7 H_2O$ was oxidized in an autoclave. Ferric sulphate was dissolved in a quantity that corresponded to the desired concentration of Fe^{2+} in the solution.

Oxidations were performed in an acid-resistant autoclave with one liter of the solution. The autoclave was electrically heated and a constant temperature maintained automatically. The solution was intensively mixed with a metal mixer built into the autoclave. Before heating, gaseous O_2 was introduced into the autoclave to the desired pressure.

At the end of the oxidation time (measured from when the desired temperature was reached), the mixing was discontinued and the autoclave air-cooled to room temperature. The cooling time lasted on average about five hours. After cooling the excess of O_2 was released and the solution taken out and filtered to separate the iron precipitate.

The quantities of oxidized and hydrolyzed iron were determined by measuring the bivalent and the total iron in the filtrate. The change of solution acidity was determined by measuring the pH with a pH-meter.

a) *Influence of temperature*

Runs were made at 50, 80, 110, 140, 170, and 200°C. The working specification of the autoclave did not allow temperatures higher than 200°C.

The results are shown in Table 1 and Fig. 1.

TABLE 1

Influence of temperature on quantities of oxidized and hydrolyzed iron

Concentration of solution: 1.45 g Fe^2 x /*l*;
Oxidation time: 3 hours; Po_2 15 atm;
Initial pH of solution: 3.5

Temp %	Pressure (atm)	Conc. Fe^{2+} after oxidat. (g/l)	Oxidized Fe^{2+} (g/l)	Oxidized Fe^{2+} (%)	Conc. $Fe^{2+}+Fe^{3+}$ after oxidat. (g/l)	Hydr. Fe^{3+} (g/l)	Hydr. Fe^{3+} (%)	Diff. between hydrol. and oxidiz. Fe (%)	pH after oxidat.
20	15	1.368	0.081	6.68	1.413	0.036	1.79	4.89	3.28
50	15.5—16.5	0.921	0.531	36.67	1.086	0.366	25.20	11.47	2.51
80	18 —19	0.279	1.173	80.90	0.387	1.065	73.42	7.48	2.02
110	20 —21.5	0.095	1.355	93.50	0.116	1.305	91.01	2.49	1.85
140	24 —25.5	0.060	1.392	95.86	0.088	1.364	93.93	1.93	1.80
170	30.5—32.5	0.044	1.406	96.96	0.072	1.388	95.71	1.25	1.77
200	41 — 43	0.022	1.428	98.46	0.023	1.427	98.41	0.00	1.75

It can be seen from the results that for a given time the percentage of oxidized iron increases with increasing temperature.

The quantity of trivalent iron increases most rapidly in the temperature range up to 110°C. Above this the percentage of oxidation continues to rise, but considerably slower as it approaches 100.

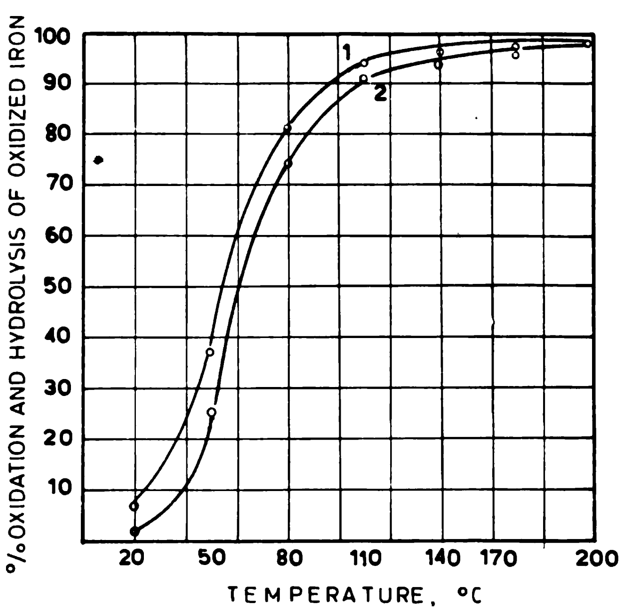

Fig. 1. Dependence of quantity of oxidized and hydrolyzed Fe on temperature

1. Oxidized Fe
2. Hydrolyzed Fe

Likewise the hydrolysis rate of oxidized iron also increases with increasing temperature. The temperature dependence of hydrolysis relative to the initial concentration of Fe^{2+} in solution is the same as the temperature dependence of oxidation. Up to 110°C hydrolysis proceeds intensively and above this slows down considerably. This means that most of the iron is extracted from the solution (91%) below this temperature.

The curve in Fig. 2 shows the relation between the oxidation and hydrolysis processes. At low temperatures (up to 50°) the difference between the quantities of oxidized and hydrolyzed iron is considerable. This means that in this temperature range hydrolysis goes considerably slower. However, with increasing temperature the rate of hydrolysis increases faster than that of oxidation, reducing the difference. At 200°C, under the given working conditions, the difference disappears, all the ferric sulphate hydrolyzes and the oxidized iron precipitates.

Hydrolysis during autoclave oxidation forms free H_2SO_4 which reduces the pH of the solution. Under the given conditions at 200°C the initial pH of 3.5 is reduced to 1.75.

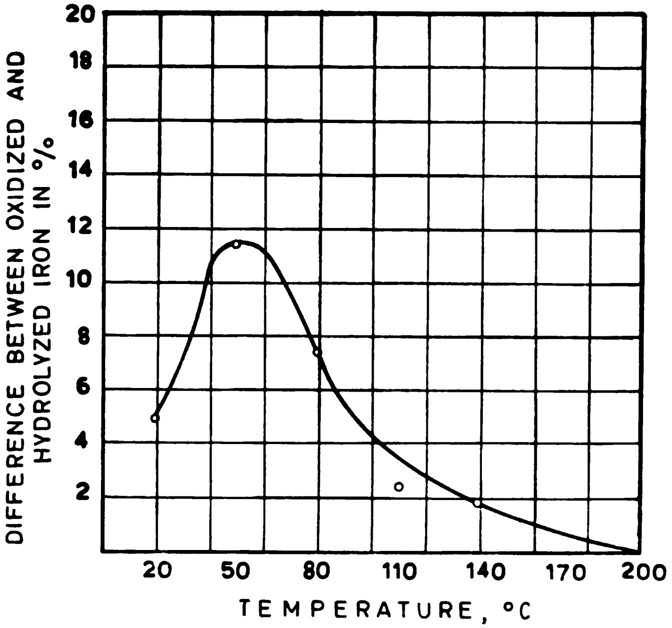

Fig. 2. Difference between oxidized and hydrolyzed Fe as a function of temperature

b) *Influence of oxidation time*

The above results show that for a concentration of 1.45 g Fe^{2+}/l of the solution it is not possible to obtain quantitative oxidation even if oxidation lasts 3 hours at a temperature of 200°C.

TABLE 2

Influence of oxidation time on quantity of oxidized Fe^2
Concentration of solution: 1.45 g $Fe^2 x/l$
Temperature 200°C, Po_2 15 atm, $P_{working}$ 41—43 atm
pH of solution before oxidation: 3.5

Oxid. time (h)	Concentr. of Fe^{2+} after oxid. (g/l)	Oxidized Fe^{2+} (g/l)	Oxidized Fe^{2+} (%)	Hydrolyzed fraction of oxidized Fe (%)	pH after oxidation
1	0.046	1.404	96.83	100.00	1.80
2	0.031	1.419	97.89	100.00	1.77
3	0.023	1.427	98.48	100.00	1.75
4	0.014	1.436	99.07	100.00	1.73
5	0.002	1.448	99.87	100.00	1.70

Since the specification of the autoclave did not allow the use of higher temperatures, further studies were made to see whether it is possible to get complete oxidation and how in a longer time oxidation changes with time in general.

Experiments were carried out at the optimal temperature of 200°C for periods of 1, 2, 3, 4, and 5 hours.

Complete oxidation of bivalent iron in a starting concentration of 1.45 g/l of solution is possible (Table 2) under the given conditions if the process lasts 5 hours.

The above results also show that the bulk of the Fe^{2+} (96.83%) oxidizes in the first hour and in this period the oxidation rate is maximum. The rest of it oxidizes much more slowly. The oxidation rate decreases and much more time is required for the completion of the process.

Hydrolysis of oxidized iron was complete in all the investigated periods of time. This implies that hydrolysis practically depends only on temperature and the acidity of the solution.

c) *Influence of the bivalent iron concentration*

It may be seen from the above that a concentration of 1.45 g Fe^{2+}/l completely oxidizes in a period of five hours. To simplify study of the influence of the starting concentration of Fe^{2+}, experiments were made with an oxidation time of 2 hours. It was found that oxidation was complete even at a concentration of 4.52 g Fe^{2+}/l at 200°C. Therefore a series of experiments were made to study the influence of the Fe^{2+} starting concentration on the time required for complete oxidation.

It was found that a concentration above about 5 g Fe^{2+}/l completely oxidizes in a period of one hour, so this was adopted as optimal for investigating the influence of the Fe^{2+} concentration on oxidation and hydrolysis. This fact leads to the important conclusion that an increased Fe^{2+} concentration reduces the time required for complete oxidation.

TABLE 3

Influence of concentration of Fe^{2+} on oxidation and hydrolysis of oxidised iron.
Time of oxidation 1 *hr*, temperature 200 °C. P_{O_2}, 15 *atm* P_{working} 41—43 *atm*
pH of solution before oxidation 3,5

Conc. Fe^{2} (*g/l*)	Conc. of Fe^{2+} after oxidation (*g/l*)	Oxidised Fe^{2+} (*g/l*)	Oxidised $Fe^{2}{}_{+}$ (%)	Conc. of $Fe^{2+}+Fe^{3+}$ aft oxid. (*g/l*)	Hydr. *Fe* (*g/l*)	Hydr. part of oxid (%)	*pH* after oxidation
1.45	0.046	1.40	96.83	0.046	1.404	100.00	1.80
4.52	0.00	4.52	100.00	0.000	4.520	100.00	1.15
9.30	0.00	9.30	100.00	0.265	9.036	97.09	0.95
14.34	0.00	14.34	100.00	1.240	13.100	91.14	0.85—0.90
18.90	0.04	16.86	99.84	5.030	13.870	73.95	0.80—0.85
46.20	0.14	46.06	99.70	32.240	13.960	31.21	0.80—0.85

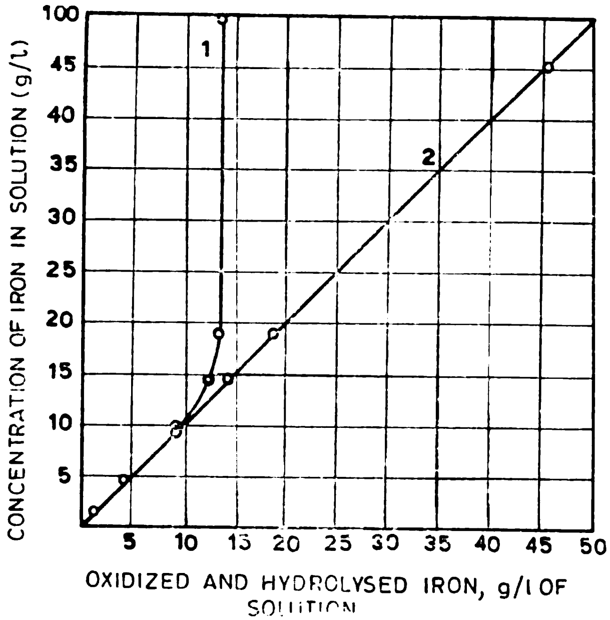

Fig. 3. Dependence of quantity of hydrolyzed and oxidized Fe on concentration of Fe^{2+} in solution

1. Quantity of hydrolyzed Fe
2. Quantity of oxidized Fe

Table 3 and Fig. 3 show that the quantity of oxidized iron increases with increasing Fe^{2+} concentration in the solution, in which case all concentrations greater than or equal to 4.52 g/l of the solution completely oxidize in one hour.

Likewise, the quantity of hydrolyzed iron increases with increasing Fe^{2+} up to about 14 g/l of solution. However, for concentrations larger than 14 g/l it remains constant.

This influence of the Fe^{2+} starting concentration on the process of hydrolysis is due to change of acidity of the solution. The more Fe^{2+} there is in the solution, i.e., the more Fe^{3+} hydrolyzes, the more free H_2SO_4 there is. At a sufficiently high concentration, so much sulphuric acid will separate that the pH will reach a value at which further hydrolysis is not possible.

From the above results it follows that for a starting pH 3.5 the limiting Fe^{2+} concentration is aproximately 14 g/l of solution. By oxidation and subsequent hydrolysis of this quantity, the free H_2SO_4 reduces the pH value to 0.80—0.85, at which the process of hydrolysis completes.

Thus the pH change is a quantitative measure of the quantity of hydrolyzed iron. The greater the change, the more iron hydrolyzed.

Data in the literature, which also confirm our results⁽⁵⁾, show that at room pressure and temperature in acidified aqueous solutions trivalent iron begins to hydrolyze at pH 2. Therefore the lower pH limit at which Fe^{3+} can hydrolyze is at about 2.

In case of hydrolysis in an autoclave, the higher temperature and pressure bring about change of the conditions of hydrolysis, which proceeds in considerably more acid media, shifting the lower pH limit way down to 0.80—0.85. This represents an important characteristic of hydrolysis of Fe^{3+} at elevated temperature and pressure.

d) *Influence of solution acidity on hydrolysis*

The above finding that Fe^{3+} hydrolyzes in an autoclave down to pH 0.80—0.85 was checked by investigating the influence of the solution acidity on hydrolysis. It has already been pointed out that the maximum quantity of iron that can hydrolyze at starting pH 3.5 is about 14 g/l.

The influence of the solution acidity was also investigated to find out to what value the quantity of hydrolyzed iron can be increased by increasing the starting pH.

TABLE 4

Influence of solution acidity on hydrolysis of Fe^{3+} autoclave

Concentration of solution 18.90 g Fe^{2+}/l
Oxidation time one hour; temperature 200°C
P_{O_2} 15 atm. $P_{working}$ 41—43 atm

pH of solution	Conc. of Fe^{2+} after oxid. (g/l)	Oxidized Fe^{2+} (g/l)	Oxidized Fe^{2+} (%)	Conc. of $Fe^{2+}+Fe^{3+}$ after ox. (g/l)	Hydrolyzed Fe (g/l)	Hydr. fraction of Fe (%)	pH after oxidation
0.80—0.85	0.00	18.90	100.00	18.90	0.00	0.00	0.80—0.85
2	0.00	18.90	100.00	7.72	11.80	59.15	0.80—0.85
3.5	0.04	18.86	99.84	5.03	13.87	73.96	0.80—0.85
6	0.00	18.90	100.00	0.06	18.84	99.71	1.10

Obviously, the oxidation of iron does not depend on the solution acidity. It is complete at all the pH values investigated.

The experiments made at pH 0.80, 2, and 3.5 at concentrations of 18.90 g Fe^{2+}/l of the solution confirm that hydrolysis in an autoclave takes place at considerably higher acidity than that at room temperature and pressure and the lower pH limit at which ferric sulphate is hydrolyzed is 0.80—0.85.

As was expected, the quantity of hydrolyzed iron increased with increasing solution pH because in this case the pH range in which Fe^{3+}

is hydrolyzed is increased. Increase of solution pH from 3.5 to 6 increases the quantity of hydrolyzed iron by about 5 g/l of solution, so that the maximum quantity of iron that can be separated by hydrolysis is 19 g/l solution.

e) *Influence of the partial pressure of oxygen*

The partial pressure, i. e. the amount of oxygen is one of the factors that influences Fe^{2+} oxidation.

Since complete oxidation of iron at a concentration higher than about 5 g/l of solution is achieved at P_{O_2} 15 atm in one hour, investigations of the influence of Po_2 were only carried out to see whether under these conditions the iron can be oxidized with even less O_2.

f) *Characteristics of the precipitate obtained by hydrolysis*

No unified opinion can be found in the literature concerning the mechanism of the hydrolysis of ferric sulphate. In the introduction of this paper we give reactions of hydrolysis, from which it follows that hydrated iron oxide is formed by hydrolysis of $Fe_2(SO_4)_3$. However, in acidified aqueous solutions hydrolysis usually proceeds with the formation of basic salts, whose form depends on the conditions. Posnjak and Merwin(7) studied the equilibrium of the Fe_2O_3—SO_3—H_2O system and found that in hydrolysis Fe_3^+ can form six kinds of basic salts. Other authors(8) found that with high acidity of the solution hydrolysis produces a basic salt of the $FeSO_4(OH)$ type.

In our experiments, at temperatures higher than 140°C, we obtained a characteristic brownish-red precipitate. It has the form of tiny grains, and its filtering and sedimentation properties are good. These characteristics make it similar to a crystalline material.

Chemical analysis of the precipitate showed that it contains 61.4% Fe and 2.2% S. The high iron content and the small sulphur content, and the above physical properties, show that the precipitate is a mixture of the dehydrated oxide Fe_2O_3 and a small amount of a basic salt.

At temperatures lower than 140°C the precipitate is light red and its separation from the solution is more difficult. The same content of sulphur and 52% of iron imply that there is no dehydration of the precipitate and the basic component is in the form of $Fe_2O_3 . nH_2O$.

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GLASNIK HEMIJSKOG DRUŠTVA, Vol. 29, No. 3—4, 1964, pp. 95—105

MINOR CONSTITUENTS IN NATIVE NATURAL PRODUCTS, ASHES AND SLAGS. VI.

SEMIQUANTITATIVE SPECTROGRAPHIC DETERMINATION OF SECONDARY CONSTITUENTS IN NATURAL MATERIALS AND THEIR PRODUCTS

P. S. TUTUNDŽIĆ and V. Č. ŠĆEPANOVIĆ

Besides their principal components, all natural materials — ores, minerals, soils, rocks, coal, plants, etc. — contain small quantities of a large number of elements. These are called secondary constituents. The determination of these elements can be important both for pure and applied science. From the point of view of pure science their determination in natural materials can contribute to the knowledge of the composion of the earth's crust, and also to the knowledge of the distribution of given atomic species on the earth (4,9,12,13,14). From the practical point of view, their determination in natural materials can help towards more complete utilization of the products of these materials, and also to the discovery of new raw materials, especially for rare metals. Also, by determining them in soils, plants and related materials, their biochemical role can be discovered, which is very important with regard to the nutrition of plants, and also of animals and man (1,2,3,5,8,10).

In view of its multiple importance we tried to work out a semiquantitative spectrographic method for the determination of microelements. We required the method to satisfy three principle conditions: 1, it should be suitable for determining a large number of elements; 2, the procedure should be preferably simple and suitable for routine analysis; 3, the accuracy should be as high as possible for a semiquantitative spectrographic determination.

In choosing the elements to be determined, we wanted from the first to include the rare metals. We also tried to include elements whose determination lines all lie within a given spectral region, which could be photographed all on one plate in a high dispersion apparatus. In this way we arrived at 20 elements whose lines are covered by the spectral region 2450 to 3500 Å. These elements and the wavelengths of their spectral lines are given in Table 1.

TABLE 1

The elements determined and their spectral lines

Element	Wavelength Å	Element	Wavelength Å
Ag	3280.68	Mn	2576.10
B	2496.78	Mo	3170.35
Be	3131.06	Nb	2950.88
Cd	3261.06	Ni	3002.49
Co	3044.01	Pb	2833.07
Cr	2843.25	Sn	3175.02
Cu	3247.54	Ti	3372.80
Ga	2943.64	V	3102.30
Ge	3256.09	Zn	3345.02
In	2651.18	Zr	3438.23

The determination of line intensities and the construction of the analytical curves in quantitative spectral analysis is rather complicated and time-consuming, and so is not convenient for routine application. We therefore sought to simplify the determination of line intensities, by visual estimation. Our method involves counting the degrees of the spectral line on a spectrogram obtained with a rotating logarithmic step-sector(6,7).

It is well known that the elements of the base, i. e. the principle constituents of the material examined, exercise a great influence on the accuracy of spectrochemical determinations. The influence of secondary component elements is generally negligible. To get the highest possible accuracy, the chemical composition of the base for the standards should be as close as possible to that of the material to be analysed. For this reason we used for the standard base a mixture of the oxides of the elements which are the principal components of igneous rocks. The proportions of these elements were the same as in igneous rocks, these proportions being taken as average for the elements in the earth's crust(4,12). The composition of the mixture for the standard base is given in Table 2.

TABLE 2

Average quantities of principle components in igneous rocks
(average concentrations in the earth's crust)

Compound	SiO_2	Al_2O_3	Fe_2O_3	CaO	Na_2O	K_2O	MgO	SO_3
%	59.1	15.1	13.3	4.6	3.37	2.98	2.8	0.225

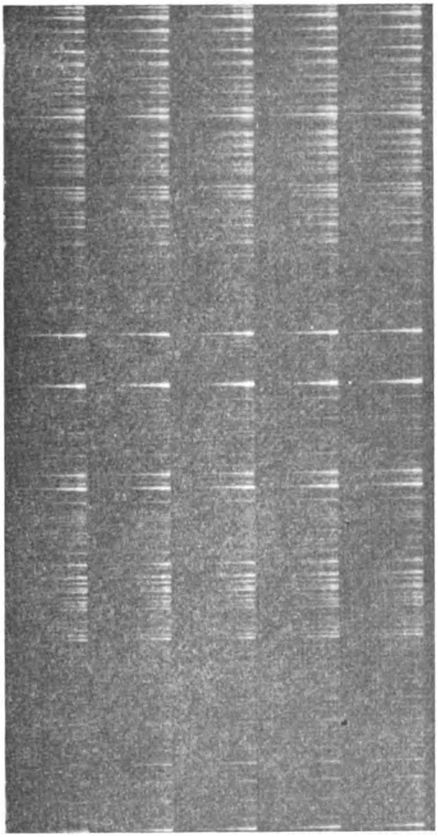

Fig. 1. Appearance of a spectrogram obtained with the 7° rotating logarithmic step-sector.

We introduced known concentrations of the elements to be determined into the standard base, by adding Spex-G_1 powder, which contains 43 chemical elements in a graphite base(7). This powder includes all the elements we had selected for determination except gallium and indium. We made a special standard for these two, using their pure oxides and our base. The concentrations of the 20 elements to be determined in our standards were as follows:

0.1% 0.01% 0.001% 0.0001%.

In preparing the standards we also added 3% of bismuth oxide, bismuth serving as a sort of internal standard, or a control element. In successful spectrograms the lines of bismuth appear in well-determined degrees, as may seen from Table 3.

TABLE 3

Bismuth lines and their degrees

Wavelength (Å)	Degree	Wavelength (Å)	Degree
2627.9	5	2938.3	7
2780.5	5	3024.6	6.8
2809.6	5	3397.2	6.5

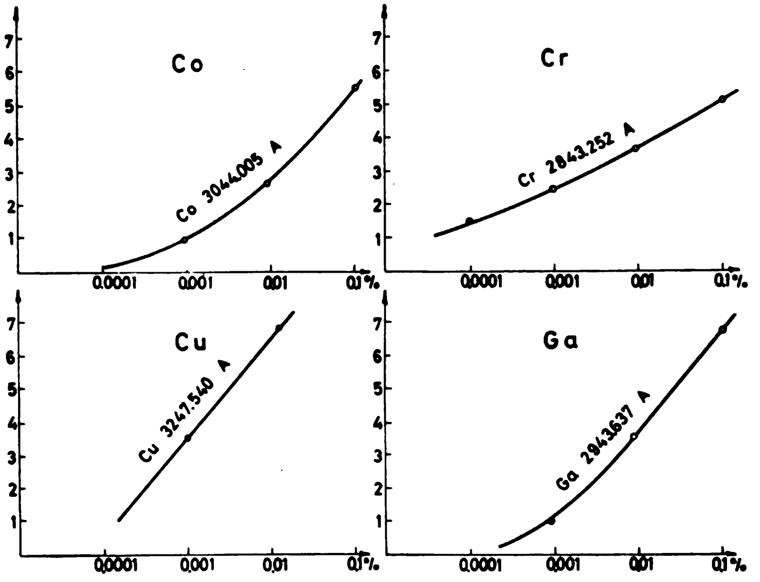

Fig. 2 a. Calibration curves.

Using the standards we plotted calibration curves for the semiquantitative determination of the 20 elements. These curves are given in Fig. 2.

As may be seen, most of the curves are straight lines. This indicates that good accuracy should be obtained. It may be pointed out that it is possible to determine a large number of elements in a wide concentration range, from 10^{-1} to 10^{-4}%.

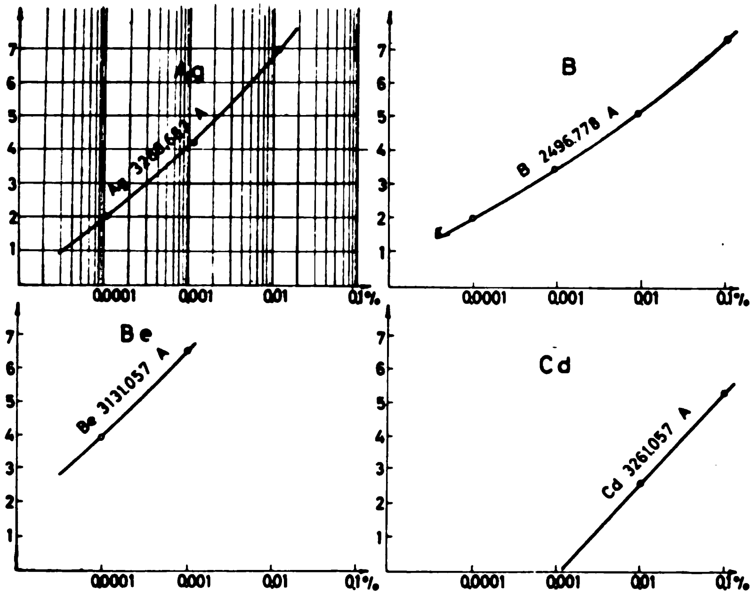
Ag
Ag 3280.683 A
B
B 2496.778 A
Be
Be 3131.057 A
Cd
Cd 3261.057 A
1
2
3
4
5
6
7
0.0001
0.001
0.01
0.1 %

Fig. 2 b

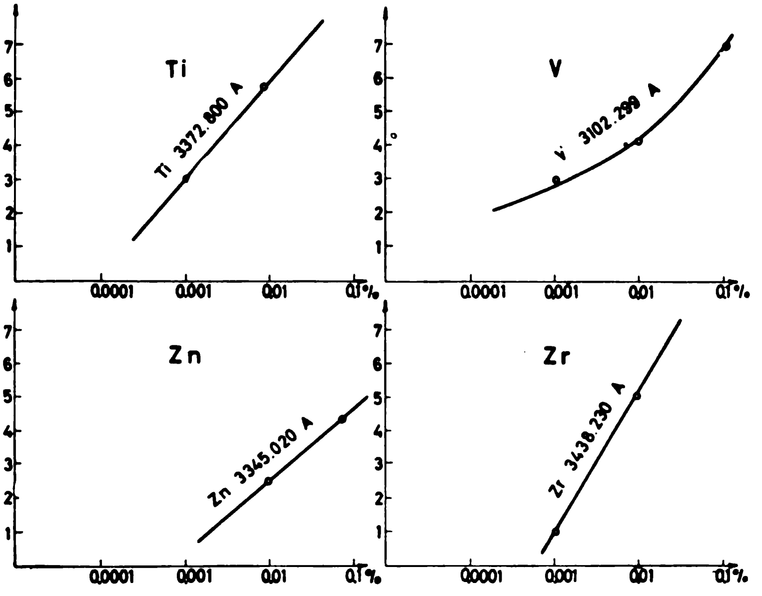
Ti
Ti 3372.800 A
V
V 3102.299 A
Zn
Zn 3345.020 A
Zr
Zr 3438.230 A
1
2
3
4
5
6
7
0.0001
0.001
0.01
0.1 %

Fig. 2 c

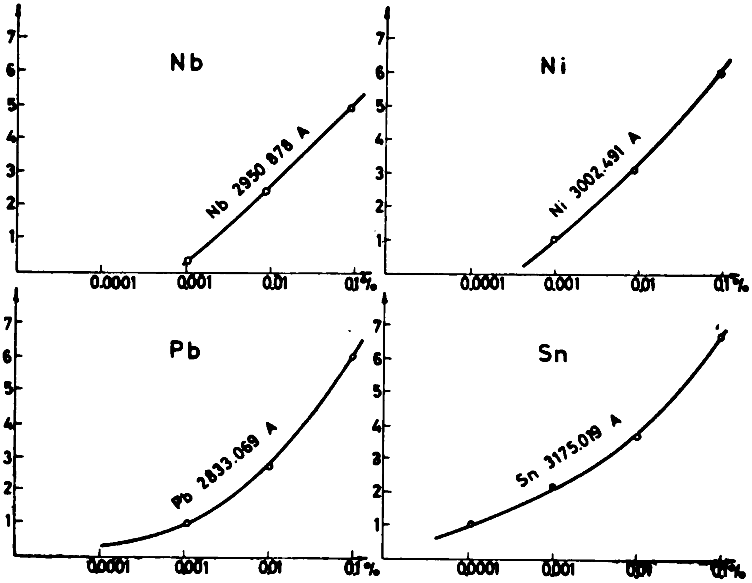
Nb
Nb 2950.878 A
Ni
Ni 3002.491 A
Pb
Pb 2833.069 A
Sn
Sn 3175.019 A
1
2
3
4
5
6
7
0.0001
0.001
0.01
0.1%

Fig. 2 d

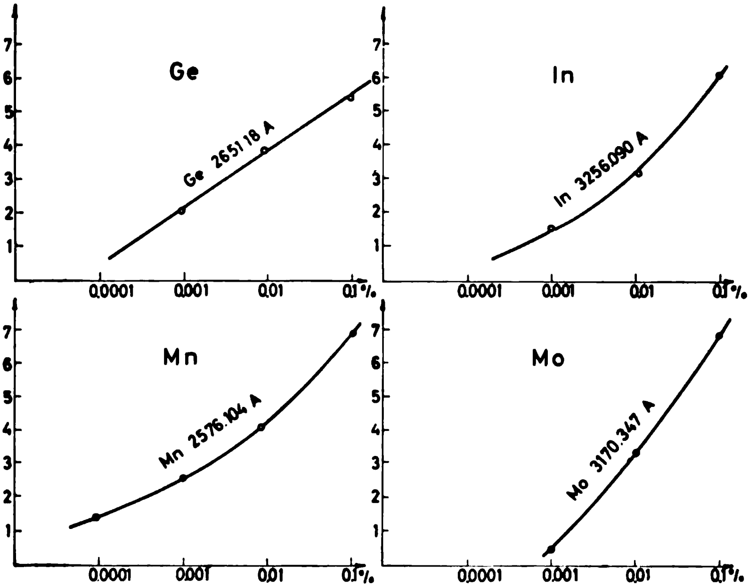
Ge
Ge 2651.18 A
In
In 3256.090 A
Mn
Mn 2576.104 A
Mo
Mo 3170.347 A
1
2
3
4
5
6
7
0.0001
0.001
0.01
0.1%

Fig. 2 e

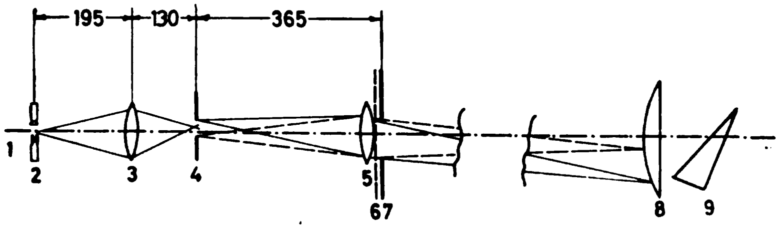

Fig. 3. Optical setup of the illumination of the spectrograph. 1-optical axis, 2-electrodes, 3-F-958 lense, 4-intermediate diaphragm, 5-lense on the sector, 6-rotating sector, 7-slit, 8-lense, 9-prism.

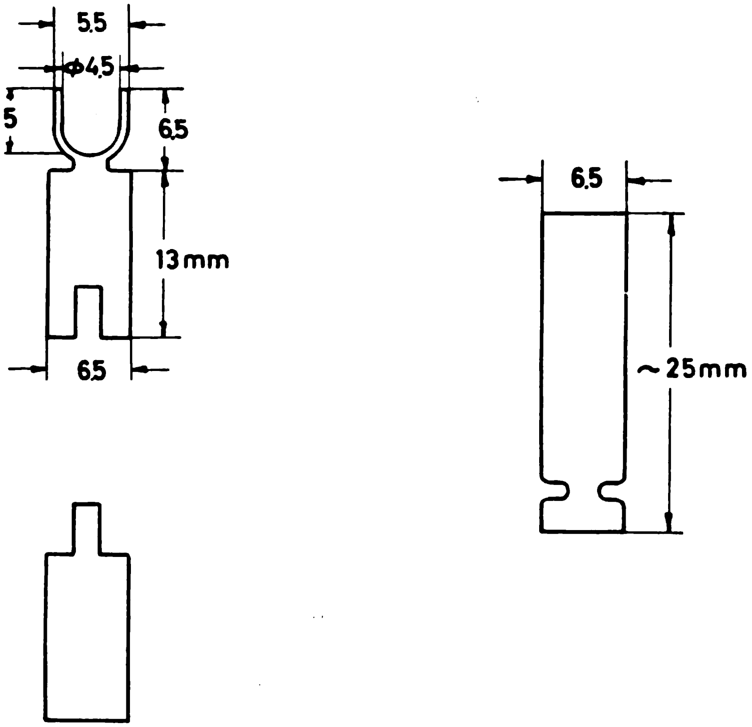

Fig. 4. Form of the electrodes.

The operating conditions were as follows:
Spectrograph: Hilger E 478
Excitation: continuous arc, stabilized
Current: 10 amps
Optical setup: as for quantitative determination (Fig. 3)
Rotating step-sector: 7° step, ratio 2 : 1; 1600 t/min
Interelectrode gap: 9 mm, constant

Charge: 20 mg of mixture, in the form of a well-homogenized powder
Exposure time: about 2.5 min, until complete combustion
Spectral range: 2450—3500 Å
Photographic plates: Kodak B.10

The form of the electrodes is shown in Fig. 4.

We found that the errors were not higher than 30%. In some cases we got accuracies as high as with quantitative spectrochemical methods, with errors of less than 10%. For example, with a few improvements, we got an accuracy in the determination of germanium as high as that obtained by quantitative methods, i. e. errors always less than 10%(11).

The method described may be recommended for the semiquantitative determination of small quantities of elements in soils, rocks, wastes from the treatment of ores, the ashes of coal and of crude oil, and similar materials.

School of Technology,
Physical Chemistry and Electrochemistry Institute
and Inorganic Chemistry Institute, Beograd

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GLASNIK HEMIJSKOG DRUŠTVA Vol. 29, No. 3—4, 1964, pp. 107—113

A CONTRIBUTION TO THE COMPLEXOMETRIC DETERMINATION OF METALS. VII. POTENTIOMETRIC DETERMINATION OF IRON, COPPER, NICKEL, ZINC, MAGNESIUM, MANGANESE, LEAD, COBALT AND CADMIUM*

by

TIBOR A. KISS

In our earlier works(1,2) we used visual indicators for direct titration of copper, nickel, zinc, magnesium, manganese, lead, cobalt, cadmium and iron with ethylenediaminetetraacetic acid (EDTA), and then checked, compared and modified different known methods. We got results for metals by various methods in good agreement. In these works(1,2) we also developed inverse titration methods, i. e. titrations of EDTA with metals. The results of these titrations were also consistent, but in all determinations they were slightly lower than those obtained by titrations of EDTA with metals. We ascribed this disagreement to the indistinct color change.

To find out whether this indicator error was the only cause of the inconsistency, in this work we carried out titrations with the same metal solutions and EDTA, indicating the titration end point potentiometrically. The volumetric factors of the metal solutions obtained by different methods of direct potentiometric titration with EDTA were in good agreement, but slighly lower than those obtained with metal indicators.

For potentiometric titrations of higher metal concentrations we modified the usual methods by first titrating acidified metal solutions to near the equivalence point. Then by adding a buffer we were easily able to keep the rest of the metal in solution and titrate it to the end point. The results obtained by these methods were consistent and in good agreement with those obtained by the unmodified methods.

We developed potentiometric methods of inverse titration, i. e. titration of EDTA with metals, for both dilute and concentrated solutions. The results for metals agreed were consistent but slighly lower than those obtained by potentiometric titrations of the metals with EDTA, and slighly higher than those of EDTA titration with the metals in the presence of visual indicators.

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* Part VI., Glasnik hemijskog društva (Beograd) 28 (5—6), 1963.

TABLE 1

Metal solution volumetric factors got by different methods. Results are a means of 6—9 estimations of different amount of metal: up to 50 ml 0.1 M and 0.01 M of metal solution or EDTA.

	iron	copper	nickel	zinc	magnesium	manganese	lead	cobalt	cadmium
Metal titration with EDTA in presence of indicator$^{10)}$ potentiometrically	1.0985	1.0499	1.0584	1.0087	1.1023	1.0922	0.9995	1.2012	1.0132
	1.0981$^{5a)}$	1.0460$^{2a)}$	1.0565$^{2a)}$	1.0050$^{2a)}$	1.0093$^{2a)}$	1.0921$^{2a)}$	0.9993$^{2a)}$	1.2007$^{2a)}$	1.0128$^{2a)}$
	1.0977$^{6b)}$	1.0456$^{2b)}$	1.0571$^{3)}$	1.0054$^{3)}$	1.0089$_{1)}$		0.9991$^{3)}$		1.0130$^{3)}$
	1.0979$^{7c)}$	1.0458$^{3)}$							
		1.0461$^{6)}$							
		1.0457$^{8)}$							
average	1.0979	1.0458	1.0568	1.0052	1.0091	1.0921	0.9992	1.2007	1.0129
EDTA titration with metal in presence of indicator potentiometrically	1.0963	1.0404	1.0538	1.0009	1.0050	1.0917	0.9983	1.1992	1.0119
	1.0972$^{5a)}$	1.0433$^{1a)}$	1.0552$^{1a)}$	1.0033$^{1a)}$	1.0075$^{1a)}$	1.0918$^{1a)}$	0.9988$^{1a)}$	1.1998$^{1a)}$	1.0120$^{1a)}$
	1.0971$^{6b)}$	1.0430$^{1b)}$	1.0548$^{4)}$	1.0027$^{4)}$	1.0069$^{4)}$		0.9984$^{4)}$		1.0124$^{4)}$
		1.0424$^{4)}$							
		1.0427$^{7)}$							
		1.0426$^{9)}$							
average	1.0970	1.0430	1.0550	1.0030	1.0072	1.0918	0.9986	1.1998	1.0122

1) By method after (3)
2) Analogous to method after (3)
3) By method after (8)
4) Analogous to method after (8)

a) with mercury electrode
b) with platinum electrode

a) with mercury electrode
b) with platinum electrode

5) By method after (4)
6) By method after (5)
7) Analogous to method after (5)

a) at pH 3 at 20 °C
b) at pH 3 at 80 °C
c) at pH 5 at 20 °C

8) By method after (6)
9) Analogous to method (6)
10) Methods described in papers (1.2)

From Table 1 it may be concluded that the inconsistency of the results of metal titrations with EDTA and of EDTA titrations with metals is mainly due to an error in the color change determination.

EXPERIMENTAL

Preparation of standard solutions

For the potentiometric titrations we used the same standard solutions as in our earlier works(1,2), in which we described their preparation.

All reagents were Merck, p. a.

Instruments and equipment

A Radiometer PHM 22p pH-meter and a Radiometer TTA 1 potentiometric titration set were used.

Radiometer P 100 and K 100 electrodes were used for the potentiometric redox titrations of iron and copper, and for the determination of the other elements a K 100 electrode and a mercury electrode (platinum sheet coated with electrolytically deposited mercury) prepared by Siggia's method(3).

For titrations with a bimetal electrode pair(4) we used a platinum and a tungsten electrode.

Determination of iron

Iron (III) was titrated by the methods of Přibil and co-workers(5) at pH 3 at room temperature. The equilibrium redox potential of the indicator electrode was established more quickly if the titrated solution was heated at 80°C and if titration was done at pH 5 in a solution buffered with ammonium acetate.

Large concentrations of iron were titrated in acidified solution to near the equivalence point, then the pH was adjusted to 3 or 5 and the titration completed.

Inverse titrations were done under similar conditions.

The results are shown in Table 1.

Determination of copper

By the method of Siggia and co-workers(3) EDTA was titrated with 0.1 M copper sulphate in presence of pyridine at pH 7.5 with a platinum and mercury indicator electrode. Analogous to the above method we developed inverse methods, i. e. titrations of copper sulphate with EDTA, in small and large concentrations.

Up to 30 mg of copper in 60 ml of titrated solution buffered with ammonia and ammonium acetate was titrated at room temperature without ammonium rodanide(6) and at 40°C with the addition of ammonium rodanide(°). Titrations up to 120 mg of copper in 60 ml of the solution and inverse titrations were performed in similar ways.

By titrating at pH 10 in ammoninum buffer(8) we could not obtain a satisfactory potential rise at the equivalence point(6).

The results are shown in Table 1.

Determination of nickel, zinc, magnesium, manganese lead, cobalt and cadmium

Siggia and co-workers(3) titrated EDTA with 0.1 M solution of nickel nitrate, zinc nitrate, magnesium chloride, manganese chloride, manganese acetate and lead nitrate in solutions buffered with 50% pyridine, using a mercury and a saturated calomel electrode. Under these conditions we got a good potential rise even if we used other salts such as the sulphates of nickel, magnesium, manganese and cadmium, zinc chloride and lead nitrate.

Inverse titrations of a 0.1 M metal solutions with EDTA were performed in a similar way.

Copper, nickel, zinc, magnesium, lead and cadmium were potentiometrically titrated directly in an ammonium medium in presence of tartaric acid by the methods of Budanova and Platonova(4). The end point was determined with a bimetal electrode pair (platinum, tungsten). We also titrated EDTA with metal solutions in a similar way.

The results are shown in Table 1.

DISCUSSION

When elements are determined by retitration the added excess of EDTA is titrated with a standard metal solution. This metal solution is usually standardized by titration with EDTA but not inversely by titration of EDTA with the metal. Since we found (Table 1) that the titer of the metal solution obtained by EDTA titration with the metal is different from that obtained by inverse titration it is recommended that the metal solutions with which retitration is performed be standardized by titrating EDTA with the metals.

Department of Chemistry
University of Novi Sad

Received March 7, 1964

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GLASNIK HEMIJSKOG DRUŠTVA, Vol 29, No. 3—4, 1964, pp. 115—120

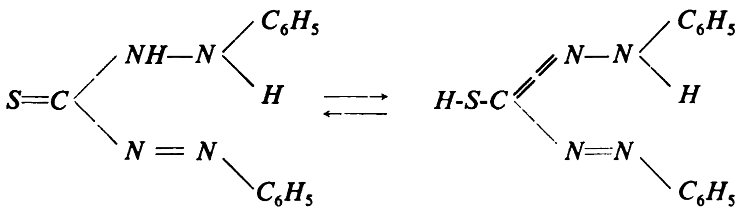
THIN-LAYER CHROMATOGRAPHY OF INORGANIC IONS II. — SEPARATION OF METAL DITHIZONATES

by

MIRJANA HRANISAVLJEVIĆ-JAKOVLJEVIĆ, IVANKA PEJKOVIĆ-TADIĆ,
KOSTA JAKOVLJEVIĆ and JELENA MILJKOVIĆ-STOJANOVIĆ

In recent years thin layer chromatography has been applied for analyzing mixtures of inorganic salts. By this method Seiler *et al.* (1) have separated cations of almost all analytical groups. However, in the separation of elements of H_2S-group tailing of spots occurred and in case of the $(NH_4)_2S$ group and the alkaline earth metal group zones of some cations overlapped. Solvent systems used in these separations were mixtures of polar solvents containing a large amount of water or acid (up to 20%), thus prolonging the running time to as much as 3 hours.

To avoid the difficulties encountered by Seiler and coworkers we have studied the separation of metal ions in the form of their complexes with organic compounds(2). Such metal complex compounds may be expected to behave like organic substances on a silica gel layer, i. e. to be separated by nonpolar solvents in a short time. We have decided to use dithizone [diphenylthiocarbazone, HDz, (I)] as the complexing agent, since it is a nonspecific reagent which reacts with a great number of metal ions forming colored complexes soluble in organic solvents.



I

Communicated at XXXIVth International Congress of Industrial Chemistry, Beograd, 1963.

Acording to Fischer(3) the dithizone complexes formed in acid and neutral media have the following formulae:

$$M_{I}HDZ,\ M_{II}\ (HDz_2)\ \text{and}\ M_{III}\ (HDz)_3$$

where M_I is a monovalent, M_{II} a divalent and M_{III} a trivalent metal. HDz represents the monovalent thioketone residue of dithizone. In alkaline media, it is assumed that complexes of the following type are formed:

$$M_I\,Dz/2,\ M_{II}Dz$$

where Dz is the divalent dithizone residue.

The separation of metals from mixtures in the form of metal dithizonates has already been done in a few cases by other chromatographic methods. In 1954, Venturello and Ghe(4) studied the behavior of some metal dithizonates on paper impregnated with buffer solutions, but they only succeeded in separating three metals: silver, mercury and zinc. The separation of dithizonates on a column of alumina was performed back in 1942(5), but in fact T. Ashizava,(6) in 1961, was the first to carry out a systematic chromatographic investigation of metal dithizonates on aluminum oxide columns.

By thin-layer chromatography we have separated the dithizonates of the following metals: mercury, copper, bizmuth, zinc, lead, cadmium, nickel and cobalt.

An aqueous solution of metal ions is first extracted with a chloroform solution of dithizone; the pH of the aqueous solution determines the order in which the metal dithizonates get extracted. At pH 3 dithizone reacts with mercury, copper and bizmuth, at pH 5 with zinc, lead and cadmium, and at pH 7 with nickel and cobalt. These three chloroform extracts are separately chromatographed on a thin layer of silica gel in benzene-methylene chloride (50 : 10, v/v). The separation takes 15 to 30 minutes (Fig. 1).

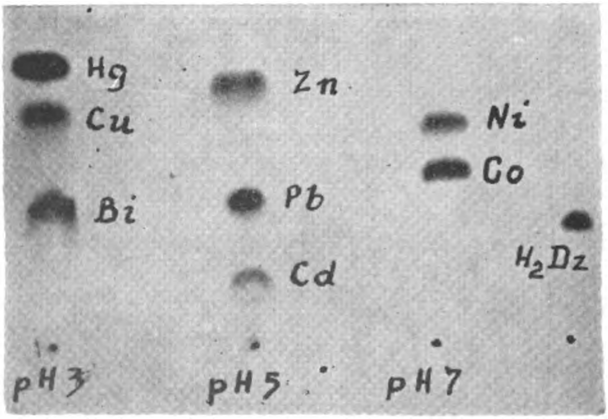


Fig. 1

Since the separated complexes are colored, no detecting reagent is necessary and the course of separation can be followed visually. The colors of complexes are different and characteristic for each element and determination of R_f-values is not necessary (Table 1).

TABLE 1

pH	Complex (8)	Colour	$R_f \times 100$
3	$Hg(HDz)_2$	orange	54
	$Bi(HDz)_3$	pink-brown	37
	$Cu(HDz)_2$	dark violet-brown	47
5	$Zn(HDz)_2$	light violet	50
	$Pb(HDz)_2$	red	34
	$Cd(HDz)_2$	yelow orange	13
7	$Ni(HDz)_2$	dark gray	41
	$Co(HDz)_2$	dark violet	32

* Copper dithizonate at *pH* 5-6 (*CuDz*) is green-brown and has the other R_f value ($R_f \times 100 = 38$)

It should be noted that sometimes co-extraction of metal ions can take place. This is because not all metal dithizonates react simultaneously or quantitatively; in addition, on prolonged shaking of aqueous and chloroform solutions, metal dithizonates can pass into the aqueous phase. An excess of dithizone does not interfere with the identification of cations, since the blue spot of dithizone itself (Fig 1.) does not coincide either in color or in R_f-value with any metal dithizonate in the mixture. Since by this method microgram amounts of metals can be determined, it can be used for their determination in biological material and water.

EXPERIMENTAL

Materials: 0.1% aqueous solutions of acetate or chloride of mercury, copper, cadmium, lead, nickel and cobalt; 0.1% aqueous solution of $Bi(OH)CO_3$ with a few drops of acetic acid.

Solvent system: benzene-methylene chloride (50 : 10, v/v)

Running time: 15—35 minutes depending on the number of cations present in the mixture.

Procedure: One milliliter of the solution of each salt is put into a small separatory funnel and the mixture (total 8ml) is acidified with acetic acid to pH 3. To 2 ml of this mixture 2 ml of 0.1% solution of dithizone in chloroform is added and the obtained mixture is vigorously shaken for one minute. The lower organic layer is separated and the aqueous layer is shaken once more with 2 ml of dithizone solution. The chloroform layer is again separated and combined with the first extract. These two extracts make solution I which contains dithizonates of mercury, copper and bismuth. To remove the traces of these cations from the aqueous solution it is necessary to extract the remaining aqueous solution twice more, each time with 2 ml of chloroform dithizone solution and once with 3—4 ml of pure chloroform; these chloroform solutions are discarded.

The remaining aqueous solution is adjusted to pH 5 by adding dilute ammonia, and then it is vigorously shaken twice, each time with 2 ml of dithizone solution in chloroform. The separated chloroform layers are united and they make solution II which contains dithizonates of cadmium, lead and zinc. The remaining aqueous solution is extracted twice again, each time with 2 ml of chloroform dithizone solution and once with 3—4 ml of pure chloroform and these chloroform solutions are again discarded.

The aqueous solution is then adjusted to pH 6 by the addition of dilute ammonia and extracted twice, each time with 2 ml of 0.1% solution of dithizone in chloroform. The united chloroform extracts make solution III, which contains dithizonates of cobalt and nickel.

20 μ 1 of each solution (I, II and III) is applied by means of a micropipette to a chromatoplate (20 × 13 × 0.5 cm) coated with a thin layer of silica gel (0.2 mm thick). Original "Silicagel G nach Stahl" or a mixture of 87 parts of silica gel (240—270 mesh) and 13 parts of gypsum is used. The chromatoplates are air dried for 12 hours. They are developed in chromatographic tanks (24 × 16 × 8 cm) previously saturated with solvent mixture.

Received March 7, 1964

School of Science
Institute of Chemistry
Beograd

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GLASNIK HEMIJSKOG DRUŠTVA, Vol. 29, No. 3—4, 1964, pp. 121—129

THE REACTION BETWEEN SODIUM TUNGSTATE AND *L*-ASCORBIC ACID

by

M. V. ŠUŠIĆ, D. S. VESELINOVIĆ and D. Ž. SUŽNJEVIĆ

The reaction between sodium tungstate and L-ascorbic acid has been little studied. In the literature there are some data[1,2] which indicate that the tungstate interferes with the spectrophotometric determination of niobium from L-ascorbic acid solution and that the reaction product of tungstate and L-ascorbic acid is adsorbed on anionic ion-exchange resin. The aim of our work was a more detailed study of this reaction.

Since in the reaction of sodium tungstate and L-ascorbic acid a colored compound is formed, we studied its absorption spectrum in the region from 1000 to 330 mμ. The measurements were carried out at room temperature, in cuvettes of 1 cm (glass cuvettes for the visible and quartz for the UV region), using water as the reference solution.

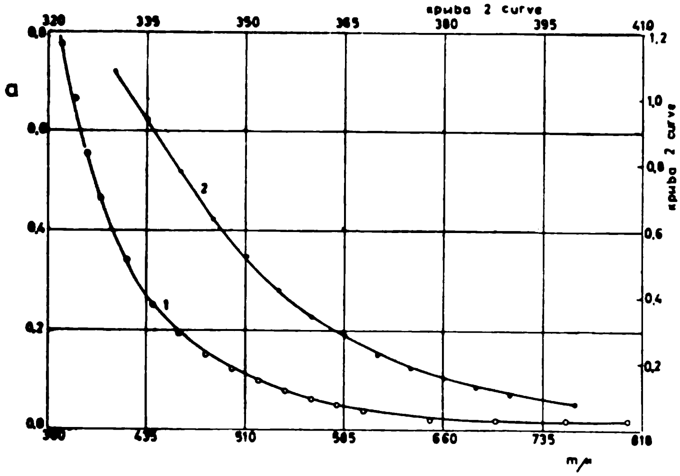

Fig. 1

From the spectrophotogram shown in Fig. 1 it may be seen that there is no absorption maximum in the studied wavelength region and that the absorption increases with decreasing wavelength. The absorption at shorter wavelengths was not measured since L-ascorbic acid absorbs below 330 mμ.

The color intensity of the solution increases on standing. Investigation of the dependence of the absorbance on time (Fig. 2) have shown that the absorbance become practically constant after six hours.

The ratio of tungstate to *L*-ascorbic acid in the compound obtained was determined by Job's method of continuous variation(3,4). The determinations were made with 0.01 M solutions of ascorbic acid and sodium tungstate. By mixing these two standard solutions mixtures containing different molar ratios — L-ascorbic acid/sodium tungstate $= a$ — were obtained and their absorbances were measured with a spectrophotometer after standing from 10 to 12 hours. The measurements were performed at room temperature.

From the results given in Fig. 3 it may be seen that a sharp maximum is obtained for $a=2$ and an inflexion point for $a=1$ at all the wavelengths studied. Accordingly, sodium tungstate reacts with L-ascorbic acid in two ways: 1. — with one molecule of L-ascorbic acid, and 2. — with two molecules of L-ascorbic acid. Compound 2 is colored.

The reaction of sodium tungstate with L-ascorbic acid was also studied by the molar ratio method after Harwey and Manning(5,6) The absorbance was plotted against the molar ratio of L-ascorbic acid and sodium tungstate, *n*, at a constant concentration of sodium tungstate (0.035 M).

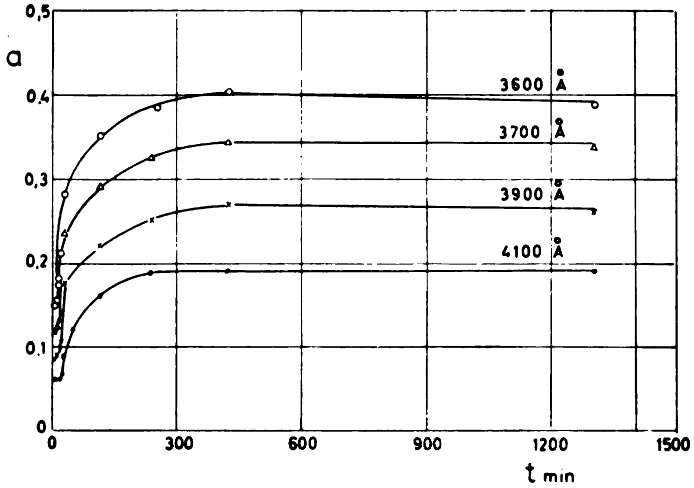

Fig. 2

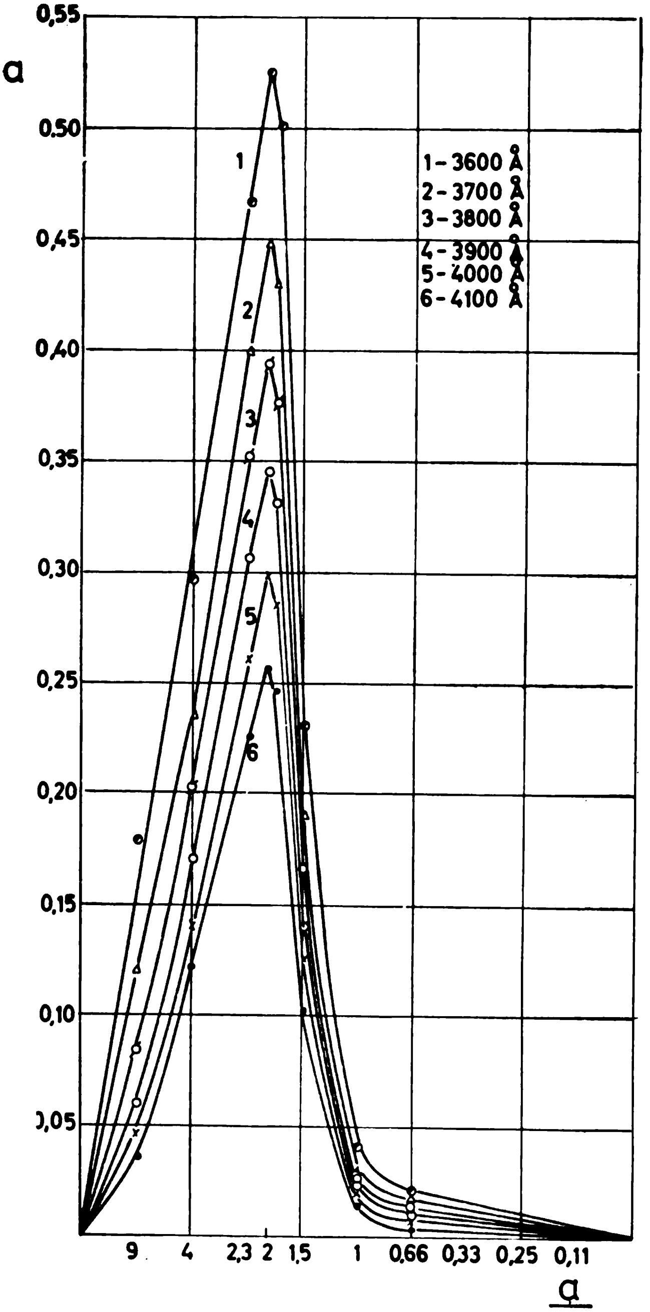
a
0,55
0,50
0,45
0,40
0,35
0,30
0,25
0,20
0,15
0,10
0,05
1
2
3
4
5
6
1-3600 Å
2-3700 Å
3-3800 Å
4-3900 Å
5-4000 Å
6-4100 Å
9
4
2,3
2
1,5
1
0,66
0,33
0,25
0,11
q

Fig. 3

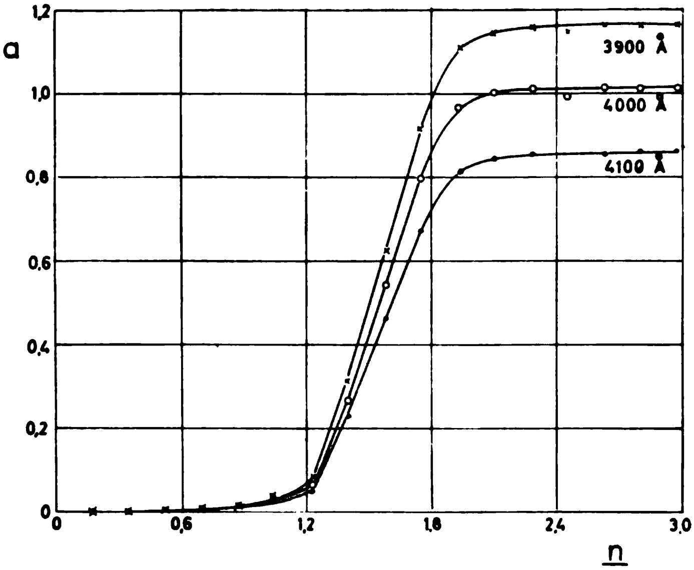
a
1,2
1,0
0,8
0,6
0,4
0,2
0
0
0,6
1,2
1,8
2,4
3,0
n
3900 Å
4000 Å
4100 Å

Fig. 4

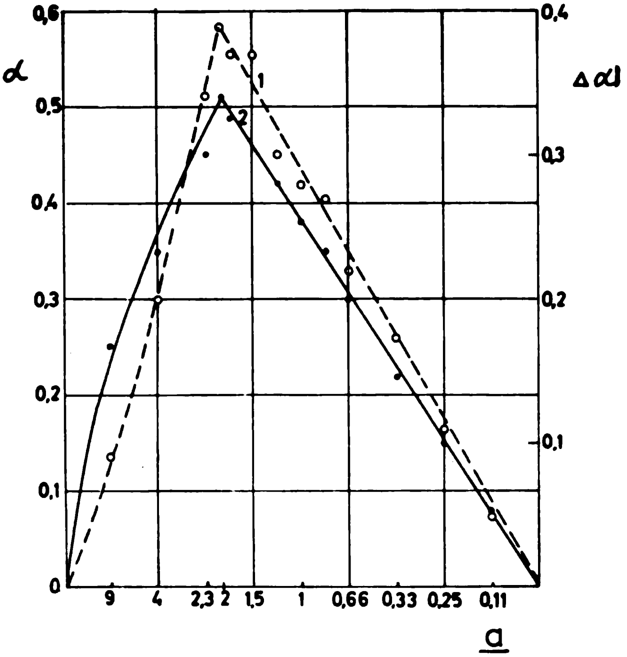
α
Δα
0,6
0,5
0,4
0,3
0,2
0,1
0
0,4
0,3
0,2
0,1
1
2
9
4
2,3
2
1,5
1
0,66
0,33
0,25
0,11
a

Fig. 5

The curve in Fig. 4 shows two distinct inflexions, at $n=1.2$ and $n=1.96$ for all the wavelengths studied. These findings are in accordance with the results obtained by Job's method and they prove that sodium tungstate may react with either one or two molecules of L-ascorbic acid.

Since L-ascorbic acid is optically active with a specific rotation $[\alpha]_D = 22°$ for the undissociated form (in 2 N sulphuric acid) and $[\alpha]_D = 105°$ for the dissociated form (sodium salt)(7), a change of the angle of optical rotation may be expected if the reaction with sodium tungstate gives rise to the formation of anions of L-ascorbic acid from undissociated molecules. A similar effect should be obtained in case a compound is formed from L-ascorbic acid and sodium tungstate but only if the newly formed compound and the undissociated acid have different specific rotations. From the aforesaid it follows that the method of continuous variation could be applied by measuring the optical rotation in dependence on the molar ratio a.

For this purpose solutions were prepared by mixing 0.035 M standard solutions of L-ascorbic acid and sodium tungstate in the same way as in the determination of Job's curve by spectrophotometry. In addition, L-ascorbic acid solutions of concentrations corresponding to the acid concentrations in the mixed solutions were prepared. After standing 6—10 hours, to allow equilibration, the optical activity of each solution was measured. The measurements were performed with a polarimeter of 0.02° accuracy, in cuvettes of 1 dm. The light source was a spectral sodium lamp.

The results are shown in Fig. 5 and in Table 1. From the angles of rotation given in Table 1 it may be seen that the rotation is considerably augmented in the presence of sodium tungstate. Curve 1 in Fig. 5 shows the dependence of the optical rotation on the molar ratio a. Curve 2 shows the dependence of the difference between the angle of rotation of the mixed solution and that of the ascorbic acid solution, $\Delta\alpha$, on a. From the both curves it may be seen that the maximum is at $a=2$, which is in accordance with the spectrophotometric determinations. The inflexion point at $a=1$ could not be precisely determined since the changes lie within the limits of experimental error.

The change of the optical rotation, under the given experimental conditions, could not be augmented by increasing either the concentration or the cuvette length, since in both cases the light from the sodium lamp was absorbed and measurements were not possible.

The reaction products of L-ascorbic acid and sodium tungstate were also investigated by paper chromatography, using methanol as the mobile phase. The spots of L-ascorbic acid were detected with silver nitrate solution or acid iodine solution and strach, and those of tungstate with stannous chloride solution.

The chromatography was performed with solutions obtained by mixing 0.25 M solutions of L-ascorbic acid and sodium tungstate in ratios 4 : 1 and 1 : 4. 0.01 ml of each solution was applied to the chromatographic paper. The solvent front advanced to 17.2 cm, in two hours.

The chromatograms of the solutions containing an excess of L-ascorbic acid over sodium tungstate had three spots of L-ascorbic acid with

TABLE 1

Molar ratio	*Solution mixture in ml			(room temperature)	
a	W	HA	H_2O	α°	Δα
9	5.5	45	—	0.25	0.09
	—	45	5	0.16	
4	10	40	—	0.35	0.20
	—	40	10	0.15	
2.33	15	35	—	0.45	0.34
	—	35	15	0.11	
2	16.65	33.35	—	0.51	0.39
	—	33.35	16.65	0.12	
1.87	17.50	32.50	—	0.49	0.37
	—	32.50	17.50	0.12	
1.5	20	30	—	0.47	0,37
	—	30	20	0.10	
1.22	22,50	27.50	—	0.42	0.30
	—	27.50	22.50	0.12	
1	25	25	—	0.38	0.28
	—	25	25	0.10	
0.82	27.50	22.50	—	0.35	0.27
	—	22.50	27.50	0.08	
0.66	30	20	—	0.30	0.22
	—	20	30	0.08	
0.43	35	15	—	0.22	0.17
	—	15	35	0.05	
0.25	40	10	—	0.15	0.11
	—	10	40	0.04	
0.11	45	5	—	0.08	0.05
	—	5	45	0.03	

* Concentration of parent solutions 0.0350 M.

R_f-values 0.0, 0.37 and 0.73. The spot with R_f=0.0 corresponded to the compound formed from L-ascorbic acid and sodium tungstate, since tungstate was also found to have R_f=0.0. R_f=0.37 corresponded to sodium ascorbate and R_f=0.73 to ascorbic acid, as was established on separate chromatograms of L-ascorbic acid and a mixture of sodium ascorbate and L-ascorbic acid.

On the chromatograms of solutions containing an excess of sodium tungstate over L-ascorbic acid, the presence of L-ascorbic acid was established by a spot with $R_f = 0.35$. This finding indicated that all the ascorbic acid was present in the form of its sodium salt. The R_f—of tungstate was also found to be 0.0.

These results show that in the presence of an excess of sodium tungstate sodium ascorbate forms, indicating that the reaction between these two compounds involves their Na^+ and H^+ ions. However, in the presence of an excess of L-ascorbic acid, in addition to the above reaction, the formation of a compound from L-ascorbic acid and sodium tungstate is observed.

DISCUSSION

The results show consistently that the reaction between sodium tungstate and L-ascorbic acid takes place in two ways — one molecule of sodium tungstate reacts either with two molecules or with one molecule of L-ascorbic acid. The first path results in the formation of a colored compound whose absorption spectrum is shown in Fig. 1. Since neither sodium tungstate nor L-ascorbic acid are colored, it is evident that a compound of L-ascorbic acid and sodium tungstate is formed. This was confirmed by the chromatographic investigations which showed that in solutions containing a molar ratio L-ascorbic acid: sodium tungstate > 1, the ascorbic acid portion exhibited the same R_f—value as the tungstate ion, i. e. an R_f which differed from those of L-ascorbic acid and sodium ascorbate.

From the literature it is known that sodium tungstate reacts with organic acids (oxalic, tartaric, citric) giving rise, according to some authors(8), to a complex ion:

$$Na_2\,WO_4 + H_2C_2O_4 \rightleftharpoons Na_2\,(WO_3C_2O_4) + H_2O \qquad (1)$$

or to colloidal tungstic acid according to others:(9)

$$Na_2WO_4 + H_2C_2O_4 \rightleftharpoons H_2WO_4 + Na_2C_2O_4. \qquad (2)$$

Both types of reaction bring about an increase of the pH of the solution. We observed the same effect with L-ascorbic acid, i. e. the pH of the mixed solution of L-ascorbic acid and sodium tungstate was considerably higher than that of the L-ascorbic acid solution of the same dilution. Therefore, in our opinion, the reaction between sodium tungstate (1 molecule) and L-ascorbic acid (2 molecules) takes place according to the following equation:

$$Na_2\,WO_4 + 2\,HA \rightleftharpoons Na_2\,(WO_3\,A_2) + H_2O \qquad (3)$$

The spectrum of the complex anion is shown in Fig. 1. The possibility of tungstic acid formation, which also satisfies the above stoichiometric relation, is excluded since the colored compound would represent tungstic acid, and the other organic acids should also give rise to a colored compound with the same absorption spectrum. However, this has not been observed in reactions with a number of organic acids stronger and weaker than L-ascorbic acid (10). In addition, the chromatographic analysis would give only the R_f-values of L-ascorbic acid and sodium ascorbate whereas the R_f-value common to tungstate and ascorbic acid would not be found. The appearance of the third R_f-value undoubtedly confirms the hypothesis that a compound of L-ascorbic acid and sodium tungstate is formed.

The reaction between tungstate and L-ascorbic acid in which the ratio of molecules entering into the reaction $a = 1.2$ results in the formation of a polyanion by the action of the H^+ ion of the acid:

$$6\,WO_4{}^{2-} + 7\,HA \rightleftharpoons H\,(W_6O_{21})^{5-} + 7\,A^- + 3\,H_2O \qquad (4)$$

In the literature this reaction is well-known as the reaction of tungstate with mineral acids(11,12,13). In this reaction the molar ratio of L-ascorbic acid and sodium tungstate in $a = 1.17$ and this is in good agreement with the found ratio $n = 1.3$. This reaction is also confirmed by the chromatographic identification of only sodium ascorbate in case the reaction is carried out in the presence of an excess of sodium tungstate.

APPARATUS AND REAGENTS

Measurements were made with a Unicam SP 500 spectrophotometer and a Zeiss (Jena) "Kreispolarimeter" polarimeter. Chromatographic separations were performed on Whatman -MM 1 paper. All reagents used were p. a., produced by Kemika and Merck.

School of Science
Institute of Physical Chemistry
Beograd
Institute of Chemistry,
Technology and Metallurgy
Beograd

Received May 15th, 1964

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GLASNIK HEMIJSKOG DRUŠTVA, Vol. 29, No. 3—4, 1964, pp. 131—137

DETERMINATION OF TERTIARY AMINES AND SALTS OF ORGANIC ACIDS IN GLACIAL ACETIC ACID BY CONDUCTOMETRIC TITRATION

by

VILIM VAJGAND and TIBOR PASTOR

The quantitative determination of organic substances, by measurement of the high frequency conductance of their solutions has recently been increasingly applied. On account of its simplicity and rapidity, high frequency titration has relegated conductometric titration to a subordinate role. However this latter method often gives better results in nonaqueous media than in aqueous solutions. Thus the titration of sulphuric acid in glacial acetic acid gives to two end-points, and in the same solvent, the titration of a mixture of sulphuric and hydrochloric acid was successful(1).

Conductometric titrations of weak bases in different nonaqueous solvents were carried out by McCurdy and Calt(2). They observed that in the course of the titration the conductance changed more rapidly in in a mixture of 1,4-dioxane and formic acid than in acetic acid, and thus easier and more precise determination of the titration end-point was possible. They therefore recommend this solvent for the determination of individual components of a mixture. However, this is only possible when the difference in the basicity of individual components is greater than one pK_b unit.

Lippincott and Timnick(3) titrated aniline in acetic acid. Good results were obtained in individual determinations but in the titration of a mixture of amines the end-point corresponded to the total amount of bases in the solution. More detailed investigations on the determination of weakly basic amines in acetic acid were performed by Škodin and co-workers(4). They succeeded in titrating very weak bases such as for example diphenylamine ($pK = 13.2$ in water). This success they ascribed to the basicity of weak bases in water ($pK \approx 10—14$) being increased several times in acetic acid ($pK \approx 6—10$). They also successfully titrated a mixture of bases in the same solvent.

The aim of the present work was to determine by conductometric titration a series of organic bases which are important pharmaceutical products, including novalgin, which could not be satisfactorily determined either by potentiometric, biamperometric or derivative polarographic titrations. In addition, the possibility of using antimony electrodes in conductometric titrations in glacial acetic acid was studied.

EXPERIMENTAL

The investigations were performed with a Ludwig Seibold type LFM conductometer. The electrodes used were the platinum electrodes of the apparatus and two bright platinum electrodes of 1 cm^2. The distance between them was 4 mm. In addition, Radiometer antimony electrodes at a distance of 15 mm were employed.

The solution was placed in a vessel of diameter 3 cm and height about 12 cm. It was stirred with a magnetic stirrer and its temperature was kept constant at 23±0.26° by means of Thermostat type NB ultrathermostat. The volume of the titrated solutions was about 30 ml.

The preparation of standard solutions and the purification of the solvent are described in a previous paper$^{(5)}$.

The comparative method was potentiometric titration but novalgin was determined gravimetrically$^{(6)}$.

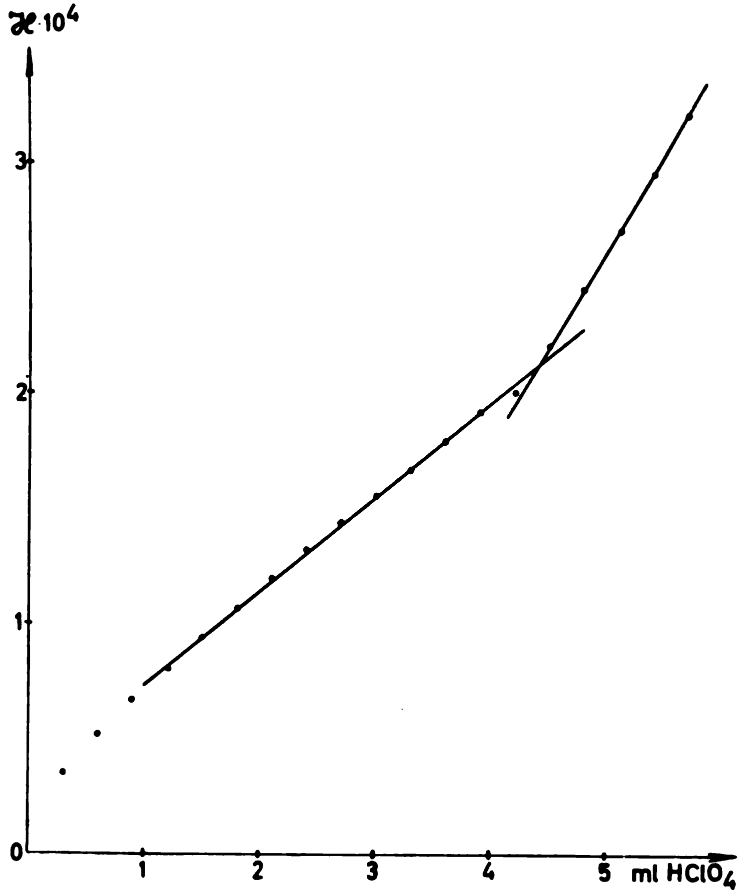

Fig. 1

Our investigations were aimed at the study of the direct titration and retitration methods. The direct titration was performed with perchloric acid solution and gave good results in the determination of alkaloids and salts of organic acids. However, with the other bases given in Table 1, the results were too high. The shape of the curves obtained in the direct titration method is shown in Fig. 1.

On account of the limited applicability of direct titration we investigated the retitration method. In these determinations an excess of perchloric acid was added to the solution of the base, and the unconsumed acid was retitrated with sodium acetate solution. By this method it was possible to determine a greater number of organic bases, including novalgin. The behavior of novalgin differed from that of other titrated substances. The shape of curves obtained in the determination of bases by this method are given in Fig. 2 and correspond to the titration of strong

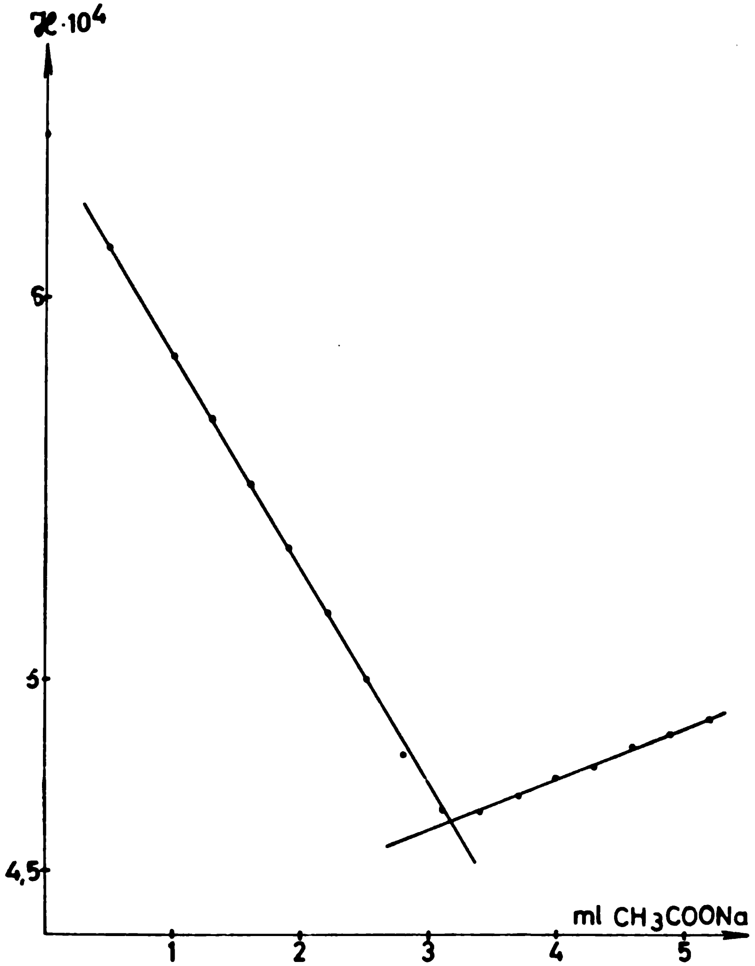

Fig. 2

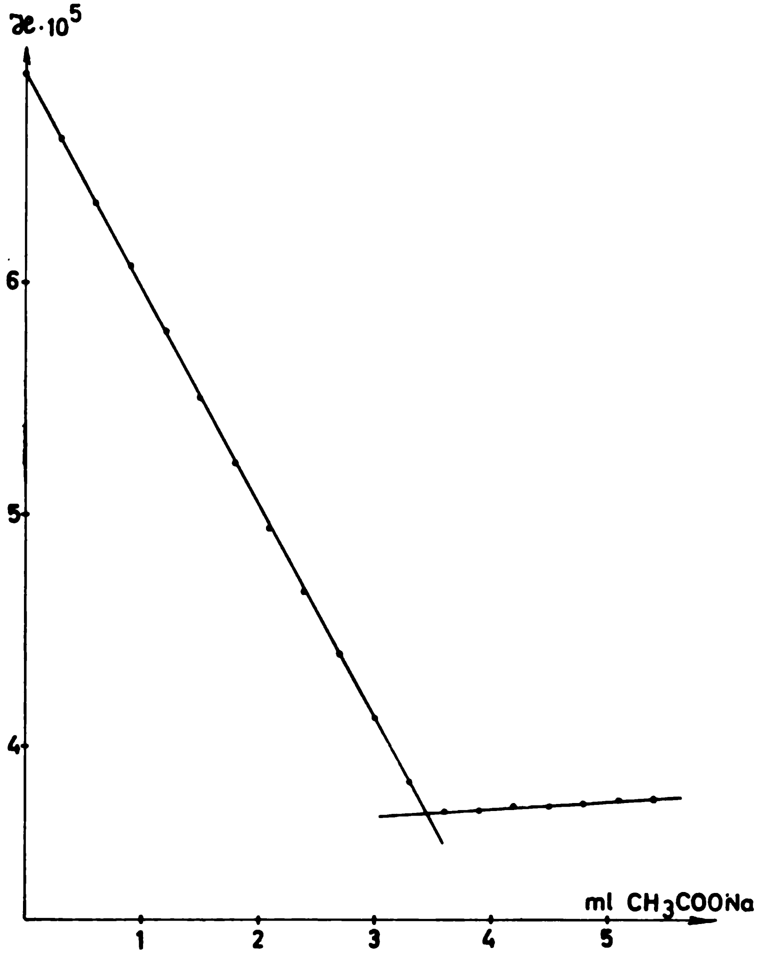

Fig. 3

acids with strong bases. (Fig. 3) However, the shape of the curve for novalgin is quite different. This might be explained by the hypothesis that after addition of an excess of perchloric acid, novalgin reacts with more than two acid equivalents (consumes two acid equivalents) and gives rise to a compound which behaves as a weak acid. However the shape of the titration curve also depends on the amount of perchloric acid added. If the excess of perchloric acid solution is great, the conductance first decreases and then increases (Fig. 4). If it is small the conductance increases steadily from the beginning of the titration. The amount of the titration agent corresponding to the ascending part of the curve depends on the time interval between the addition of perchloric acid to the novalgin solution and the beginning of the titration. If the titration is carried out immediately after the addition of perchloric acid, this

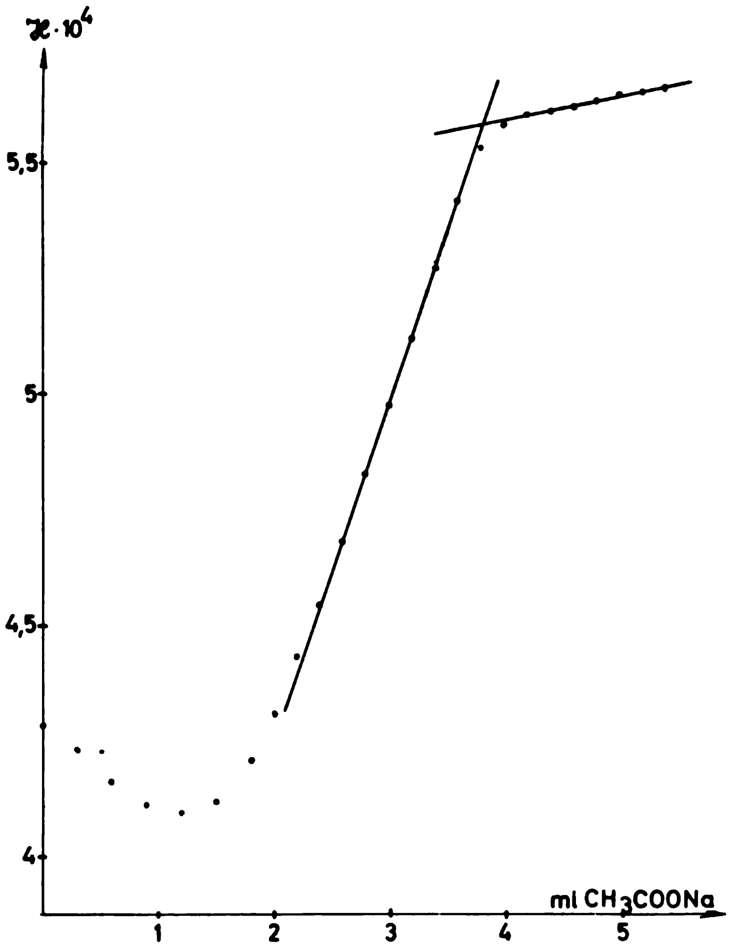

Fig. 4

amount is small and determination of the titration end-point is very difficult. Therefore, it is best to titrate the solution 10—15 minutes after the addition of perchloric acid.

Of all the titrated substances only novalgin and niamide consume two equivalents of perchloric acid. It is of interest to note that in potentiometric determination niamide consumes only one acid equivalent. In the determination of brucine (basicity constants $Kb = 7.2 \times 10^{-4}$ and 2.5×10^{-11}) only one titration endpoint was obtained and it corresponded to the consumption of one equivalent of the titration reagent. Such a behavior of brucine was established by Hara and West(7) by high frequency titration.

Acetic acid anhydride increases the conductance of the solution of the investigated substance in acetic acid. According to Bel'skii and

TABLE 1

Titrated substance	Taken g	Found by potent. titr. or gravim. g	Conductometric titration in the presence of Pt electrodes				Conductometric titration in the presence of Sb electrodes			
			Direct titration		Indirect titration		Direct titration		Indirect titration	
			No. of titr.	Found g	No. of titr.	Found g	No. of titr.	Found g	No. of titr.	Found g
Sodium salicylate	0.1000	0.0991	5	0.1001 ± 0.0001	6	0.0992 ± 0.0003	3	0.1003 ± 0.0000	3	0.0994 ± 0.0003
Sodium p-amino salicylate	0.1000	0.0994			7	0.0999 ± 0.0004			3	0.0997 ± 0.0001
Sodium benzoate	0.1000	0.0981			8	0.0986 ± 0.0003			4	0.0985 ± 0.0003
Narcotine	0.1000	0.0988	3	0.1004 ± 0.0003			5	0.0988 ± 0.0005		
Brucine	0.1000	0.0985	5	0.0996 ± 0.0002			4	0.0993 ± 0.0002		
Strychnine	0.1000	0.0984	3	0.0992 ± 0.0004			4	0.0999 ± 0.0006		
Struchnine nitrate	0.1000	0.0994	7	0.0997 ± 0.0004			7	0.0996 ± 0.0003		
Nicotinamide	0.1000	0.0991	3	0.0997 ± 0.0002	5	0.0994 ± 0.0002	4	0.0997 ± 0.0002	5	0.0992 ± 0.0002
Antipyrine	0.1000	0.0992			4	0.1001 ± 0.0013			13	0.0993 ± 0.0003
Niamide	0.1000	0.0984			10	0.0988 ± 0.0003			3	0.0983 ± 0.0004
Novalgin	0.1000	0.0994			16	0.0989 ± 0.0005			6	0.0993 ± 0.0008

Vinnik(8), in a mixture of acetic acid and acetic acid anhydride, the greatest conductance is obtained when the ratio of the components is 1 : 1. The dielectric constant of the mixture increases from 6.1 (constant of pure acetic acid at 25°C) to 20.7 (constant of the pure anhydride).

In addition to platinum electrodes, which were used in our previous works, antimony electrodes proved convenient for conductometric titration. On account of their shape the changes of conductance due to the stirring of the solution were considerably smaller than in case of platinum electrodes.

The titrated substances and the results obtained with platinum and antimony electrodes are given in Table 1.

The titration of theobromine was not successful on account of the precipitate formed. Procaine hydrochloride, quinine, and pyridoxine could not be titrated in the presence of mercuric acetate.

School of Science
Institute of Chemistry
Beograd

Received 14 July, 1964,

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CONTRIBUTION TO THE STUDY OF BENZOTHIAZOLES, BENZIMIDAZOLES AND BENZOXAZOLES.

II. BENZOTHIAZOLES OBTAINED BY CONDENSATION OF *o*-AMINOTHIOPHENOL WITH PYRIDINECARBOXYLIC ACIDS

by

BORIVOJE L. BASTIĆ and MIROSLAV V. PILETIĆ

Pyridylbenzothiazoles can be prepared in different ways(1). Zubarovski and Voronina have synthesized them by heating a mixture of pyridinemonocarboxylic acid with *o*-aminothiophenol several hours in a sealed tube at elevated temperatures(2).

To simplify the procedure and to improve the yields of pyridylbenzothiazoles we attempted to synthesize them from the same starting components (pyridinemonocarboxylic acid and *o*-aminothiophenol) but at a lower temperature (on account of partial decomposition at higher temperatures), avoiding using sealed tubes and trying to shorten the time of heating.

Attempts to carry out the condensation in an open vessel either in the presence or absence of the usual solvents were unsuccessful. After heating the starting acids were always isolated and *o*-aminothiophenol was oxidized giving rise to the corresponding disulphide.

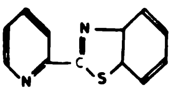
In recent years Hein, Alheim and Levitt(3) and Rau and Braunwartth(4) have employed polyphosphoric acid as catalyst and solvent in syntheses of similar compounds. By employing polyphosphoric acid in the synthesis of benzothiazoles, the condensation of *o*-aminothiophenol with picolinic, nicotinic or izonicotinic acid, furnished better yields of the corresponding benzothiazoles. The reaction was carried out in an open vessel, at a lower temperature and the period of heating was shortened.

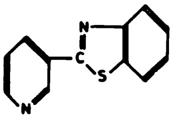
Table 1 shows Zubarovski and Veronina's results and those which we obtained using polyphosphoric acid as catalyst and solvent.

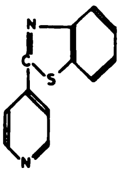
TABLE 1

Components	Temperature	Time in hrs	Yield in %	Method
Picolinic acid and	140—200°	6	33	Zubarovski
o-aminothiophenol	120—140°	3	76	Ours
Nicotinic acid and	230°	4	34	Zubarovski
o-aminothiophenol	140—150°	3	61	Ours
Izonicotinic acid and	210—240°	4	65	Zubarovski
o-aminothiophenol	140—150°	3	70	Ours

In the above condensation reactions the following products were obtained; 2—(pyridyl—2)—benzothiazole, 2—(pyridyl—3)—benzothiazole and 2—(pyridyl—4)—benzothiazole.







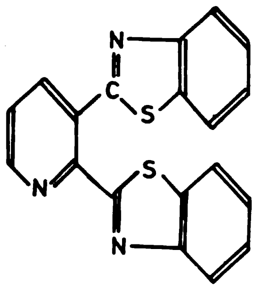
From Table 1 it is evident that polyphosphoric acid not only improves the yields of pyridylbenzothiazoles but also shortens the reaction time and lowers the reaction temperature. Thus, a more simple procedure involving heating in an open vessel instead of under pressure in a sealed tube is made possible.

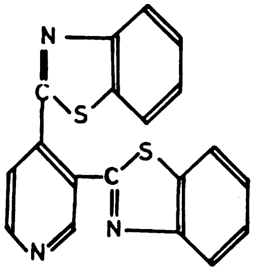
The same condensation reaction was further applied to quinolinic and cinchomeronic acids by heating them with *o*-aminothiophenol in the presence of polyphosphoric acid as catalyst.

Earlier(1) we established that free quinolinic acid does not react with *o*-aminothiophenol and that it must first be transformed into its anhydride. Quinolinic acid anhydride reacts with *o*-aminothiophenol giving 2-(benzothiazyl-2)-3-pyridinecarboxylic acid as the reaction product.

Similarly free cinchomeronic acid does not react with *o*-aminothiophenol either. It must also first be transformed into its anhydride.

However, by heating equimolecular amounts of *o*-aminothiophenol with quinolinic or cinchomeronic acid in the presence of polyphosphoric acid the corresponding 2,3-bis-(benzothiazolyl-2)-pyridine or 3,4-bis-(benzothiazolyl-2)-pyridine, respectively, were obtained:





Although we heated equimolecular amounts of the components in the presence of polyphosphoric acid at the relatively low temperature of 120—140° for only one hour, expecting that only one carboxylic group would enter into the reaction, both carboxylic groups reacted, probably due to the catalytic action of the polyphosphoric acid.

These findings, together with the already mentioned catalytic action of polyphosphoric acid, undoubtedly indicate that this acid is a very useful agent in the condensation reactions of *o*-aminothiophenol with pyridinecarboxylic acids.

The catalytic action of polyphosphoric acid in similar reactions producing benzothiazoles, benzimidazoles and benzoxazoles is under investigation.

EXPERIMENTAL

Melting points are not corrected
Industrial polyphosphoric acid (Fluka) was used.

1: *Condensation of o-aminothiophenol with picolinic acid*

In a 100 ml flask equimolecular amounts of *o*-aminothiophenol (2g) and finely powdered dry picolinic acid (2g) were mixed together and then polyphosphoric acid (9 ml) was added. The flask was connected to an upright condenser fitted with a calcium chloride tube. The reaction mixture was heated at 120—140° in a paraffin oil bath 3 hrs, with occasional shaking. At a temperature of about 120° water started to separate and to condense on the inner walls of the flask, dissolution became complete and the solution gradually turned dark-colored. At the end of heating the separation of crystalline needles on the walls of the flask was observed. The hot solution was immediately poured into cold water (200 ml) whereby a resinous product was precipitated, which however soon transformed into a white crystalline precipitate. After standing a short while the crystals were filtered off and dried. The yield of the crude product was 76% (2.6 g).

The crude product was dissolved in hot alcohol (30 ml) and recrystallized with addition of active charcoal. The crystals (1.6 g) melted at 136 °C and the addition of water to the filtrate furnished an additional amount (0.5 g) of crystals of the same m. p. The total yield of light gray crystals was 61% (2.1 g). The mixed melting point of this compound with a specimen of 2-(pyridyl-2) benzothiazole showed no depression.

2. *Condensation of o-aminothiophenol with nicotinic acid*

In a 100 ml flask equimolecular amounts of *o*-aminothiophenol (2 g) and nicotinic acid (2 g) were mixed and then polyphosphoric acid (9 ml) was added. The further procedure was as above, the reaction mixture being heated at 140—150° for 3 hrs. At about 120° water started to separate, everything dissolved and the solution gradually turned dark. The hot solution was then poured into water (300 ml) and left to cool. Slow addition of KOH until the reaction mixture was strongly alkaline resulted in the separation of a greenish precipitate which after standing a short while was filtered off and dried. The yield of the crude product was 61% (2.1 g).

The crude product was dissolved in hot alcohol (30 ml) and treated with active coal. Water was added to the hot filtrate. The deposit which separated on cooling was filtered, washed with water and dried. The yield of greenish crystals melting at 128° was 40% (1.4 g); the m. p. corresponds to that of 2-(pyridyl-3)-benthiazole.

3. *Condensation of o-aminothiophenol with izonicotinic acid*

In a 100 ml flask equimolecular amounts of *o*-aminothiophenol (2 g) and izonicotinic acid (2 g) were mixed and then polyphosphoric acid (9 ml) was added. The further procedure was as above, the reaction mixture being heated at 140—150° for 3 hrs. At about 120° water started to separate, everything dissolved and the solution gradually turned dark. At the end of heating, separation of a yellow sublimate on the inner walls was observed. The hot solution was poured into water (400 ml) and left to stand for 2 hrs. Since only a small amount of a deposit was separated, KOH was added until the reaction mixture was strongly alkaline, whereby an additional precipitate was obtained. The yield of the crude product was 70% (2.4 g).

The crude product was dissolved in hot alcohol (120 ml), active charcoal was added and the mixture was filtered hot. After cooling water was added to the filtrate, which was warmed until dissolution, and then it was left to stand. The deposit which separated on cooling was filtered off and dried: m. p. 134–135°, corresponding to the m. p. of 2-(pyridyl-4) benzothiazole. The yield of light green crystals was 47% (1.6 g). The mixed melting point of this compound and the compound obtained by the decarboxylation of the condensation product of *o*-aminothiophenol and cinchomeronic acid anhydride showed no depression.

4. *Condensation of o-aminothiophenol with quinolinic acid*

In a 100 ml flask equimolecular amounts of *o*-aminothiophenol (1.25 g) and finely powdered dry quinolinic acid (1.65 g) were mixed and then polyphosphoric acid (9 ml) was added. The flask was connected to an upright condenser fitted with a calcium chloride tube. The reaction mixture was heated at 120—140° in a parrafin oil bath for one hour with occasional shaking. At 115° water started to separate. Heating was continued until the evolution of bubbles from the liquid surface ceased. The hot solution was poured into cold water (200 ml) whereby a resinous precipitate was obtained which soon transformed into a white crystalline deposit. The latte was left to stand for 3 hrs and then filtered off.

The crude product was dissolved in hot alcohol (150 ml), active charcoal was added and after filtration the filtrate was left to cool. The separated crystals were filtered off. Water was added to the filtrate, whereby a further amount of crystals was obtained. The yield was 23% (0.8 g): m. p. 193°. The mixed melting point of this compound with 2,3-bis-(benzothiazyl-2)-pyridine obtained by an other method(1) showed no depression.

5. *Condensation of o-aminothiophenol with cinchomeronic acid*

In a 100 ml flask equimolecular amounts of *o*-aminothiophenol (2.5 g) and finely powdered dry cinchomeronic acid (3 g) were mixed and then polyphosphoric acid (9 ml) was added. The procedure was further carried out as above described, heating the reaction mixture at 120—140° for one hour. At 120° water started to separate, everything dissolved and the reaction mixture turned dark-colored. The hot solution was poured into water (400 ml) whereby a resinous precipitate was obtained. After short standing it was filtered off.

The crude product was dissolved in a small amount of alcohol, active charcoal was added, and after filtration, water was added to the filtrate. The separated precipitate was filtered off, dissolved in alcohol and the solution was filtered again. On cooling the filtrate furnished crystals, which were filtered off and dried: m. p. 157°. The yield was 26% (0.90 g).

Analysis:
Calculated for $C_{19}H_{11}N_3S_2$: C 66.06%; H 3.21%; N 12.17%
Found : C 66.17%; H 3.10%; N 11.98%

School of Technology
Institute of Organic Chemistry

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CHEMICAL INVESTIGATION OF WHEAT

10*

NUCLEOTIDE COMPOSITION OF RIBONUCLEIC ACID OF WHEAT LEAVES**

by

MIHAILO LJ. MIHAILOVIĆ, STOJAN GRUJIĆ and DIMITRIJE HADŽIJEV

INTRODUCTION

Our preliminary study(1) of wheat shoots showed that about 34 percent of the total phosphorus present in shoots was incorporated in Na***.

These investigations also demonstrated that in shoots of high-yield varieties there is more extensive accumulation of RNA than in low yield varieties, when the age of the shoots, nutritional conditions, light factors, etc., are equal. This finding might explain the more intensive processes, related to protein biosynthesis, cell division, photosynthetic and oxidative phosphorylation, and respiration capacity, which take place in the high-yield varieties, but on the other hand, many other biological-varietal characteristics of wheat varieties would still remain unexplained.

The participation of uridine derivatives in sugar, *i. e.* starch biosynthesis is well known. Our preliminary observation that these derivatives are present in increased amounts in the leaves of high-yield varieties led us to think that a possible difference in the rate of incorporation of free uridylic acid in RNA might represent qualitative characteristic of the RNA composition of low and high-yield varieties.

It is of interest to note that while the nucleotide composition of DNA and RNA isolated from wheat germ has already been investigated (2,3,4,5) the nucleotide composition of wheat-leaf RNA has not yet been determined. The reason for this is probably the exceptionally easy isolation of these acids from wheat germ, while the isolation of RNA either from green leaves or ripe whole grain involves many difficulties.

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* Paper 9 : *Glasnik hemijskog društva Beograd* 28, 1963.

** Preliminary communication: *Biochimica et Biophysica Acta* (Amsterdam) 87 : 499—502, 1964.

*** NA, nucleic acids; DNA, desoxyribonucleic acid; RNA, ribonucleic acid.

The present study was therefore undertaken with the purpose of investigating the nucleotide composition of RNA of green wheat leaves, and at the same time, of devizing a convenient method for this kind of research.

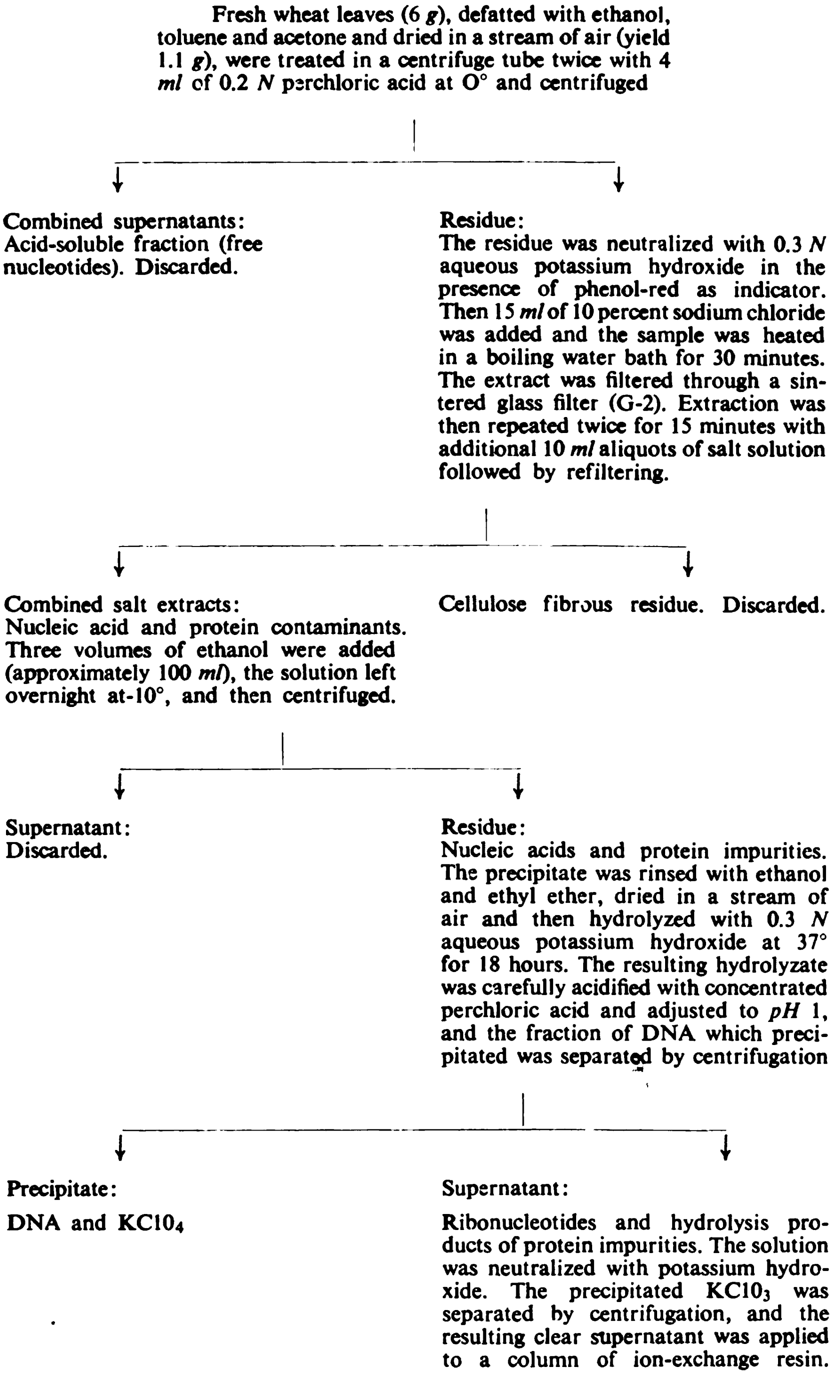
MATERIALS AND METHODS

For the study of the nucleotide composition of RNA the following wheat varieties were used: Yugoslav low-yield varieties *Bankut* 1205 and *Novosadska* 1446, and the high-yield varieties *San Pastore* (Italian) and *Etoile de Choisy* (French). For analysis, young shoots 10—12 days old were used.

As previously confirmed, the method of Ogur and Rosen does not separate selectively and quantitatively the DNA from RNA in green wheat leaves(1). A very convenient and satisfactory method for this purpose appeared to be that of Schmidt and Thannhauser(6). However, recent investigations have shown that by using the original extraction procedure, in alkaline digest, partial destruction of mononucleotides occurs(7). This concerns especially cytidylic acid, which is deaminated to uridylic acid, but a similar decomposition, which follows first order reaction kinetics, is also characteristic for adenylic acid and to a lesser extent even for uridylic acid(7). For this reason, in the present work the extraction of NA was performed using the sodium chloride procedure, since this salt solution efficiently disrupts the electrovalent bonds supposed to exist between NA and proteins, but does not affect NA. Therefore extraction with 10 percent sodium chloride was applied, according to Williams(8), followed by precipitation of NA with ethanol at a lower temperature, according to the procedure of Scholtisseck(9). The precipitated acids were then treated with potassium hydroxide, and the RNA present in the mixture was hydrolyzed to mononucleotides by a modified procedure of Schmidt and Thannhauser, which has already been satisfactorily applied by Davidson and Smellie(10), and Thomas and Sherratt(3). By using such a modification we expected to get RNA and DNA fractions which would be suitable for purine and pyrimidine determinations. Details of the entire procedure for the isolation of RNA from green wheat leaves and its hydrolysis to mononucleotides are presented in Scheme 1.

Mononucleotides were separated on a short column of ion-exchange resin — commercial Dowex 1×10 (Cl^-), 200—400 mesh particle size, previously transformed into the formate form, as outlined by Hurlbert(11). The column was prepared from a dilute water suspension of ion exchange resin in chromatographic glass tubes of 5 and 6 *mm*, diameter respectively. The column length was 7 *cm*, after Cohn and Volkin(12).

The elution was performed by the discontinuous technique with the following eluents: 0.05 *M* HCOOH for cytidylic acid, 0.5 *M* HCOOH for adenylic acid, a mixture of 0.1 *M* $HCOONH_4$ and 0.05 *M* HCOOH for uridylic and pseudouridylic acids, and a mixture of 0.2 *M* $HCOONH_4$ and 0.5 *M* HCOOH for guanylic acid.



Fresh wheat leaves (6 *g*), defatted with ethanol, toluene and acetone and dried in a stream of air (yield 1.1 *g*), were treated in a centrifuge tube twice with 4 *ml* of 0.2 *N* perchloric acid at 0° and centrifuged

Combined supernatants:
Acid-soluble fraction (free nucleotides). Discarded.

Residue:
The residue was neutralized with 0.3 *N* aqueous potassium hydroxide in the presence of phenol-red as indicator. Then 15 *ml* of 10 percent sodium chloride was added and the sample was heated in a boiling water bath for 30 minutes. The extract was filtered through a sintered glass filter (G-2). Extraction was then repeated twice for 15 minutes with additional 10 *ml* aliquots of salt solution followed by refiltering.

Combined salt extracts:
Nucleic acid and protein contaminants. Three volumes of ethanol were added (approximately 100 *ml*), the solution left overnight at-10°, and then centrifuged.

Cellulose fibrous residue. Discarded.

Supernatant:
Discarded.

Residue:
Nucleic acids and protein impurities. The precipitate was rinsed with ethanol and ethyl ether, dried in a stream of air and then hydrolyzed with 0.3 *N* aqueous potassium hydroxide at 37° for 18 hours. The resulting hydrolyzate was carefully acidified with concentrated perchloric acid and adjusted to *pH* 1, and the fraction of DNA which precipitated was separated by centrifugation

Precipitate:

DNA and $KC10_4$

Supernatant:

Ribonucleotides and hydrolysis products of protein impurities. The solution was neutralized with potassium hydroxide. The precipitated $KC10_3$ was separated by centrifugation, and the resulting clear supernatant was applied to a column of ion-exchange resin.

Scheme 1. — Method for the isolation of RNA nucleotides from green wheat leaves.

The amount of ion-exchange resin used to fill the column, the concentration of the nucleotide hydrolyzate, the elution rate of collected eluates and other details of analysis, were described by Petrović and Janković[13]. The absorbancies of the eluates were recorded on a Beckman Model DU spectrophotometer, with quartz cells of 1 *cm* length.

RESULTS AND DISCUSSION

The efficiency of the separation of mononucleotides achieved by the above procedure on columns of 5 and 6 *mm* diameters, are given in Figs. 1 and 2.

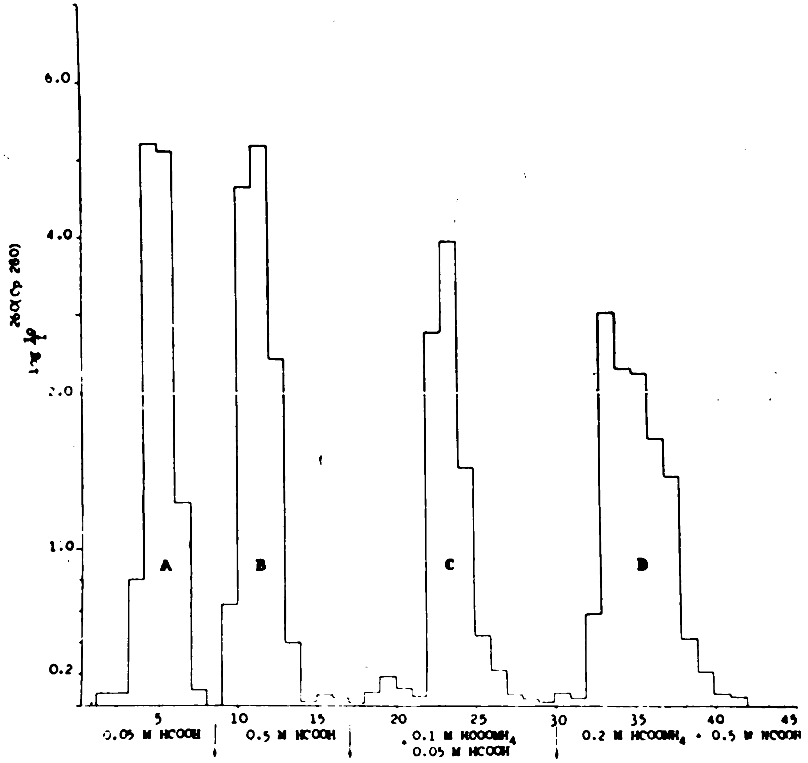


Figure 1. — Elution diagram of RNA nucleotides isolated from wheat leaves of the Yugoslav low-yield variety *Bankut* 1205. Column diameter 6 *mm*. Fraction volume 5*ml*. A — cytidylic acid; B — adenylic acid; C — uridylic acid; D — guanylic acid.

As may be seen from the elution diagrams, both columns gave satisfactory separation, the narrower column being particularly efficient.

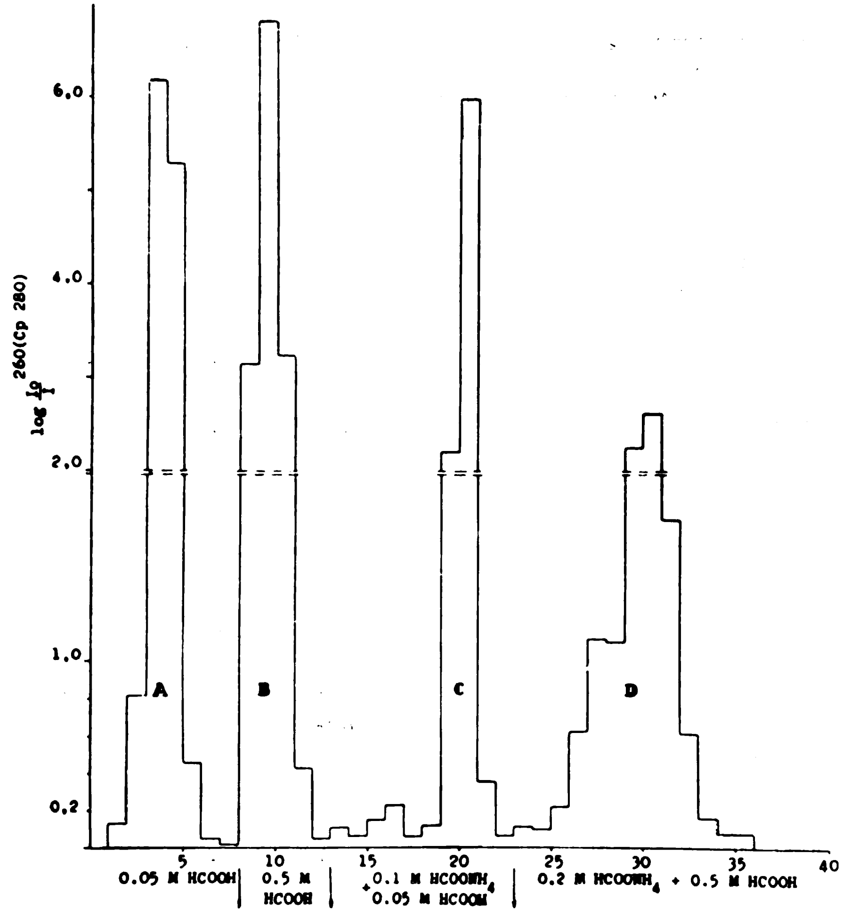


Figure 2. — Elution diagram of RNA nucleotides isolated from wheat leaves of the Italian high-yield variety
San Pastore. Column diameter 5 *mm*. Fraction volume 5 *ml*.
A — cytidylic acid; B — adenylic acid; C — uridylic acid; D — guanylic acid.

For instance, in the separation of nucleotides of *San Pastore* practically all the uridylic acid was present in only two eluates of 5 *ml*. Similar sharp separations were also obtained in the case of cytidylic and adenylic acids, while guanylic acid was eluted from the column, somewhat slowler, thus confirming the finding of other authors(13).

The appearance of small amounts of pseudouridylic acid (eluted just before uridylic acid) in the eluates of both varieties (low-yield and high-yield), suggests that this acid might also play an important role in the formation of wheat RNA.

The purity of the separated nucleotides was checked by reading their absorbancies at corresponding wavelengths. As may be seen from Table 1, the spectral ratios of the individual acids were either identical or very close to the theoretical values.

TABLE 1

Spectrophotometric constants of RNA nucleotides obtained from wheat leaves

Wheat varieties (and pure compounds)		Nucleotide	Spectral ratios at *pH* 2		
			$D^{250/260}$	$D^{280/260}$	$D^{290/260}$
Yugoslav low-yield varieties	Bankut 1205	Ap*	0.85	0.21	0.05
		Cp	0.45	1.89	1.31
		Up	0.82	0.35	0.07
		Gp	0.93	0.69	0.30
	Novosadska 1446	Ap	0.88	0.22	0.03
		Cp	0.48	1.89	1.30
		Up	0.80	0.31	0.04
		Gp	1.14	0.69	0.29
High-yield varieties	Etoile de Choisy	Ap	0.86	0.21	0.04
		Cp	0.44	1.87	1.23
		Up	0.79	0.32	0.04
		Gp	1.15	0.69	0.34
	San Pastore	Ap	0.86	0.21	0.03
		Cp	0.47	1.93	1.31
		Up	0.80	0.30	0.03
		Gp	1.15	0.68	0.35
Chemically pure compounds**		Ap (2')	0.85	0.23	0.03
		Ap (3')	0.85	0.22	0.03
		Cp (2')	0.48	1.80	1.22
		Cp (3')	0.43	2.00	1.43
		Up (2')	0.80	0.28	0.03
		Up (3')	0.76	0.32	0.03
		Gp (2')	0.90	0.68	0.40
		Gp (3')	0.93	0.69	0.40

* Abbreviations used: Ap — adenylic acid; Cp — cytidylic acid; Up — uridylic acid; Gp — guanylic acid. All acids were mixtures of 2' — and 3; — nucleotides.

** Data according to Cohn, W. E., in "*Methods in Enzymology*", *Vol. III.* edited by Collowick, S. and N. O. Kaplan, — New York: Academic Press, 1957, p. 740.

Although in previous investigations of the purine and pyrimidine composition of RNA or DNA hydrolyzates the methods of paper chromatography or paper electrophoresis were mostly used for the separation of the bases(14), the application of the ion-exchange technique offers great advantages when plant materials tissues are to be analyzed. This goes especially for wheat material, which gives nucleic acid hydrolyzates contaminated with considerable amounts of proteins, such as globulins or their hydrolysis products. These impurities are easily removed from the column simply by rinsing with water. Furthermore, the use of this technique might possibly facilitate further research concerning the occurence and content regularities of pseudouridylic acid in plant tissues in general.

Disadvantages attributed to this method of separation, such as long elution times, a large number of fractions and spectrophotometer readings, were essentially overcome by using weighed samples of defatted leaf, and technical details described recently by Petrović and Janković(13). Since the elution of cytidylic, adenylic and uridylic acids was usually completed with 25 *ml* of eluate per acid, and guanylic acid

TABLE 2

Nucleotide composition of RNA isolated from leaves of some low-yield and high-yield wheat varieties

Nucleotide	Low-yield varieties		High-yield varieties	
	Novosadska 1446	Bankut 1205	San Pastore	Etoile de Choisy
	Micromoles*			
Cp	5.19	4.91	5.01	5.85
Ap	5.31	4.70	4.83	5.13
Up	5.16	4.61	4.87	5.76
Gp	6.32	5.52	5.72	7.83
Sum	**21.98**	**19.74**	**20.42**	**24.57**
	In molar %			
Cp	23.62	24.87	24.50	23.80
Ap	24.15	23.81	23.67	20.89
Up	23.48	23.36	23.84	23.45
Gp	28.74	27.97	27.98	31.86
Purine (pyrimidine bases (Ap + Gp) / (Cp + Up)	1.12	1.07	1.07	1.12
6-amino / 6-oxo bases (Ap + Cp) / (Gp + Up)	0.91	0.94	0.94	0.81

* For 6 *g* fresh leaves

with 50 *ml* of eluate, the total separation of ribonucleotides did not last more than eight hours.

In addition, the application of the ion-exchange technique allowed us to separate as much as 25 micromoles of ribonucleotides, without losses and overlapping of the individual acids, by using a column which contained only 2 *ml* (volume) of packed wet resin (see Figures 1 and 2).

Our results also confirm the applicability of Williams' method(8) for the preliminary extraction of NA. Although this extraction is not always quantitative, as recently found on materials such as Euglena or Chlorella(15), in the comparative investigation of nucleotide composition this disadvantage was of negligible importance, as was the lower selectivity of this method when applied to wheat tissue(1,16).

The content of individual acids in RNA, calculated from the corresponding molar extinction coefficients for pure 2' — and 3' — nucleotides, are listed in Table 2.

Although our preliminary study has shown that high-yield varieties, as compared to Yugoslav low-yield varieties, are richer in free nucleotides, especially in adenine and uridine derivatives, no significant differences were found in the nucleotide composition of their RNA. This concerns particularly uridylic acid, *i. e.* the acid component which might be expected to show a significant difference.

The mean value of the ratio of purine to pyrimidine bases, *i. e.* (Ap+Gp)/(Cp+Up), was 1.09, while the ratio of 6-amino to 6-oxo bases, *i. e.* (Ap+Cp)/(Gp+Up), was less than unity, varying in the range 0.81 to 0.95 (see Table 2). The ratio (Gp+Cp)/(Ap+Up) was 1.15 (mean value), and the ratio (Gp+Up)/(Ap+Cp) had a mean value 1.11, *i. e.* these ratios were somewhat different from those of wheat germ established recently by Vanyushin and Belozerskiĭ(5). Similar values for the RNA composition of plants were reported not long ago by other authors (17–21). These results show that RNA isolated from wheat leaves, regardless of variety, belongs to the GC (guanine, cytosine) type, and as such follows Chargaff's rule(22). In both varieties the sum of guanylic and cytidylic acids is higher than the sum of adenylic and uridylic acids, and the amount of purine bases is larger then the amount of pyrimidine bases.

Department of Chemistry
School of Sciences
Beograd
Department of Chemistry
University of Novi Sad
Novi Sad

Received June 1, 1964.

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GLASNIK HEMIJSKOG DRUŠTVA, Vol. 29, No. 3—4, 1964, pp. 157—193

THE EFFECT OF INSULIN ON THE METABOLISM OF PROTEINS, LIPIDS AND GLUCIDES. VIII. THE ACTION OF SUCCESSIVE HYPERINSULINEMIA ON BLOOD SERUM LIPOPROTEINS

by

JELENA J. BOJANOVIĆ, ANKA D. JEVTOVIĆ and MILANKA O. ČORBIĆ

It is known that insulin reduces alimentary hyperinsulinemia (insulin clearing effect) and chlolesteremia (4,6) shortly after its administration. On the other hand it has been found that in patients subjected to long therapy with insulin shocks (in schizophrenia), the level of total lipids and especially that of neutral fats in the circulation is considerably above normal(2). These data prompted us to investigate the ratio of serum lipoprotein fractions in the course of successive administration of large quantities of insulin over a long period of time, and to observe the delayed insulin effect (several hours after administration). In our opinion these data might be of interest not only for the observation of metabolic processes and their interrelations with respect to the insulin effect, but also they might be of importance in case of long application of insulin therapy with regard to side-effects and the disturbances they cause.

MATERIALS AND METHODS

Electrophoretic investigations of serum lipoprotein fractions were made on six shizophrenic patients (female) aged from 20 to 30 years. Other diseases were excluded by examination. During the insulin shock therapy blood was taken just before injection and 20 minutes after insulin coma began (about two and a half hours after injection). Insulin was given intramuscularly, the dose being determined individually, ranging from 100 to 160 units. Before the first insulin coma, the patients were given small amounts of insulin. Patients were wakened from coma by the i. v. administration of glucose. The serum was taken in the usual way(1).

Paper electrophoresis of lipoprotein fractions was done by the method of Swahn(7). Spots of 0.03 ml of serum were applied to 4 × 40 cm. strips of Schleicher Scüll 2043 bM paper. The electrophoresis was performed in a veronal-sodium veronal, buffer pH $= 8.6$, $\mu=0.1$, at a voltage of 170 V, over five hours. Fractions were detected by staining with solution of Sudan black B in 50% ethanol. The staining time, was 45 minutes. After this the strips were washed with 50% ethanol. The dried strips were impregnated with glycerol and the optical density of the spots was measured photometrically. The amounts of individual fractions are given in percentages. The results were statistically evaluated by the basic methods(1).

RESULTS AND DISCUSSION

The relative amounts of serum lipoprotein fractions in shizophrenic patients before insulin shock therapy and found in healthy persons of the same sex and age do not essentially differ(3). However, in insulin coma and in conditions attained several hours after insulin administration we found considerable differences in the lipoprotein electrophoresis patterns. We also found that these values vary during the therapy period observed.

Insulin Effect in Successive Shocks

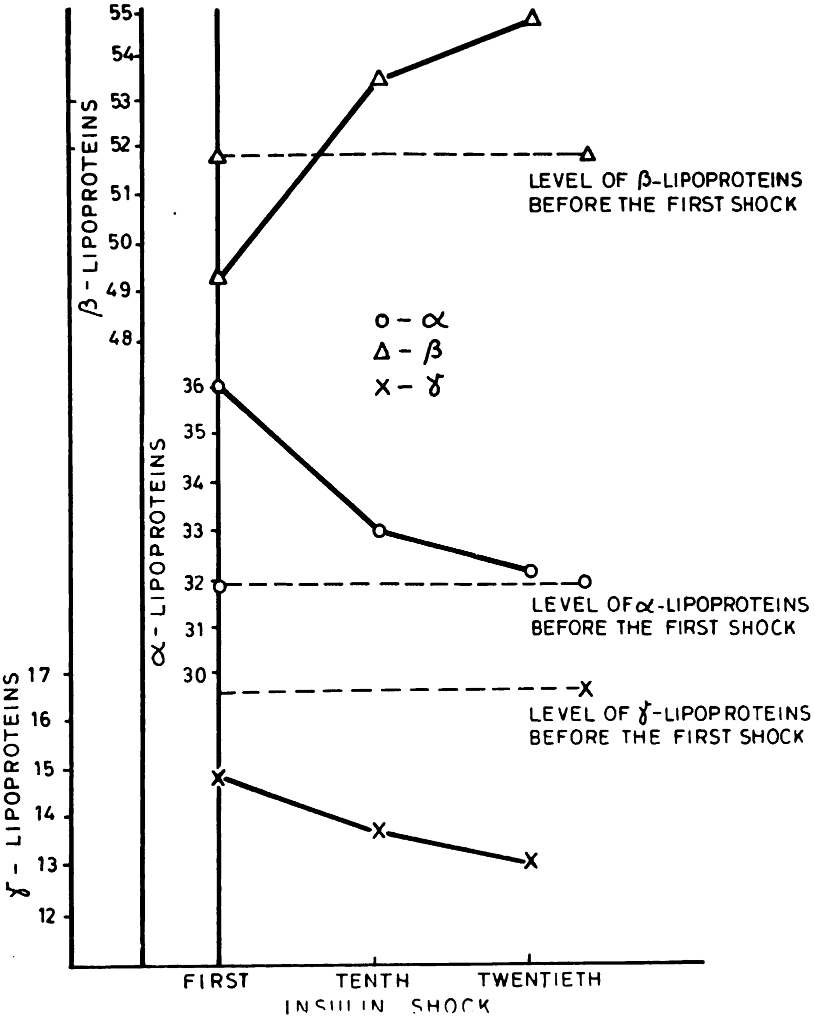
Daily administration of insulin in quantities sufficient to produce deep comas resulted in increase of the percentage of α-lipoproteins. In all periods observed the changes of α-lipoproteins were of the same sense but of different intensities. The greatest increase relative to other fractions was found in the tenth successive shock (the change is statistically highly significant). In the first and twentieth shock the increase was considerably smaller (in the first the change is statistically significant, in the twentieth shock it is unsignificant). However, although the α-lipoprotein fraction was increased in insulin coma its level in the blood decreased in the course of the therapy. Thus in the twentieth shock, although it was increased, its relative level was of the same order as before the first insulin coma.

The relative values of the β-lipoprotein level was decreased in insulin shocks. The changes were of the same sense in all periods observed but of different intensities. In the tenth shock the relative decrease was the greatest and the change was statistically significant. In the first and twentieth shock the decrease was small and not statistically significant. However, although the relative values of the β-lipoproteins were decreased in insulin shocks, they was increased in the course of therapy, so that in the twentieth shock they were higher than before the first shock.

The γ-lipoprotein fraction was decreased in all insulin shocks observed, but the changes were small and not statistically significant. The serum γ-lipoprotein level decreased in the course of the therapy so that in the twentieth coma it was lower than before the first shock.

Delayed Insulin Effect Observed 24 Hours After Insulin Administration

Investigation of lipoproteins 24 hours after insulin administration, in the period in which the optimal functions in tissues should be attained, showed that the delayed insulin effect is manifested in changes whose sense and degree depend upon the duration of therapy.


β - LIPOPROTEINS
55
54
53
52
51
50
49
48
α - LIPOPROTEINS
36
35
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33
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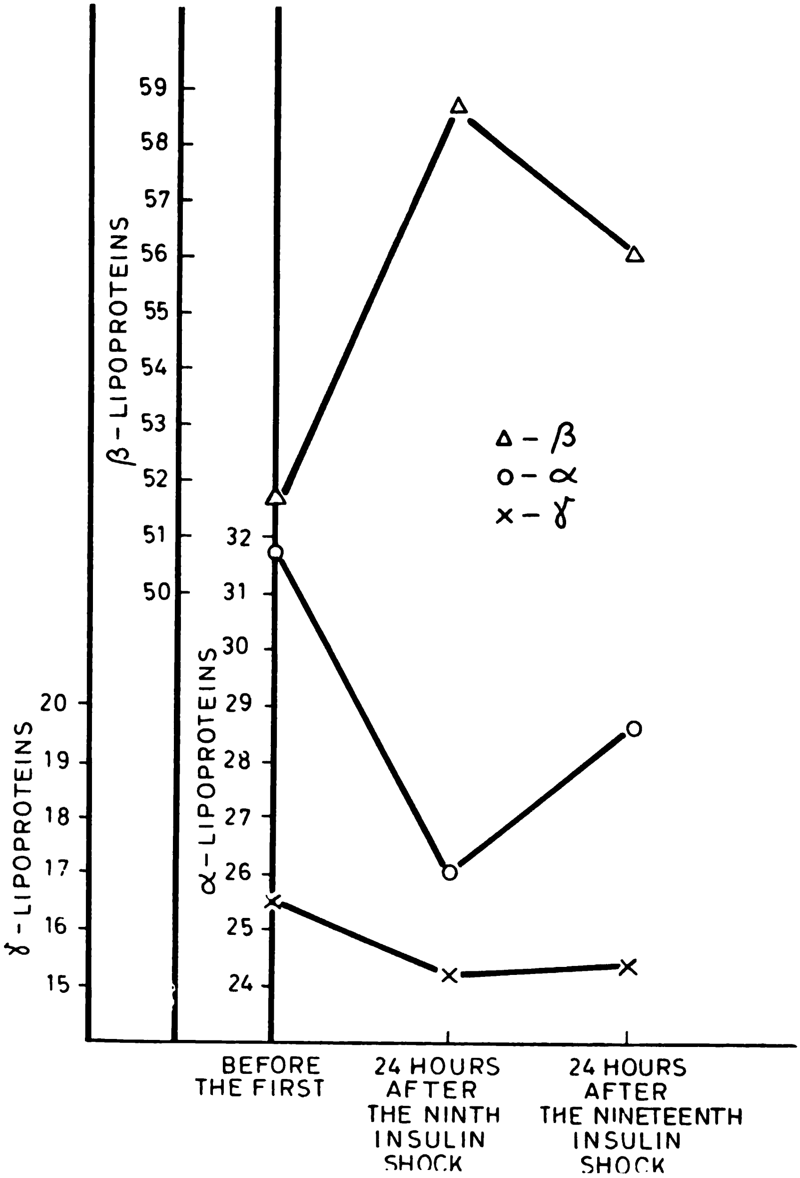
31
30
γ - LIPOPROTEINS
17
16
15
14
13
12
o – α
Δ – β
x – γ
LEVEL OF β-LIPOPROTEINS BEFORE THE FIRST SHOCK
LEVEL OF α-LIPOPROTEINS BEFORE THE FIRST SHOCK
LEVEL OF γ-LIPOPROTEINS BEFORE THE FIRST SHOCK
FIRST
TENTH
TWENTIETH
INSULIN SHOCK

Fig. 1


β-LIPOPROTEINS
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γ-LIPOPROTEINS
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16
15
Δ – β
o – α
x – γ
BEFORE THE FIRST
24 HOURS AFTER THE NINTH INSULIN SHOCK
24 HOURS AFTER THE NINETEENTH INSULIN SHOCK

Fig. 2

TABLE 1

Statisticaly calculated results for relative levels of serum lipoprotein fractions in schizophrenic patiens (female) before the injection of insulin and in insulin shock

Subject of investigation		Values before in shock	Number of cases	Range of values	Mean values —standard deviation	Standard error	Coefficient of variation in %	% of decrease or increase*	Level of significance
Lipoprotein fraction	α	before first	6	26.60—36.47	31.70±3.49	1.43	11.01	+ 13.65	$p = 0.05$
		in first	6	31.35—39.44	36.03±3.37	1.37	9.35		
		before tenth	6	21.84—32.42	26.08±3.65	1.49	13.99	+ 26.46	$p < 0.01$
		in tenth	6	29.38—35.93	32.98±2.64	1.08	8.00		
		before twentieth	6	21.07—31.49	28.47±3.75	1.53	13.17	+ 12.26	$p > 0.05$
		in twentieth	5	21.48—36.39	31.96±6.02	2.69	18.84		
	β	before first	6	48.05—56.55	51.78±2.91	1.18	5.62	—4.73	$p > 0.05$
		in first	6	46.48—52.00	49.33±2.28	0.93	4.62		
		before tenth	6	57.39—61.01	58.75±1.41	0.52	2.40	—9.04	$p < 0.05$
		in tenth	6	46.26—58.87	53.44±4.83	1.97	9.04		
		before twentieth	6	51.35—61.36	56.07±3.67	1.50	6.54	—1.62	$p > 0.05$
		in twentieth	5	47.69—61.83	55.16±5.05	2.26	9.15		
	γ	before first	6	13.55—20.43	16.50±2.66	1.09	16.12	—11.33	$p > 0.05$
		in first	6	10.00—18.65	14.63±2.82	1.15	19.27		
		before tenth	6	10.03—19.34	15.29±3.47	1.42	22.69	—11.18	$p > 0.05$
		in tenth	6	10.52—17.80	13.58±3.26	1.33	24.00		
		before twentieth	6	10.20—17.56	15.44±2.78	1.13	18.00	—16.64	$p > 0.05$
		in twentieth	5	7.30—16.92	12.87±4.02	1.80	31.23		
	β α	before first	6	1.37— 1.99	1.65±0.25	0.10	15.15	—16.36	$p = 0.05$
		in first	6	1.18— 1.60	1.38±0.18	0.70	13.04		
		before tenth	6	1.77— 2.71	2.29±0.32	0.13	13.97	—28.82	$p < 0.01$
		in tenth	6	1.29— 2.00	1.63±0.26	0.11	15.95		
		before twentieth	6	1.63— 2.91	2.02±0.45	0.18	22.28	—9.90	$p > 0.05$
		in twentieth	5	1.35— 2.88	1.82±0.61	0.27	33.52		

*% Decrease or increase and level of significance are given relative to values before the shock

TABLE 2

Statisticaly calculated results for relative levels of serum lipoprotein fractions in schizophrenic patients (female) 24 hours after the administration of insulin

Subject of investigation		Values before 24 hours after shock	Number of cases	Mean value	% decrease or increase relative to values before the first shock	Level of significance relative to values before the first shock	% decrease or increase relative to values 24 hours after the nineth shock	Level of significance relative to values 24 hours after the nineth shock
Lipoprotein fraction	α	before the first	6	31.70	—	—	—	—
		after the nineth	6	26.08	−17.73	$p<0.05$	—	—
		after the nineteenth	6	28.47	−10.19	$p>0.05$	+9.16	$p>0.05$
	β	before the first	6	51.78	—	—	—	—
		after the nineth	6	58.75	+13.46	$p<0.001$	—	—
		after the nineteenth	6	56.07	+8.28	$p - 0.05$	−4.56	$p>0.05$
	γ	before the first	6	16.50	—	—	—	—
		after the nineth	6	15.29	−7.33	$p>0.05$	—	—
		after the nineteenth	6	15.44	−6.42	$p>0.05$	+0.98	$p>0.05$
	$\frac{\beta}{\gamma}$	before the first	6	1.65	—	—	—	—
		after the nineth	6	2.29	+38.79	$p<0.01$	—	—
		after the nineteenth	6	2.02	+22.42	$p>0.05$	−11.79	$p>0.05$

Insulin shock two and a half hours after injection, was characterized by a decreased large molecule lipoprotein level relative to the other lipoprotein fractions, while after 24 hours we found that the level of β-lipoproteins in the entire observed period of the therapy was higher than before the first shock. The changes were statistically significant The greatest increase of β-lipoproteins and the β/α ratio was found 24. hours after the ninth sucessive shock. After nineteen shocks some decrease of the level of this fraction was observed but it was still considerably higher than before the first shock.

It is interesting to note that in analogous experiments on animals the delayed effect of insulin on nonesterified and esterified serum fatty acids was a considerable increase of their concentration (unpublished data obtained in our laboratory).

The decrease of the α-lipoprotein level was greatest and statistically significant 24 hours after nine successive shocks. However, the increase of the relative value of the α-lipoprotein fraction which appeared on further administration of the same quantities of insulin was small and not statistically significant.

The decrease of the γ-lipoprotein relative to the other fractions in the course of successive administration of insulin was small and not statistically unsignificant; after nineteen shocks the changes were practically negligible.

The changes of the serum lipoprotein fractions in the period of the delayed insulin effect are evidently due to altered metabolic processes in the liver, whereby it is necessary to take into consideration not only the direct effect of insulin on these processes but also an increased amount or an increased activity of insulin antagonists under these conditions.

Chemical Institute
School of Medicine
Beograd

Received May 13, 1964

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SRPSKO HEMIJSKO DRUŠTVO (BEOGRAD)

BULLETIN OF THE CHEMICAL SOCIETY Belgrade

(Glasnik Hemijskog društva — Beograd)
Vol. 29, No. 5 - 6, 1964.

Editor:
MILOŠ MLADENOVIĆ

Published by
SRPSKO HEMIJSKO DRUŠTVO (BEOGRAD)
1966.

Translated and published for U. S. Department of Commerce and
the National Science Foundation, Washington, D. C., by
the NOLIT Publishing House, Terazije 27/II, Belgrade, Yugoslavia
1966

Translated by
DANICA LADJEVAC and ALEKSANDRA STOJILJKOVIĆ

Edited by
PAUL PIGNON

Printed in Beogradski Grafički Zavod, Belgrade

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GLASNIK HEMIJSKOG DRUŠTVA, Vol. 29, No. 5—6, 1964, pp. 169—180

REFRACTOMETRIC INVESTIGATIONS of 2—2 bis (*p*-chlorophenyl) — 1 — 1 — 1 — TRICHLOROETHANE (*p*, *p'* —*DDT*) IN VARIOUS ORGANIC SOLVENTS. III.

by

SLOBODAN M. RISTIĆ and VIDOSAVA M. GEORGIJEVIĆ

1. INTRODUCTION AND REFERENCE TO EARLIER COMMUNICATIONS

Our earlier investigations of the refractive index of solutions of the insecticide 2—2—bis (*p*—chlorophenyl) — 1 — 1 — 1 — trichlorethane, better known as *DDT*, have shown some interesting details about the behavior of this molecule in different organic solvents. The present communication in part completes our earlier works(1, 2) and partly extends them.

First of all we would like to correct an omission made in the second paper (II) of our investigations by publishing here Table 1, which contains a summary and a survey of our earlier work, but brought up to date with the results of later measurements (cf. Table 1). The numeration on the lines in Fig. 1 of paper II correspond to the solvents in the order given in Table 1. As can be seen, before the present communication the behavior of the *p*, *p'* — isomer of DDT was refractometrically investigated in 25 organic solvents. All the measurements were made at constant temperature $t = 25.0^\circ$ ± 0.05 and with sodium light (*D* line). The φ — value, as defined in paper I, is given for all these solutions. From these φ-values an attempt was made(2) to find a relation between φ and some other constants, and indeed certain rough relations are given in the table which can be checked by the data in the other columns.

2. REFRACTOMETRIC DETERMINATION OF DDT IN NEW SOLVENTS

In the work reported here nine further solvents were investigated under experimental conditions as similar as possible to those of the earlier communications. Specifications of these solvents are given in the list below.

SOLVENTS USED (Paper III):

1. *Cyclohexanol* — "Carlo Erba S. A., Milano, p. a." — Refractive index directly determined at 25.0°C, $n_D^{25} = 1.46425$.
2. *Decalin* — "Carlo Erba S. A., Milano p. a." — Refractive index directly determined at 25.0°C, $n_D^{25} - 1.47488$.
3. *Tetralin* — supplied by the Chemistry Institute of this Faculty. Refractive index directly determined at 25.0°C, $n_D^{25} = 1.54614$.
4. *Nitrobenzene* — "Norwood, O., USA", p. a. — Refractive index directly determined at 25.0°C, $n_D^{25} = 1.54996$.
5. *Phenyl hydrazine* — "Judex Chemicals". Refractive index directly determined at 25.0°C, $n_D^{25} - 1.60161$.
6. *Quinoline* — "Glavkoks, USSR", purum. Refractive index directly determined at 25.0°C, $n_D^{25} - 1.62206$ (redistilled); two other samples had $n_D^{25} = 1.62170$ and $n_D^{25} - 1.61687$.
7. *Carbon disulfide* — "Carlo Erba S. A., Milano, p. a." Refractive index directly determined at 25.0°C, $n_D^{25} - 1.62384$.
8. *Acetylene tetrabromide* — "E. Merck", Darmstadt, p. a. Refractive index directly determined at 25.0°C $n_D^{25} - 1.63426$.
9. α—*Monobromine naphtalene* — "Carlo Erba, S. A., Milano, p. a.". Refrective index directly determined at 25.0°C, $n_D^{25} = 1.65661$.

Refractometric curves of *p, p'* — DDT solutions in these solvents are given in Fig. 1. Except for quinoline solution, where the φ-value is about ±0, which will be discussed later (Figs. 2 and 3), these are high refractive index solvents.

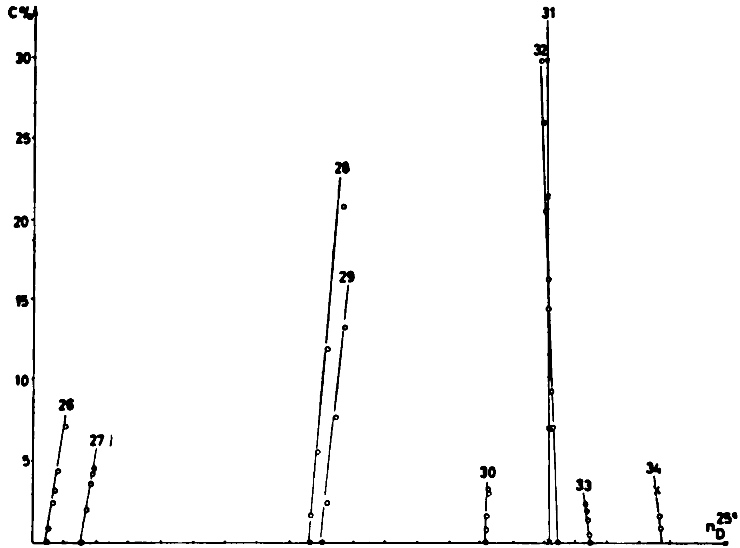

Fig. 1

As can be seen in Fig. 1, the slopes of the curves on either side of quinoline have a different direction, *i. e.* the φ-value clearly changes sign in case of solvents such as quinoline.

TABLE 1

Investigated solutions of p, p′—DDT

	Solvent	$\varphi - \frac{\Delta n}{\Delta c}$	n_D^{25}		$d_4^{25°}$	M
			Found	lit.		
1.	Chloroform	0.00188_5	1.44200	1.44270	1.47992	119.389
2.	Carbon tetrachloride	0.00182_9	1.45747	1.45759	1.5842	153.838
3.	Methyl alcohol (obs.)	0.00177_0	1.32736	1.3267	0.78740	32.042
3.a	Methyl alcohol	0.00152_0	1.32857	1.32773	0.78643	32.042
4.	Methyl acetate	0.00176_0	1.35818	1.35935+	0.92740	74.078
5.	Ethyl acetate	0.00163_4	1.36981	1.36979	0.89455	88.104
6.	Acetone	0.00156_4	1.35687	1.35660	0.78508	58.087
7.	Ethyl alcohol	0.00150_0	1.35934	1.35941	0.78554	46.086
7.a	Ethyl alcohol	0.00142_0	1.36184	1.36790	0.8066	46.086
8.	Paraldehyde	0.00144_1	1.40226	1.40486+	0.9943+	132.16
9.	Ethyl ether	0.00137_1	1.35055	1.3497	0.7135+	74.14
10.	Petrol ether	0.00134_1	1.36193	—	—	74.14
11.	Piperidine	0.00123_9	1.45087	1.45035	0.8606+	85.15
12.	Dioxane	0.00121_0	1.42000	1.42025	1.02687	88.104
13.	Benzene	0.00113_7	1.40108	—	0.7165	—
14.	Acetyl acetone	0.00107_5	1.44917	1.45178+	0.9712	100.11
15.	Cyclohexanine	0.00093_6	1.44947	1.4460	0.94206	98.140
16.	Oleic acid	0.00089_5	1.45877	1.4571+	0.8870	282.452
17.	Toluol	0.00082_5	1.49340	1.49405	0.86220	92.134
18.	Benzene	0.00081_5	1.49787	1.49790	0.87368	78.108
19.	Pyridine	0.00069_4	1·50712	1.5067	0.9786	79.098
20.	Monochlorbenzol	0.00064_6	1.52143	1.52211	1.10630	112.557
21.	Benzyl chloride	0.00063_8	1.53668	1.54151+	1.1026+	126.58
22.	Acetophenone	0.00054_6	1.53136	1.5322	1.2382	120.144
23.	Bromoform	0.00034_5	1.59288	1.5980+	2.890+	252.766
24.	Benzyl benzoate	0.00029_8	1.56718	1.5681+	1.114+	212.236
25.	Aniline	0.00015_1	1.58365	1.58318+	1.01750	93.124
26.	Cyclohexanol	0.00087_7	1.46425	$1.46560^{22.6}$	0.9449	100.16
27.	Decalin	0.00085_7	1.47488	1.48280	0.8960	$138.1^{138.25}$
28.	Tetralin	0.00051_3	1.54602	1.54614	0.9710	132.20
29.	Nitrobenzene	0.00052_6	1.54996	1.55045+	1.1950	125.1
30.	Phenyl hydrazine	0.00017_5	1.60161	$1.60813^{20.3}$	1.0884	108.14
31.	Quinoline	0.00004_7	1.62206	1.62450	1.0896	129.1
32.	Carbon disulfide	0.00016_2	1.62384	1.62950^{18}	1.2628	76.14
33.	Acetylene tetrabromide	0.00059	1.63426	1.63795	2.9638	345.70
34.	α-monobrome-naphthalene	0.00045	6.65661	$1.65876^{19.4}$	1.4875	207.0

Table 1 also contains data for checking relations (4—7) of paper II. The considerable fluctuations in the constant *W* (expression 7, Paper II), persist here, so it is still impossible to find out the cause for this fluctuations. However, the number of substances for which the product in the last column falls far outside a fairly wide average is relatively small.

3. INVESTIGATION OF THE INFLUENCE OF TEMPERATURE AND WAVELENGTH ON THE φ-VALUE

In our earlier investigations we tried to get the steadiest possible temperature ($t = 25.00 \pm 0.05$°C) and monochromatic wavelength (Na_D). In this work, with a carbon disulfide solution of p, p' – DDT we determined *the temperature coefficient of* $\varphi \left(\frac{d\varphi}{dt}\right)$, and its *wavelength coefficient*, $\left(\frac{d\varphi}{d\lambda}\right)$. These quantities were measured especially for the practically important temperature region 20 – 25 – 30°C, and the λ-region of the Fraunhofer lines $C - D = G'$ (*i.e.* 6563, 5893 and 4340 Å). Because of the lack of a special monochromator the refractive index of the solution was determined at various wavelengths using the monochromator system of a Bonet-Maury absolute colorimeter. This was done by removing selenium cell detector, so that the beam of monochromatic light (with the smallest slit) selected by means of the wavelength drum was directly incident on the prism of the Pulfrich refractometer. Since the Bonet-Maury instrument has one grating as the dispersion system, the monochromaticity was satisfactory for our purposes. Tables 2 and 3 show these determinations and the result.

TABLE 2

Influence of temperature on φ for CS_2-solution of DDT

C%	n_D^{20}	φ^{20}	C%	n_D^{25}	φ^{25}	C%	n_D^{30}	φ^{30}
0.00	1.62704		0.00	1.62384		0.00	1.61983	
		$1.8\cdot10^{-4}$			$1.3\cdot10^{-4}$			$3.4\cdot10^{-4}$
5.73	1.62598		7.07	1.62295		3.35	1.61867	
		$1.6\cdot10^{-4}$			$1.7\cdot10^{-4}$			$1.4\cdot10^{-4}$
8.47	1.62571		9.32	1.62223		12.69	1.61804	
		$1.8\cdot10^{-4}$			$1.7\cdot10^{-4}$			$1.2\cdot10^{-4}$
17.86	1.62384		18.58	1.62072		22.17	1.61714	
		$1.6\cdot10^{-4}$			$1.6\cdot10^{-4}$			$1.2\cdot10^{-4}$
20.96	1.62375		20.71	1.62045		26.20	1.61669	
					$1.5\cdot10^{-4}$			
			26.19	1.61983				
		mean value			mean value			mean value
		$1.69\cdot10^{-4}$			$1.56\cdot10^{-4}$			$1.30\cdot10^{-4}$

$$\left[\frac{d\varphi}{dt}\right]_{20/25} = 2.6\cdot10^{-4} \qquad \left[\frac{d\varphi}{dt}\right]_{25/30} = 5.8\cdot10^{-4}$$

TABLE 3

Influence of wavelength on φ for CS_2-solution of DDT

C%	n_C^{20}	φ_C	n_D^{20}	φ_D	$n_{G'}^{20}$	$\varphi_{G'}$
0.00	1.61771		1.62704		1.67517	
		$1.4 \cdot 10^{-4}$		$1.7 \cdot 10^{-4}$		$4.7 \cdot 10^{-4}$
5.27	1.61699		1.62616		1 67269	
		$1.6 \cdot 10^{-4}$		$1.8 \cdot 10^{-4}$		$4.6 \cdot 10^{-4}$
5.73	1.61681		1.62598		1.67253	
		$1.3 \cdot 10^{-4}$		$1.6 \cdot 10^{-4}$		$3.3 \cdot 10^{-4}$
8.47	1.61664		1.62571		1.67235	
		$1.4 \cdot 10^{-4}$		$1.8 \cdot 10^{-4}$		$3.8 \cdot 10^{-4}$
17.86	1.61529		1.62384		1.66831	
		$1.2 \cdot 10^{-4}$		$1.6 \cdot 10^{-4}$		$3.9 \cdot 10^{-4}$
20.96	1.61511		1.62375		1.66684	
		mean value $1.36 \cdot 10^{-4}$		mean value $1.69 \cdot 10^{-4}$		mean value $4.09 \cdot 10^{-4}$

$$\left[\frac{d\varphi}{d\lambda}\right]_{C/D} = 4.9 \cdot 10^{-7} \qquad \left[\frac{d\varphi}{d\lambda}\right]_{D/G'} = 1.8 \cdot 10^{-6}$$

As can be seen: 1 — *in carbon disulfide solution of $p, p'-DDT$ φ decreases with increasing temperature* in the investigated temperature intervals (although not much: 0.03 and 0.06×10^{-4}/degree): 2 — for the same solution φ increases with decreasing monochromatic wavelength for the wavelength interval used here 6563—4340 Å ($H_\alpha - H_\gamma - \lambda -$ lines).

4. DETERMINATION OF THE SOLUBILITY, DENSITY AND n_D OF SOME SATURATED DDT SOLUTIONS

In order to be able to acquire some additional information on the process of dissolution in the systems investigated, we tried the concentrations up to saturation in order to determine some values of the *solubility of $p, p'-DDT$* which could not be found in the available literature(3). We also determined pycnometrically the

TABLE 4

Some characteristics of saturated solutions of $pp'-DDT$ in some organic solutions

Solvent	C_{sat}	d_4^{25}	n_D^{25}	sat.
Carbon disulfide	35.82	1.3458	1.61903	$-1.3 \cdot 10^{-4}$
Chloroform	31.54	1.4783	1.50183	$+1.9 \cdot 10^{-3}$
Quinoline	32	1.1956	1.61929	± 0.00

density of the solution at constant temperature ($t = 25.00°C$). These and the corresponding n_D values are shown in Table 4. As can be seen, the solubilities at this temperature are considerable for all three solvents, so they are quite suitable for refractometric determination of solute concentration in view of their suitable numerical values (except for quinoline which will be discussed in section 6).

5. CHECK OF THE REFRACTIVITY FORMULA

The various well-known, mainly empirical relations between refractive index and density can still provide *additional data on the dissolution process* when applied to the solutions, because *molecular refractivities have an additive character, if the dissolution is a physical process.*

For some solutions, for which we determined concentrations until saturation (carbon disulfide and chloroform solutions) we checked the additivity of the molecular refractivity formula by the Lorentz-Lorentz formula

$$R_L = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d}$$

The additivity of all the solvents used is good, and that of the solutions is satisfactory. Good agreement of the R_L for the pure solvents with some literature data further confirms our results (for both n_D and d_4^t). Table 5 gives the determined specific and molecular refractivities of the solvents and solutions, from which we could get not only the molecular refractivity of the solid solute, *i. e. p, p'* − DDT, but also its refractive index, provided the normal molecular weight for this compound is valid ($M_{DDT} = 354.5$).

TABLE 5

Solvent Solution or Solvate	R_L^M	r_L^s
Carbon disulfide	21.17	0.2781
Chloroform	21.01	0.1762
$CS_2 + DDT_{sol.\ sat.}$	45.84	0.2607
$CHCl_3 + DDT_{sol.\ sat.}$	38.64	0.1996
DDT_{solid}. (theory)	84.30	0.2378
DDT_{solid} (exper.)	87.56	0.2470

This obviously confirms what was stated at the beginning of this section. However, it should be pointed out that even values with above 10% deviation are satisfactory, since saturated solutions were used and deviations are expected.

6. REFRACTOMETRY OF QUINOLINE DDT SOLUTION

The *p*, *p*′ – DDT solution in quinoline is particularly interesting since our first investigations showed that its φ is extremely low, practically zero. Using two other samples of quinoline, we purified it by distillation but the results did not change. The solution showed a very small, if any one, practically constant φ-value, despite the high solubility of *p*, *p*′ – DDT in quinoline. Figure 2 shows the analytical refraction curves for this case, the left curve being for nondistilled and the right for distilled quinoline of the same origin.

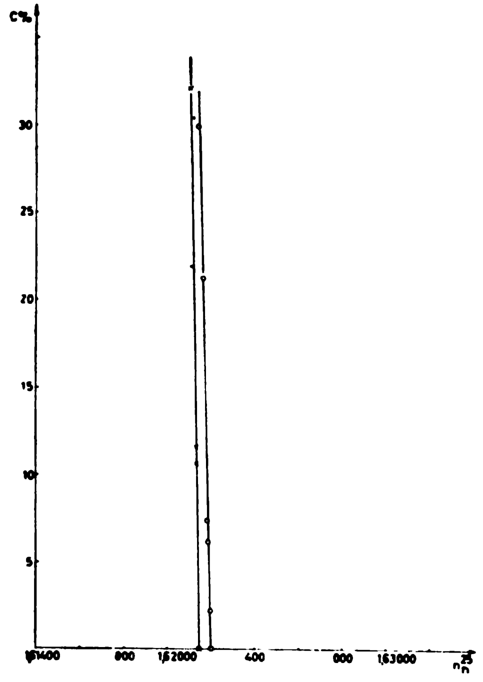

Fig. 2

This represents, as far as we know, the first certain case where the additivity of molecular refractivities does not hold: the density of the solution increases ovbiously with increasing concentration, while n_D remains constant or changes only slightly.

The fact that the concentration coefficient of the quinolinic solution of *p*, *p*′ – DDT is practically zero is to some extent predictable from data for the refractive index of the solid substance published by E. L. Gooden (1045)$^{(5)}$, and a group from the Armor Research Foundation (Illinois)$^{(6)}$: the two indices of solid *p*, *p*′—DDT $n_\alpha = 1.618$ and $n_\beta = 1.626$ are very close to the refractive index of the solvent (1.61687 – 1.62206). This obviously implies that the dominant factor determining φ should be considered to be the difference between the refractive indices of the solute and the solvent $(n-n_0)$ rather than the refractive index of the solvent (n_0) itself. Nevertheless, the refractometric behavior of the quinoline solution of $p, p'-$DDT is still rather obscure, since the usual mean refractive index $\bar{n}=\sqrt[3]{\bar{n}_\alpha \bar{n}_\beta \bar{n}_\gamma}=1.663$, which can be useful for determining the molecular refractivity of solid compounds, is not suitable for interpreting the refractivity of the saturated solution.

7. DISCUSSION OF RESULTS AND CONCLUSION

Aside from nine new solvents the influences of temperature and wavelength on φ were investigated. These influences are similar as on the refractive index, but latter being clearly more important.

The quinolinic solution is thus in so far interesting at present, just because this dominant component of the φ-value is inactivated, and it may be possible to define more precisely the importance of the other components whose effect is otherwise not obvious.

Work on this problem will be continued.

Institute for Physical Chemistry
School of Sciences
University of Beograd
(Yugoslavia)

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GLASNIK HEMIJSKOG DRUŠTVA, Vol. 29, No. 5—6, 1964, pp. 181—189

SPECTROPHOTOMETRIC INVESTIGATIONS OF CRYSTALLOHYDRATES AND CRYSTALLODEUTERATES OF SOME TRANSITION ELEMENTS AND THEIR SOLUTIONS IN H_2O AND D_2O*

by

ANKICA M. ANTIĆ-JOVANOVIĆ and MILORAD G. JEREMIĆ

It is known that the color of transition element ions depends on the type of ligands surrounding them. Tsuchida(1) empirically arranges the ligands in a series according to their abilities to shift the maximum of their absorption spectrum. The sequence in this series does not change with change of the central ion. Of special interest is the investigation of the substitution of ordinary water by heavy water, a rather similar ligand but with different nuclear mass.

The influence of heavy water on the color of hydrated salts was first studied by Joos and Böhm(2) on potassium-chromium-selenium and potassium-chromium-sulfate alum. Later Bell(3) studied this effect on copper sulfate. However, these authors only observed changes in color intensity and made some qualitative measurements of the color tint, in both cases colorimetricaly.

By spectrophotometric measurements with a Cary Model 14 recording spectrophotometer, Halpern and Harkness(4) recently obtained some more precise data on the shift of the absorption band maxima for a number of ions in solution in ordinary and heavy water in the form of perchlorate salts.

We have not found any exact data on absorption expressed for instance terms of absorptivity.

The purpose of the present work was to investigate the substitution of H_2O by D_2O in crystallohydrates and crystallodeuterates of ions of some elements of the first transition series and their solutions, using absorption and reflection spectra. Our aim was to obtain more complete quantitative data on absorption spectra and their changes in these two strongly polar solvents. For this purpose we made spectrophotometric measurements of the absorption of hydrate crystals of Ni^{++}, Co^{++}, Fe^{++}, Cr^{++}, Cu^{++} and Mn^{++} and their solutions in ordinary and heavy water in the region 2.000 to 10·000 Å using a Unicam SP 500 spectrophotometer.

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* Reported at the 11th International Spectroscopy Colloqium in Beograd, October, 1963.

EXPERIMENTAL

Saturated solutions of the above ions were prepared from anhydrated sulfate salts, p. a., by dissolution in ordinary and heavy water at a constant temperature of 25±0.05°C, at which temperature all spectrophotometric measurements were made too. An exception was ferous sulfate which was not first anhydrated but directly dissolved in weakly acidified water, pH = 5.0. To investigate the influence of dilution and the validity of Lambert-Beer's law we also made measurements at considerably lower concentrations — 0.5 to 2*M*.

Crystals were obtained by slow evaporation from saturated solutions. For the formation of deuterohydrates evaporation was carried out in a closed system with constant monitoring of the vapor pressure and at constant temperature. Ferrosulfate crystals were formed from weakly acid solutions in a nitrogen atmosphere so to prevent any oxidation of ferrous to ferric ions. After three or four weeks growth, we got crystals with 1 – 2 cm edges which could be used for optical measurements. For this purpose the crystals were normally cut in the direction of the main optical axis and were polished into thin plates of 0.2 to 1.5±0.05 mm.

The absorption spectra of the solutions and the crystals are shown in Figs. 1, 2, 3, 4, 5.

The spectrophotograms show changes in absorption, both in the solution and the crystals, on the replacement of ordinary water

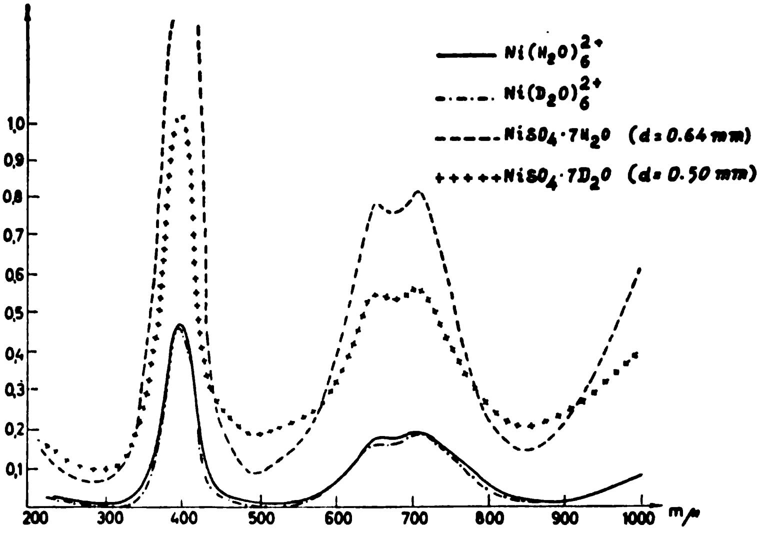

Fig. 1. Absorption spectra of $NiSO_4 \cdot 7H_2O$ and $NiSO_4 \cdot 7D_2O$ crystals and their solutions in H_2O and D_2O.

by heavy water, manifested in a hyperchromic effect on the one hand and change of the absorption minimums on the other. This is particularly clear if the absorption is expressed as transmittance as a function of wavelength, as shown for cobalt sulfate in Fig. 2 (curves 1 and 2).

The absorptivities for each solution and crystal at the absorption maxima are given in Table 1.

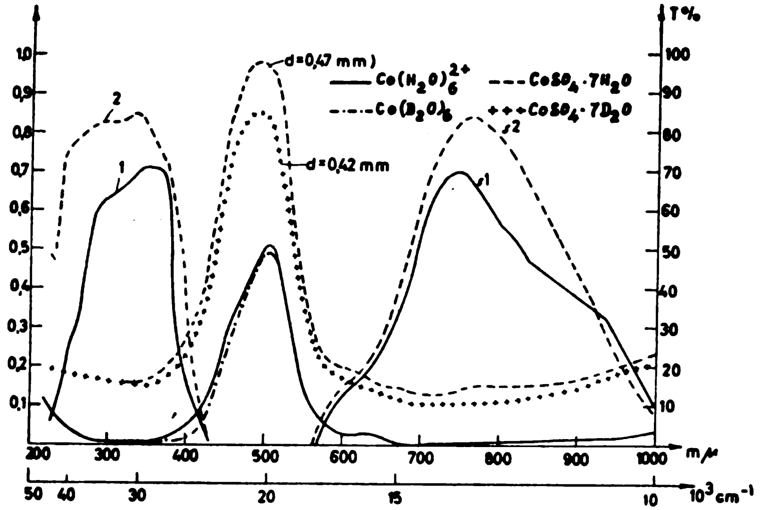

Fig. 2. Absorption spectra of $CoSO_4 \cdot 7H_2O$ and $CoSO_4 \cdot 7D_2O$ crystals and their solutions in H_2O and D_2O. Curves 1 and 2 show transmittance of Co++ ion in H_2O and D_2O solutions.

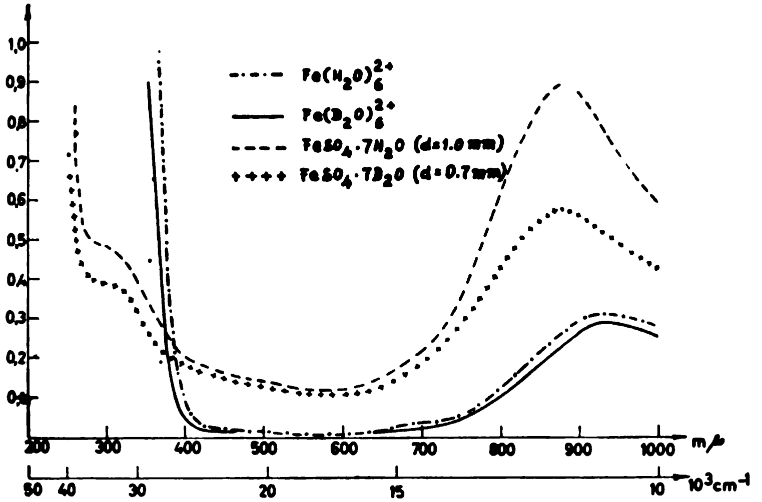

Fig. 3. Absorption spectra of $FeSO_4 \cdot 7H_2O$ and $FeSO_4 \cdot 7D_2O$ and their solutions in H_2O and D_2O.

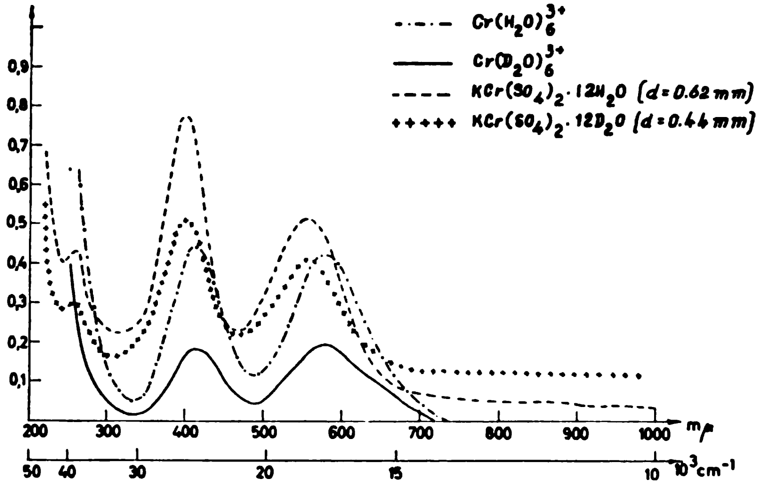

Fig. 4. Absorption spectra of chrome alum and solutions in H_2O and D_2O

TABLE 1

Absorptivity of crystals and their solutions in H_2O and D_2O

Sample	max mμ	Absorptivity in H_2O	Absorptivity in D_2O
$Ni(H_2O)_6^{2+}$	710	2.09 ±0.05	1.98 ±0.05
	650	1.84 ±0.05	1.73 ±0.05
	390	4.85 ±0.05	4.60 ±0.05
$NiSO_4 \cdot 7H_2O$	700	12.1 ±0.1	11.3 ±0.1
	640	11.5 ±0.1	10.5 ±0.1
	390	27.3 ±0.1	27.0 ±0.1
$Co(H_2O)_6^{2+}$	505	5.12 ±0.05	4.99 ±0.05
$CoSO_4 \cdot 7H_2O$	500	21.0 ±0.5	20.0 ±0.5
$Fe(H_2O)_6^{2+}$	950	1.62 ±0.05	1.55 ±0.05
$FeSO_4 \cdot 7H_2O$	875	8.8 ±0.5	7.8 ±0.5
$Cr(H_2O)_6^{3+}$	580	5.80 ±0.05	5.45 ±0.05
	410	6.20 ±0.05	6.05 ±0.05
$KCr(SO_4)_2 \cdot 12H_2O$	560	10.8 ±0.5	9.9 ±0.5
	400	12.3 ±0.5	11.4 ±0.5
$Cu(H_2O)_6^{2+}$	800	12.62 ±0.1	11.80 ±0.1
$CuSO_4 \cdot 5H_2O$	760	15.0 ±0.8	46.3 ±0.8
$Mn(H_2O)_6^{2+}$	400	0.040±0.01	0.030±0.01

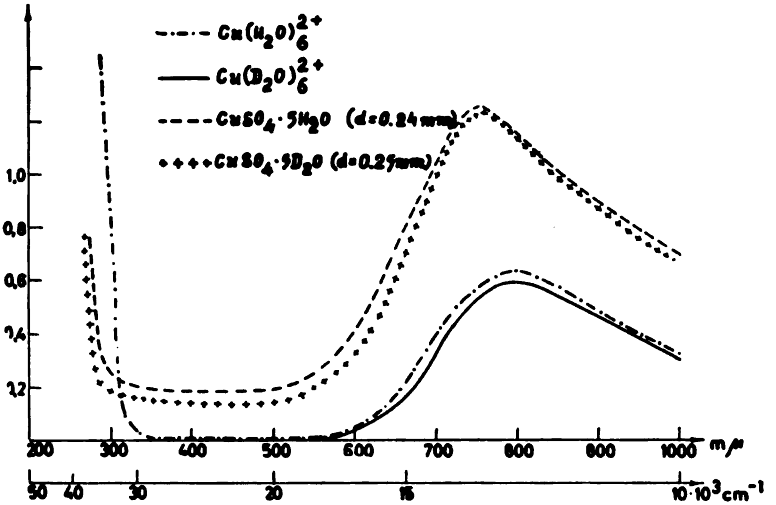

Fig. 5. Absorption spectra of $CuSO_4 \cdot 5H_2O$ and $CuSO_4 \cdot 5D_2O$ and their solutions in H_2O and D_2O.

The differences in absorptivity between solutions in ordinary and heavy water vary from 2.5% for $Co(D_2O)_6^{2+}$ to 6.5% for $Cu(D_2O)_6^{2+}$, while for crystals this difference is about twice as big.

For more precise determination of the absorption maximum we also used emission spectrophotography. Photographs were taken on a PGS 2 spectrograph with a plane diffraction grating and a recording microphotometer. Thus we got the position of the maxima to considerably higher accuracy and determined the shifts caused by the substitution of ordinary water by heavy water. Results are shown in Table 2.

TABLE 2

Shifts of absorption band maxima on replacing H_2O by D_2O

Sample	Wave number of band maximum in H_2O (cm^{-1})	Shift in cm^{-1}
$Ni(H_2O)_6^{2+}$	25468	$+62 \pm 20$
$Co(H_2O)_6^{2+}$	19774	$+30 \pm 12$
$Cr(H_2O)_6^{3+}$	17384	$+45 \pm 15$
”	24190	$+63 \pm 20$
$Mn(H_2O)_6^{2+}$	14939	$+6 \pm 3$

This table shows that there are shifts towards higher energies, *i. e.* smaller wavelengths, which is in good agreement with the first qualitative observation(2, 3, 5) and other recent measurements(4).

According to ligand field theory this effect arises from the difference in field intensity produced by ordinary and heavy water as ligands surrounding the central ion. On the other hand, this difference can be explained by the hypothesis(4) that differences in the dipole moment of ordinary and heavy water cause changes in the energy of the ligand-central ion bond, which is higher with

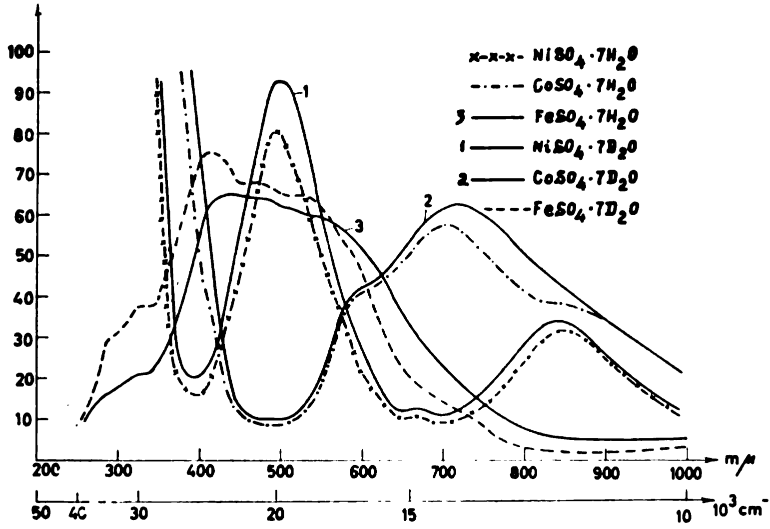

Fig. 6

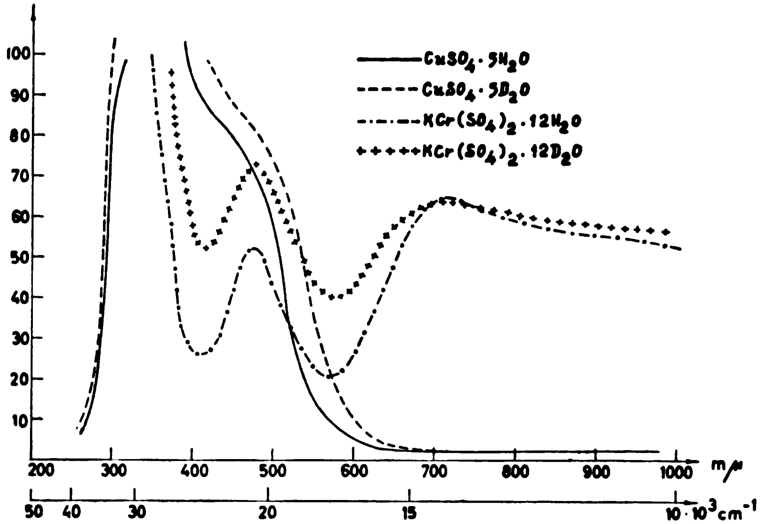

Fig. 7 — Reflection spectra of crystals

heavy water, thus shifting the absorption maximum to a shorter wavelength.

Besides absorption spectra we also measured reflection spectra of crystals using a Unicam SP 500 spectrophotometer. Measurements on crystals of different densities gave data which are, at least qualitatively, in agreement with the absorption spectrophotometric measurements. Figures 6 and 7 show reflection spectra of crystals of the same density.

As can be seen the intensity of reflection of crystals with heavy water is greater than with ordinary water, while the shift of reflection maximum is similar to the shift of the absorption maximum.

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GLASNIK HEMIJSKOG DRUŠTVA, Vol. 29, No. 5—6, 1964, pp. 191—197

THE SPACE GROUP DETERMINATION OF 2 AMINO 4′ BROMO BENZOPHENONE AND 2 AMINO 4′ CHLORO BENZOPHENONE

J. MIŠOVIĆ, S. RAMASECHAN, Indian Institute of Science, India.

INTRODUCTION

This investigation was undertaken as part of a project at the Physics Department of the Indian Institute of Science for the accurate determination of the crystal structures of the substituted benzophenones, with a view to determination how substitution of groups in various positions and the formation of inter and intra molecular hydrogen bonds affect the angle between the planes of the two benzene rings[1,2,3,4] (1940, 1945, 1954, 1954). It became increasingly clear that the steric hiderance between the hydrogens in the 6.6′ positions would prevent the molecule from being coplanar.

These compounds were prepared in the Organic Chemistry Department of the Indian Istitute of Science, by Dr. M. V. Bhatt[5] (1953), who was interested in the mechanisms of substitution in the benzophenones. By thorough analysis using various organic techniques[6] (1936) he was able to definitely fix the positions of the amino, bromo and chloro positions. The crystals were needle shaped and yellow. Good crystals were grown by slow evaporation from the saturated petroleum-benzene solution.

The crystals appeared to be orthorhombic on examination under a polarisation microscope.

MORPHOLOGICAL MEASUREMENT

The crystal was fixed on to the goniometer head of a Unicam two-circle goniometer and the needle axis was made to coincide with the axis of rotation. The centering etc., were done by the usual procedure. The best developed face of the crystal was the *b*-pinacoid; some of the prism faces (*m*, *l*, *n*) were also quite well developed. The *a* and *c* faces were extremely small. The brachydome *f* and the pyramid *o* were easily recognisable. The only two other forms recognisable, although very small, were the macrodome (*d*) and the pyramid (*i*).

Table 1 gives the ρ and φ values for the different planes observed on the surface of the crystal. There were a few other very tiny faces but the angles were not measured. The angles given are accurate to +15′ arc. This low accuracy was due to the great flakiness of the crystal, so that the reflections were not sharp.

TABLE 1

Data from the goniometer measurements of 2 amino — 4′ bromo benzophenone crystal

Forms			Indices
a	0	90°	100
m	16°50′	90°	110
l	31°10′	90°	120
n	42°10′	90°	130
b	90°	90°	010
n	137°55′	90°	$\bar{1}30$
l	148°30′	90°	$\bar{1}20$
m	163°15′	90°	$\bar{1}10$
a	180°	90°	$\bar{1}00$
m	196°58′	90°	$\bar{1}\bar{1}0$
l	211°15′	90°	$\bar{1}\bar{2}0$
n	222°10′	90°	$\bar{1}\bar{3}0$
b	270°	90°	$0\bar{1}0$
n	317°52′	90°	$1\bar{3}0$
l	228°50′	90°	$1\bar{2}0$
m	343°12′	90°	$1\bar{1}0$
a	0°	90°	100
o	16°50′	57°20′	221
o	163°50′	57°20′	$\bar{2}21$
o	196°50′	57°20′	$\bar{2}\bar{2}1$
o	343°50′	57°20′	$2\bar{2}1$
d	0°	36°15′	101
d	180°	36°15′	$\bar{1}01$
f	90°	25°	021
f	270°	25°	$0\bar{2}1$
i	31°10′	24°	122
i	148°50′	24°	$\bar{1}22$
i	211°10′	24°	$\bar{1}\bar{2}2$
i	328°50′	24°	$1\bar{2}2$

The stereographic projection for the crystal is given in Fig. 1.

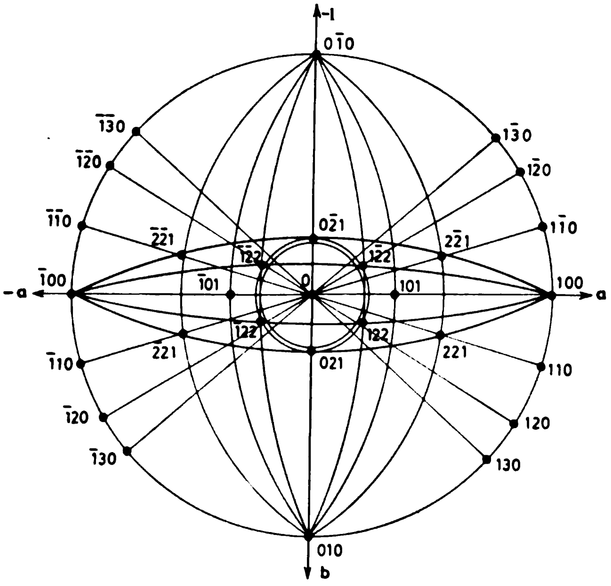


Fig. 1. Stereographic projection of 2 amino-4' benzophenone crystal

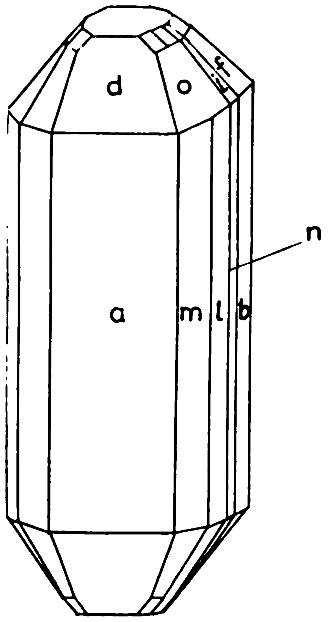


Fig. 2. Crystal habit of 2 amino-4' bromo benzophenone

The face marked in the projection as 221, because of its size, was first taken to be the parametral plane (111). From this we got the axial ratios

$$0.31:1:0.45,$$

but later *X*-ray measurements showed that the actual index of this plane is (221) and not (111). The indexing in the projection follows this identification and the axial ratios come out to be

$$0.3070:1:0.2294.$$

From the symmetry one can see that the crystal most probably belongs to the point group mm^2 (C_2^v).

Figure 2 gives the crystal habit of amino-4′ brome benzophenone. The crystals of 2 amino −4′ chloro benzophenone were extremely fine needles. However, when grown from alcohol-water solution under isothermal conditions very good crystals could be obtained. Measurements of the angles for this crystal on the two--circle goniometer gave practically identical results to those obtained for 2 amino −4′ bromo benzophenone. The crystal habit of this crystal was also very similar to that of the bromo compound.

Since the angular measurement were by no means very accurate it was not possible to determine the differences in the axial ratios by the morphological method.

UNIT CELL AND SPACE GROUP

A rotation picture about the needle axis and Weissenberg zero, first and second layer photographs were taken. In this experiment copper K_α radiation filtered through a nickel filter was used. The linear absorption coefficients of 2 amino-4’ bromo benzophenone and 2 amino-4’ chloro benzophenone are 52.83 cm^{-1} and 35.60 cm^{-1}, respectively. In order to reduce the absorption error very small crustals of diameter 2 mm were used for taking the photographs.

For getting the systematic absences the zero, first and second level Weissenberg photographs about the c axis were taken. They showed no systematic absences of general (hkl) reflections. Hence the cell type is primitive (P). Zero-level photographs reveal the extinctions noted in Table 2. Tables 2 and 3 give the crystallographic data for 2 amino 4’ bromo benzophenone and 2 amino 4’ chloro benzophenone.

TABLE 2

Crystallographic data for 2 amino — 4' bromo benzophenone

$a = 7.84$ Å $\quad b = 25.54$ Å $\quad c = 5.86$ Å

$\alpha = \beta = \gamma = 90°$

Axial ratios are 0.3070:1:0.2294
Number of molecules per unit cell:4
Conditions limiting possible reflections:

hkl	No conditions
*h*00	$h = 2n$
0*k*0	$k = 2n$
00*l*	$l = 2n$
0*kl*	$k + l = 2n$
*h*0*l*	$h = 2n$
*hk*0	No conditions.

This show that the space group is *Pna* 2_1 (No. 33 in the International Tables for X-ray Crystallography — 1952).

TABLE 3

Crystallographic data for 2 amino-4'- chloro benzophenone

$a = 7.896$ Å $\quad b = 25.21$ Å $\quad c = 5.74$ Å

$\alpha = \beta = \gamma = 90°$

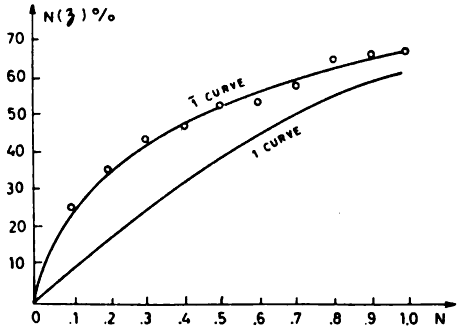
Axial ratios 0.3132:1:02277
Number of molecules per unit cel: 4
Conditions limiting possible reflections:

hkl	No conditions
*h*00	$h = 2n$
0*k*0	$k = 2n$
00*l*	$l = 2n$
0*kl*	$k + l = 2n$
*h*0*l*	$h = 2n$
*hk*0	No conditions

Hence group is *Pna* 2_1 (No 33 in the International Tables for X-ray Crystallography — 1952).

The specific grivities of 2 amino —4' bromo and 2 amino —4' chloro benzophenone are 1.59 and 1.37, respectively. From the specific gravity and molecular weight the number of molecules per unit cell is 4 for both compound.

The $\sin^2\theta$ values were calculated using the formula for an orthorhombic system. For the zero layer the Lorentz and polarisations corrections were read from Buerger's Tables. For the higher layers the curve of $\left(1 - \frac{s^2}{4\sin^2\theta}\right)^{\frac{1}{2}}$ against $\sin^2\theta$ was drawn and the 1/L. P. factor was calculated X-ray diffraction data.



Distribution for 2 amino-4' bromo benzophenone *hk*0 reflections, 3 ranges, compared with theoretical curves 1 and $\bar{1}$

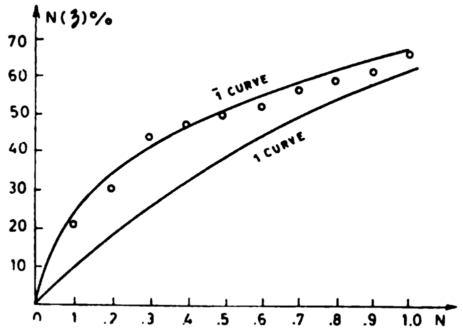


Fig. 3. Distribution for 2 amino-4' bromo benzophenone *hk*0 reflections, 6 ranges compared with theoretical curves 1 and $\bar{1}$

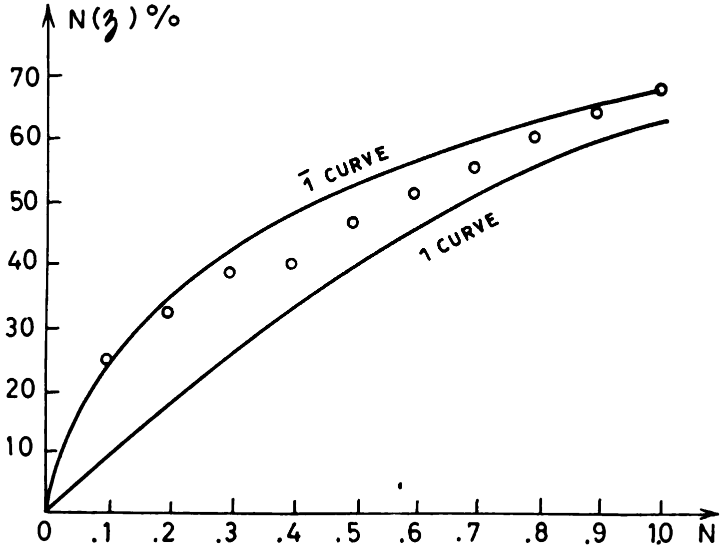


Fig. 4. Distribution for 2 amino-4' bromo benzophenone *hk*1 reflections, 3 ranges, compared with theoretical curves 1 and $\bar{1}$

TABLE 4

N(Z), in percentage, for hk0 reflections of 2 amino-4′ bromo benzophenone

Z

Range	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
I	21.00	35.00	44.00	52.00	55.00	59.00	62.00	69.00	69.00	70.00
II	16.33	30.61	38.76	44.90	49.90	48.98	56.12	64.29	66.33	68.37
III	39.81	41.67	48.15	48.15	53.70	55.56	57.41	64.81	64.81	66.67
Mean	25.71	35.76	43.64	48.35	52.87	54.51	58.51	66.03	66.71	68.35

N(Z), in percentage, of the two functions for N(Z) (theoretical values)

Z

	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	
$l-exp(-Z)$	9.52	18.13	25.92	32.97	39.35	45.12	50.34	55.07	59.34	63.21	(curve 1)
$erf\left(\frac{1}{2}Z\right)^2$	24.81	34.53	41.87	47.38	52.05	56.14	59.72	62.89	65.72	68.33	(curve 1)

TABLE 5

N(Z), In percentage, for hk0 reflections of 2 amino-4′ bromo benzophenone

Z

Range	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
I	23.40	34.04	46.81	51.06	55.32	57.45	59.57	63.83	68.09	68.09
II	18.87	30.19	45.28	52.83	52.83	56.60	53.49	62.26	62.26	67.92
III	13.04	30.43	43.48	43.48	43.48	43.48	47.83	52.17	52.17	60.87
IV	19.23	30.77	38.46	42.31	46.15	46.15	53.84	57.69	67.31	78.85
V	0	34.55	41.82	45.45	52.73	60.00	63.64	63.64	63.64	67.27
VI	0	20.75	50.94	49.24	54.72	54.72	62.26	62.26	62.26	62.26
Mean	21.64	30.12	44.46	47.40	50.87	53.07	57.60	60.31	62.62	67.54

The data for the intensity measurements were gotten by the multiple film technique of Robertson[7] (1943). The *hk*0 and 0*kl* Weissenbergs were recorded by oscillating the crystal about the c and a axes through 200°. The time of exposure was of the order of 20—30h. A different standard intensity scale was prepared for each layer, with a given reflection for each particular layer.

The intensities of the diffraction spots were measured by comparison with the standard spots. Thus the intensities of the diffraction spots were placed on a relative numerical scale.

WILSON'S STATISTICAL METHOD

Although the space group is determined, it was necessary aplly Wilson's statistical method[8] (1949) for the detection of the center of symmetry, since the absences for *Pna* 2_1 and *Pnam* are identical.

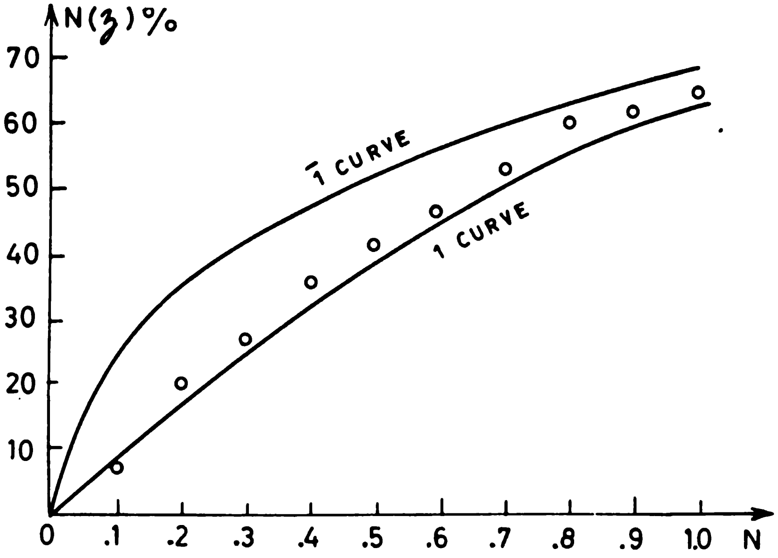


Fig. 5 Distribution for 2 amino-4' bromo benzophenone *hk*2 reflections, 5 ranges, compared with theoretical curves 1 and $\bar{1}$

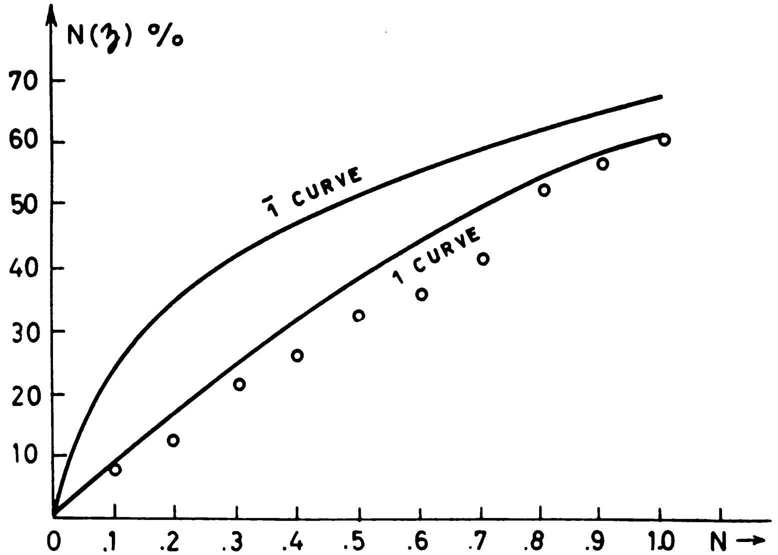


Fig. 6 Distribution for 2 amino-4' bromo benzophenone 0*k*l reflections, 8 ranges, compared with theoretical curves 1 and $\bar{1}$

The *hk*0 reflections were divided into two sets of ranges — for the first set $\sin^2\theta$ was 0—0.2, 0.2—0.4, and 0.4—0.6 with 54,51 and 55 reflections in each range, respectively. The secend set, for the same group of *hk*0 reflections, had $\sin^2\theta$ 0—0.1, 0.1—0.2, 0.2—0.3, 0.3—0.4, 0.4—0.5 and 0.5—0.6, with 25, 28, 24, 27, 28 and 27 reflections, in each range respectively. Table 1 gives the results for the two sets of ranges. In Fig. 3 the two distribution curves obtained for these and the theoretical curves for the centro and non-centro-symmetric distributions are given. In a similar manner the *h*11, *h*21, 0*k*1 reflections were divided into ranges and distribution curves drawn. The curves in Figs. 4, 5 and 6 give the distribution of intensities as compared with theoretical curves. One notices that while the *hk*1 data gives a curve close to the centro-symmetric value, the *hk*2 unequivocally shows a non-centro-symmetric distribution. Therefore, the space group for both crystals is $Pna\,2_1$.

The crystal structures of both compounds will be given in a separate paper.

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GLASNIK HEMIJSKOG DRUŠTVA, Vol. 29, No. 5—6, 1964, pp. 199—201

COULOMETRIC DETERMINATION OF MANGANOUS ION

by

SRETEN N. MLADENOVIĆ

Small amounts of manganese are most often determined colorimetrically by measuring the color intensity of permanganate ion solutions. Coulometric determination of the manganous ion either at constant current density or at limited potential is prevented by reactions taking place either before or simultaneously with the reduction and oxidation of manganous ions.

From neutral and acid solutions, before the reduction of the manganous ion, hydrogen is evolved at the platinum cathode. However, at the platinum anode several reactions can take place depending on the acidity of the solution:

$$\begin{array}{llll}
Mn^{2+} - e & \rightarrow Mn^{3+} & e_0 = 1.51\ V & (1) \\
Mn^{2+} - 2e & \rightarrow Mn^{4+} & e_0 = 1.84\ V & (2) \\
Mn^{2+} + 2H_2O - 2e & \rightarrow MnO_2 + 4H^+ & e_0 = 1.24\ V & (3) \\
Mn^{2+} + 4H_2O - 5e & \rightarrow MnO_4^- + 8H^+ & e_0 = 1.51\ V & (4) \\
2H_2O - 4e & \rightarrow 4H^+ + O_2 & e_0 = 1.23\ V & (5)
\end{array}$$

The equations show that some of these reactions increase the acidity of the solution, i. e. the hydrogen ion concentration. In the oxidation of 1 gram-ion of manganese to manganese dioxide two faradays are consumed but 4 gram-ions of hydrogen are generated. In the oxidation of 1 gram-ion of manganese to permanganate 5 faradays are consumed but 8 gram-ions of hydrogen are produced. These data show that the number of gram-ions of hydrogen generated is not equal to the number of faradays consumed. Therefore the amount of electricity required for the reduction of hydrogen ions in order to restore the original pH of the solution is not equal to the amount consumed in the oxidation of manganous ions. It is therefore possible to follow two or more reactions taking place simultaneously and to determine the extent to which they occur.

Communicated at IXth Meeting of the Serbian Chemical Society, 1961.

In a previous paper(1), we found by potential measurements that from slightly acid solutions manganese dioxide and oxygen are formed at the anode. These findings were taken as the basis for the coulometric determination of manganous ion by measuring the increase of the electrolyte acidity. The increase of hydrogen ion concentration in the course of the separation of manganese dioxide is given by equation (3): 4 gram-ions of hydrogen are equivalent to 1 gram-ion of manganese.

However, since the separation of manganese dioxide takes place with simultaneous evolution of oxygen, whereby the acidity of the electrolyte is increased, the coulometric determination of manganese involves the following operations:

1. Quantitative separation of manganese dioxide;
2. Coulometric determination of H-ions after the separation of manganese dioxide;
3. Calculation of the amount of hydrogen ion produced in the course of manganese dioxide separation.

The procedure of the coulometric determination of manganous ion is as follows:

In a neutral solution of sodium sulphate which serves as the anolyte and which is separated from the catholyte by means of a conveniently arranged bridge with sodium suphate solution, manganous ions separate on the platinum anode in the form of manganese dioxide with simultaneous evolution of oxygen: the cessation of the separation of brown manganese dioxide indicates that all the manganese from the anolyte has precipitated. After the precipitation of manganese dioxide, the anode is taken out of the solution and washed with a small amount of water above the anolyte. Then another platinum electrode which is connected as the cathode, is put into the solution. The acid produced in the course of manganese dioxide precipitation is coulometrically determined in the usual way in the presence of methyl red. The amount of manganese is calculated from the equation

$$\frac{(c-a)A}{2F}=x$$

where A = the atomic weight of manganese

b = the amount of electricity consumed in the oxidation of manganous ion

c = the amount of electricity consumed in the reduction of H ion,

x = the amount of manganese in g

Table 1 shows the results obtained by coulometric determination of manganese in amounts ranging from 1.730 to 2.595 mg. The error ranged from −1.11% to 0.63%.

TABLE 1

Current m A	Time sec.	Manganese Taken	 Found	Error %
8.35	719.1	1.730	1.712	−1.11
8.35	731.8	1.730	1.741	0.63
8.35	730.0	1.730	1.737	0.39
8.35	727.7	1.730	1.731	0.10
8.35	728.0	1.730	1.732	0.11
8.35	729.0	1.730	1.734	0.25
8.35	721.9	1.730	1.717	−0.63
8.35	1080.6	2.595	2.571	−0.85
8.35	1092.2	2.595	2.598	0.21
8.35	1091.8	2.595	2.597	0.17

This determination indicates that the consumption of one faraday may not always produce one equivalent of a given ion (hydrogen ion in this case) in the electrolyte. This is of practical and theoretical importance for new determinations of stoimetric relations.

Institute of Physical Chemistry
and Electrochemistry
School of Technology,
Beograd

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GLASNIK HEMIJSKOG DRUŠTVA, Vol. 29, No. 5—6, 1964, pp. 203—206

POLAROGRAPHIC DETERMINATION OF COPPER IN THE PRESENCE OF LEAD*

by

SRETEN N. MLADENOVIĆ

Up to the present there has been no suspicion as to the accuracy of polarographic determination of copper in an ammoniacal medium in the presence of lead or in lead. This can be ascribed mainly to the low solubility of lead hydroxide in ammonium hydroxide, cited in all analytical chemistry textbooks, and to the conviction that the solubility is low since there are a lot of data in the literature on the insolubility of lead hydroxide. The good results obtained so far by polarographic determination of copper in ammonium chloride and ammonium hydroxide (1,2,3) show that suspicion as to the reliability and accuracy of the method would certainly be groundless.

We have, found, however, that the quantities of copper in solutions of different ores which also contain lead determined electrogravimetrically and polarographically were not in good agreement: the quantity of copper found polarographically in ammoniac medium was always slightly larger than that obtained electrogravimetrically.

We also found that the quantity of copper in zinc found polarographically in ammoniac medium was always larger than that obtained polarographically or electrogravimetrically in acid medium. Since this zinc contained lead and lead was the biggest impurity, we considered this the reason for the disagreement of the results, as has been confirmed by a number of experiments on a polarograph. This is shown in Table 1.

The table shows that with increasing quantity of lead in the supporting electrolyte $4MNH_4OH+2MNH_4Cl$, the wave heights increase linearly with lead concentration, although the copper content is constant. Besides copper, lead, ammonium hydroxide and ammonium chloride there were also sodium sulphite and gelatine in the

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* Reported at the 1st Yugoslav Congress on pure and applied chemistry, 1960.

TABLE 1

Supporting electrolyte: 4M. $NH_4OH + 2M. NH_4Cl + 1$ ml satur. $Na_2SO_3/50$ ml + 1 ml 0.1% gelatine /50 ml

Wave height mm	Copper 10^{-6} g/50 ml	Lead 10^{-6} g/50 ml
13.5	40	0
19.0	40	50
25.0	40	100
32.0	40	150
38.0	40	200
74.0	40	500
27.0	80	0
33.0	80	50
38.5	80	100
44.0	80	150
49.5	80	200

supporting electrolyte. This unexpected increase of the wave height may be ascribed to the composition of the electrolyte, first of all to the presence of ammonium chloride in the supporting electrolyte. The solubility product of lead hydroxide $L_{Pb(OH)_2}$ at 18° is 6.8×10^{-13}, the dissociation constant of ammonium hydroxide K at 25° is 1.79×10^{-5}. For the ammonium hydroxide and ammonium chloride concentration in the supporting electrolyte and the K of ammonium hydroxide we obtain the approximate concentration of hydroxyl ions $a_{OH^-} = 3.58 \times 10^{-5}$. From $L_{Pb(OH)_2}$ and a_{OH} the concentration of lead ions is 0.53×10^{-3} g ions/*l*, or 0.11 g lead/*l*. From this calculation it follows that 5.5 mg of lead may be found in 50 ml of the supporting electrolyte of the given composition.

From the data in Table 1 the quantity of lead in the supporting electrolyte in the presence of copper is much less than in the solution. Therefore all the lead in our experiments was in the form of ions, which could be reduced on a dripping mercury electrolyte.

Our results also show that the potential of the half-wave of lead is the same as the potential of the half-wave of copper in ammoniacal medium, and that it differs slightly from that of lead in saline acid medium (Fig. 1).

From the wave heights of solutions with the same quantity of copper and different quantities of lead it can be concluded that under the given conditions the wave height increases by about 6 mm per 50 g of lead. Accordingly the polarographic determination of lead in ammoniac medium may be assumed to be possible.

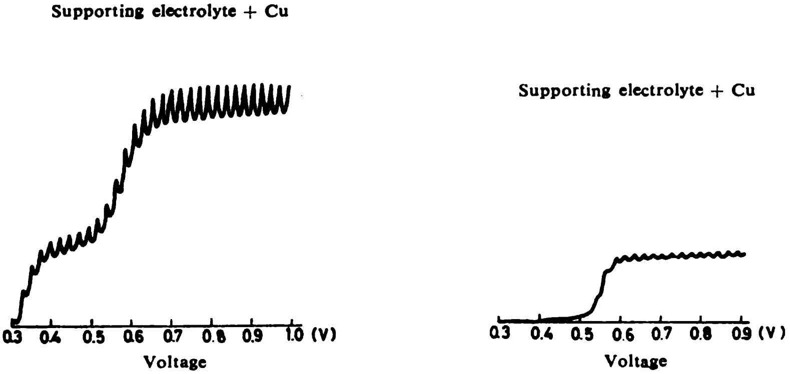

Fig. 1.

Hence we arrive at the important conclusion that in ammoniac medium of the given composition, copper cannot be determined polarographically in the presence of lead, unless the quantity of lead is much less than that of copper so that lead practically does not increase the wave height of copper.

We checked this conclusion by polarographic determination of copper in cathodic zinc with 0.013% of lead and cathodic zinc melted with 0.002% of lead. By polarographic determination of copper in acid medium we got that there was 0.0006% of copper in the cathodic zinc and 0.0004% in the melted cathodic zinc. By polarographic determination of copper in ammoniac medium (4M. $NH_4OH + 2MNH_4Cl$), we got the percentage of copper in the cathodic zinc 0.0075% and in the melted cathodic zinc 0.0022%. Therefore, polarographic determination of copper in the precence of lead gives higher (less accurate) results the greater the lead content. Therefore copper in zinc must be determined in acidic medium or by some other method in the absence of materials which disturb the determination of copper. This principle may be extended to all cases of determining copper in the absence of iron if the content of copper is not much larger than that of lead.

A further general conclusion is that by polarographic determination of substances in any medium in the presence of hardly soluble compounds, it is necessary to check whether the hardly soluble compound present does not reduce or oxidize at the same potential as the substance investigated. If so, it is necessary to determine whether its presence influences the quantitative determination and in what way.

Our results show that in polarographic determination of copper too high results are obtained in the presence of lead. Attention is drawn to this error now because of the belief that lead hydroxide is so hardly soluble in ammoniacal medium that the lead remaining in the solution can be practically neglected.

This belief was backed up by the analytical reaction of lead which shows that with ammonium hydroxide lead produces a precipitate which is insoluble in the excess of the precipitating agent, but this in fact says nothing about the quantity of lead remaining in the solution.

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GLASNIK HEMIJSKOG DRUŠTVA, Vol. 29, No. 5—6, 1964, pp. 207—211

POLAROGRAPHIC DETERMINATION OF TIN IN ZINC*

by

SRETEN N. MLADENOVIĆ

Coulometric methods of determining tin with dithiol(1, 2, 3) and phenyl fluorine(4) cannot be successful in the presence of even negligible quantities of certain impurities since many types of ions can react with the developer reagents.

The separation of tin from these ions is often uncertain and time-consuming and therefore the tin content found after the separation is unreliable.

Iodomectric determination of small quantities of tin from large sample portions (*e. g.* zinc and copper) with preliminary reduction of stannic ions and a blank test has also proved unreliable.

Polarographic determination of small quantities of tin (50 γ Sn) is possible after concentrating the tin from large sample portions.

Concentration of tin from various solutions is possible by recipitating it with ammonium hydroxide in the presence of ferric chloride, which with the ammonium hydroxide forms feric hydroxide. In this case feric hydroxide does not act as a tin collector, but in some cases (Sn in Zn or Cu) as an agent for extracting tin from a large quantity of the main, primary compound of the sample. On the other hand, in case tin does not separate, the elementary component of the sample with the supporting electrolyte forms a pulp which makes polarographic determination of tin impossible.

The determination of tin without preliminary concentration in a large sample portion or a large quantity of electrolyte is limited by the low tin concentration and the low sensitivity of the polarograph.

Extraction of tin by distillation and subsequent concentration is a long and tedious process, although in principle good.

Determination of tin in samples whose basic components form complex soluble compounds with ammonium hydroxide can be done without preliminary distillation. However, if lead is present

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Reported at the First Yugoslav Congress on Pure and Applied Chemistry, 1960.

in such samples as an impurity polarographic determination of tin is the more unreliable the greater the quantity of lead. Reducing lead ions on a dropping mercury electrode at almost the same potential as that at which tin ions are reduced, in a saline acidic medium, causes superposing of tin and lead waves. To determine tin in the presence of lead, Lindane(5) has developed an indirect method whose error increases the more the tin-lead concentration ratio differs from one.

In view of the fact that strontium sulfate is a collector of lead sulfate, we considered the possibility of separating tin from lead by precipitating lead sulfate and strontium sulfate, and then determining tin polarographically.

In polarographic determination of lead in the supporting electrolyte:

HCl, conc., p. a.	5 ml
1M Na_2SO_4	10 ml
$Sr(NO_3)_2$, p. a.	0.5 g
Gelatine, 1% solution	1 ml
Water	to 50 ml
Fe powder, p. a.	0.5 g

a lead wave does not appear even with considerable quantities of lead (400γ and 500γ) and high polarograph sensitivity $\left(\text{Radiometer PO 3, } \frac{1}{10}\right)^+$.

In determining tin (100γ, 200γ and 300γ) in the same supporting electrolyte in whih lead is determined, the polarograms show a linear dependence between wave height and tin concentration. This is shown in Table 1.

In polarographic determination of tin (100γ, 200γ, 300γ) from a solution constanting 400γ of lead we obtained the same wave heights as without lead (Table 1).

From these tests it can be concluded that lead does not interfere with the polarographic determination of tin from this supporting electrolyte mentioned.

The tin polarographic wave heights in this supporting electrolyte, after dissolving tin hydroxide precipitated with ammonium hydroxide from samples containing lead, in the presence of ferric chloride, are equal to those obtained by direct polarographic determination of the same quantities of tin without preliminary precipitation (Table 1).

TABLE 1

Wave height mm	Lead 10^{-6}g	Tin 10^{-6}g	Remarks
19	0	100	
38	0	200	
56	0	300	
19	400	100	
38	400	200	
56	400	300	
0	400	0	
0	600	0	
0	400	0	Determination of tin after precipitating Fe $(OH)_3$ with ammonium hydroxide
19	400	100	
38	400	200	
55	400	300	
19	400	100	Sample with 40 g Zn and 400 γ Pb

In these tests we determined the collector capacities of both ferric hydroxide, in the presence of which tin quantitatively precipitates, and strontium sulfate, the lead collector.

This procedure for the separation of tin from lead was found suitable for polarographic determination of tin in electrolytic zinc containing of the order of 10^{-4}% tin or less and 10^{-3}% or more lead.

The procedure was checked by adding 100 γ of tin to solutions with 40 g zinc and 400 γ lead. The tin wave height from such solutions was always equal that obtained with this quantity of tin in samples without zinc (Table 1).

From all these results it follows that tin in zinc in the presence of lead can be determined after separation from zinc and lead by the following procedure:

100 g of zinc is dissolved in concentrated hydrochloric acid. Near the end of dissolution several milliliters of concentrated nitric acid is added. The solution is transferred to a 500 ml measuring flask which is filled with water up to the mark and then shaken. Two portions of this solution, 200 ml each, are pipetted into two 600 ml beakers. To each beaker 25 ml 0.5% of ferric chloride solution is added and then 1 ml of a standard tin solution (1 ml – 0.0001 g Sn)

is added to one of them. Portions of 0.5 ml 0.1 n sodium permanganate are added to each beaker, and the mixture shaken, heated and precipitated with ammonium hydroxide. After filtering through ordinary filter paper (black band) the precipitate is dissolved with 10 ml of hot hydrochloric acid and the filter paper washed with hot water. The total volume of the solution (with water) should amount to 80—100 ml. This solution is heated and precipitated again with ammonium hydroxide. The solution is filtered, the precipitate dissolved with 5 ml of hot hydrochloric acid and the filter paper washed with hot water. To this solution 10 ml 1M sodium sulfate solution is added and diluted with water up to 40 ml. Then 0.5 g of strontium nitrate is added, stirred well and left to stand for at least half an hour with occasional stirring. The solution is then filtered through a filter paper (black band) and the filtrate caught in a 50 ml measuring flask. The filter paper is washed with warm water, 1 ml of 1% gelatine added and the measuring flask filled up to the mark with water. 0.5 g of iron powder is then added to the measuring flask. In half an hour, with occasional stirring, stannic and ferric ions are reduced. The solution is then filtered of iron powder and polarographed.

Tin does not interfere with the polarographic determination of lead in electrolytic zinc with 0.0001% tin and 0.003 to 0.005% lead in the supporting electrolyte, hydrochloric acid. If there is more tin, it shoud be removed by distillation.

The procedure for determining tin in zinc can be successfully used for determining it in copper containing lead.

This method is quicker and more reliable than other methods, so it can be recommended for determining tin in zinc and copper.

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GLASNIK HEMIJSKOG DRUŠTVA, Vol. 29, No. 5—6, 1964, pp. 213—217

A CONTRIBUTION TO THE COMPLEXOMETRIC DETERMINATION OF METALS.

VI — DETERMINATION OF MANGANESE, LEAD, COBALT, CADMIUM, AND IRON*

by

TIBOR A. KISS**

Extending an earlier work(1) to the direct determination of manganese, lead, cobalt, cadmium, and iron, we have checked different methods of complexometric titration of metals with ethylene diamine tetraacetic acid (EDTA) and found good agreement between the volumetric factors of the metal solutions.

For the titration of larger concentrations of metals we modified the well-known methods: first we titrated weakly acid metal solutions to near the equivalence point, then, by adding a buffer, we retained the remaining small amount of metal in the solution and titrated it to the end point. The volumetric factors obtained by the modified methods agree well with those obtained by the unmodified methods.

We also worked out the methods of reverse titration, *i. e.* titration of a standard EDTA solution with a tested metal solution. Although the volumetric factors of metal solutions obtained by such titrations are mutually consistent they are lower than those obtained by titrating metals with EDTA: by 0.1% in the case of manganese, lead and cadmium, and 2% in the case of cobalt and iron. This difference is probably due to the fact that the solutions cannot be titrated until color change but instead must be titrated until the disappearance of the tint of the initial color. Whether or not this error of the indicator is the sole factor causing the difference, or whether it may be ascribed to other factors, will probably be shown by potentiometric determinations now under way.

For comparison purposes the metals were determined by some of the usual gravimetric methods. The results are in good agreement with those obtained by titration of EDTA with metals.

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* Part V: Glasnik hemijskog društva (Beograd) (in press).

** School of Technology, Novi Sad

EXPERIMENTAL PROCEDURE

Preparation of standard solutions

0.1 M EDTA solution. Purified EDTA, p. a. Merck (Titriplex III), was dried at 80° C and used as the primary standard(2, 3). 37.225 g of the salt was dissolved in water and diluted to 1000 ml. The factor of the EDTA solution did not change in several months(4, 5).

Approximately 0.1 *M* manganese, cobalt, cadmium and ferric sulphate and lead nitrate solutions were prepared by dissolving 0.1 M of the salts in water and diluting to one liter.

0.01 M metal solutions and 0.1 M EDTA solution were prepared by diluting 0.1 M solutions. The preparation of the solutions was checked by preparing several solutions by the same procedure and titrating each solution by the same method. The factors of such solutions remained unchanged in several months.

All the solutions were prepared with water purified with ion exchangers(6) and kept in polyethylene bottles(2, 5, 7).

The volumetric flasks were calibrated in the usual way. Temperature corrections of volumes of metal and EDTA solutions were also made.

Determination of manganese

In the presence of eriochrome black T. Of the various methods of complexometric titration of manganese available(8a, 9a, 10a, 11a, 12) we chose the following to determine small concentrations: without the addition of tartrate at room temperature(12a) and at 80° C(12a), in the presence of potassium sodium tartrate at room temperature and at 80° C(12b, c), and with the addition of triethanolamine(9a). Titrations performed at room temperature without the addition of tartrate, did not give a sharp color change of the indicator and the blue color was not marked. More noticeable color changes were obtained at 80° C both without and with the addition of tartrate. With the addition of triethanolamine a sharp color change was obtained even at room temperature.

We modified the above methods to determine larger concentrations of metals and to titrate EDTA with manganese.

In the presence of pyrocatechol violet. Smaller concentrations were titrated by the methods of Malát and Suk(13a, b). These were adapted for the determination of larger concentrations and for the titration of EDTA with manganese.

Manganese was determined by the usual gravimetric methods in the form of manganese sulphate(14) and manganese pyrophosphate(15a).

TABLE 1

	Manganese		Lead		Cobalt		Cadmium		Iron	
Molarity	0.1	0.01	0.1	0.01	0.1	0.01	0.1	0.01	1.0	0.01
Metal titration with EDTA in presence of:										
Pyrocatechol Violet	1.0918	1.0912	0.9995	0.9992	1.2010	1.2014	1.0131	1.0134	1.0984	1.0980
Eriochrome Black T	1.0916	1.0911	0.9994	0.9993			1.0133	1.0130		
Various indicators					1.2012	1.2015(1)			1.0985	1.0980(2)
									1.0987	1.0982(3)
									1.0983	1.0987(4)
									1.0981	1.0986(5)
EDTA titration with metal in presence of:										
Pyrocatechol Violet	1.0924	1.0922	0.9983	0.9981	1.1993	1.1991	1.0118	1.0116	1.0960	1.0965
Eriochrome Black T	1.0920	1.0921	0.9983	0.9984			1.0120	1.0119		
Various indicators					1.1990	1.1994(1)			1.0965	1.0961(2)
									1.0961	1.0965(3)
									1.0966	1.0960(4)
									1.0964	1.0961(5)
Gravimetrically	1.0717(6) 1.0710(7)		0.9981(8)		1.1995(9)		1.0110(6) 1.0117(9)		1.0560(10)	

Volumetric factors of metal solutions got by different methods. Results are means of 6—9 estimations of different amounts of metals. Measurements were made up to 50 ml 0.1 M and 0.01 M of metal solution or EDTA.

1.) In presence of Muroxide
2.) In presence of salicylic acid
3.) In presence of sulfosalicylic acid
4.) In presence of variamine blue B
5.) In presence of Chrome Azurol S
6.) As sulphate
7.) As pyrophosphate
8.) As chromate
9.) Electrogravimetrically
10.) As oxide

Determination of lead

In the presence of eriochrome black T(8b, 9b, 10b, 11b, 16). Up to 30 mg of lead was determined by the methods given in(16a, b,c) at 40° C in the presence of potassium sodium tartrate. Larger concentrations of lead were determined and reverse titrations performed by modified methods.

For comparison, lead was determined gravimetrically in the form of lead chromate(17) by the method in (15b).

Determination of cobalt

Smaller concentrations of cobalt were determined in the presence of murexide(8c, 9c, 10c, 11c, 18), in the presence(6) and absence(8c) of sodium acetate and in the presence of pyrocatechol violet(13a, b).

From 0.1 M cobalt sulphate solution, cobalt was determined electrogravimetrically by the method in (19a). Larger concentrations of cobalt, and EDTA with cobalt sulphate, were titrated by modified methods.

Determination of cadmium

Small concentrations of cadmium were titrated in the presence of eriochrome black T(6, 16b, 20) at room temperature without the addition of ammonium chloride(20a) and at 40° C in the presence of amonium chloride(20b), and in the presence of pyrocatechol violet(13a, b).

For comparison cadmium was determined gravimetrically in the form cadmium sulphate(21a) and electrogravimetrically(21b).

Determination of iron

Iron (III) was determined in the presence of salicylic acid(22), sulphosalicylic acid(23), variamine blue B: smaller concentrations by the method of (24a) and larger by that of (24b), in the presence of chrome azurol S(25) and in the presence of pyrocatechol violet by the method(26). By modifying each of the above methods we determined large concentrations of iron and titraed EDTA with iron.

We determined iron gravimetrically in the form of iron oxide(21c).

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GLASNIK HEMIJSKOG DRUŠTVA, Vol. 29, No. 5—6, 1964, pp. 219—228

DETERMINATION OF THE DIFFUSION COEFFICIENT AND ITS TEMPERATURE DEPENDENCE IN DEALKALIZATION OF SODIUM FROM Na—Ca—SILICATE GLASS

by

D. DELIĆ and M. A. JOVANOVIĆ

DETERMINATION OF DEALKALIZED SODIUM

One-liter milk bottles produced in Yugoslavia were used. We chose these bottles to get a large enough area of glass (580 cm^2) exposed to the action of water and a sufficient ratio of the volume of dealkalizing medium to the area of glass(1, 2) provided. This enabled us to obtain the desired accuracy.

The glass had the following characteristics:

— chemical composition: 71.08% SiO_2; 0.71% Al_2O_3; 0.18% Fe_2O_3; 9.20% CaO; 1.22% MgO; 17.21% Na_2O; 0.28% SO_3.
— transformation point: $T_g = 512° \pm 3$
— specific weight: $= 2.4954 \pm 0.0002$

The inner surfaces of the bottles were exposed to the action of fresh distilled water at temperatures of 40, 60, 80 and 98°.

The quantity of sodium removed was determined by flame photometry.

Three bottles were simultaneously investigated each time.

The results (mean values for three samples) are shown in Tables 1, 2, 3 and 4.

THE PROCESS OF SODIUM DISSOLUTION IN DEALKALIZATION WITH WATER

Processes which take place when a glass surface is treated with water must be considered from the point of view of the glass structure. According to present-day knowledge glass has an anion net in which alkalis deposit as ions. Therefore, the action of water may be such that molecules or ions of water interact with the alkalis in one of the ways described below.

Reaction between water and alkalis proceeds very rapidly compared with the rate of travel of ions, in our case sodium ions, into or out of the glass. The quantity of sodium which transfers into the water as a function of time is therefore determined either by the rate of diffusion of water ions through the boundary layer to sodium capable of reacting, or by the rate at which sodium ions can travel from their original place to the surface(3). The slower of these two processes determines the whole dealkalization process(4). It is here assumed that the anion net retains the form of a porous boundary layer for some time.

By losing sodium ions, the glass should become electronegative. An electrical double layer would form on the surface, holding up further removal of sodium ions. As this is not the case it is obvious that electrical neutrality is maintained by counter-diffusion of other ions, replacing the sodium(4). Since calculation of double diffusion is very difficult and since one diffusion constant is much smaller than the other, the process will be considered as simple diffusion. The constant used will not differ much from the constant of the slower diffusion, and in our case sodium diffusion.

TABLE 1

Quantities of sodium removed at 40°

	Dealkalization time h		Quantity of sodium removed mol. cm^{-2}	
	each	total	each × 10^8	total × 10^8
1	3	3	4.03	4.03
2	3	6	3.39	7.42
3	3	9	2.57	9.99
4	3	12	2.04	12.03
5	3	15	1.04	13.07
6	3	18	0.91	13.98

TABLE 2

Quantities of sodium removed at 60°

	Dealkalization time h		Quantity of sodium removed mol. cm^{-2}	
	each	total	each × 10^8	total × 10^8
1	3	3	5.32	5.32
2	3	6	4.03	9.35
3	3	9	3.16	12.51
4	3	12	2.64	15.15
5	3	15	2.10	17.25
6	3	18	1.61	18.86

TABLE 3

Quantities of sodium removed at 80°

	Dealkalization time h		Quantity of sodium removed mol. cm^{-2}	
	each	total	each × 10^8	total × 10^8
1	3	3	7.74	7.74
2	3	6	6.29	14.03
3	3	9	5.45	19.48
4	3	12	4.39	23.87
5	3	15	3.84	27.71
6	3	18	3.10	30.81

TABLE 4

Quantities of sodium removed at 98°

	Dealkalization time h		Quantity of sodium removed mol. cm^{-2}	
	each	total	each × 10^8	total × 10^8
1	3	3	19.52	19.52
2	3	6	15.07	34.59
3	3	9	12.97	47.56
4	3	12	10.32	57.88
5	3	15	8.71	66.59
6	3	18	8.32	74.91

DISSOLUTION OF SODIUM AS A DIFFUSION PROCESS

From Fick's second law we have

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \tag{1}$$

where

c — concentration of Na in the boundary surface of glass (mol/cm^3)

x — distance of the layer from the boundary surface (cm)

D — diffusion coefficient (cm^2/sec)

t — time (sec)

Taking the initial concentration as c_0, so that $c = c_0$ for all $x > 0$ for $t = 0$, and assuming a sodium concentration $c = 0$ for $t = 0$ and $x = 0$, we get the following solution of eg. (1):

$$c(x, t) = \frac{c_0}{2}\left[1 - \Phi\left(\frac{x}{2\sqrt{Dt}}\right)\right] \tag{2}$$

For investigating thin layers(5) the quantity removed m (in moles) from a layer of cross-section q, whose coordinates go from x_1, to x_2, is given by

$$m = q \int_{x_1}^{x_2} c(x, t)\,dx \tag{3}$$

Substituting for $c(x, t)$ from eq. (2) we obtain

$$m = q\frac{c_0}{2} \int_{x_1}^{x_2} \left[1 - \Phi\left(\frac{x}{2\sqrt{Dt}}\right) dx\right] \tag{4}$$

If we write $\eta = \frac{x}{2\sqrt{Dt}}$, so that $dx = 2\sqrt{Dt}\,d\eta$ we obtain

$$m = q \cdot c_0\sqrt{Dt} \int_{x_1}^{x_2} [1 - \Phi(\eta)]\,d\eta \tag{5}$$

For the limiting values $x_1 = 0$ and $x_2 = \infty$ we have

$$m = q \cdot c_0 \cdot \sqrt{Dt} \int_{0}^{\infty} [1 - \Phi(\eta)]\,d\eta \tag{6}$$

In this case

$$\int_{0}^{\infty} [1 - \Phi(\eta)]\,d\eta = \frac{1}{\sqrt{\pi}}$$

so that

$$m = q \cdot \frac{1}{\sqrt{\pi}} \cdot c_0\sqrt{Dt} \tag{7}$$

From $m/q = Q$ it follows that the total quantity of sodium removed per cm^2 in time t

$$Q = \frac{1}{\sqrt{\pi}} \cdot c_0 \cdot \sqrt{Dt}\,[\mathrm{mol} \cdot \mathrm{cm}^{-2}] \tag{8}$$

i.e. the diffusion coefficient is

$$D = \frac{Q^2 \cdot \pi}{c_0^2 \cdot t}\,[\mathrm{cm}^2 \cdot \mathrm{sec}^{-1}] \tag{9}$$

The above relation shows a linear dependence between the quantity dissolved and the square root of the time, with slope

$$\frac{1}{\sqrt{\pi}} \cdot c_0 \cdot \sqrt{D},$$

which depends on the diffusion coefficient.

Our experimental results show that the quantity of sodium dissolved depends linearly in time except in the initial phase of the reaction (Fig. 1). This confirms the findings of some authors that dealkalization behaves as a diffusion process.

Hence, from the experimental results in Tables 1, 2, 3 and 4 we can calculate the diffusion coefficient (eq. 9).

The concentration of sodium is calculated assuming that it is the same throughout the glass, from the percentage of sodium in the glass and its density.

Hence we obtain that the initial concentration of sodium is

$$c_0 = 0.012559 \text{ [mol. cm}^{-3}\text{]}$$

The experimental results for the diffusion coefficient are calculated statistically by the least squares method. From the data given in Tables 5, 6, 7 and 8 the arithmetic mean of the diffusion coefficient for each temperature is found to correspond to a "one sigma" law(6).

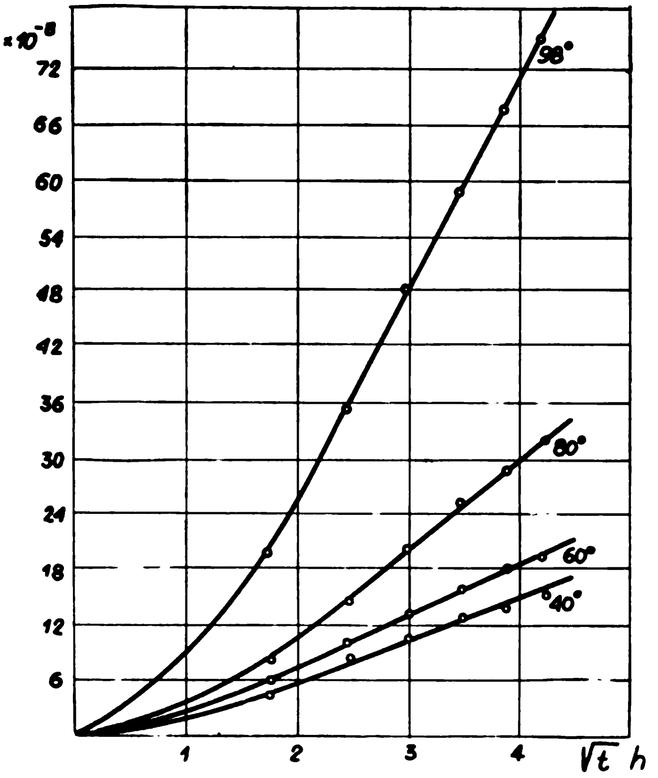

Fig. 1. Relation between dissolved quantity of sodium and the square root of the duration removed

TABLE 5

Diffusion coefficient at 40°

Measurement	D cm^2. sec^{-1} $x\ 10^{15}$	$\bar{D}-D$ $x\ 10^{15}$	$(\bar{D}-D)^2$ $x\ 10^{30}$
1	2.99	+2.47	6.10
2	5.06	+0.40	0.16
3	6.12	−0.66	0.44
4	6.66	−1.20	1.44
5	6.29	−0.83	0.69
6	5.64	−0.18	0.03

TABLE 6

Diffusion coefficient at 60°

Measurement	D cm. sec^{-1} $x\ 10^{15}$	$\bar{D}-D$ $x\ 10^{15}$	$(\bar{D}-D)^2$ $x\ 10^{30}$
1	5.21	+3.90	15.21
2	8.04	+1.07	1.15
3	9.60	−0.49	0.24
4	10.56	−1.45	2.10
5	10.95	−1.84	3.39
6	10.27	−1.16	1.35

TABLE 7

Diffusion coefficient at 80°

Measurement	D cm^2. sec^{-1} $x\ 10^{14}$	$\bar{D}-D$ $x\ 10^{14}$	$(\bar{D}-D)^2$ $x\ 10^{28}$
1	1.10	+1.14	1.30
2	1.81	+0.43	0.18
3	2.33	−0.09	0.01
4	2.62	−0.38	0.14
5	2.83	−0.59	0.35
6	2.74	−0.50	0.25

TABLE 8

Diffusion coefficient at 98°

Measurement	D cm^2. sec^{-1} $x\ 10^{14}$	$\bar{D}-D$ $x\ 10^{14}$	$(\bar{D}-D)^2$ $x\ 10^{28}$
1	7.01	+6.30	39.69
2	11.01	+2.30	5.29
3	13.88	−0.57	0.32
4	15.41	−2.10	4.41
5	16.31	−3.00	9.00
6	16.21	−2.90	8.41

TABLE 9

Mean values of the diffusion coefficient

Temperature	D_{mean} cm$^2\cdot$sec^{-1}
40°	$5.95\cdot10^{-15}\pm1.33\cdot10^{-15}$
60°	$9.88\cdot10^{-15}\pm2.47\cdot10^{-15}$
80°	$2.47\cdot10^{-14}\pm0.67\cdot10^{-14}$
98°	$14.56\cdot10^{-14}\pm3.66\cdot10^{-14}$

Table 9 shows the mean diffusion coefficients for each temperature. From the diffusion coefficients and the relation giving their temperature dependence

$$D=D_0\cdot e^{-E/RT} \tag{10}$$

we can calculate the activation energy of Na-ions.

Integrating eg. (10) we get

$$\ln D=\ln D_0-\left[\frac{1}{T}\right]\frac{E}{R} \tag{11}$$

The activation energy is calculated by the least squares method using the data in Table 10.

TABLE 10

Data for calculating the activation energy

D	T	$\ln D$	$\frac{1}{T}$ $x\,10^3$	$\frac{1^2}{T}$ $x\,10^6$	$\frac{1}{T}\ln D$ $x\,10^3$
$5.95 \cdot 10^{-15}$	313	−32.755	3.195	10.208	−104.652
$9.88 \cdot 10^{-15}$	333	−32.248	3.003	9.018	− 96.841
$2.47 \cdot 10^{-14}$	353	−31.332	2.883	8.026	− 88.764
$1.46 \cdot 10^{-13}$	371	−29.555	2.695	7.263	− 79.651
	Σ	−125.890	11.726	34.515	−269.908

Solving the equations

$$[\ln D] = 4 \ln D_0 - \left[\frac{1}{T}\right]\frac{E}{R} \tag{12}$$

$$\left[\frac{1}{T}\ln D\right] = \left[\frac{1}{T}\right] \ln D_0 - \left[\left(\frac{1}{T}\right)^2\right]\frac{E}{T} \tag{13}$$

for $\frac{E}{R}$ we obtain that

$$\frac{E}{R} = 6.23 \cdot 10^3$$

Substituting the value for $R = 1.987$ [cal. degree^{-1} mol^{-1}] we obtain the activation energy

$$E = 12.38 \cdot 10^3 \text{ [cal. mol}^{-1}\text{]}$$

DEPENDENCE OF SODIUM DISSOLUTION ON TEMPERATURE

The influence of temperature on the ion velocity and thus on the magnitude of the diffusion coefficient is given by

$$D = D_0 \cdot e^{-E/RT} \tag{10}$$

where

E — activation energy
R — gas constant
T — absolute temperature
D — diffusion coefficient
D_0 — diffusion constant

First we calculate the diffusion constant for the temperature range 40—98°C using the data from (Table 10) and the calculated value for E. We have

$$- 125.890 = 4 \ln D_0 - 11.726 \cdot 10^{-3} \cdot 6.23 \cdot 10^3$$

The diffusion constant is

$$D_0 = 1834 \cdot 10^{-6}$$

i. e. the dependence of the diffusion coefficient on temperature for the temperature range 40—98° is

$$D = 1834 \cdot 10^{-6} \exp\left(- \frac{12380}{RT} \right)$$

School of Technology
Beograd

Received September 10, 1964

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GLASNIK HEMIJSKOG DRUŠTVA, Vol. 29, No. 5—6, 1964, pp. 229—237

DEALKALIZATION FROM GLASS AS A KINETIC PROCESS

by

D. DELIĆ and M. A. JOVANOVIĆ

We used one-liter milk bottles of Yugoslav production, made of Na-Ca-silicate glass of the following composition: 71.08% SiO_2; 0.71% Al_2O_3; 0.18% Fe_2O_3; 9.20% CaO; 1.22% MgO; 17.21% Na_2O; 0.28% SO_3.

The inner surface of the bottles was exposed to the action of fresh distilled water at temperatures of 40, 60, 80 and 98°. Each time three bottles were investigated simultaneously.

The content of removed sodium was determined by flame photometry: total quantities were determined.

Taking the inner surface area of the bottles as 580 cm^2. Tables 1, 2, 3 and 4 show results for the quantity of sodium removed per 1 dm^2 (mgNaO/dm^2).

TABLE 1

Quantity of sodium removed at 40°

Time	Quantity removed			
	Sample I	Sample II	Sample III	Mean value
3	0.128	0.129	0.120	0.125
6	0.237	0.231	0.223	0.230
9	0.314	0.315	0.302	0.310
12	0.380	0.374	0.366	0.373
15	0.408	0.405	0.402	0.405
18	0.434	0.437	0.428	0.433

We tried to apply Jander's law of the rate of reaction in the solid state⁽¹⁾ to the process of dealkalization of glass. For this purpose it was necessary to determine the thickness of the dealkalized surface layer. This is practically impossible but an effective

TABLE 2

Quantity of sodium removed at 60°

Time	Quantity removed			
	Sample I	Sample II	Sample III	Mean value
3	0.161	0.170	0.164	0.165
6	0.283	0.298	0.290	0.290
9	0.386	0.399	0.380	0.388
12	0.472	0.478	0.461	0.470
15	0.542	0.545	0.519	0.535
18	0.582	0.596	0.579	0.585

TABLE 3

Quantity of sodium removed at 80°

Time	Quantity removed			
	Sample I	Sample II	Sample III	Mean value
3	0.229	0.233	0.238	0.240
6	0.433	0.453	0.419	0.435
9	0.592	0.623	0.597	0.604
12	0.728	0.752	0.738	0.740
15	0.854	0.862	0.859	0.859
18	0.947	0.969	0.947	0.955

TABLE 4

Quantity of sodium removed at 98°

Time	Quantity removed			
	Sample I	Sample II	Sample III	Mean value
3	0.580	0.625	0.610	0.605
6	1.059	1.076	1.082	1.072
9	1.458	1.459	1.503	1.474
12	1.795	1.801	1.784	1.794
15	2.034	2.094	2.064	2.064
18	2.305	2.329	2.332	2.322

or theoretical thickness can be calculated assuming that all the sodium is removed from this layer. Then, knowing the total quantity of sodium removed experimentally, we can calculate the theoretical thickness of the dealkalized layer.

The content of Na_2O is given by

$$G = a \cdot y \cdot m \cdot \gamma$$

where

G = quantity of Na_2O removed (mg/cm^2)

a = dealkalized area of glass surface (cm^2)

y = thickness of dealkalized layer (cm)

m = quantity of Na_2O in glass (weight %)

γ = specific weight of glass (g/cm^2)

We have therefore

$$G_x = 10 \cdot 10 \cdot y_x \cdot 17.21 \cdot \frac{1}{100} \cdot 2.4954$$

or

$$y_x = \frac{G_x}{43.025} \qquad \text{[cm]}$$

where

G_x = quantity of Na_2O removed (mg/dm^2) at the given temperature and time

y_x = theoretical thickness of the layer dealkalized (cm) at the given temperature and time

The theoretical layer thicknesses are given in Table 5.

According to Jander's theory the reaction rate in the solid state is given by

$$y^2 = k \cdot t$$

where

y — thickness of the reaction layer

t — time

k — constant

The reaction rate constants are given in Table 6.

The reaction rate constants were calculated by the least squares method. From the data given in tables 7, 8, 9 and 10 it was found that the arithmetical mean of the rate constants for each temperature corresponds to "one sigma" conditions(2).

TABLE 5

Theoretical thickness of the dealkalized layer

Temperature of removal, °C	Duration of removal, h	Thickness of the dealkalized layer, $y \cdot 10^4$ cm
40	3	0.029
40	6	0.053
40	9	0.072
40	12	0.087
40	15	0.094
40	18	0.100
60	3	0.038
60	6	0.067
60	9	0.090
60	12	0.109
60	15	0.124
60	18	0.136
80	3	0.056
80	6	0.101
80	9	0.140
80	12	0.172
80	15	0.200
80	18	0.222
98	3	0.141
98	6	0.249
98	9	0.342
98	12	0.415
98	15	0.485
98	18	0.540

TABLE 6

Reaction rate constants

k ($cm^2 \cdot cec^{-1}$)	Temperature			
	40° $x\,10^{16}$	60° $x\,10^{16}$	80° $x\,10^{15}$	98° $x\,10^{14}$
k_1	7.41	12.96	2.87	1.84
k_2	12.96	20.83	4.72	2.87
k_3	16.05	25.00	6.05	3.61
k_4	17.59	27.55	6.85	3.99
k_5	16.30	38.52	7.41	4.36
k_6	14.83	26.89	7.17	4.24

TABLE 7

Reaction rate constant at 40°

Measurement	k $cm^2 \cdot sec^{-1}$ ($x\ 10^{16}$)	$\bar{k}-k$ ($x\ 10^{16}$)	$(\bar{k} = k)^2$ ($x\ 10^{32}$)
1	7.41	+6.78	45.97
2	12.96	+1.23	1.51
3	16.05	−1.86	3.46
4	17.59	−3.40	11.56
5	16.30	−2.11	4.45
6	14.83	−0.64	0.41

TABLE 8

Reaction rate constant at 60°

Measurement	k $cm^2 \cdot sec^{-1}$ ($x\ 10^{16}$)	$\bar{k}-k$ ($x\ 10^{16}$)	$(\bar{k}-k)^2$ ($x\ 10^{32}$)
1	12.96	+10.66	113.63
2	20.83	+ 2.79	7.78
3	25.00	− 1.48	1.90
4	27.55	− 3.93	15.44
5	28.52	− 4.90	24.01
6	26.89	− 3.27	10.69

TABLE 9

Reaction rate constant at 80°

Measurement	k $cm^2 \cdot sec^{-1}$ ($x\ 10^{15}$)	$\bar{k}-k$ ($x\ 10^{15}$)	$(\bar{k}-k)^2$ ($x\ 10^{30}$)
1	2.87	+2.97	8.82
2	4.72	+1.12	1.25
3	6.05	−0.21	0.04
4	6.85	−1.01	1.02
5	7.41	−1.57	2.46
6	7.17	−1.33	1.77

TABLE 10

Reaction rate constant at 98°

Measurement	k $cm^2 \cdot sec^{-1}$ $(x\ 10^{14})$	$\bar{k}-k$ $(x\ 10^{14})$	$(\bar{k}-k)^2$ $(x\ 10^{28})$
1	1.84	+1.64	2.69
2	2.87	+0.61	0.37
3	3.61	−0.13	0.02
4	3.99	−0.51	0.26
5	4.36	−0.88	0.77
6	4.24	−0.76	0.58

Table 11 shows the mean *k*-values at each temperature.

TABLE 11

Mean values for reaction rate constants

Temperature °C	k_{mean} $cm^2 \cdot sec^{-1}$
40	$15.54 \cdot 10^{-16} \pm 3.67 \cdot 10^{-16}$
60	$25.76 \cdot 10^{-16} \pm 5.89 \cdot 10^{-16}$
80	$6.44 \cdot 10^{-15} \pm 3.07 \cdot 10^{-15}$
98	$3.81 \cdot 10^{-14} \pm 0.94 \cdot 10^{-14}$

In an earlier paper(3) we treated this process as a diffusion process and determined the diffusion coefficient.

The dependence of the reaction rate constant on the diffusion coefficient can be expressed as follows:

$$k = k' \cdot D$$

Table 12 shows the results for k and D and the calculated values for k'.

TABLE 12

Dependence of the reaction rate constant on the diffusion coefficient

Temperature °C	k $cm^2 \cdot sec^{-1}$	D $cm^2 \cdot sec^{-1}$	k'
40	$15.54 \cdot 10^{-16}$	$5.95 \cdot 10^{-15}$	0.26117
60	$15.76 \cdot 10^{-16}$	$9.88 \cdot 10^{-15}$	0.26072
80	$6.44 \cdot 10^{-15}$	$2.47 \cdot 10^{-14}$	0.26071
90	$3.81 \cdot 10^{-14}$	$14.57 \cdot 10^{-14}$	0.26095

$$k'_{\text{mean}} = 0.261$$

Hence

$$k = 0.261 \cdot D$$

In the same work⁽³⁾ we determined the dependence of the diffusion coefficient on temperature:

$$D = 1834 \cdot 10^{-6} \exp\left(-\frac{12380}{RT}\right)$$

Therefore the process can be expressed as follows:

$$k = 0.48 \cdot 10^{-6} \exp\left(-\frac{12380}{RT}\right)$$

where

k — rate constant
R — gas constant
T — absolute temperature

Hence the process of the removal of sodium from glass can be interpreted by Jander's theory.

School of Technology
Beograd

Received September 10, 1964

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GLASNIK HEMIJSKOG DRUŠTVA, Vol. 29, No. 5—6, 1964, pp. 239—246

EXTRACTION OF MANGANESE FROM POOR MANGANOUS ORES BY REDUCTIVE ROASTING AND LEACHING IN AMMONIACAL SOLUTION

by

DUŠAN VUČUROVIĆ, RAJKO Ž. VRAČAR and ILIJA B. ILIĆ

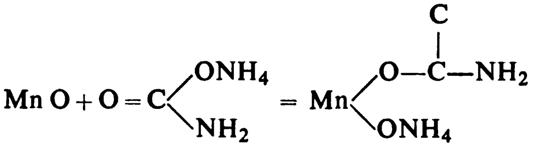
Manganese is mainly produced by pyrometallurgical methods. The chemical affinity of manganese for oxygen, especially in case of its lowest oxide MnO, is considerably stronger than that of a number of other metals, such as lead, nickel, iron, zinc, etc. For this reason to break the chemical bond between Mn and oxygen in MnO requires a high temperature and a strong reductive atmosphere, which is hard to get with conventional reducing apparatuses. In the production of ferromanganese in blast or arc furnaces in the presence of carbon, reduction is followed not only by high temperatures but also by carbonization of the ferromanganese. Carbon-free metallic manganese is produced by silicothermal and alumothermal reduction. However, the production of ferromanganese or manganese by these procedures can only be economical if the ore is rich, with a manganese content of not less than 35%.

Since many countries, including Yugoslavia, have deposits of poor manganese ores, efforts have been made to find out possibilities of extracting manganese by hydrometallurgical procedures. The literature data show that the following procedures have been studied most: leaching manganese ore with sulphuric, sulphurous and nitric acid solutions; leaching with water and introducing SO_2; roasting with ammoniac salts, or with SO_2, with subsequent water leaching of the soluble manganese compounds formed(1,2,3,4,5).

Recent attempts to extract manganese with solutions of ammoniac salts have attracted particular attention. It has been noticed that MnO has the property of oxides of copper and some other metals of dissolving in solutions of ammoniac salts, in which case Mn goes into solution in the form of a complex ammoniac ion.

This procedure was first used by Bradley and Fitch(1). They first roasted ore in a reducing atmosphere to convert MnO_2 to soluble MnO and then leached it with ammonium sulphate solutions. Concentrations up to 10% $(NH_4)_2SO_4$ were used and the maximum manganese extraction was 70%.

As distinct from earlier authors, Dean used an ammoniac solution of ammonium carbonate for leaching the reduced roasted ore⁽⁶⁾. By treating MnO, manganese is converted to a soluble complex according to the following reaction:



$$\mathrm{Mn\,O + O{=}C}\left\langle {\mathrm{ONH_4} \atop \mathrm{NH_2}} \right. = \mathrm{Mn}\left\langle {\mathrm{O{-}\overset{\overset{\mathrm{C}}{|}}{\mathrm{C}}{-}NH_2} \atop \mathrm{ONH_4}} \right.$$

By diluting the filtrate after leaching, or by introducing CO_2, the complex can be precipitated to manganese carbonate. Dean's process is promising because it gets good dissolution of MnO, up to 80—100 g Mn/l solution. The ammonium carbonate solution can be simply prepared by introducing CO_2 into ammoniac solution, and its regeneration after use is easy. This especially cuts costs.

Systematic research has been done at the Nonferrous Metallurgy Department of the School of Technology in Beograd on possibilities of processing the poor manganese ore from Kopaonik (Yugoslavia). The method of ammoniacal leaching one of the methods investigated and optimum conditions were sought.

EXPERIMENTAL

Ore composition and methods oj investigation. — Laboratory tests were made with "Novo Brdo" — Kopaonik manganese ore whose chemical composition is given in Table 1. The sample was ground 100%—60 mesh.

TABLE 1.

Chemical composition of the ore in %

Mn	Fe	Pb	Zn	Cu	As	Sb	Mg O	Al_2O_3	
21.10	30.71	3.32	1.35	0.10	0.35	1.20	6.10	20.48	11.53

Mineralogical analysis showed that ore contained: psilomelane, pyrolusite, mangansiderite, chalcopyrite, cerussite, limonite, sphalerite, galenite, smithsonite, pyrite, calcite, quartz, etc.

From these analyses it is obvious that the ore is poor. Manganese is mainly present in the quadrivalent form, mainly in psilomelane. The fact that manganese is present in the form of a mineral is significant for its reduction and extraction with ammoniac solution.

Ore was reduced with hydrogen in a cylindrical electric oven with automatic temperature regulation, to convert high manganese oxides to MnO. The hydrogen flow-rate was regulated by a capillary meter. After reduction the ore was cooled to room temperature in a hydrogen atmosphere and then transferred to the solution for leaching.

Leaching was carried out with an ammoniacal solution of ammonium carbonate in a neutral atmosphere, agitated with an electric mixer. The protective atmosphere was to prevent oxidation of manganese to Mn^{4+} which by hydrolysis converts to a leaching residue thus decreasing the extraction.

The solution was prepared by dissolving ammonium carbonate in an aqueous solution of ammonia. After leaching, the pulp was filtered and both the solution and the leaching residue were analysed for calculation of the balance of elementary manganese. The investigations were aimed at finding out optimal conditions of roasting and leaching. To this end we investigated:

a) Effect of roasting temperature and time;

b) Effect of the quantity of the reducing agent;

c) Effect of the leaching conditions (time; liquid: solid ratio, concentration of the solution).

EFFECT OF ROASTING CONDITIONS ON EXTRACTION WITH AMMONIACAL SOLUTION

a) *Effect of roasting temperature and time.* — The reduction was performed at temperatures from 400 to 900°C for 15 to 120 minutes. The hydrogen flow-rate was 250 ml/min. The leaching conditions were the same in all experiments (leaching time: 30 min; l:s = 4:1, concentration of solution 25% NH_3, and equivalent + 120% of ammonium carbonate).

Results are shown in Table 2 and Fig. 1.

TABLE 2.

Effect of roasting temperature and time on % extraction

Temperature °C	% extraction after roasting time					
	15′	30′	45′	60′	90′	120′
400	48.7	62.8	49.5	23.6	—	—
500	71.2	71.7	67.7	68.7	75.0	76.0
600	72.5	73.2	72.6	75.6	80.0	80.3
700	73.8	74.2	74.4	80.0	84.7	84.7
800	68.0	74.4	80.0	78.9	68.5	64.2
900	78.5	71.3	71.4	68.8	61.5	58.5

The above results show that with an increase of temperature from 500 to 700°C and time from 12 to 120 minutes, the extraction increases, and is a maximum at 700°C and 90 minutes. Prolonging the time does not increase extraction further. With an increase of temperature to 800°C the extraction increases to a maximum of about 80% for 45 minutes. Increase of the temperature to 900°C decreases extraction.

Accordingly, the best experimental conditions are a temperature of 700—800°C, in which case the same results are obtained for 60 minutes at the former and 45 minutes at the latter respectively, while if at 700°C the reduction time is prolonged to 90 minutes, the maximum extraction is 84.7%. If the economy of the process is better the shorter the reduction time, then the optimum conditions are 700—800°C and 45—60 minutes respectively. For laboratory conditions the optimum parameters are 700°C and 90 minutes.

The decrease at 900°C is probably due to complex crystallographic changes in the ore and bonding of MnO to other components in compounds insoluble in the ammoniac solution.

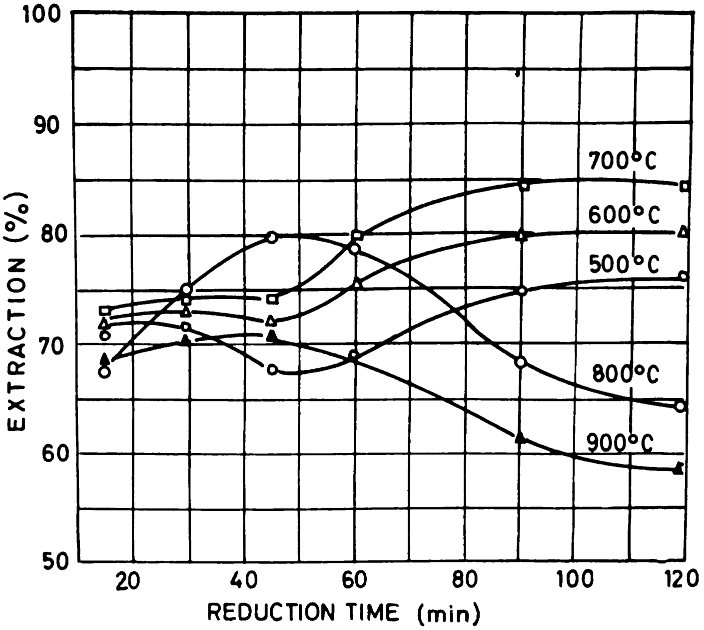


Fig. 1. Dependence of manganese extraction on reduction conditions

b) *Effect of the quantity of reducing agent.* — At the optimum reduction temperature of 700°C and time of 90 minutes, and other conditions unchanged, we investigated the effect of the hydrogen flow-rate on extraction. Results are shown in Table 3. 250 ml/min may be taken as optimal.

TABLE 3.

Effect of H_2 flow-rate during reduction on extraction

H_2 flow-rate (ml/min)	200	250	300
Extraction	83.50	84.70	84.70

EFFECT OF LEACHING CONDITIONS

The optimum parameters of reduction roasting were investigated under constant leaching conditions. Since in hydrometallurgical processes, leaching of useful components depends on variable leaching factors, we investigated their influence on manganese extraction for the given optimum roasting conditions.

c) *Effect of leaching time.* — With the same l:s ratio and concentration of the solution we investigated leaching for 15, 30, 60, 120, and 180 minutes. The results are given in Table 4.

TABLE 4.

Effect of leaching time on extraction

Leaching time (min)	15	30	60	120	180
Extraction (%)	81.80	84.70	86.70	87.20	87.66

The above results obviously show that MnO dissolves quickly in concentrated ammoniac solution. Even after leaching for only 15 min 81.80% of the manganese is extracted. With further increase of time the extraction increases considerably slower. Thus, 87.66% is obtained after three hours, which is only 6% more than after 15 minutes. The optimum leaching time adopted was one hour (86.70% extraction).

d) *Effect of concentration of the solution.* — From the literature data it is known that manganese ore processing by this procedure requires a strong solution, because the manganese ammoniacal complex is not stable enough in dilute solution. Furthermore, the more concentrated the solution the more successful is the dissolution of MnO. For this reason it was interesting to find out what solution concentration, i.e., what ratio of NH_3 to $(NH_4)_2SO_4$ in the solution would give the best extraction.

To investigate the effect of the amount of ammonium carbonate we took 25% ammoniac solution and in it dissolved $(NH_4)_2CO_3$ in an amount equivalent to manganese, plus a variable amount. With the determined optimum quantity of ammonium carbonate we changed the ammonia concentration to find its optimum. Results are shown in Tables 5 and 6.

TABLE 5

Effects of amonium carbonate concentration in the leaching solution on extraction

$(NH_4)_2CO_2$	Equiv. + 25%	Equiv. + 50%	Equiv. + 80%	Equiv. + 120%	Equiv. + 150%
g/l	23.00	27.60	33.12	40.00	46.00
Extraction %	52.40	62.30	78.60	86.70	86.70

TABLE 6

Effect of the free ammonium concentration in the leaching solution on manganese extraction

NH_3 concentration (%)	15	20	25
Extraction (%)	56.0	86.7	86.7

The above results confirm that successful extraction requires a high solution concentration of ammonia and ammonium carbonate. Optimum quantities of these components were equiv. +120% $(NH_4)_2CO_3$ and 20% NH_3.

e) *Fffect of the l:s ratio.* — All the above experiments were made at a constant l:s ration 4:1. Since manganese extraction also depends on this factor a number of experiments were made to determine its effect. Leaching was performed with optimum solution concentration [20% NH_3 and equiv. +120% $(NH_4)_2SO_3$] and optimum leaching time (60 min).

TABLE 7

Effect of the leaching solution l:s ratio on extraction

l:s	2:1	4:1	6:1	8:1	10:1
Extraction (%)	39.70	86.70	91.30	94.00	94.10

The above results show that increasing the liquid to solid ration to 8:1 increases extraction.' With this ratio the extraction is 94.00%. Therefore, for successful dissolution of MnO from the roast and convertion of Mn to ammoniac complex, one of the necessary conditions is a relatively high l:s ratio in leaching.

f) *Behavior of the other ore components in ammoniacal leaching.* — From the chemical analysis it can be seen that the manganese ore contained 30.71% Fe, 3.32% Pb, 1.35% Zn, and small quantities of Cu, Sb, and As. Except for iron all the other metals are in the form of native or complex sulfides, insoluble in ammoniac solution. This is mainly why these metals are not found in the filtrate after leaching. Iron is in the form of an oxide, mainly limonite. Fe_2O_3 and FeO are soluble in ammoniac solution. However, by reductive roasting Fe_2O_3 is mainly reduced to Fe_3O_4 which is insoluble in ammoniac solution. Due to this, only some of the iron goes into solution. With optimum roasting and leaching conditions about 4—5% Fe dissolves.

This behavior of the accompanying components in ammoniac leaching makes this procedure highly selective, especially relative to leaching with mineral acids. The selectivity and the possibility of regenerating the solution are two highly important characteristics of this leaching process.

School of Technology

Received November 3, 196

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GLASNIK HEMIJSKOG DRUŠTVA, Vol. 29, No. 5—6, 1964, pp. 247—254

EXTRACTION OF MANGANESE FROM POOR ORES BY ROASTING WITH AMMONIUM SALTS

by

DUŠAN M. VUČUROVIĆ, ILIJA B. ILIĆ, and RAJKO Ž. VRAČAR

In an earlier work(8) we presented some of the most important procedures for processing poor manganese ores, and pointed out the possibilities of processing. According to Keys and Klegg these procedures can in many cases compete with usual melting on ferromanganese from high-quality ores. Yugoslavia has considerable deposits of poor manganese ores, whose processing is becoming a more and more important problem. Therefore, besides the process of reduction roasting and leaching with ammoniac solutions, we have studied roasting ore with ammonium salts.

This procedure has been studied by a number of authors(3, 4, 5, 6, 7). Their investigations have proved that 75—90% of manganese can be extracted by roasting and leaching of the roast in water. The economical advantages of these procedures are the greater because they allow regenerating of expensive reagents.

Several authors have worked on treating poor manganese ores of different mineralogical compositions to get a manganese concentrate. This work has lead to the development of corresponding procedures. Sweet and Cartly(1) suggest a procedure for roasting complex ores with$(NH_4)_2SO_4$. By roasting, NH_3 and CO_2 are extracted, which are condensed in water, and the $(NH_4)_2CO_3$ solution obtained is later used for precipitating manganese. After $(NH_4)_2SO_4$ solution has been separated from the precipitate, it is regenerated and the salt used again. In 1957, Williams(3) patented a procedure for the processing of oxido-silicate ores and manganese slag. Besides ammonium sulfate he added $(NH_4)_2SO_3$, NH_4HSO_3, NH_4Cl to the mixture, and for silicate manganous slag NH_4F which converts $MnSiO_3$ to MnO during the roasting. This procedure yielded good results, the percentage of manganese extracted even exceeding 90%.

In view of the current importance of manganese extraction from Yugoslav ores, we have made extensive investigations, with regard the specific characteristics of Yugoslav raw material etc. to determine which parameters of ore roasting with ammonium salts influence the degree of manganese extraction.

EXPERIMENTAL

The "Novo Brdo" — Kopaonik ore used was the same as in previous work[8]. The main components were:

Mn^{2+} — 2.51%
Mn^{4+} — 18.84%
Fe — 15.90%
SiO_2 — 11.50%

The total content of arsenic, antimony, lead, copper and zinc did not exceed 3%. Microscopic examination in reflected light showed that psilomelane was the main bearer of manganese. The particle size distribution of the ore was 100%—60 mesh.

The ore was roasted with $(NH_4)_2SO_4$ and NH_4Cl in a horizontal electric resistance furnace and then the roast leached in water.

To determine optimal roasting conditions the effects of the following factors on the degree of manganese extraction were investigated.

a) temperature and time
b) $(NH_4)_2SO_4$ and NH_4 Cl content
c) leaching conditions

a) EFECT OF TEMPERATURE AND TIME

To investigate the effect of temperature and time on the degree of sulfatizing roasting of manganese, we only roasted the ore with $(NH_4)_2SO_4$. The quantity of the salt was the quantity equivalent to the manganese in the ore plus 20%. The conditions of leaching in water were always the same (liquid-solid ratio = 6:1, time 2 hours). Experimental results are shown in Fig. 1 and Table 1.

TABLE 1

Effect of temperature and time of roasting on manganese extraction in %.

Temperature °C	Time of roasting in min. 30	45	60	90
400	41.20	52.75	45.20	56.80
450	65.00	65.45	61.20	62.10
500	59.80	62.20	63.20	66.06
550	68.20	67.20	66.60	68.30
600	68.90	—	70.00	72.00
700	75.70	—	74.10	77.40
800	73.20	—	71.60	71.40

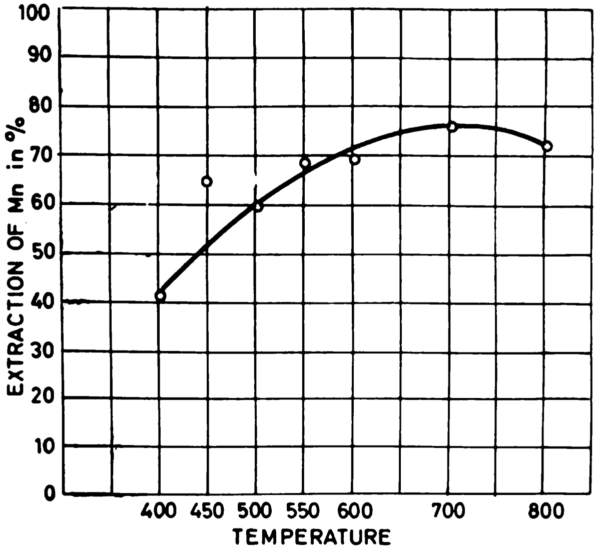

Fig. 1. Dependence of manganese extraction on roasting temperature. Time of roasting — 30 minutes.

By roasting at temperatures from 400° C to 800°C the MnO_2 present dissociates to MnO, while $(NH_4)_2SO_4$ decomposes at 350°C according to reaction

$$(NH_4)_2SO_4 = 2NH_3+H_2O+SO_3 \qquad (1)$$

The released SO_3 reacts with MnO:

$$MnO+SO_3 = MnSO_4 \qquad (2)$$

By increasing the temperature, reactions (1) and (2) are shifted to right and the kinetics of the process is stepped up.

As can be seen from Fig. 1 and Table 1, the convertion of manganese oxide to sulfate increases up to 700°C. Further increase of the temperature reduces it, since $MnSO_4$ decomposes strongly at about 800°C.

The effect of roasting time at higher temperatures is small, because, as can be seen from Table 1, if the roasting time is prolonged from 30'to 90' at 700°C, the percentage of extraction increases by only 2%. At lower temperatures the kinetics of the process is slower.

The purpose of investigating the effect of temperature and time on the degree of sulfatizing roasting was to find conditions where only manganese gets converted to a soluble sulfate form while the other accompanying metals remain in insoluble form. As iron is the most frequent of the non-gangue components in the ore besides manganese, we followed up iron extraction in the solution parallel with manganese.

By investigating the conditions of sulfatizing iron roasting it can be concluded that its water soluble forms $FeSO_4$, $Fe_2(SO_4)_3$ and FeS_2O_8 are resistant only at roasting temperatures below 550°C. Above this temperature iron extraction sharply decreases (Table 2, Fig. 2). By analysing the decomposition pressures of the above soluble iron compounds, it was found that $FeSO_4$ dissociates intensely even at 480°C while the somewhat more resistant forms $Fe_2(SO_4)_3$ and FeS_2O_8 decompose strongly at temperatures between 530 and 560°C.

Comparison of the results in Tables 1 and 2 obviously indicates that the selectivity between manganese and iron is almost total at the optimal temperature of 700°C. Thus, an almost pure solution of manganese sulfate with an extraction degree of about 76% is obtained in a relatively short roasting time of thirty minutes at 700°C.

TABLE 2

Effect of temperature and time of roasting on iron extraction in %

Temperature °C	Time of roasting in min. 30	45	60	90
400	19.31	18.21	17.99	21.07
450	15.00	13.80	14.26	17.90
500	14.00	10.20	4.60	2.90
550	4.61	3.30	—	2.52
600	2.20	—	2.50	1.95
700	0.54	0.00	0.00	0.00
800	0.00	0.00	0.00	0.00

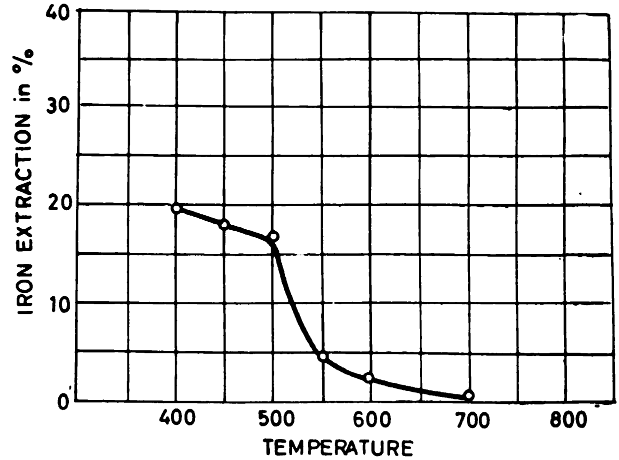

Fig. 2. Dependence of iron extraction on temperature of roasting. Roasting time 30 minutes.

b) EFFECT OF THE QUANTITY OF $(NH_4)_2SO_4$ AND NH_4Cl

Our subsequent investigations were aimed at determining optimal quantities of ammonium sulfate at the optimal roasting temperature and time. The results are shown in Table. 3.

From the table it may be seen that increasing the quantity of ammonium sulfate from 20% to 30% more than the equivalent gives a slight increase, about 2.5%, while further increase does not influence extraction any more. Nevertheless, in our further work we used the latter quantity.

TABLE 3

Effect of quantity of $(NH_4)_2SO_4$ *on manganese and iron extraction in %*

$(NH_4)_2SO_4$	Equiv. + 10	Equiv. + 20	Equiv. + 30	Equiv. + 40
(g)	11.14	12.15	13.17	14.18
%Mn	77.0	77.4	79.7	79.8
%Fe	0.00	0.00	0.00	0.11

Obviously that it is not possible to convert all the manganese to a sulfate form suitable for further extraction with ammonium sulfate. According to the literature data it is rather difficult to convert bound MnO to $MnSO_4$. MnO may be bound in a compound with higher undissociated manganese oxides, and with SiO_2 and FeO, where it forms compounds of the xMnO. $y SiO_2$and xMnO. $y SiO_2 . z$FoO type. In addition, the particle size distribution of the ore also influences the extraction. If the particle size is small, in our case fractions smaller than 60 mesh, the chemism of roasting goes easier, while manganese oxide trapped in large particles reacts hardly at all.

However, it is known that MnO reacts rather strongly with chlorine and some of its compounds forming highly water-soluble manganous chloride. In this case roasting in the presence of ammonium chloride goes according to the reaction.

$$MnO + 2NH_4Cl = MnCl_2 + 2NH_3 + H_2O \qquad (3)$$

To study the influence of ammonium chloride on manganese extraction, other conditions being constant roasting was carried out with different additions of this compound. Results are shown in Table 4.

Table 4 shows that ammonium chloride considerably increases manganese extraction up to a quantity equivalent to half the optimum quantity of $(NH_4)_2SO_4$. Transfer of iron to the solution under these conditions is negligibly small so a pure solution of manganous sulfate is obtained. The extraction decreases with further increase of the quantity of ammonium chloride. In our case the optimum quantity is 1/4 of the optimum quantity of $(NH_4)_2SO_4$, with a maximum extraction of 89.5—90% under the above roasting conditions.

TABLE 4

Effect of NH_4Cl *on manganese and iron extraction degree in %*

	quantity of NH_4Cl as fraction of optimum quantity of $(NH_4)_2SO_4$					
NH_4Cl	1/8	1/4	1/2	1	1 + 10%	1 + 20%
(g)	1.646	3.292	6.584	13.169	14.486	15.800
%Mn	82.00	89.50	90.30	74.70	71.80	71.40
%Fe	0.44	0.60	0.00	0.00	0.00	0.87

CONDITIONS OF ROAST LEACHING

After each roasting the roast was leached in water with agitation. The quantity of water and leaching time during the investigations of the optimal roasting conditions were: liquid-solid ratio = 6:1, time 2 hours.

For the optimal roasting conditions we investigated the conditions of extracting manganous sulfate and manganous chloride from the roast. The extraction of these salts depends mainly on the l:s ratio and the leaching time. Data on the effect of the l:s ratio are shown in Table 5. The table shows that the maximum extraction, 92.3%, is obtained with a small quantity of water, i.e. with a 2:1 l:s phase ratio. This is due to the high solubility of the salts in water. The leaching time was 2 hours.

TABLE 5

Effect of l:s ratio on manganese and iron extraction in %

l:s	2:1	4:1	6:1	8:1
% Mn	92.30	89.75	89.50	91.50
% Fe	0.44	0.33	0.60	0.65

The effect of leaching time on manganese extraction was also investigated under optimal roasting conditions and optimal l:s ratio =2:1. Results are shown in Table 6. It can be seen that manganese salts obtained by roasting dissolve quickly, i.e. the optimal leaching time is only 30 minutes. With prolonged leaching, like with increased l:s ratio, somewhat lower extractions are obtained, which can be ascribed to hydrolysis of manganese salts.

TABLE 6

Effect of leaching time on manganese and iron extraction in %

Time in min.	15	30	60	120	180
% Mn	88.88	93.00	91.40	91.50	90.90
% Fe	0.53	0.44	0.30	0.40	0.15

After leaching the solution was separated from the precipitate by filtering. The filtering rate considerably dependeb on the roasting conditions. Roasting at 550°C gives a roast which precipitates on leaching and is not easily filtered because of the presence of colloidal Fe^{3+} ions. The roast obtained at higher temperatures is easily filtered after leaching. The iron in it is in the form of an oxide which does not cause trouble, so filtering proceeds quickly and the solution remains clear.

Further research is in progress on sulfatization roasting of the same ore plus pyrite in an SO_2 gas stream.

School of Technology
Beograd

Received November 3, 1964

SRPSKO HEMIJSKO DRUŠTVO (BEOGRAD)

BULLETIN OF THE CHEMICAL SOCIETY Belgrade

(Glasnik Hemijskog društva — Beograd)
Vol. 29, No. 7, 1964.

Editor:
MILOŠ MLADENOVIĆ

Published by
SRPSKO HEMIJSKO DRUŠTVO (BEOGRAD)
1966.

Translated and published for U. S. Department of Commerce and
the National Science Foundation, Washington, D. C., by
the NOLIT Publishing House, Terazije 27/II, Belgrade, Yugoslavia
1966

Translated by
DANICA LADJEVAC and ALEKSANDRA STOJILJKOVIĆ

Edited by
PAUL PIGNON

Printed in Beogradski Grafički Zavod, Belgrade

CONTENTS

GLASNIK HEMIJSKOG DRUŠTVA, Vol. 29, No. 7, 1964, pp. 283—299.

EFFECT OF SOLUTION pH ON THE ABSORPTION SPECTRA OF PELARGONIDOL, DELPHINIDOL AND MALVINOZIDE

by

SLOBODAN M. RISTIĆ and JELISAVETA M. BARANAC

1. INTRODUCTION

The present paper deals with the investigation of absorption spectra of some important anthocyanidols as a function of the pH of the buffered solutions in which they are observed.

2. EXPERIMENTAL

The absorption spectra in the region from 200 to 1000 mμ were obtained on a UNICAM S.P. 500 spectrophotometer. All pH-measurements were performed with a Beckmann pH-meter, type H-2 (glass electrode). pH-buffered solutions were prepared according to Sorensen and Clark⁽¹⁾, concentrations of the solute were of the order 10^{-5}mμ except when otherwise stated. Samples of anthocyanidols used were mainly commercial products whose purity was checked chromatographically.

A. *Investigations in acid media* were carried out with seven buffer solutions with pH-values in the range 1 to 5. These solutions were prepared by dissolving p.a. reagents in redistilled water, and were kept in paraffined bottles for liquid reagents. One important difficulty encountered was *the fading of the red forms of anthocyanidols.* The further the pH away from the optimal stability region, the more rapidly the fading took place, so that for some pH-values ordinary, direct-reading spectrophotometry was impossible. However, since we first established the possible limiting values of "the fading effect" (which will be discussed later in more detail) we were able to define precisely the spectrophotograms of the red forms of the anthocyanidols.

Characteristic absorption spectra of these compounds which can be relatively observed in strongly acid media (pH = 1—2) are characterized by an intense red color which is visually observable. Figure 1 shows the spectrophotograms of these colored forms (see caption).

As seen in Fig. 1 the red forms of the anthocyanidols show *three absorption maxima* (λ_{maxI}, λ_{maxII} and λ_{maxIII} starting from long waves) which are well-defined and which can be differentiated from the corresponding values in aqueous and nonaqueous solvents⁽²⁾. Characteristic values of these maxima are more accurately and more clearly given in Table I (together with the spectra of blue and colorless forms which will be discussed later). It may be assumed that the *individuality of the "red" anthocyanidol forms is satisfactorily defined spectrophotometrically*; some spectrophotometric features of these forms, and their correlation with the structure and the behavior of these compounds, will be discussed later.

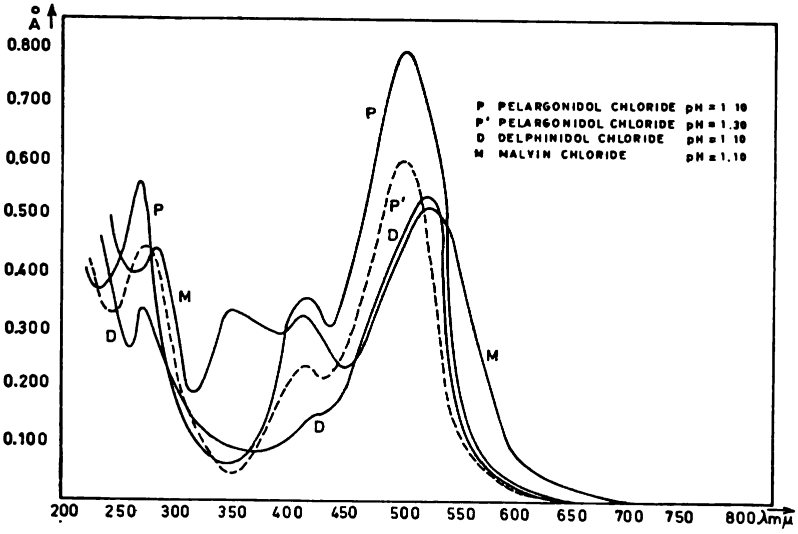

Fig. 1 Absorption spectra of "red" cationic forms of anthocyanidols and anthocyanosides

The effect of fading was studied by systematically following the changes of absorption spectra with well-buffered different pH-values of the solutions. We also measured directly the absorption spectra of faded forms at some well-defined constant pH-values. Figures 2 and 3 show these observations in case of pelargonidol solutions and Fig. 4 in case of delphinidol solutions.

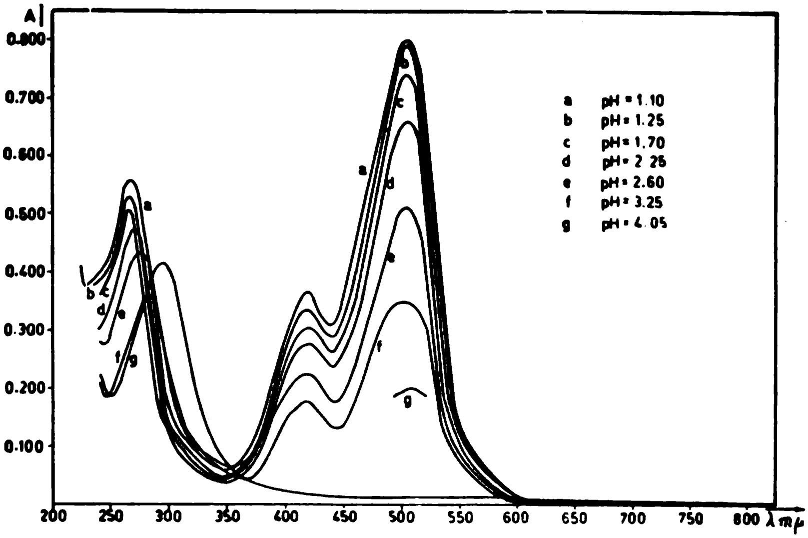

Fig. 2 Absorption spectra of pelargonidol chloride in dependance on solution pH

TABLE I

Absorption spectra of the main colored forms of anthocyanidols and anthocyanozides

RED CATIONIC FORMS										CORRESPONDING COLORLESS FORMS									
Ionic form	pH	λmax. I.	λmax. II	λmax. III	λmax. IV	a_1	a_2	a_3	a_4	Noo-ionized ionic forms	pH	λmax. I	λmax. II	λmax. III	emax. IV	a_1	a_2	a_3	a_4
PK+	1.10	505.0	420.0	265.0	—	10,500	4800	7300	—	IPB$_p$	2.60	—	—	290.0	—	—	—	6700	—
PK$^+$	1.30	505.0	420.0	265.0	—	9400	5000	7000	—	IPB$_p$									
DK$^+$	1.10	520.0	—	270.0	—	11,500	—	7100	—	IPB$_D$	2.60	—	—	290.0	—	—	—	5500	—
MK+	1.10	520.0	415.0	275.0	350.0	10,600	6600	8900	6900	IPB$_M$	4.05	—	—	350.0	—	—	—	5600	—

BLUE ANIONIC FORMS									CORRESPONDING COLORLESS FORMS							
Ionic form	pH	λmax. I	λmax. II	λmax. III	a_1	a_2	a_3		Non-ionized ionic forms	pH	λmax. I	λmax. II	λmax. III	a_1	a_2	a_3
PA-	12.20	600.0	450.0	295.0	12,000	5000	9000		IPK$_p$	12.20	—	—	330.0	—	—	10,000
DA-	8.00	600.0	—	—	9500	—	—		IPK$_D$	8.00						
MA-	10.22	600.0	600.0	325.0	9500	7800	7500		IPK$_M$	10.22						

Figure 2 clearly shows that with decreasing acidity of the buffered pelargonidol solution, the first absorption maximum in the visible region ($\lambda^{PC+}_{max\,I}$ = 505.0 mμ and the second ($\lambda^{PC+}_{max\,II}$ = 420.0mμ) are less pronounced. However, in spite of the decreased absorbance, the characteristic wavelengths remain unchanged. Simultaneously the formation of a new absorption maximum ($\lambda^{IPB}_{max\,III}$ = 290.0 mμ) may be observed and it seems that the absorbances of the disappearing maxima are "leaking out" into the newly formed one. It is evident that this maximum belongs to the product of the fading reaction. On account of the proximity of the new absorption maximum, the height of the third maximum of the pelargonidol cation ($\lambda^{PC+}_{max\,III}$ = 265.0 mμ) is not the same at different pH-values of the solution. This makes difficult the estimation of the precize characteristic wavelength of the newly formed maximum. Genetic correlation of the absorption spectra of pelargonidol cation with the basic colorless form is more directly shown by the appearance of the isosbestic point in Fig. 3, where spectrophotograms of pelargonidol and the corresponding faded forms at different pH-values are given.

The process and mechanism of the effect of pH on the absorption spectra of anthocyanidols and anthocyanosides can be explained if *two important assumptions* are made (howewer, their validity should be checked in the given case). *Firstly*, according to the theory formulated by Lewis and Calvin(3), and Pauling (1939/1946)(4), anthocyanidol cations appearing in acid media have *the structure of resonance hybrid* in which different electrometric structures participate in various amounts; formerly it was assumed that the only electrometric structures present were those of the oxonium and carbenium types. It is very likely *that the colored forms are charged* and *that they have the betainoid valence structure* of a resonance hybrid, since they originate from the ionic form of a pseudo-base, whereas the colorless forms have the nonchromophoric valence structure in ionogenous but nonionized form(5), since all the oxonium and carbenium combinations are excluded by the hydroxylation of the C_2 of the flavylium chromophoric grouping. — *Secondly*, the colored resonance hybrid cations (and anions) can be in equilibrium with the undissociated ionogenous form of the pseudo-base (or pseudo-acid) provided the applicability of the law of mass action is established, i.e. the constancy of K^b_{dis} and K^a_{dis}, or the pK--values for the investigated compound is confirmed. Taking into account all the aforesaid, a tentative but probable *scheme of the main processes* may be put forward; for the time being it will fairly reliably define the existence of an ionic equilibrium between the red cation (or the blue anion) and the ionic form of the corresponding pseudo-base (or pseudo-acid). However, this scheme will be less complete in case of violet and colorless forms whose individualities are already spectrophotometrically well established.

Such investigations of equilibria between spectrophotometrically active forms (hybrid cation) and ionic forms of pseudo-bases which in the visible region are spectrophotometrically inactive have already been carried out with pH-metric indicators, but not with anthocyanosides. However, Sondheimer and Kertesz (1953)(6) have applied this method of investigations to pelargonoside (pelargonine). In view of the fact that such investigations make possible the quantitative estimation of the ratio between the colored and the colorless form, we applied them to pelargonidol, delphinidol and malvinoside. From the measured absorbance values of spectrophotometrically active forms of pelargonidol, delphinidol and malvinoside at different pH-values and applying them to the ionic equilibrium (I) between the resonance hybrid cation (RHC+) and ionic form of the pseudobase (IPB) —

$$(\mathrm{RHC})^+ + \mathrm{H_2O} \rightleftharpoons (\mathrm{IPB}) + \mathrm{H_3O^+} \qquad \text{(I)}$$

we can calculate the quantitative relation between the dissociated and the undissociated anthocyanidols from the equation

$$\mathrm{pK^b} = \mathrm{pH} + \log\left(\frac{\mathrm{RHC^+}}{\mathrm{IPB}}\right) \qquad (1)$$

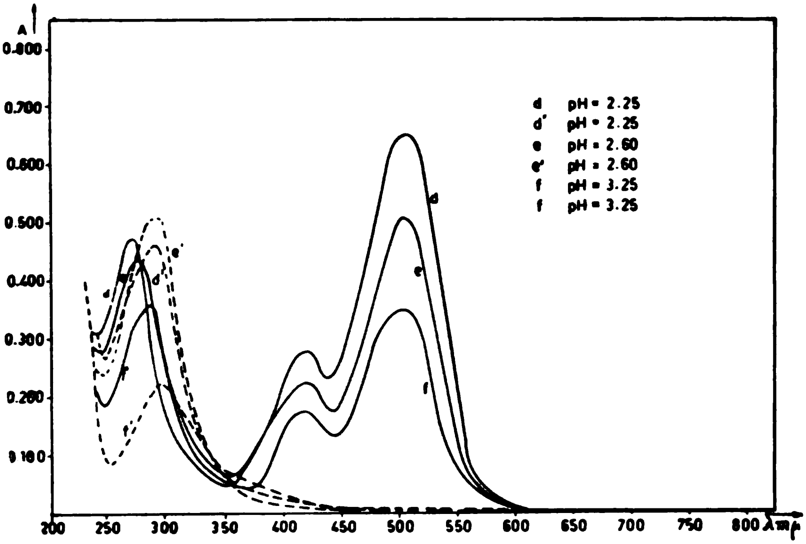

Fig. 3 Absorption spectra of the “red” cationic form of pelargonidol chloride and of its faded forms.

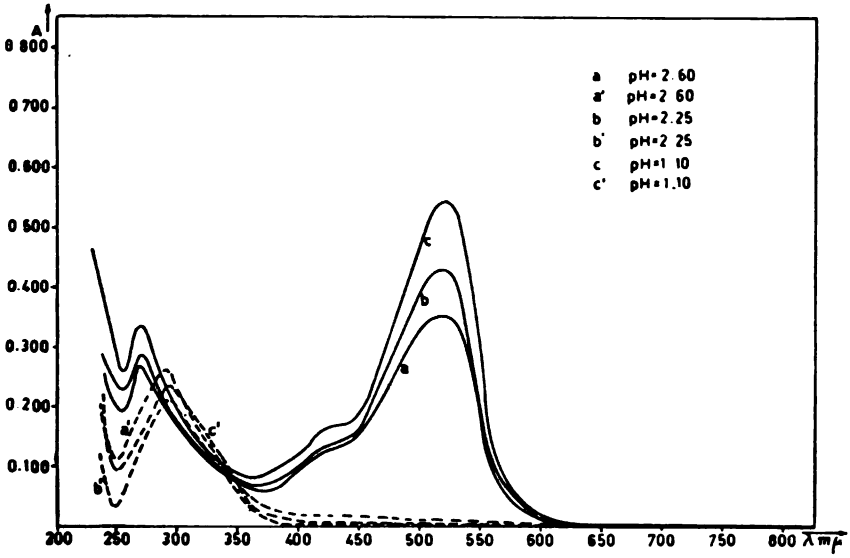

Fig. 4 Absorption spectra of the “red” cationic form of delphinidol chloride and of its faded forms.

TABLE 2.

Jonic equilibrium between pelargonidol red cations (PC+) and blue anions (PA−) and the corresponding colorless nonionized ionic pseudobase (IPB) or pseudoacid (IPA)

PC+ λ max I = 505.0 m μ					PA− λ max I = 600.0 m μ				
pH = 1.10 a_{PC+} = 10.500; pH = 4.05 a_{IPB} = 2.600					pH = 12.20 a_{A-} = 24,000; pH = 9.05 a_{IPA} = 6.800				
pH	A	PC+%	IPB%	pK^b	pH	A	pA−%	IPA%	pK^a
1.25	0.796	99.16	0.84	2.32	11.95	0.650	86.40	13.6	11.15
1.70	0.740	90.01	9.91	2.66	11.70	0.507	58.60	41.4	11.45
2.25	0.660	76.67	23.33	2.77	11.45	0.355	29.10	70.9	11.81
2.60	0.510	51.66	48.34	2.63	11.10	0.298	18.00	82.0	11.75
3.25	0.350	25.00	75.00	2.77	10.22	0.265	11.60	88.4	11.10
pK^b_{mean} = 2.63					9.80	0.240	6.80	93.9	11.94
					pK^a_{mean} = 11.36				

The results are given in Table II (together with the data for the electrolytic dissociation of the blue anion which are to be mentioned later). These results are important since they offer the possibility of determining the percentages of the colored form present. For example, at pH = 1.25 under the specified conditions PK+ = 99.16%, DK+ = = 98.60% and MK+ = 96.55% i.e. the differences in behavior of the investigated hybrid cations are small but perceptible.

B. *Investigations in basic media* were carried out analogously as described under A, with eight buffered solutions of pH in the range 8 to 12. The absorption spectra of investigated blue forms under optimal stability conditions are shown in Fig. 5; the effect of pH on the absorbance of pelargonidol is demonstrated in Fig. 6, while the appearance of the "faded" form is indicated in Fig. 7.

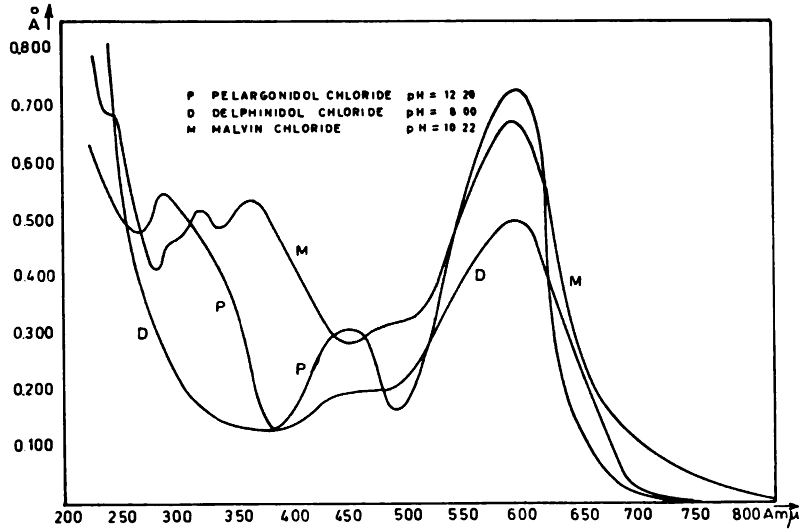

Fig. 5. Absorption spectra of anionic blue forms of anthocyanidols and anthocyanosides

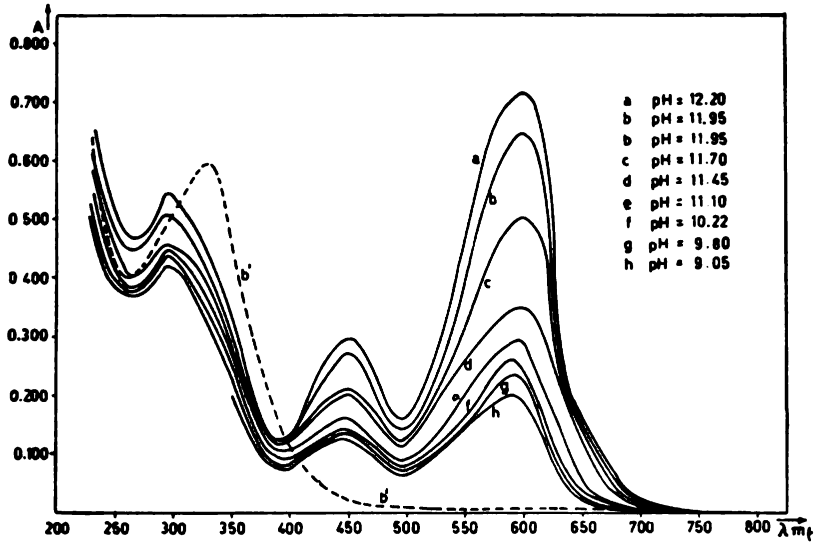

Fig. 6. Absorption spectra of the blue form of pelargonidol chloride as a function of solution pH

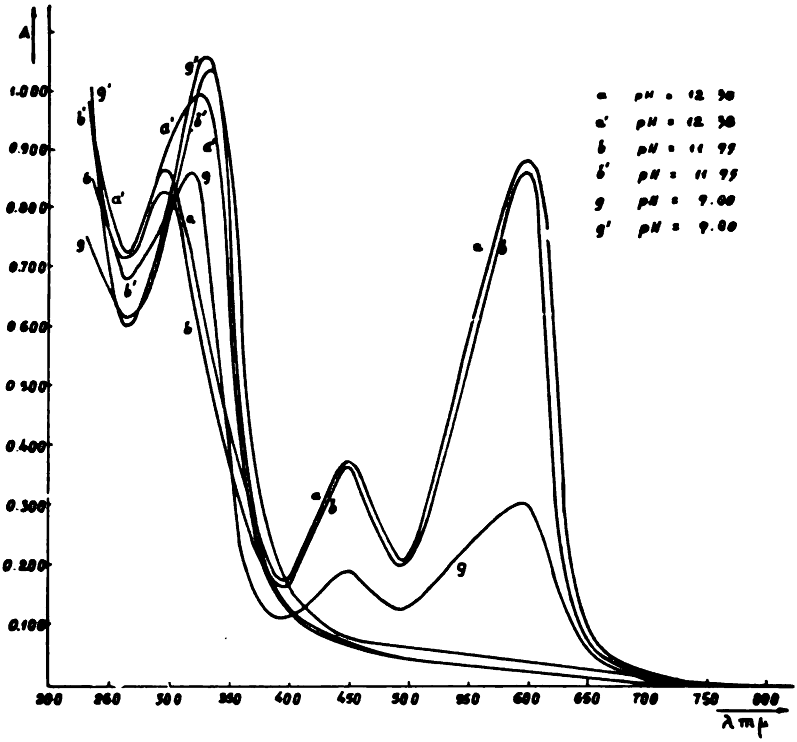

Fig. 7. Absorption spectra of anionic blue forms of pelargonidol chloride and of its faded forms.

Characteristic parameters of these spectra are given in Table I. The effect of fading was followed here too as earlier described, and is seen in the spectrophotograms (Fig. 7). On the basis of the above assumptions the following ionic equlibrium between the resonance hybrid anion (RHA^-) and the ionic form of the pseudo-acid, in a basic medium,

$$(IPA) + H_2O \rightleftharpoons (RHA)^- + H_3O^+ \qquad (II)$$

can be interpreted in the same way as before. Analogously, the equation

$$pK^a = pH + \log\left(\frac{IPA}{RHA^-}\right) \qquad (2)$$

can be used to calculate the percentage concentrations of the resonance hybrid anion and the colorless, undissociated but ionogenous form of the pseudo-acid conjugated with it. The data and the results of these calculations are summarized in Table II. However, conclusions concerning the conjugate faded blue forms cannot be formulated on the basis of our present investigations. From data given in Table II in which the constancy of the pK-value in the pH-region from 9 to 11 (variations about 5%) is shown, the existence of these forms is evident since their spectroscopic absorptions do not overlap to any extent with the characteristic maxima of the blue form ($\lambda^{PA^-}_{max\,I} = 600°$ mμ; $\lambda^{PA^-}_{max\,II} = 450°$ mμ; $\lambda^{PA^-}_{max\,III} = 295°$ mμ. The colorless forms of the red cation and the blue anion of pelargonidol are shown in Fig. 8. Without any deeper analysis it may be concluded that the faded forms of the red and the blue ions are clearly distinct. This practically means that the pseudo-acid and the pseudo-base possess clearly distinct absorption spectra.

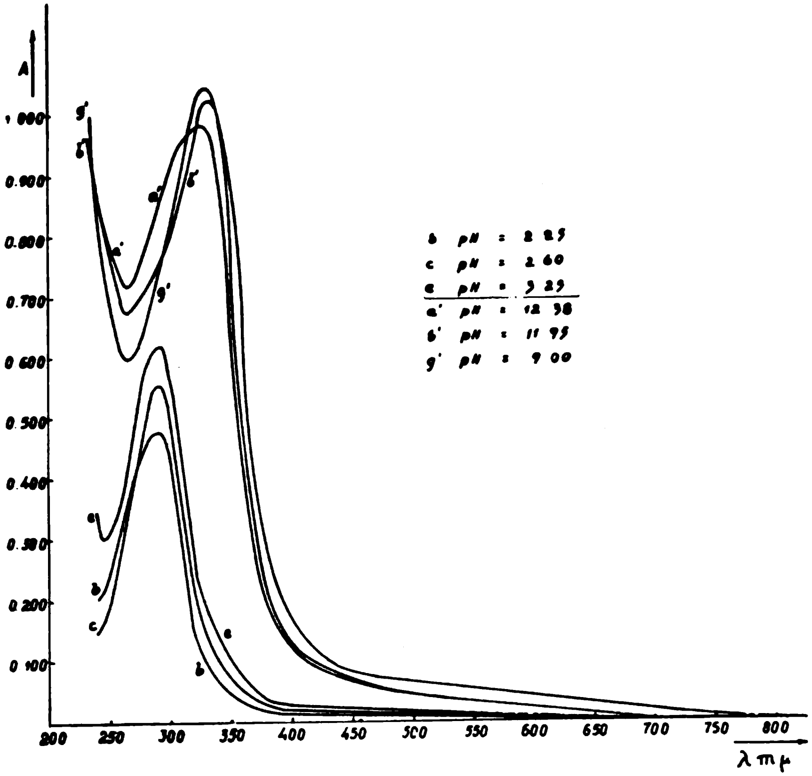

Fig. 8 Absorption spectra of the colorless, red and blue forms of pelargonidol chloride

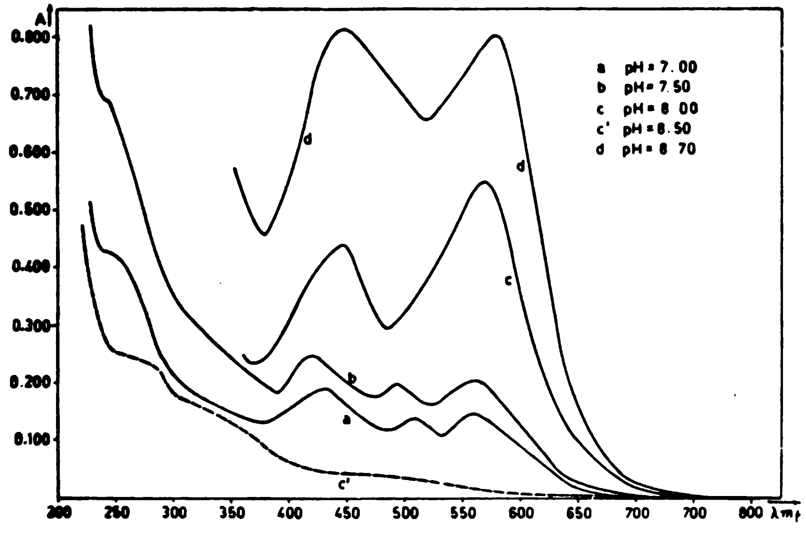

Fig. 9 Absorption spectra of the violet form of pelargonidol chloride

C. *Spectrophotometric investigations* in the pH-region between strongly acid and strongly basic, where there exist stability regions for resonance hybrid cations and anions, are very delicate on account of the ever lower stability of the active chromophoric systems. For the present we only give the absorption spectra of the violet form of pelargonidol (Fig. 9). which could be measured in the pH-region from 7.00 to 8.00.

DISCUSSION

From the absorption spectra of the main colored forms of anthocyanidols, i.e. the red cation and of the blue anion (Figs. 2 and 6) it may be seen that, in spite of drastic pH-changes, some absorption maxima remain at the same wavelength. For example *in acid media,* the red resonance hybrid cation (Figs. 1 and 5) of pelargonidol (PK) is defined *with three absorption maxima* $\lambda^{PK+}_{\max I} = 505.0 m\mu$, $\lambda^{PK+}_{\max II} = 420 m\mu$, $\lambda^{PK+}_{\max III} = 265.0 m\mu$, and the *blue* resonance hybrid anion by the three maxima $\lambda^{PA-}_{\max I} = 600.0 m\mu$, $\lambda^{PA-}_{\max II} = 450{,}0 m\mu$, $\lambda^{PA-}_{\max III} = 295.0 m\mu$. The specificity of these maxima in basic media is unchanged provided they are not disturbed by the appearance of some new maxima in their proximity which might arise from other spectrophotometrically active forms. Such an example was encountered with the maxima $\lambda^{PK+}_{\max III} 256.0$ mμ and $\lambda^{PA-}_{\max III} = 295.0$ mμ which were disturbed by the maxima $\lambda^{IPB}_{\max III}$ and $\lambda^{IPK}_{\max III}$ of the "faded" forms. To obtain more reliable values of $\lambda^{PK+}_{\max III}$ and $\lambda^{PA-}_{\max III}$ it is indispensable to measure the absorption spectra in pH-regions which are optimal for the stability of the cation or anion, i.e. regions in which the concentration of the interfering "faded" form is minimal (Table II). The same situation is encountered with delphinidol and malvinoside, although greater complexity of their chromophoric systems necessarily makes the characteristics discussed here less clear.

The "violet" and "faded" forms are less precisely defined in our investigations, although we were able to measure their absorption spectra (Fig. 9). In fact, the characteristic absorption maxima of the violet form are not only subject to disturbances but they are also considerably less stable than those of the other forms.

Without going here into too much detail, we can indicate and provisionally interpert the course of indicator color changes in buffered anthocyanidol solutions, for example those of pelargonidol. From our observations of the indicator curve of pelargonidol, obtained in strongly acidic and strongly basic media (Fig. 10), where an almost direct transition of the red into the violet and blue forms, and vice versa, is observed, it may be concluded that the violet form is probably in direct interaction with the red resonance hybrid cation, or with the blue resonance hybrid anion in neutral and near-neutral pH-regions. This would be in good agreement with Pauling's theory of the essentially ionic nature of the respective chromophores. The faded form of pelargonidol with a deteriorated K-chromophoric grouping would absorb only in the ultraviolet region (Fig. 8) and would be formed by the hydratation of the amphipolar K-chromophoric violet structures. Such

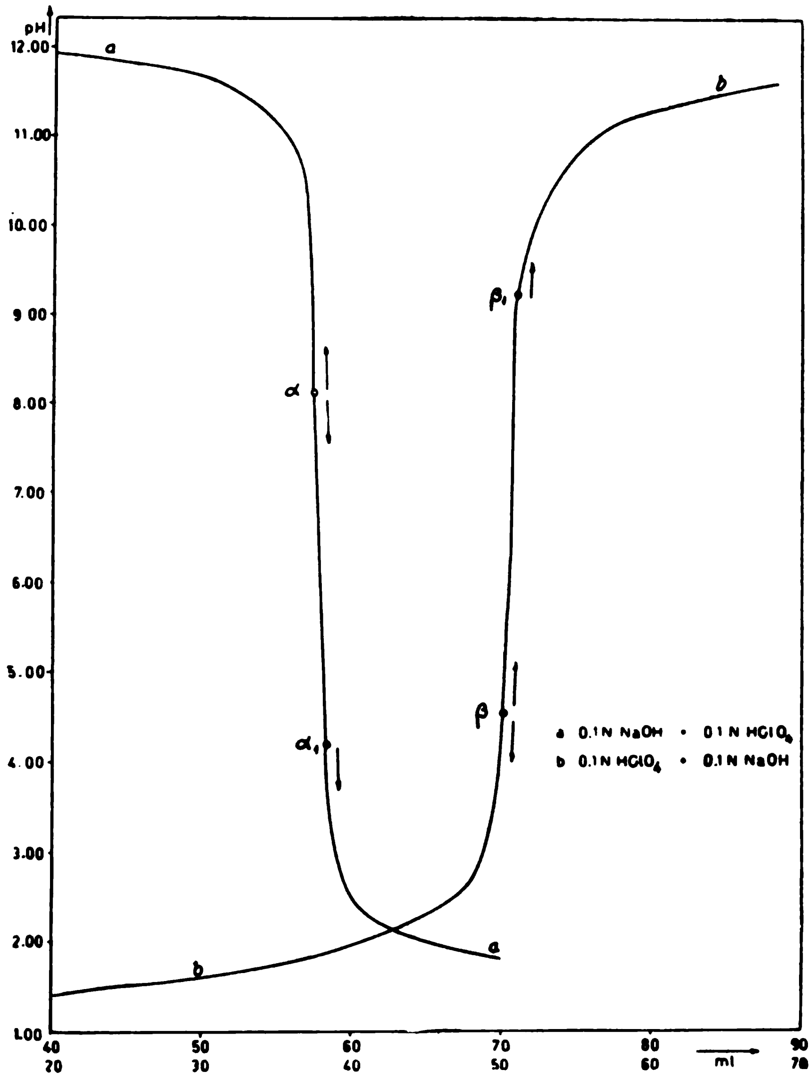

Fig. 10. Indicator curve of pelargonidol chloride

α -point of transition of blue to violet
α_1-point of transition of violet to red
β -point of transition of red to violet
β_1-point of transition of violet to blue

an interpretation of the course of indicator color changes is in many details consistent with the observations made by L. di Bella (7) mecocyanine by visual spectrometry.

The main colored forms of the investigated substances are considerably sensitive to pH-changes (Fig. 11). In Fig. 11 the absorption spectra of a classical indicator (lithmus) and pelargonidol in the pH-range

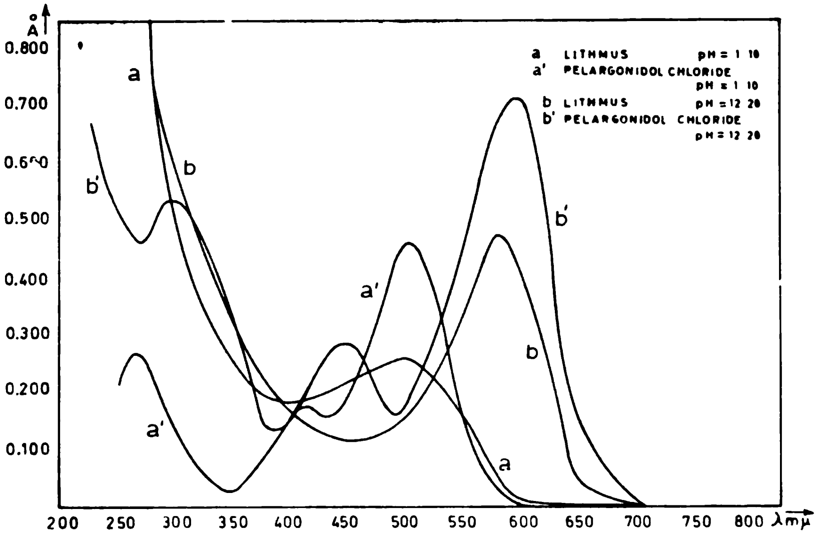

Fig. 11. Absorption spectra of lithmus and pelargonidol chloride in buffered solutions.

are presented. From this it follows that, with respect to intensity of the color change, pelargonidol could be used as an indicator, as has already been recommended for a number of anthocyanidols. However, on account of optical instability in critical neutral regions, the use of anthocyanidols as indicators would be limited. Other applications, based on this photochemical instability are of course not excluded. Photochemical changes of anthocyanidol absorption spectra are evidently of specific significance for the natural environment in which they were formed.

4. CONCLUSIONS

The behavior of anthocyanidols and anthocyanosides, studied from their absorption spectra in solutions with different but controlled pH-values indicates the existence of at least four different forms. Apart from their absorption spectra (Figs. 1 and 5, Table I) the red resonance hybrid cation and the blue resonance hybrid anion could be fairly precisely defined by the electrochemical equilibria in which they take part (Table II), thanks to their relatively higher stability in solutions of optimal acidity. The violet and the colorless forms of anthocyanidols have been defined only by their absorption spectra.

The use of anthocyanidols and anthocyanoside as indicators, as studied and recommended by some authors, is relatively small and limited to special cases.

School of Science
Department of Physical Chemistry
Beograd University

Received February 26, 1965

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GLASNIK HEMIJSKOG DRUŠTVA, Vol. 29, No. 7, 1964, pp. 301—309

DETERMINATION OF URANIUM AND THORIUM CONCENTRATIONS AND THEIR DISTRIBUTION IN SOME MINERAL DEPOSITS BY MEANS OF PHOTO-NUCLEAR METHOD*

by

BOŠKO PAVLOVIĆ and DRAGANA PETROVIĆ

Photo-nuclear methods for determining the concentration of radioactive elements in natural deposits have been applied more or less successfully by a great number of research workers (1,2,3,4). By using a photo-nuclear technique we studied the distribution of radioactive inclusions and the concentrations of uranium and thorium in some natural sediments (travertines), some igneous rocks (andesite and granodiorite) and in some samples of coal.

The photo-nuclear method we used is based on the registration of tracks in emulsion at a 2 π steradian angle. A finely ground sample of the studied rock was dried and then placed in a layer on the emulsion. The powder was left on the emulsion for 15 to 20 days at room temperature. The time of exposure depended on the activity of the investigated sample. In the case of coal we did not use powder, but on account of its specific properties, small sticks were finely polished and their polished sides were placed on the emulsion. The time of exposure and further treatment of the photo-nuclear plate were the same as for samples in powder.

Ilford C_2 and home-made IFSRS photo-nuclear plates were used. Ilford plates were developed by means of the standard ID 19 developer, and IFSRS plates with amidol reagent. The counting of the tracks and the measurement of their lengths was carried out by means of a Zeiss microscope (magnification 10×10).

The powder was poured uniformly on the emulsion so that the thickness of the layer was not larger than the greatest range, R, of investigated α-particles. According to Poole and Mathews(5), when the registration of tracks in emulsion is made at an angle of 2π steradian and the thickness of l is greater than R, then each square centimeter of the sample's surface will emit N_x α-particles per time unit, regardless of the thickness of the layer. If N_i decays take place per volume unit of the radioactive source whose thickness $l > R$, the number, N_x, of α-particles registered in the emulsion per time unit will be

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* Communicated at the XI Meeting of the Serbian Chemical Society.

$$N_x = \frac{N_l}{4} K R - \rho) \qquad (1)$$

where $K = \frac{R'}{R} = \frac{\text{the range of } \alpha\text{-particles in the investigated sample}}{\text{the range of } \alpha\text{-particles in the air}}$

and $\rho = \frac{\text{the range of } \alpha\text{-particles in the emulsion}}{\text{the relative range of } \alpha\text{-particles in the emulsion}}$

Since the investigated samples of rocks contained radioelements from series $^{238}U + ^{235}U$ and ^{232}Th, many of which were α-emitters, the equation (1) had to be transformed, and for example, for one radioactive series it was written as

$$N_x = \frac{N}{4} K \sum (R - \rho) \qquad (2)$$

where N is the total number of α-particles emitted per time unit by radioelements of one series occuring in the volume unit of the investigated sample, and $\sum \left(R - \frac{\rho}{1}\right)$ is the sum of $R - \rho$ ranges of the α-particles.

If we know the number n of α-particles emitted per time unit by each radioactive parent (i.e. ^{238}U, ^{235}U, and ^{232}Th) when in radioactive equilibrium with its decay product, and the ratio $^{238}U/^{235}U$, as well as the density d of the examined sample and the concentrations C of uranium 234, uranium 235 and thorium 232, we find that the number N of α-particles emitted per volume unit per unit time will be

$$N = ndC \qquad (3)$$

for each of these elements. Inserting the numerical values in equations (2) and (3) we find that each square centimeter of the sample surface will emit the following number of α-particles originating from uranium and thorium, respectively:

$$N_U = 9.21 \; x \; 10^4 \; d \, C_u \, K \qquad (4)$$

$$N_{Th} = 2.44 \; x \; 10^4 \cdot d \cdot C_{Th} \, K \qquad (5)$$

Since the investigated samples consisted of different components, each of which had a certain stopping force, s, for α-particles, the constant K in equations (4) and (5) should be expressed as a function of the concentration of idnividual elements present in the sample and their stopping forces.

From Coppens'(2) calculations it follows that

$$K = \frac{0.85 \; x \; 10^{-4}}{d \; \frac{C_i S_i}{A_i}} \qquad (6)$$

From equations (4), (5) and (6) it is found that

$$N_U = 9.2 \, C_U \, K' \qquad (7)$$

$$N_{Th} = 2.64 \, C_{Th} \, K' \qquad (8)$$

where

$$K' = \frac{0.85}{\frac{C_i S_i}{A_i}} \qquad (9)$$

The equations (7) and (8) show that it is possible to calculate the concentrations C_U and C_{Th} by counting the number of tracks of α-particles and knowing the value of K'. If the examined sample contains the elements of both uranium and thorium series, the number of α-particles emitted per surface unit per time unit will be

$$N = (9.2\, C_U + 2.64\, C_{Th})\, K' \tag{10}$$

Since this equation contains two unknown quantities, Cu and C_{Th}, it is necessary to form another equation for the ratio of $C_{Th} : C_v$, and then on the basis of these two equations to calculate C_v and C_{Th}.

Comparing the lengths of many tracks registered in the emulsion it is observed that they fall into a rather wide range. The longest tracks originate from ThC′ (^{212}Po), RaC′ (^{214}Po) and AcA (^{215}Po). Tracks whose lengths in the emulsion are equivalent to a length of more than 7 cm in air belong to ThC′, whereas those whose lengths are equivalent to lengths from 5.8 to 7 cm, in air originate from α-particles emitted by AcA and RaC′. In view of the fact that the atoms of ThC′ and other radioelements present in the sample are not located only in the layer contiguous with the emulsion but throughout the sample, it is evident that some of the shorter tracks belong to α-particles retarded during their passage through the sample.

If the lengths of the tracks in the emulsion are equivalent to lengths of 7 cm in air, from equations (1) and (3) it is found that the number of α-particles emitted by Th and ThC′ per time unit per surface unit is

$$n_1 = 0.25\, N_{Th}\, K' \tag{11}$$

If the lengths of the tracks in the emulsion are equivalent to lengths between 5.8 and 7 cm in air, the number of α-particles per time unit per surface unit is

$$n_2 = 0.25\, K'\, (0.78\, N_{Th} + 1.14\, N_U) \tag{12}$$

The final equation for the determination of thorium and uranium concentration is obtained from equations (11) and (12)

$$\frac{C_{Th}}{C_U} = \frac{3.3}{\frac{n_2}{n_1} - 0.8} \tag{13}$$

To successfully apply equation (13) and in order to reduce the error (to less than + 20%) it is necessary to measure the lengths of some hundreds of tracks.

The concentrations C_v and C_{Th} can be determined from equations (4), (5), (10) and (13) if we know the number and the lengths of the tracks as well as the absorption coefficient. Equation (9) shows that the value of coefficient K′ can be obtained only if we know the quantitative chemical composition of the studied sample; otherwise we have to use the data for K′ published in literature.

Since no data on the coefficient K′ for travertine, andesite and coal had been reported so far, we performed the quantitative analysis of the samples. The results are given in Table 1, and on the basis of these we have calculated the values of the coefficient K′ for travertine, andesite and coal. We also verified the published data of K′ for granodiorites⁽⁶⁾. Table 2 shows the calculated values of K′ and the concentrations of uranium and thorium.

As already mentioned, the aim of our investigations was not only to determine the uranium and thorium concentrations, but also to study the distribution of radioactivity in mineral fractions of travertine. In addition, we wanted to find out whether the radioelements found in andesite, grandiorites and coal occur in inclusions or are uniformly distributed. Techniques used in these investiagtions are described in a previous publication⁽⁷⁾.

The experiments showed that α-emitters are distributed in travertine components of higher specific gravity as well as in those of lower specific gravity. However, in andesite and granodiorites, the radioelements are mainly concentrated in inclusions of higher specific gravity.

In the coal samples we found that the activity was uniformly distributed throughout the mass.

TABLE I

Quantitative Analyses of Samples in which U and Th Concentrations Were Determined

Elements	TRAVERTINE		ANDESITE	GRANODIORITE		COAL	
	Niška banja	Debarska banja	Bor	Prilep	Ravno Vučje	Pićan	Podlabin
Ca	33.10	23.68	5.85	2.87	2.58	3.16	2.24
Si	2.47	3.04	26.64	30.0	30.0	0.64	0.44
Al	1.69	2.70	9.86	8.62	7.95	0.86	0.55
Fe	0.98	0.40	*	3.03	3.56	1.63	1.90
Mn	0.35	0.30	0.15	*	*	*	*
Na	0.30	0.74	2.17	2.57	2.65	0.41	0.03
K	*	*	1.47	3.26	3.24	0.35	0.03
Ba	*	0.17	*	*	*	*	*
S	*	1.34	0.08	*	*	2.07	2.07
Ti	*	*	0.36	0.48	0.28	*	*
P	*	*	0.04	0.22	0.38	*	*
N	*	*	*	*	*	0.60	0.72
H	0.59	0.67	*	0.11	0.13	2.30	2.64
C	49.66	50.16	46.19	48.1	47.62	10.93	11.60
C	10.40	11.98	0.54	*	*	76.20	76.57

* Concentrations smaller than 0.03%.

TABLE 2

Values of K′ Coefficient and Concentrations of Uranium and Thorium

	TRAVERTINE		ANDESITE	GRANODIORITE		COAL	
	Niška banja	Debarska banja	Bor	Prilep	Ravno Bučje	Pićan	Podlabin
$\frac{C \quad S}{A}$	6.04	6.09	6.14	5.98	5.92	7.27	7.12
K′	14.07	13.95	13.85	14.39	14.36	11.56	11.54
C_u (n 10^{-6}g/g)	47.8	17.2	1.5	2.3	2.5	90.6	83.7
C_{Th} (N 10^{-6}g/g)	26.3	1	5.8	11.9	16.5	50.7	46.2

DISCUSSION

The data on uranium and thorium concentrations in samples of travertine, andesite, granodiorite and coal obtained by the photo-nuclear method were not found to agree with the results obtained by other methods. In travertines, uranium has been determined fluorometrically and thorium by means of the emanometric method; in other rock samples and in coals, uranium and thorium have been determined by the radiometric method.

TABLE 3

Comparison of Results Obtained for Uranium and Thorium Concentrations by Means of Photonuclear, Fluorometric and Radiometric Methos

Results obtained by photonuclear method

Elements	TRAVERTINE		ANDESITE	GRANODIORITE		COAL	
	Niška banja	Debarska banja	Bor	Prilep	Ravno vučje	Pićan	Podpićan
$C_U g/g$	4.78×10^{-5}	1.72×10^{-5}	1.54×10^{-5}	2.30×10^{-6}	2.51×10^{-6}	9.06×10^{-5}	8.37×10^{-5}
$C_{Th} g/g$	2.63×10^{-5}	—	5.85×10^{-6}	11.96×10^{-6}	11.56×10^{-6}	5.07×10^{-5}	—
$C_{Th/U}$	0.55	—	3.8	5.2	6.6	0.56	—
$C_{Ra} g/g$	16.1×10^{-12}	5.80×10^{-12}	$0{,}52 \times 10^{-12}$	0.78×10^{-12}	0.84×10^{-12}	30.5×10^{-12}	28.2×10^{-12}
Results obtained by fluorometric method for uranium and emanometric method for radium and thorium							
$C_U g/g$	3.0×10^{-7}	1.3×10^{-6}					
$C_{Th} g/g$	1.4×10^{-6}	10^{-6}					
$C_{Th/U}$	0.47	—					
$C_{Ra} g/g$	13.2×10^{-12}	2×10^{-12}					
Results obtained by radiometric method							
$C_U g/g$			1.7×10^{-6}	2.1×10^{-6}	3.5×10^{-6}	4.02×10^{-5}	4.20×10^{-5}
$C_{Th} g/g$			10.6×10^{-6}	9.0×10^{-6}	17.5×10^{-6}	—	—
$C_{Th/U}$			6.2	4.3	5.0	—	—
$C_{Ra} g/g$			0.57×10^{-12}	0.71×10^{-12}	1.18×10^{-12}	1.35×10^{-12}	1.41×10^{-12}

The data given in Table 3 show that the differences in the values of uranium concentrations in travertines, obtained by photo-nuclear and fluorometric method are greater than the order of concentrations established. Such differences were obtained to a lesser extent in coal samples as well. Since the differences are greater than the error of the photo-nuclear method, the explanation of these results should be looked for in the methods themselves. For example, in the fluorometric method the determination of uranium concentration is based on its properties, i.e. on the fluorescence of uranium salts, whereas the determination by photo-nuclear method involves counting the tracks of α-particles and measuring their lengths. If the individual members of one radioactive series are not in radioactive equilibrium, the number of tracks and the ratio of their lengths will not be the same as when all the radioelements are in equilibrium. Hence, the results obtained from the number of α-particles by the method described do not represent the actual concentrations of uranium.

According to the radioactive equilibrium the following concentrations of radium correspond to the uranium concentrations in travertines determined by the photo-nuclear method: for the sample from Niška Banja — calculated 1.61×10^{-11} gRa/g, measured — 1.32×10^{-11} gRa/g; for travertine from Debarska Banja, calculated 5.8×10^{-12} gRa/g, measured 2.1×10^{-12}. Thus, the concentrations of radium calculated on the basis of uranium concentrations determined by the photo-nuclear method do agree at least in order of magnitude with the radium concentrations determined by other methods. This indicates that the concentration of radium is in fact determined by the number of tracks of α-particles and that Coppens' formulae (equations 10 and 13) cannot be applied in all cases. Since the calculated concentrations of radium in travertine do agree with those obtained by measurement, and the calculated concentrations of uranium are not consistent with those obtained by measurement, it follows that in these sediments uranium and radium are not in radioactive equilibrium. From data given in Table 3 it is evident that there is no radioactive equilibrium between uranium and radium in the samples studied, and that from the number of α-particles the concentration of radium is determined, although Coppens' formula is used. The discrepency between the results of the photo-nuclear method and other methods might be explained by assuming that the daughter radioelements are not in radioactive equilibrium with the parents. The photo-nuclear method can be applied for the determination of uranium and thorium concentrations only in those samples in which U and Th are in radioactive equilibrium with their decay products.

It has been established that radioactive elements are differently distributed in individual components of travertines, igneous rocks and coals. We have already found earlier(7) that all the components of travertine are radioactive to a greater or lesser extent. Since travertine is formed by precipitation from aqueous solutions, it is very likely that the radioelements are adsorbed by all its components. Similar findings have been established with coal too. However, in igneous rocks, uranium, thorium and their decay products are located in inclusions which are usually of higher specific gravity than the main mass of the rock.

School of Technology
University of Beograd
Institute of Physics, SR Srbija
Beograd

Recieved February 11, 1965

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GLASNIK HEMIJSKOG DRUŠTVA, Vol. 29, No. 7, 1964, pp. 311—320

REACTIONS OF ORGANIC AND INORGANIC ACIDS WITH SODIUM TUNGSTATE. I. pH-METRIC AND CONDUCTOMETRIC TITRATIONS

by

MILENKO V. ŠUŠIĆ, DRAGAN S. VESELINOVIĆ and DESANKA SUŽNJEVIĆ

According to the data available in the literature, in the reaction of organic and inorganic acids with sodium tungstate two types of compound are formed: polyanions of tungstic acid and complexes of tungstic acid with reacting acids. The formation of polyanions has been observed mainly in reaction with inorganic acids. Decrease of the pH of the solution and the increase of the reactant concentration result in the formation of hexatungstate ($HW_6\,0_{21}^{5-}$)(1,2,3) and metatungstate ($W_4O_{13}{}^{2-}$) and $W_{10}O_{32}{}^{2-}$ and $W_{20}O_{61}^{2-}$)(5-) polyanions. In acetic and phenylacetic acid(4) solution $W_3O_{12}^{2-}$ polyanion is formed.

Most authors have reported that organic acids give complexes with tungstate (6,7,8). The oxalato complex was found to have the composition $[WO_3C_2O_4]^{2-}$. However, there are some data indicating that oxalic acid separates collodial tungstic acid without complexing (11).

In a previous paper(8) we established that L-ascorbic acid reacts with sodium tungstate and gives, depending on the ratio used, two types of compound: hexatungsate polyanion $HW_6O_{21}^{5-}$ (formed by the action of H^+ of the acid) and the complex $[WO_3A_2]^{2-}$ (A^- is the monobasic anion of L-ascorbic acid). These findings indicate that other, particularly organic acids may also react with sodium tungstate giving two types of compound. Therefore we investigated the reaction of sodium tungstate with the following acids: formic, L-ascorbic, acetic, propionic, hydrochloric and nitric.

The reaction of sodium tungstate with L-ascorbic acid, represented by equations (1) and (2), is accompanied by a decrease of the total number of ions, especially H^+-ions. This effect was

$$7\,H^+ + 7\,A^- + 12\,Na^+ + 6\,WO_4^{2-} \rightleftharpoons HW_6\,0_{21}^{5-} + 12\,Na^+ + 7\,A^- + 3\,H_2O \qquad (1)$$

$$2\,H^+ + 2\,A^- + 2\,Na^+ + WO_4^{2-} \rightleftharpoons [WO_3A_2]^{2-} + 2\,Na^+ + H_2O \qquad (2)$$

also observed in the reaction of tungstate with other acids and it could be followed by pH-metric and conductometric measurements.

The investigations were carried out by the method of continual variation(12), pH-metric and conductometric titration, and by pH and conductivity measurement.

The method of continual variation, in which the increase of H^+-ion concentration is measured as a function of the molar ratio of components, has been applied for the study of complexes of metal ions with weak acids(13,14). In the reaction of tungstate with acids the decrease of H^+-concentration is proportional to the amount of complex or polyanion formed. Hence this method could be applied by measuring the decrease of H^+-concentration as a function of the molar ratio of components. The procedure we used was as follows: solutions containing different molar ratios of acid and tungstate were prepared by mixing *a* ml of tungstate solution with *b* ml of acid solution, so that $a+b=$ const. (both solutions were of the same concentration). Thus the molar ratio of acid and tungstate in the mixture was equal to the ratio of ml taken: $n = b/a$. Apart from these solutions, solutions of acid and tungstate in which the concentration of each substance corresponded to that in the mixture were prepared; they were obtained by mixing *a* ml of water with *b* ml of acid, and *a* ml of tungstate with *b* ml of water. After measuring the pH of all the three solutions, the decrease of H^{+}-ion concentration was computed from the equation

$$\Delta C_{H^+} = C^{s}_{H^+} - (C^{Ac}_{H^+} + C^{W}_{H^+}) \tag{3}$$

where $C^{s}_{H^+}$ denotes the concentration of H^+ ion in the mixture solution, $C^{Ac}_{H^+}$ -the H^+-ion concentration in the acid solution and $C^{W}_{H^+}$- the H^+-ion concentration in the tungstate solution.

By plotting-ΔC_{H^+} against *n* a curve with maxima or points of inflection was obtained. The values corresponding to these points give the ratio of the components in the compounds formed in the reaction.

The reaction of tungstate with acids was investigated by the method of continual variation and by conductivity measurements using the procedure applied in the study of chloroberyllates(15,16). The procedure involved the measuremet of the specific conductivity of the mixture solution and of solutions of pure components, prepared as in the pH-metric investigations. The change of onductivity, $\Delta\varkappa$, was obtained from the equation

$$\Delta\varkappa = \varkappa^{s} - (\varkappa^{Ac} + \varkappa^{W}) \tag{4}$$

where $\varkappa^{s}$ denotes the specific conductivity of the mixture solution, and, $\varkappa^{Ac}$ and $\varkappa^{W}$ the specific conductivities of the acid solution and tungstate solution, respectively. By plotting $\Delta\varkappa$ against *n* a curve was obtained whose maxima or inflections correspond to *n*-values which denote the ratio of the components in compounds formed.

The reaction of tungstate with acids was also studied by pH-metric and conductometric titrations. The slow rate of the reaction, observed in the study of L-ascorbic acid and tungstate(8), required some alteration of the usual procedure. Solutions with the same tungstate but different acid concentrations were prepared. After equilibration the conductivity and the pH-values of these solutions were measured. From the results the pH-metric and conductometric titration curves were constructed.

EXPERIMENTAL

In the method of continual variation 0.0100 M solutions of tungstate and acid were used. By mixing these solutions, solutions with different *n* were obtained. Titrations were always carried out with 50 ml of 0.0200 M sodium tungstate solution and different amounts of 0.200 M acid solution. The mixtures were diluted to 100 ml with water so that the final tungstate concentration was 0.0100 M. The consumption of the acid was calculated with respect to this concentration.

Solutions were left to equilibrate for at least 10 hours at 25 ± 0.02°C, except in experiments with L-ascorbic acid when the equilibrating time was reduced to six hours in order to avoid losses due to air oxidation.

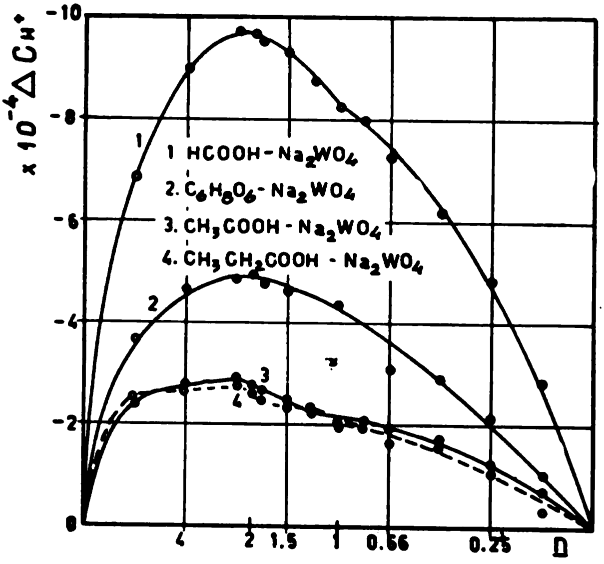

Fig. 1. Dependence of — Δ C_{H^+} on *n* for the 0.01 M organic acid-0.01 M Na_2WO_4 system

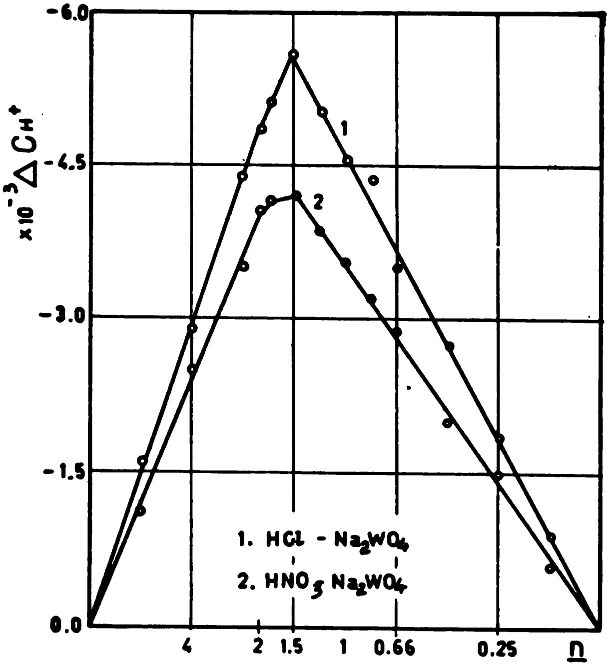

Fig. 2. Dependence of — Δ C_{H^+} on *n* for the 0.01 M mineral acid-0.01 M Na_2WO_4 system

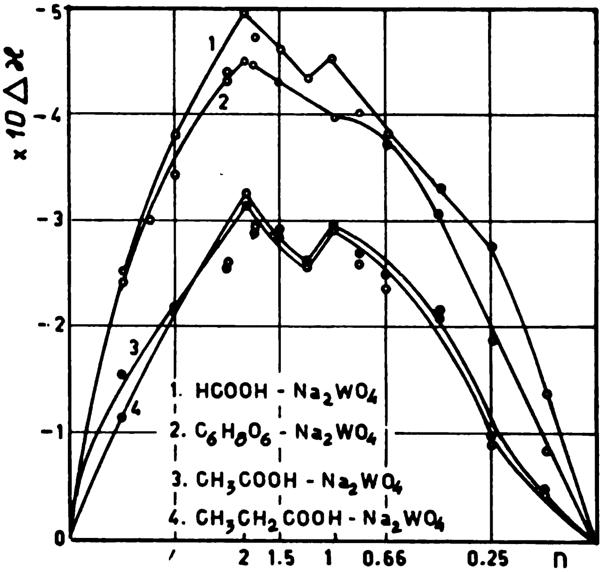

Fig. 3. Dependence of — Δ K on *n* for the 0.01 M organic acid-0.01 M Na$_2$ WO$_4$ system

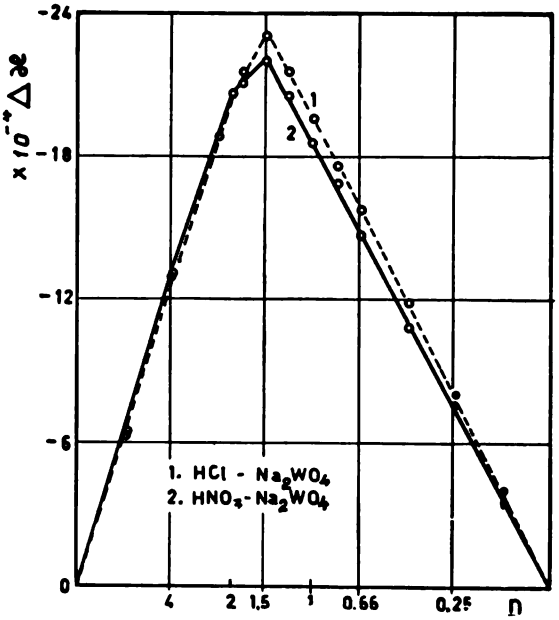

Fig. 4. Dependence of — Δ ϰ on *n* for the 0.01 M mineral acid-0.01 M Na$_2$WO$_4$ system

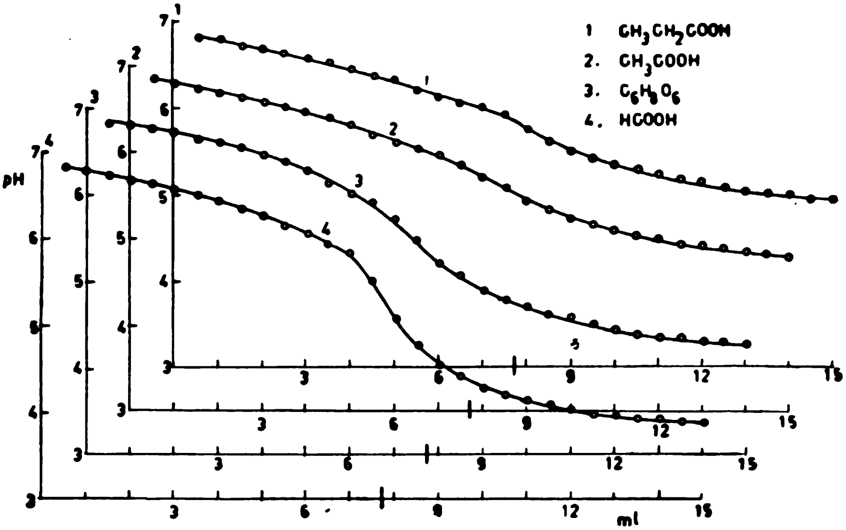

Fig. 5. pH metric titrations of 100 ml 0.01 M Na_2 WO_4 with 0.2 M organic acids

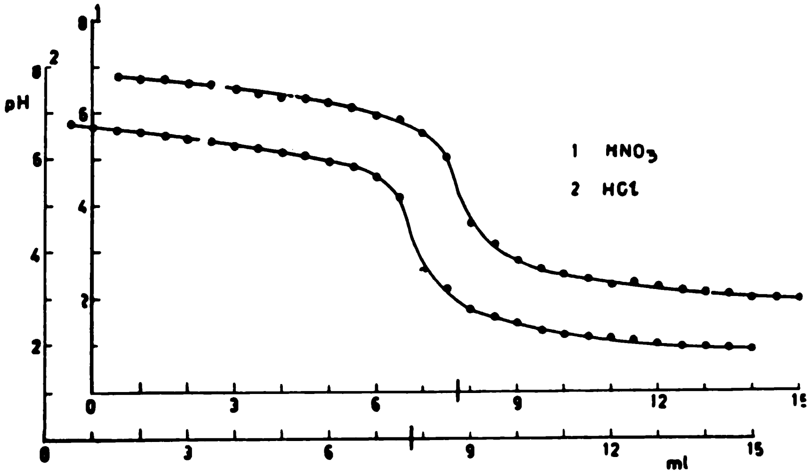

Fig. 6. pH metric titrations of 100 ml 0.01 M Na_2 WO_4 with 0.2 M mineral acids

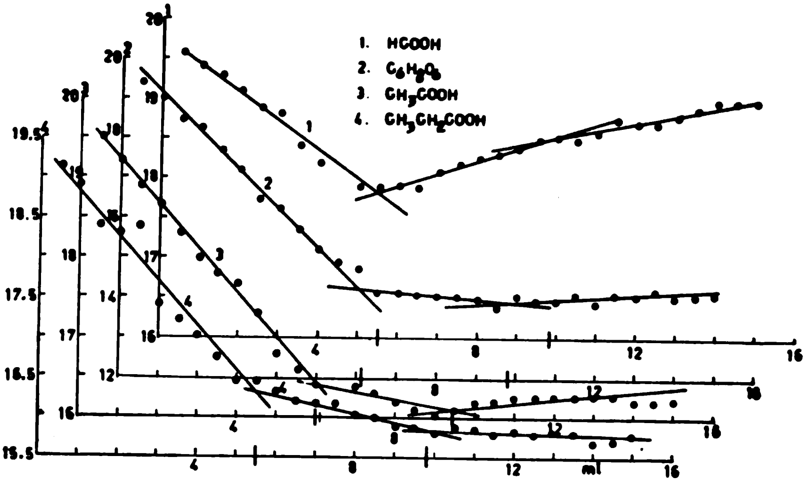

Fig. 7. Conductometric titrations of 100 ml 0.01 M Na_2WO_4 with 0.2 M organic acids

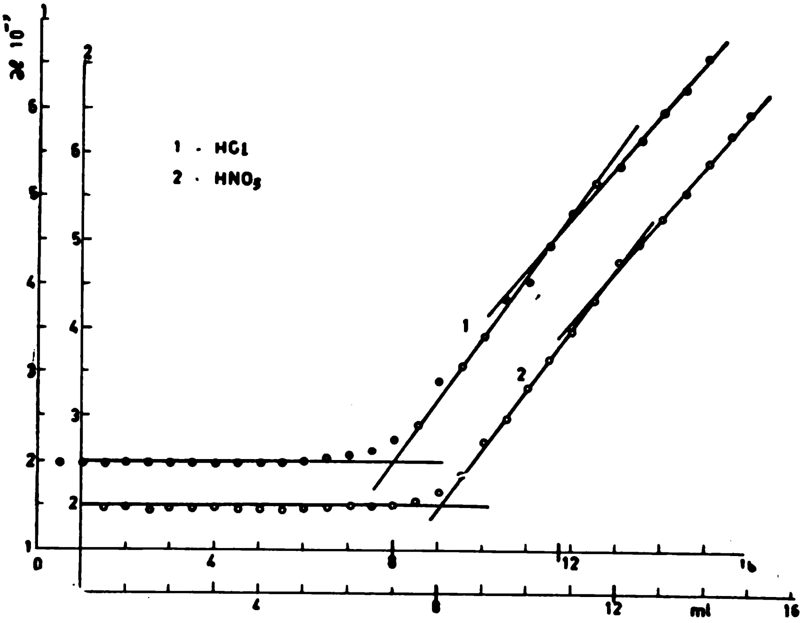

Fig. 8. Conductometric titrations of 100 ml 0.01 M Na_2WO_4 with 0.2 M mineral acids

Curves obtained by the method of continual veriation from pH-values are shown in Figs. 1 and 2, and those obtained by means of conductivity measurements are given in Figs. 3 and 4. Curves obtained by means of potentiometric and conductometric titrations are presented in Figs. 5, 6, 7 and 8.

The shapes of the curves obtained by the method of continual variation show that by decreasing the strength of the acid the absolute values of ΔCH^+ and $\Delta\kappa$ are also decreased, and the assymetry of the curve is greater. This is explainable since the absolute pH-value of the solution increases with decreasing acid strength, whereby ΔC_{H^+} and $\Delta\kappa$ are decreased. The assymetry of the curve is due to different degrees of dissociation of the acid in the reaction mixture and in the pure solution.

The same effect was also observed in titrations. Increase of the acid dissociation constant brings about a greater change of potential in pH-metric and a greater change of conductivity in conductometric titrations.

The molar ratios, *n*, corresponding to reaction products of sodium tungstate and the acids are given in Table I.

TABLE I

Valeus of the molar n, obtained by different methods

	Continual variation methods				Titrations		
	From pH-measurements		From κ measurements		pH-metric	conductometric	
acid	n_1	n_2	n_1	n_2	n	n_1	n_2
HCOOH	2	1	2	1	1.5	1.1	2
$C_6H_8O_6$	2	1	2	1	1.5	1.2	2
CH_3COOH	2	1	2	1	1.5	1.2	1,9
CH_3CH_2COOH	2	1	2	1	1.5	1.1	2
HCl	1,5	—	1.5	—	1.5	1.6	2.3
HNO_3	1.5	2	1.5	2	1.5	1.6	2.4

DISCUSSION

From Table I it may be seen that the values of *n* for organic acids obtained by the method of continual variation and by conductometric titrations are $n = 2$ and $n = 1.1 - 1.2$, respectively. These values correspond to complex formation and to hexatungstate anion formation with L-ascorbic acid. No separation of colloidal tungstic acid was observed. Hence it follows that the investigated monobasic organic acids react with Na_2WO_4 giving the complex anion $/WO_3AC_2/^{2-}$ ($n = 2$; $A\bar{c}$ = anion of monobasic acid) whereas the action of H^+ ion produces hexatungstate polyanion $HW_6\,O_{21}{}^{5-}$.

For mineral acids all methods give the following n-values: $n = 2-$ -2.5 and $n = 1.5-1.6$. The former value corresponds to colloidal tungstic acid formation, confirmed by the opalescence of the solution, and the latter ($n = 1.5-1.6$) to the formation of metatungstate anion obtained by the action of acid H^+ ion. The value $n = 1.5-1.6$ was also obtained for organic acids in pH-metric titration.

The formation of hexatungstate anion takes place at $pH \approx 6-7$. Metatungstate and complex anion are formed simultaneously at lower pH. Accordingly, it might be expected that mineral acids would also give hexatungstate polyanion at pH greater than 6. This was not experimentally confirmed since these effects, being masked by other reactions, cannot be observed by the methods used.

The formation of other types of polyanion was not observed. Their existence in the solution has been reported as established by pH-metric titration using a quinhydrone electrode. However, we have found that quinhydrone, and other compounds containing an enol group (L-ascorbic acid, pyrogallol, etc., react with sodium tungstate; hence the data obtained with a quinhydrone electrode cannot be taken as satisfactorily reliable, especially for small pH variations.

APPARATUS AND REAGENTS

A Beckman pH-Meter Model H-2, VEB Prüfgeräte Model NB thermostat and laboratory apparatus for conductivity measurements with an accuracy of 0.5% were used. All reagents were p.a., made by "Kemika" and "Merck".

School of Science

Department of Physical Chemistry, Beograd
Institute of Chemistry, Technology and
Metallurgy, Beograd

Received January 7, 1964

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GLASNIK HEMIJSKOG DRUŠTVA, Vol. 29, No. 7, 1964, pp. 321—326

REACTIONS OF MONOBASIC ORGANIC AND INORGANIC ACIDS WITH SODIUM TUNGSTATE.

II. DETERMINATION OF HEXATUNGSTATE POLYANION POLYMERIZATION CONSTANT

by

DRAGAN S. VESELINOVIĆ, DESANKA Ž. SUŽNJEVIĆ AND MILENKO V. ŠUŠIĆ

In a previous paper⁽¹⁾ it was shown that hexatungstate anion, $HW_6O_{21}^{5-}$, is formed regardless of the type of organic or inorganic acid used, provided solution pH = 6—7. This condition is fulfilled when the concentration of sodium tungstate is greater than that of the acid; then, the following equilibrium reactions take place in the solution:

$$6\,WO_4^{2-} + 7\,H^+ \rightleftharpoons HW_6O_{21}^{5-} + 3\,H_2O \tag{1}$$

$$H^+ + Ac^- \rightleftharpoons HAc \tag{2}$$

Ac^- denotes the anion of the monobasic acid used. Since the hexatungstate anion is formed by the polymerization of WO_4^{2-} ion under the influence of the acid, the constant of this reaction, which will be named the hexatungstate anion polymerization constant, is given by the following expression:

$$K = \frac{[C_{WO_4^{2-}}]^6\,[C_{H^+}]^7}{[C_{HW_6O_{21}^{5-}}]} \tag{3}$$

The dissociation constant of the acid is given by

$$k = \frac{[C_{H^+}] \times [C_{Ac^-}]}{[C_{HAc}]} \tag{4}$$

The total concentration of tungstate in the solution is

$$\overset{\bullet}{C}_{WO_4^{2-}} = C_{WO_4^{2-}} + 6\,C_{HW_6O_{21}^{5-}} \tag{5}$$

and that of the acid

$$\overset{\bullet}{C}_{HAc} = C_{HAc} + C_{Ac^-} \tag{6}$$

The C° denote the initial molar concentrations of tungstate and the acid used, and the C the equilibrium concentrations of the corresponding ions.

The concentration of the acid anion is given by the equation

$$C_{Ac^-} = C'_{Ac^-} + 7\,C_{HW_6O_{21}^{5-}} \tag{7}$$

in which C′Ac denotes the concentration of the acid anion formed by dissociation. In case of monobasic acids this concentration is equivalent to the H+ ion concentration:

$$C'_{Ac^-} + C_{H^+} \tag{8}$$

From equations (6) and (4) the following expression is obtained:

$$C_{HAc} = \frac{C_{H^+} \times \overset{\circ}{C}_{HAc}}{k + C_H^+} \tag{9}$$

which gives the concentration of the undissociated acid provided the values of $\overset{\circ}{C}_{HAc}$ and *k* are known, while C_{H^+} is measured directly. By substituting the obtained C_{HAc} value in equation (6), the concentration of the acid anion C_{Ac^-} is obtained.

Equations (8) and (7) give

$$C_{HW_6O_{21}^{5-}} = \frac{C_{Ac^-} - C_{H^+}}{7} \tag{10}$$

from which the polyanion concentration can be obtained. If the calculated concentration is put in equation (5) the concentration of tungstate $C_{WO_4^{2-}}$ is obtained, provided its initial concentration, $\overset{\circ}{C}_{WO_4^{2-}}$, is known.

From the values obtained for $C_{WO_4^{2-}}$, $C_{HW_6O_{21}^{5-}}$ and C_{H^+}, by means of equation (3), the hexatungstate anion polymerization constant can be calculated.

In determining the pH of the solution by means of a glass electrode we measure the activity of hydrogen ions, and therefore the $a_H{}^+$ obtained should be corrected for the activity factor in order to obtain the actual concentration of H+ ions. For that, we carry out an approximate calculation of the concentration of the all ions assuming that the activity of hydrogen ions is equivalent to the concentration. From the values obtained, provided the concentration of sodium ion is known, the ionic strength of the solution is obtained by means of the equation

$$\mu = 1/2 \sum C_i n_i^2 \tag{11}$$

The activity coefficient f_{H^+} for the given ionic strength is calculated from the Debye-Hückel equation:

$$\log f_{H^+} = -0.51 \sqrt{\mu} \tag{12}$$

which may be assumed to be sufficiently accurate for $\mu < 0.1$. The experimental H^+-ion activity, corrected for the activity factor, gives the concentration of hydrogen ions C_{H^+} which is used for the calculation of the hexatungstate anion polymerization constant.

The extrapolation of the straight line giving the dependence of pK/-log K on $\sqrt{\mu}$ yields the value of pK for $\mu = 0$.

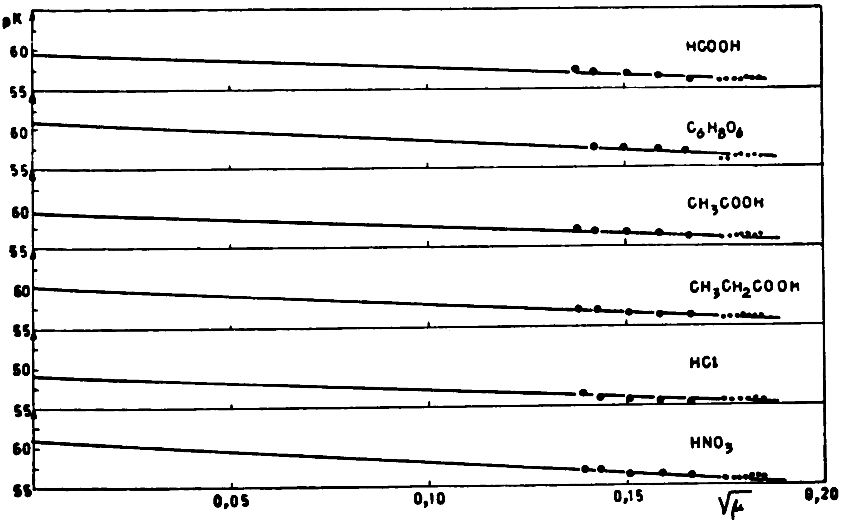

Fig. 1 Dependence of pK on $\sqrt{\mu}$ for different acids. ●-titrations; ●-method of continual variation

TABLE I

pH-values of solutions with different $C^{o}_{WO_4^{2-}}$, *and* C^{o}_{HAc}, *at* 25°C.

	$C^{o}_{WO_4^{2-}}$	C_{HAc}	pH					
			HCOOH	$C_6H_8O_6$	CH_3COOH	CH_3CH_2COOH	HCl	HNO_3
	0.01	0.001	6.85	6.89	6.85	6.83	6,78	6.75
	0.01	0.002	6.80	6.83	6.80	6.78	6.70	6.70
I	0.01	0.003	6.73	6.78	6.75	6.72	6.62	6.64
	0.01	0.004	6.67	6.75	6.70	6.67	6.58	6.60
	0.01	0.005	6.64	6.68	6.64	6.62	6.52	6.56
	0.01	0.006	6.58	6.62	6.56	6.57	6.45	6.47
	0.01	0.007	6.50	6.55	6.52	6.51	6.38	6.36
	0.009	0.001	6.97	7.00	6.86	6.88	6.70	6.80
	0.008	0.002	6.79	6.90	6.74	6.72	6.60	6.68
II	0.007	0.003	6.62	6.75	6.60	6.59	6.44	6.51
	0.006	0.004	6.43	6.57	6.42	6.42	6.25	6.34
	0.0055	0.0045	6.34	—	6.30	6.30	6.20	6.22

I. Titrations
II. Method of continual variation

The hexatungstate polymerization constant was calculated from data obtained by pH-metric investigation of the reaction of tungstate with monobasic acids⁽¹⁾. The values of pH, $C^{\circ}_{WO_4^{2-}}$ and C°_{HAc} for formic, acetic, propionic, hydrochloric and nitric acid are given in Table I. The dependence of pK on $\sqrt{\mu}$ is graphically represented in Fig. 1 for each of the acids. The values of pK for $\mu = 0$ are shown in Table II.

TABLE II

pK-values ($\mu = 0$) for $HW_6O_{21}^{5-}$ obtained with different acids

Acid	HCOOH	$C_6H_8O_6$	CH_3COOH	CH_3CH_2COOH	HCl	NHO_3	t = 25°C
pK	59.5	60.75	59.5	60.0	59.0	60.75	60 ± 1

The results show that pK is not dependent on the type of the acid used; hence, all the acids react with sodium tungstate in the same way producing polymerization of tungstate anion by the action of H^+.

Since the polymerization reactions are mainly irreversible it is essential to establish the reversibility of hexatungstate anion formation; only then will the pK-values obtained be thermodynamically valid. However, apart from the consistency of the pK for different acids, there are no other data on the reversibility of this reaction. Hence, this result represent an apparent pK-value (pK′).

School of Science
Department of Physical Chemistry, Beograd,
Institute of Chemistry, Technology and
Metallurgy, Beograd

Received January 7, 1964

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SRPSKO HEMIJSKO DRUŠTVO (BEOGRAD)

BULLETIN OF THE CHEMICAL SOCIETY Belgrade

(Glasnik Hemijskog društva — Beograd)

Vol. 29, No. 8-9-10, 1964

Editor:
MILOŠ MLADENOVIĆ

Published by
SRPSKO HEMIJSKO DRUŠTVO (BEOGRAD)
1966.

Translated and published for U. S. Department of Commerce and
the National Science Foundation Washington, D. C., by
the NOLIT Publishing House, Terazije 27/II, Belgrade, Yugoslavia
1966

Edited by
PAUL PIGNON

Printed in Beogradski Grafički Zavod, Belgrade

11th MEETING OF THE CHEMISTS OF THE SR. OF SERBIA

AND

ANNUAL CONVENTION OF THE SERBIAN CHEMICAL SOCIETY

January 25—27, 1965

HELD AT THE SCHOOL OF TECHNOLOGY
UNIVERSITY OF BEOGRAD

CONTENTS

ABSTRACTS

BASES OF MODERN CHEMICAL ENGINEERING AND ITS DEVELOPMENTAL TRENDS

S. KONČAR - ĐURĐEVIĆ

School of Technology, Beograd

A short survey of the theoretical bases of chemical engineering, its fundamental conceptions and characteristic methods, is presented.

The present importance and the future prospects of chemical reaction techniques, automatization and analogous and digital techniques in chemical engineering is underlined.

The need for creative work and for creative training of chemical engineers is indicated.

I — 1

AN APPROXIMATE MATHEMATICAL MODEL FOR TRINITRATION OF TOLUENE

M. BOGOSAVLJEVIĆ

School of Technology, Novi Sad

An analog mathematical model which approximately corresponds to the process of mono-, di-, and trinitration of toluene with sulphuric-nitric acid mixture is presented. The process proceeds continuously in a system of mixer and separator units which makes possible the recyclization of spent acids. The set of equations obtained in the form of functions G(s) makes it possible to determine, by means of an analog computer, all the main factors which affect the dynamic characteristics of the process and the system units.

I — 2

DYNAMIC CHARACTERISTICS OF THE PROCESS OF o-CRESOL DINITRATION

M. BOGOSAVLJEVIĆ

School of Technology, Novi Sad

The usual procedure for the preparation of dinitro-o-cresol consists in the sulphonation and nitration of o-cresol. However, experiments have shown that the same product may also be obtained by direct nitration with a sulphuric-nitric acid mixture. To determine more closely the principles governing the simplified procedure of direct nitration of o-cresol, it was of interest to define the characteristics of the process itself. These dynamic characteristics are given in the form of corresponding functions, G(s), for each phase of the process separately. The obtained analog mathematical scheme of the process makes it possible to determine the characteristics of the process by means of an analog computer.

I — 3

HEAT TRANSFER FROM A SHORT HEATING ELEMENT TO WATER FLOW IN AN ANNULUS

M. MITROVIĆ

School of Technology, Beograd

Heat transfer from a heated element which is part of the inner tube of an annulus to water flowing in the annulus was examined.

The length of the heated element was of the same order of magnitude as the hydraulic diameter of the annulus. Experiments were performed with small temperature difference between the heated element and the water, so that effects of natural convection were neglegible and isothermal conditions could be assumed. The heat flux or the temperature of the element surface were held constant. The results in the laminar flow region for three annuli with different equivalent diameters fitted the known expression

$$Nu = 1.86\ Re^{1/3}\ Pr^{1/3}\ (L/D_h)^{-1/2}$$

while in the turbulent region

$$Nu \sim \tau_0^{1/3}$$

where τ_0 is the wall shear stress on the inner tube.

I — 4

INVESTIGATION OF CORROSION OF SIMILAR SYSTEMS IN A MOBILE FLUID

S. KONČAR - ĐURĐEVIĆ, and O. VUKOVIĆ

Institute for Chemistry, Technology and Metallurgy. Department of Chemical Engineering, Beograd; School of Technology, Beograd

We sought correlation factors between the rate of corrosion of geometrically similar models when the corrosion is produced by a mobile fluid.

The systems studied were dynamically as well as geometrically similar.

The models were thin plates in the ratios 1 : 2 : 4. They were corroded in a mobile solution of sulphuric acid. The following magnitudes were kept constant: Reynolds number, the period of corrosion, the concentration of sulphuric acid, the temperature.

The results indicate the existence of correlation factors.

I — 5

AN EXPERIMENTAL STUDY OF HEAT AND MASS TRANSFER INVOLVING THE HUMID AIR - P_2O_5 SYSTEM

M. MITROVIĆ, and M. STRUNK

University of Missouri at Rolla, School of Technology, Beograd

Heat and mass transfer between humid air and a partially hydrated P_2O_5 layer deposited on a cylindrical surface were examined.

The H_3PO_4 produced was continually decomposed by electrolysis and P_2O_5 regenerated. The influences of air humidity, Re-number of air streaming near element, element and air temperatures, and electrolysis voltage on the coefficients of transfer were examined. Correlation diagrams for heat and mass transfer as a function of the Re-number show that countercurrent diffusion of H_2O vapor and H_2 and O_2 decrease mass and increase heat transfer in comparison with a similar system without gaseous reaction products.

These investigations open up new possibilities for air humidity measurements and measurement of eddy diffusivity in gas flows.

I — 6

APPLICATION OF DIMENSIONAL ANALYSIS TO CONSTRUCTION OF GRAPHS FOR DETERMINATION OF DIRECT DUCT EQUIVALENT DIAMETERS FOR GIVEN FLOW RATE AND PRESSURE DROP

S. CVIJOVIĆ, AND I. VRANIĆ

School of Technology, Beograd

Dimensional analysis is applied to turbulent flow of fluids and a new variable $Q = (wd^2_e)$ is introduced which is a function of the duct cross section and the flow rate.

The following criteria are obtained, expressed in terms of Reynolds number, the friction factor and the relative roughness:

$$K_1 = (fRe^2)^{1/3}, \ (K_2 = (fRe^5)^{1/3}$$

and

$$K_3 = (fRe^2 \ n^3)^{1/3}$$

where

$$K_1 = d_e a, \ K_2 = \frac{Q\rho}{\mu} \cdot a \text{ and } K_3 = \varepsilon \cdot a \qquad a = \left[\frac{\Delta_p \rho}{l\mu^2}\right]^{1/3}$$

Using these results and the known correlation $f = f(Re, n)$ the function $K_1 = f(K_2)$ is plotted with K_3 as a parameter.

This graph allows direct determination of the equivalent diameter for a given duct instead of the trial and error method commonly used.

I — 7

LOCAL MASS TRANSFER TO THIN FLAT PLATES SUBMERGED IN A MOVING FLUID

S. KONČAR-ĐURĐEVIĆ, and O. POPOVIĆ

Institute for Chemistry, Technology and Metallurgy, Beograd School of Technology, Beograd

Local mass transfer to flat plates fixed perpendicularly or at small angles to the normal to direction of flow of the fluid was studied.

Particular attention was paid to qualitative differences in mass transfer to the front and rear sides of plates under the same flow conditions. The flow rate and plate dimensions were changed. The plates were circular. Local mass transfer coefficients were determined as a function of radius. The relationship between the local coefficient and the hydrodynamic conditions is presented graphically in the form

$$Ah = ARe^{n}$$

I — 8

HEAT TRANSFER WITH SIMULTANEOUS ENDOTHERMIC CHEMICAL REACTION

S. KONČAR-ĐURĐEVIĆ, M. MITROVIĆ and S. CVIJOVIĆ

School of Technology, Beograd

The conditions of heat transfer with simultaneus catalytic decomposition of methanol into formaldehyde and hydrogen in a nitrogen atmosphere were examined. The reaction took place on a silver tube which served as the catalyst and constituted the inner tube of an annulus. The heat transfer as a function of catalyst temperature and methanol concentration in nitrogen is compared with that without chemical reaction.

The influence of the flow rate and reactant preheating was also examined.

I — 9

APPLICATION OF ADSORPTION METHOD TO THE STUDY OF MASS TRANSFER IN ULTRASONIC FIELD

R. JOVANOVIĆ and S. KONČAR-ĐURĐEVIĆ

School of Technology, Beograd

The effect of the parameters of the ultrasonic field on mass transfer from a dye solution to an anodically oxidized surface of aluminum was studied by the adsorption method developed at the School of Technology in Beograd (Depa tment of Chemical and Metallurgical Engineering). This method is based on the measurement of dye intensity by light reflected from surfaces coated with suitable adsorbents. The results obtained by this method were checked by dissolving the adsorbed dye and by carrying out the colorimetry of this solution. The accuracy in direct colorimetry of surfaces and in colorimetry of the desorbed dye differed by 0.7 to 1.9% in favor of the latter method.

The dependance of the quantity of the adsorbed dye upon the temperature, adsorption time and parameters of the ultrasonic field is shown graphically.

I — 10

APPLICATION OF ADSORPTION METHOD TO FLOW MODELING IN HEAT EXCHANGERS

S. KONČAR-ĐURĐEVIĆ, and R. RADOSAVLJEVIĆ

Institute for Chemistry, Technology and Metallurgy, Department of Chemical Engineering, School of Technology, Beograd

By adsorption of methyleneblue on silica gel conditions of hydrodynamic similarity were investigated on geometrically similar models. The models were plate heat exchangers with aluminum plates as the heat-trasfer areas coated with silica gel.

Under the conditions defined by equality of the Reynolds numbers $Re_1 = Re_2 = Re_3$ which theoretically ensure similarity of the flow, diffusion and thermal fields of the system, methyleneblue solution was introduced to the exchangers.

By reflectance measurements along the length and width of the plates the function reflectance against Re-number was obtained for geometrically symmetric points. From the results the flow field was indirectly determined, which allows determination of the thermal field by analogy.

Conditions for similarity of flow and thermal fields in the exchangers were investigated and determined.

The experiments are the starting point for the calculation of heat transfer coefficients using experimentally obtained mass transfer coefficient, and hence for flow and heat transfer modeling.

I — 11

CLASSIFICATION OF METHODS FOR CALCULATION OF WATER COOLING TOWERS

V. ALIĆ, and S. KONČAR-ĐURĐEVIĆ

School of Technology, Beograd; Prva Iskra Enterprise, Barič

It is pointed out that the many published methods for calculation of water cooling towers have not been classified, which makes their application difficult.

By systematic study of 38 published methods it has been shown that they can be classified from the following aspects:

1) the purpose; 2) the principles; 3) the way the theoretical expressions are worked out; 4) the theoretical expressions; 5) the way the parameters are defined and interpreted; 6) the accuracy.

Classification schemes according to these aspects are given.

I — 12

SOME EXPERIENCE WITH AUTOMATIC MONITORING OF BOILER FEED WATER

M. IVANIŠEVIĆ

Kombinat nafte i plina, Zagreb, Rafinerija nafte, Rijeka

The Rijeka Petroleum Refinery has its own steam power plant which provides steam for the refinery and also produces some of the electrical energy. The water to feed this plant is pumped from a stream which passes through the Refinery. The water is softened by decarbonization and ion-exchange. The water quality is checked in a laboratory. The total hardness used to be determined by the old method with soap-suds. Two years ago this check was made semi-automatic, so that the total hardness is continuously monitored and the number of operators reduced. At the same time the efficiency and accuracy is increased.

Some analytical data for the feed water and the results of the earlier and the automatic monitoring are presented.

I — 13

EXPERIMENTAL EVALUATION OF METHODS FOR CALCULATING WATER COOLING TOWERS

S. KONČAR-ĐURĐEVIĆ, and V. ALIĆ

School of Technology, Beograd, Prva Iskra, Enterprise, Barič

10 methods were evaluated experimentally.
Experimental and calculated results are compared.
In the calculations the Merkel criterion was used.
Correction factors are given.

I — 14

ESTIMATION OF THE LENGTH OF A VERTICAL PNEUMATIC DRYING TUBE

B. PEROVIĆ

Prva Iskra Enterprise, Barič

The necessary time of contact between moist particles and the stream of hot air in pneumatic drying plants is very short. Generally the drying time varies from one to eight or nine seconds, according to the moisture content of the feed material and its distribution in individual particles.

This short drying time makes it necessary to rigorously determine factors affecting it. One of these is the drying tube length.

Using the basic kinematic laws, a formula for estimating the vertical tube length has been worked out. It has the form

$$H = f(t, w, d_e)$$

where

H is the tube length;
t the required drying time;
w the necessary air velocity;
d_e the equivalent particle diameter.

I — 15

A NEW AERATION SYSTEM FOR CONTINUOUS MICROBIOLOGICAL PROCESSES

V. KRAJOVAN, S. VESELINOVIĆ, and S. GAĆEŠA,
School of Technology, Novi Sad

In modern continuous microbiological processes the energy spent on aeration and all other operations is minimized. There are many different aeration systems which meet the needs of production more or less successfully. Data about the performance of these systems are often contradictory and incomplete.

The velocity of oxygen dissolution during aeration depends mostly on rate of renewal of the liquid-gas interface. Aeration devices must create sufficiently large interface areas to allow rapid renewal of the contact area. Therefore air mixing must be such that the air is introduced tangentially to the direction of movement of the liquid. Inside the fermentor there should be static elements and the streams of liquid must collide. All the mass inside the fermentor must be in a state of homogenous mixing of gas and liquid in the form of foam.

A new aeration system ("Neoplanta") has been developed. In a pilot fodder yeast plant producing 300-400 kg dry yeast per day we obtained 56.5 % as dry yeast of the input of reducing substances with a concentration of reducing substances in the feed of 30 g/l and an aeration rate of 28.6 m^3 per kg dry yeast matter. With a feed concentration of 25 g/l, these figures were 61 % and 28.2 m^3 respectively.

On an industrial scale the aeration energy would be 0.4-0.5 kWh/kg dry yeast substance.

I— 16

EVALUATION OF SUGAR INDUSTRY EVAPORATION PLANT WITH STEPWISE EXPANSION OF CONDENSATE

D. ĐORĐEVIĆ

School of Technology — Beograd

The four-step evaporation plant serves to show that the consumption of vapor in the first unit of the plant with stepwise expansion is about 10 % lower than when the condensate is not expanded. To shorten the long calculation, even though an approximate method is used, the calculation should first be made without taking into account the expansion of the condensate, the calculated consumption of fresh vapor should then be decreased by 10 %, and the calculation then repeated starting from the first unit of the plant and taking into account the expansion of the condensate.

New formulas enabling an accurate evaluation of plant utilizing vapors obtained by stepwise expansion of the condensate are given.

I — 17

ENERGETIC EVALUATION OF GAS DRIERS IN THE PRODUCTION OF SULPHURIC ACID BY THE CONTACT PROCESS

D. DELIĆ and D. RADOVANOVIĆ
School of Technology — Beograd

The usual heat balances, used for obtaining the utility coefficient of a process are not always satisfactory. In recent times, energetic evaluation of a process is carried out by means of a reversibility coefficient on the basis of energy balance.

In this paper the evaluation of gas driers in sulphuric acid production by contact process is performed by means of a reversibility coefficient. The energy balance was obtained on the basis of matter, entropy and enthalpy balances, and was then used to determine the reversibility coefficient of the gas driers.

I — 18

KINETICS OF DYE PENETRATION THROUGH MASS OF TEXTILE FIBERS DYED IN ULTRASONIC FIELD

R. JOVANOVIĆ

School of Technology, Beograd

The effect of ultrasonic field parameters on the diffusion of the dye through the fiber mass was studied by measuring the position of the diffusion front microscopically, and determining the changes of dye concentrations from the surface towards the fiber center. The distribution of dye concentration on a cross-section of the fiber was measured by means of a specially constructed microphotometer. Investigations have shown that the ultrasound affects the depth of dye penetration through fiber mass in two ways.

The presence of cavities increases the gradient of dye concentration, on account of which the rate of mass penetration by diffusion is greater. An intense ultrasonic field in which there are no cavities produces changes in diffusion permeability of fiber and therefore the activation energy of the dyeing process is lowered.

I — 19

ABSORPTION OF CARBON DIOXIDE IN AQUEOUS SOLUTIONS OF SODIUM SILICATE

A. TASIĆ, S. KONČAR-ĐURĐEVIĆ, and V. VALENT

School of Technology, Beograd

The absorption of carbon dioxide in aqueous solutions of sodium silicate was studied.

The influence of concentration, gas flow rate and rate of mixing on the absorption involving chemical reaction, measured by means of the pH change, were studied.

The optimal initial concentration of the solution was determined, at which the end of reaction and the beginning of gel-structure formation coincide.

I — 20

STUDY OF THE POSSIBILITY OF REMOVING ABS FROM AQUEOUS SOLUTIONS BY FOAM SEPARATION

F. ZDANSKI, S. KONČAR-ĐURĐEVIĆ, and N. JOVANOVIĆ

School of Technology — Beograd

The separation of alkyl benzene sulfonate from aqueous solutions in the concentration range 0.5 g ABS/l to 0.01 g ABS/l has been studied. The separation was done by foaming achieved by blowing air into the solution.

The relationships between the enriching ratio, the air flow rate, the blowing time and the initial concentration were studied.

The reduction of the ABS concentration in the solution was up to 87 %, while the volume reduction was relatively small. The enriching ratio was up to over ten.

I — 21

PROPOSAL FOR A DEVICE FOR SUCCESSIVE WASHING AND DRYING OF SOLID MATERIALS

S. KONČAR-ĐURĐEVIĆ, B. ĐORĐEVIĆ, F. ZDANSKI, and A. TASIĆ

Institute for Chemical, Technical and Metallurgical Research, Beograd
School of Technology — Beograd

The development of a device which permits washing or extraction and drying of solid materials in the same apparatus is described.

Some characteristic measured parameters are given. The advantages of this type of apparatus compared with conventional devices are pointed out.

I — 22

DETERMINATION OF THE CONCENTRATION CHANGE OF ONE COMPONENT OF A POWDERED MIXTURE IN THE SURFACE OF A DRIED LAYER OF ITS SUSPENSION

V. RAJKOVIĆ

School of Technology

The analysis of the process in the layer of suspension during drying is outlined. A method is given for calculating the concentration change of one component of a dispersed mixture in the surface of a dried layer of its suspension.

The method was verified experimentally in the case of Sb_2O_3 and Sb by quantitative X-ray diffraction analysis.

I — 23

A CONTINUOUS BITUMEN BLOWER WITHOUT CONTAMINATION OF THE ATMOSPHERE

A. MOŠIĆ, E. KNEŽEVIĆ, J. HOLJAC, R. BUDEČ and S. CURIĆ

Rafinerija nafte — Sisak

In production capacities larger than 100 tons per day, a plant for continuous blowing of bitumen has great advantage over blowing in batches. It allows better utilization of the reactor volumen, better contact of the crude bitumen and air, uniformity of the quality of the product and easier control of the process.

Plant for continuous blowing of 150 tons of bitumen per day with two main and one accessory reactors was built in the petroleum refinery in Sisak. Air, either alone or diluted with water vapor, is introduced into the main reactor. The accessory reactor serves for completition of the reaction and the cessation of foaming of the mass. Thus, blowing of air or water vapor into the third reactor is not necessary. The crude material is heated to the starting reaction temperature indirectly by means of distilled oil which receives heat partly from worked-up bitumen and partly from a special tube oven and then transmits it to the crude bitumen in the main, entering, automatically regulated heat exchanger. This avoids the local overheatings and chemical decompositions which bring about the formation of coke and plant standstills.

The problem of atmosphere contamination was successfully solved by washing waste mists in a special scrubber and by burning up waste gases which have a bad smell and contain cancerogenic materials.

The plant was built on site from the columns and vessels of unused old tanks for the primary distillation of petroleum. The material of old distillation tanks was first examined by mechanical and metallographic methods. The idea for the plant originated in the factory with the aim of utilizing all available material and reducing expences to a minimum; in fact the existing plant was simply reconstructed.

This reconstruction was done after two-years experimentation whereby it was established that bitumen for civil engineering could be obtained from mixed-basic crude petroleum from Posavina.

II — 1

CONDITION OF EQUILIBRIUM BETWEEN A SOLID STATE AND ITS VAPOR

J. M. ŽIVOJINOV

Institute of Physics, School of Technology

From statistical and quantum mechanical consideration of the equilibrium between a solid and its vapor at temperatures between 0°K and the triple point it is found that the equilibrium condition is such that the ratio of the partition functions of vapor and solid must be constant. It is shown that this ratio is the same, however many particles (atoms or molecules) transfer from one phase to the other, provided that the total energy of the vapor-solid system is constant.

II — 2

SATURATED VAPOR PRESSURE OF MONO-ATOMIC ELEMENTS

J. M. ŽIVOJINOV

Institute of Physics, School of Technology

A theoretical equation of state is given which determines the pressure of a mono-atomic element as function of temperature. It contains constants characteristic for a given elements Pc — critical pressure, Tc — critical temperature, s — sublimation energy at 0^0K, w — melting energy at triple point, R — universal gas constants. In comparison with Van der Waals equation it may be said that now the constant s-w/RT is known for every mono atomic substance.

II — 3

MECHANISM OF THE EQUILIBRIUM PROCESS IN THE "SOLID - LIQUID" LAYER

R. DESPOTOVIĆ, LJ. A. DESPOTOVIĆ and M. J. HERAK
Ruđer Bošković Institute, Zagreb

From study of the adsorption-desorption equilibrium in solid-liquid systems the quantitative ratios for dynamic equilibrium between cations of various valencies in the adsorption layer have been determined.

These results may also be applied in the study of decontamination processes. The results of experiments on europium decontamination from polystyrol and DURAN 50 glass surfaces are given and compared with quantitative data for the model systems.

II — 4

ELECTRON-MICROSCOPIC INVESTIGATION OF POROUS STRUCTURE OF CATALYSTS IN CARBON MONOXIDE CONVERSION

P. PUTANOV, D. KARAULIĆ and Ž. JOVANOVIĆ

Institute for Chemistry, Technology and Metallurgy Beograd

The surface configuration of various catalysts for the conversion of carbon monoxide has been investigated.

Reproduction of catalyst surfaces was carried out by the method of replicas; a polystyrene film was used for the preparation of the first reprint.

Data obtained in the study of the porous structure of investigated catalysts may be used for a complex estimation of their qualities, especially with respect to optimal diffusion of reactants in the conversion process.

II — 5

RELATION BETWEEN POROSITY AND SPECIFIC SURFACE OF IRON-CHROMIUM CATALYST IN CARBON MONOXIDE CONVERSION

P. PUTANOV, A. TERLETCKI, Ž. JOVANOVIĆ and D. KARAULIĆ
Institute for Chemistry, Technology and Metallurgy
Beograd

In the study of the relation between the activity and textural properties of catalysts for the conversion of carbon monoxide, a detailed investigation of the relation between the porosity and specific surface of iron-chromium catalysts was performed.

Porosity was determined by means of apparent and actual densities, and specific surfaces were determined by the BET method. The results show that there is no strict dependence among the textural properties observed, but it would be possible to combine these magnitudes in order to achieve the desired properties of the catalyst.

II — 6

AN ATTEMPT TO INTERPRET THE MECHANISM OF THE DIRECT SYNTHESIS REACTION OF METHYL-CHLOROSILANES ON THE BASIS OF THE ELECTRONIC THEORY OF CATALYSIS

M. DRAGOJEVIĆ

School of Technology, University of Beograd

Starting from the fact that minimal quantities of admixtures can have an important influence on the rate of the direct synthesis reaction of methylchlorosilanes, a new mechanism of this reaction is proposed. The considerations are based on the semiconducting and doping properties of silicon in the light of the electronic theory of catalysis.

II — 7

THERMODYNAMICS OF THE HYDROLYSIS OF POLYVALENT METAL IONS

Z. PAVLOVIĆ and D. ĐORĐEVIĆ

School of Technology, Tuzla

The process of ion hydrolysis has been experimentally investigated by many authors. From their experimental values for the hydrolysis constants the standard free energies ΔF° (kcal/mol) for individual products of hydrolysis of metal ions have been worked out. By comparing the ΔF° value in a water solution with that for the final product of the hydrolysis, i. e. the metal hydroxide, and with the calculated ΔF° values for the hydrolysis products, a linear relationship between ΔF° for hydrolysis products and the number of bound OH^- groups was found.

According to M. W. Latimer certain metal ions, i. e. their hydrolysis products, deviate from this rule, e.g. In^{3+}. However according to Biederman and Norman the ΔF° calculated for $InOH^{++}$ from K - hydrolysis obeys the above linear relationship. Lineartity has also been confirmed for polynuclear ions which are formed by hydrolysis interaction if the OH^- groups are reduced to one metal ion. Using this linearity it is possible to predict graphically ΔF°s for metal ion hydrolysis products which have not yet been determined experimentally or for which the standard free energies are not known, using the known ΔF° values for the free ion and the metal hydroxide. Formulas have been established for calculating the standard free energy ΔF° for the hydrolysis products of metal ions.

II — 8

THEORETICAL AND EXPERIMENTAL THERMODYNAMICS OF PRECIPITATION OF Mn^{2+} IN THE PRESENCE OF AIR

Z. PAVLOVIĆ and R. POPOVIĆ
School of Technology, Tuzla

The behaviour of Mn^{2+} ions in sulphate solution during precipitation and the influence of atmospheric oxygen on an insufficiently isolated system is considered from the standpoint of electrochemical thermodynamics. The system Mn^{2+} - water solution and Mn^{3+} - water solution are theoretically treated separately. The homogeneous and heterogeneous equilibriums of the system which are observed on the log a - pH graph are considered. The equilibriums of the oxidation of manganese on the V. A. (Voltcalories) - pH graphs are also considered.

The effect of oxygen on the precipitation of $Mn(OH)_2$, and the possibility of its conversion into oxides — MnO, Mn_2O_3, Mn_3O_4, MnO_2, were examined by studying the pH and the way the final equlibrium is established.

Marked changes in the quantity of NaOH required to neutralize the N_2SO_4 present in the system and after precipitation were noted. From the obtained results it may be concluded that no one of the above oxides is the final precipitate, but that it is actually a heterogeneous mixture consisting of them.

II — 9

VARIOUS TRANSFORMATIONS IN PETROLEUM-COKE

B. PANDIĆ

Ruđer Bošković Institute, Zagreb

The process of graphitization of petroleum-coke in the temperature range 1400 to 2800 °C was investigated. Above 1900 °C, when most of the primitive crystallites formed are of hexagonal orientation, the crystallization proceeds simultaneously in two independent ways. Some of the crystallites continue to grow in rhomboidal modification which, at 2200 °C, passes over into hexagonal. At 2400 °C, these crystallites acquire an ideal arrangement, forming a graphite phase. The rest of the crystallites grow more slowly, without achieving complete order, thus forming a nongraphite phase.

The process of crystallite growth was investigated and the volume ratio of phases is given in a temperature-time diagram.

II — 10

REACTIONS BETWEEN ORGANIC AND MINERAL MONOBASIC ACIDS AND Na_2WO_4

M. V. ŠUŠIĆ, D. S. VESELINOVIĆ, and D. Ž. SUŽNJEVIĆ

School of Science, Beograd and The Institute for Chemistry, Technology and Metallurgy, Beograd

The reactions between Na_2WO_4 and HCOOH, $C_6H_8O_6$, CH_3COOH, CH_3CH_2COOH, HCl and HNO_3 have been studied by pH and conduction measurements using the continual variation method and titration. It has been found that organic acids form complex anions of the type $[WO_3Ac_2]^{2-}Ac^-$ (monobasic acid anion). Organic and mineral acids, through the influence of the H^+ ion, form two types of polyanions, $HW_6O^{5-}_{21}$ and $W_4O^{2-}_{13}$ and strong mineral acids exclude colloidal tungstic acid. Hexatungstic anion forms at pH $\approx 6 — 7$, and metatungstic and complex anion simultaneously at pH < 6. A provisional value of the hexatungstic anion polymerization constant for ionic strength $\mu = 0$ at 25 °C, $pK' = 60$ is calculated from the pH measurements.

II — 11

COMPLEX COMPOUNDS OF l-ASCORBIC ACID AND METAL IONS IN ACID MEDIUM

D. S. VESELINOVIĆ and M. V. ŠUŠIĆ

School of Sciences, Beograd and Institute for Chemistry, Technology and Metallurgy, Beograd

Studies of reactions of UO_2^{++}, Zn^{++}, Co^{++}, Ni^{++}, Mn^{++} Pb^{++}, Cd^{++}, Ca^{++} and Al^{+++} ions and l-ascorbic acid, by the continual variation method of measurement, have shown that all the bivalent ions form cationic complexes of the $[MeA]^+$ type (Me^- bivalent metal ion; A^- anion of monobasic l-ascorbic acid). Aluminum also forms an $[AlA_2]^+$ cationic complex. Dissociation constants of these complexes for ionic strength $\mu = 0$, at 25 °C, have been determined [pK = 3.04 (U), pK = 1.4 (Co), pK = 1.05 (Ni), pK = 1.1 (Mn), pK = 1.0 (Zn), pK = 1.8 (Pb), pK = 1.3 (Cd), pK = 1.05 (Ca), pK = 3.7 (Al)].

II — 12

STRUCTURAL FORMULA OF TINCALCONITE AS DETERMINED BY PROTON MAGNETIC RESONANCE

B. BELINA and Z. VEKSLI

From the proton magnetic resonance spectra of tincalconite recorded between — 153 °C and + 80 °C. OH — groups and water molecules were established. By dehydration at 88 °C over P_2O_5 in vacuum tincalconite loses three water molecules per formula unit with an amorphous remainder. The proton resonance line-shape of this dehydration product corresponds to the OH-group spectrum. The comparison of the experimental curve at low temperatures with theoretical curves for two different OH : H_2O ratios suggests that $Na_2[B_4O_5(OH)_4]. 3H_2O$ is the correct formula for tincalconite. This means the polyanion is the same as in borax, which fully agrees with crystallochemical requirements in this series of compounds.

II – 13

SOME PROBLEMS CONNECTED WITH PREPARATION OF SULPHUR - CONTAINING SAMPLES FOR MASS - SPECTROMETRIC ANALYSIS

D. STEFANOVIĆ, L. KLASINC, D. PAVLOVIĆ and S. AŠPERGER
Ruđer Bošković Institute, Zagreb

There are several methods for preparing samples for mass-spectrometric isotope analysis of sulphur. These methods were compared to find the most convenient one for organic compounds. The influence of impurities on the measured isotope ratios is discussed.

II — 14

ALKALINE OXIDIZING ROASTING OF PYROLUSITE

S. ĐORĐEVIĆ, P. M. RAKIN and M. VOJNOVIĆ

School of Technology, Beograd and Institute for Chemistry, Technology and Metallurgy, Beograd

A number of experiments have been made on oxidizing roasting of pyrolusite to find the conditions for the highest yield of potassium manganate.

To avoid difficulties which occur at the beginning of heating of the charge, a new way of heating was developed whose essential feature is alkaline oxidizing heating in two operations.

Using raw materials of specified quality, the yield of potassium manganate was examined as a function of: 1) heating temperature, 2) heating time, 3) partial pressure of oxygen and water vapor in the reaction atmosphere, 4) grain size of raw materials.

The results are presented in tables and graphs and discussed.

II – 15

ANODIC OXIDATION OF AMMONIA ON PLATINIZED PLATINUM ELECTRODE

A. R. DESPIĆ, D. M. DRAŽIĆ and P. M. RAKIN
School of Technology, Beograd

A galvanostatic method was used to follow the potential-time dependence during polarization of a platinized platinum electrode in strong alkaline solutions of ammonia at different concentrations. The experimental results were used to determine characteristic electrode parameters. Some effects were observed which have not been reported in the literature so far. Possible mechanisms of anodic oxidation are discussed.

II—16

ANODIC OXIDATION OF ETHANOL

V. DRAŽIĆ, D. DRAŽIĆ and B. NIKOLIĆ

School of Technology and Institute for Chemistry, Technology and Metallurgy, Beograd

The establishment of specific potentials at a platinized platinum electrode in 1N KOH containing ethanol has been examined. The galvanostatic method for determining the behavior structure of the total electrode overpotential at different anode currents was used.

On the basis of the results the mechanism of the electrochemical reaction of the oxidation of ethanol is discussed.

II – 17

POWDER HYDROGEN ELECTRODES

D. M. DRAŽIĆ, A. R. DESPIĆ and I. V. KADIJA

School of Technology and Institute for Chemistry, Technology and Metallurgy, Beograd

The influence of the construction of the holder of a powder electrode on the contact between the particles of the active powder and the corresponding ohmic potential drop has been investigated. A construction has been worked out which practically eliminates these effects.

It has been shown that such electrodes, beside their use in fuel cells, can be used for laboratory examination of the electrochemical activity of different catalytically active powders.

The electrochemical characteristics of three different kinds of active powder were determined: Raney-nickel, specially treated fibrous nickel, and porous nickel.

II—18

A POWDER OXYGEN ELECTRODE

A. R. DESPIĆ, D. M. DRAŽIĆ and G. A. SAVIĆ-MAGLIĆ

School of Technology and Institute for Chemistry, Technology and Metallurgy, Beograd

The catalytic activity of Raney-silver powders of different grain size distribution has been investigated. The results show that the Raney-silver powder electrode has similar electrochemical characteristics to the Justi-type sintered Raney-silver electrode.

The possibility of decreasing the weight and cost of the electrodes by using nonmetalic materials for the inactive supports of the catalytically active components was examined. It has been shown that silver-plated glass fibres and particles of a cationic exchange resin, packed in a suitable way, give electrodes of the same quality as those made with Raney silver.

II – 19

STUDY OF ELECTROLYTIC OXIDATION OF POTASSIUM MANGANATE

P. S. TUTUNDŽIĆ, M. VOJNOVIĆ and P. RAKIN

Institute for Chemistry, Technology and Metallurgy Beograd, and School of Technology Beograd

An attempt was made to follow the process of electrochemical oxidation of potassium manganate by measuring the potential of an inert electrode immersed in the electrolyte during electrolysis. This avoids the use of standard analytical methods which are not simple and do not give satisfactory results.

A platinum electrode was used. Its potential was measured relative to an Hg/HgO reference electrode and was registered continuously during the electrolysis. The results indicate that this method could be used for automatization of the process.

II—20

ADSORPTION OF ARSENIC ON FERIC HYDROXIDE

S. ĐORĐEVIĆ, LJ. RIKALOVIĆ, and M. TUCAKOV
School of Technology, Beograd

In the hydrometallurgy of zinc the solution is commonly purified of arsenic by precipitation with ferric hydroxide, but there are different opinions about how the arsenic precipitates. Some authors consider that it is adsorbed on ferric hydroxide and others that it reacts with ferric hydroxide to form compounds.

By precipitating ferric hydroxide under the same conditions as in the leach we proved that arsenious and arsenic ions are adsorbed on it, because it was possible to fit the results to Freundlich's adsorption isotherm.

II–21

LIQUID-VAPOR EQUILIBRIUM AND THERMODYNAMIC PROPERTIES OF AMMONIA-DIMETHYL ETHER AND SULFUR DIOXIDE-DIMETHYLETHERSYSTEMS

J. PUPEZIN, S. RIBNIKAR, Ž. KNEŽEVIĆ, and V. ĐOKIĆ

Liquid-vapor equilibrium data for the systems Me_2O-NH_3 and Me_2O-SO_2 are presented and used to evaluate the excess thermodynamic functions.

The system Me_2O-NH_3 forms a positive azeotrope with mole fraction 0.33 in Me_2O at the normal boiling point of —37.5 °C. The excess free energy is almost regular at —50 °C, with a maximum of 150 cal/mole. The maximum of the excess enthalpy is 110 cal/mole at a mole fraction of Me_2O 0.45.

The excess entropy is negative. The results are discussed with regard to weakening of the hydrogen bonds in liquid ammonia by addition of dimethyl ether.

The system Me_2O-SO_2 forms a negative azeotrope with mole fraction of Me_2O 0.41 at the normal boiling point of 0.4 °C. The excess free energy, enthalpy and entropy are negative, and almost symmetrical; their values in the equimolar mixture at —32.5 °C are —0.45, —1.20 and —0.75 kcal/mole, respectively. It was found that the theory of ideal associated mixtures can be successfully applied to the Me_2O-SO_2 mixture.

II – 22

MASS SPECTROMETRY ISOTOPE ANALYSIS OF CHLORINE BY THE SURFACE IONIZATION METHOD

K. ZMBOV

Boris Kidrič Institute of Nuclear Sciences, Vinča

A mass spectrometry method for isotope analysis of chlorine from solid samples is described. $BaCl_2$ samples are ionized in a surface ionization ion source.The temperature dependence of the Ba^{++} and $BaCl^+$ ion currents are measured. Ion intensities of the order of 10^{-11} amps are obtained with microgram samples, allowing precise isotope analysis.

II—23

SECONDARY α-DEUTERIUM ISOTOPE EFFECTS IN THE REACTION OF 2-PHENYLETHYLTRIMETHYLAMMONIUM ION WITH HYDROXIDE ION IN AQUEOUS SOLUTION AND WITH ETHOXIDE ION IN ETHANOL

L. KLASINC, D. PAVLOVIĆ, S. AŠPERGER

Ruđer Bošković Institute, Zagreb

Secondary α-deuterium isotope effects in the reaction of 2-phenylethyltrimethylammonium iodide with ethoxide ion in ethanol at 40.0° and with hydroxide ion in aqueous solution at 97.0° have been found to be very small. The results suggest that the hydrogen compound reacts slightly faster than the deuterium compound. The secondary α-deuterium isotope effect in the reaction of 2-phenylethyl bromide with sodium ethoxide in ethanol is appreciably larger — 9 percent per deuterium atom at 59.8°. The implications of these results with regard to the reaction mechanism are discussed.

II—24

NEW METHOD OF DETERMINING THE ACTIVITY OF THETIN-HOMOCYSTEINE METHYL-PHERASES

P. BERKEŠ-TOMAŠEVIĆ, M. SLAVIĆ, and I. BERKEŠ

The new method for determining the activity of thetin-homocysteine methylpherases is described. The homocysteine left after transmethylation is determined. Homocysteine is also assayed in an aliquot without dimethyl-β-propiothetin. Methionine is calculated from the difference. To get the differences of the concentration of homocysteine the total amount of thiol group, i.e. —S—S— and —SH functions, was measured amperometrically after Benesch and Benesch. Ten or more samples were done in parallel. The results are evaluated statistically and presented in tables.

Using this method the optimum pH and the optimum concentrations of both substrates were determined.

III – 1

THE STRUCTURE AND REACTIONS OF SOME MERCAPTOPYRIDAZINES

A. POLAK, B. STANOVNIK and M. TIŠLER

Department of Chemistry
University of Ljubljana

Among the heterocyclic compounds with thicamide groups in the ring system, 3-mercapto-6(1H)-pyridazinthione is particularly interesting with regard to structure and reactivity. The pK values determined and spectroscopic evidence show that it exists predominantly in the monomercapto monothione form with a thioamide group with a strongly dipolar character.

We tried some reactions characteristic for thiols with this compound. We perfomed some addition reactions with acrylonitrile, ethyl acrylate and cyclopentadiene. Addition of all these compounds invariably involved the 3-mercapto group, as was proved by independent synthesis involving alkylation which gave identical products. The addition product with cyclopentadiene further reacted in a Diels-Alder reaction with another molecule of cyclopentadiene; the product was identical with that of the reaction with dicyclopentadiene.

Hydroxymethylation and aminomethylation of the compound were also studied. Hydroxymethylation yielded a bis-hydroxymethyl derivative. It was established that one of the hydroxymethyl groups was bound on the ring nitrogen at position 1 of the pyridazine system and the other on the exocyclic sulfur at position 3. Aminomethylation yielded, depending on the reaction conditions, a mono-Mannich base or a bis-Mannichbase. With further chemical transformations it was shown that mono-aminomethylation proceeds at position 1 of the pyridazine system. However the bis-aminomethylated product is analogous to the bis-hydroxymethyl derivative. Further evidence which supports the proposed structures was obtained by comparing the UV spectra with those of the parent compounds. Pyridazines which contain only one thioamide group, e.g. 3-chloro-6(1H)-pyridazine-thione, are only aminomethylated at position 1.

III—2

NITRATION AND SULFOCHLORINATION REACTIONS OF N-METHYLACETANILIDE

O. STOJANOVIĆ, G. BONČIĆ-CARIČIĆ (Mrs) and Đ. DIMITRIJEVIĆ

Institute of Organic Chemistry, School of Technology Beograd

In previous papers we stated that with N-methylacetanilide it was not possible to perform the well known Friedel-Crafts reaction, which proceeds without difficulties with acetanilide. To study the effect of the N-methyl-acetyl group, we investigated the reactions of nitration and sulfochlorination of N-methylacetanilide.

Nitration of N-methylacetanilide was more difficult than nitration of acetalinide, which is in agreement with recent literature data. However it was successful, and produced a good yield of *o*-and *p*-derivative. The *o* to *p* ratio was not determined.

It was also possible to perform the sulfochlorination reactions of N-methylacetanilide, but it was noted that the necessary conditions were a little more strict. A very poor yield was obtained and according to IR spectrography mainly *o*-derivative.

III—3

REACTIVITY OF PYRIDINEDICARBOXYLIC ACID MONOMETHYLESTERS WITH DYPHENYLDIAZOMETHANE IN ETHANOL

M. MUŠKATIROVIĆ, Ž. TADIĆ and Đ. DIMITRIJEVIĆ
Institute of Organic Chemistry, School of Technology, Beograd

Earlier we studied pyridinemonocarboxylic acids by means of the rate constants of their reactions with DDM in ethanol, and concluded that their reactivities, with regard to the position of the carboxylic group, decrease in the order $4>2>3$. This order disagrees to some extent with previous opinions.

In the present work, the reaction rates of pyridinedicarboxylic acid monomethylesters with DDM in ethanol were measured. It was concluded that the relative position of the carboxylic and carbmethoxy groups being the same, the carboxylic group's reactivity depends on its position relative to the nitrogen atom in the pyridine nucleus as in the case of pyridinemonocarboxylic acids. In other words, the order of reactivity is $4>2>3$.

It was further concluded that the rate constants depend on the presence and position of the nitrogen atom in the pyridine nucleus, while the influence of the carbmethoxy group is limited almost exclusively to steric hindrance of carboxylic participation in the resonance of the pyridinecarboxylic acid molecule.

III — 4

CONTRIBUTION TO THE STUDY OF COPOLYMERS OF UNSATURATED POLYESTERS ON THE BASIS OF 2,2-(DIPHENYL-4, 4-DIHYDROXYETHYLETHER)-PROPANE

B. BASTIĆ and B. TOMIĆ

School of Technology, Beograd and Idol Chemical Products, Novi Sad

Glycolic components of unsaturated polyesters were replaced by 2,2-(diphenyl-4,4-dihydroxyethylether)-propane whereas the unsaturated (phtallic and maleic) and saturated dicarboxylic acid remained unchanged. On account of the increased distance between the ester groups, the properties of the polycondensate and of its copolymers were altered. The copolymerization of the polycondensate was first effected, and then the action of various chemical reagents was investigated. Considerable improvements of properties with respect to copolymer polycondensates containing glycolic components were established. The presence of free hydroxyl groups was proved by isocyanate; subsequent esterification of these groups with fatty acids was followed by copolymerization with monomers. Copolymers were found to be more resistent to the action of mild alkalies, glycol, glycerol and some other chemical agents.

III — 5

EFFECT OF SOLVENT ON PROPERTIES OF POLYSTYRENE OBTAINED BY STEREOSPECIFIC POLYMERIZATION

P. PUTANOV, S. PETROVIĆ and B. VUČUROVIĆ
Institute for Chemistry, Technology and Metallurgy Beograd

Polystyrene was polymerized in different solvents in the presence of Ziegler's catalyst $Al(C_2H_5)_3 — TiCl_4$. The effect of these solvents on the stereospecifity of the polymerization was investigated.

The solvents studied were benzene, toluene and xylene.

The effects of the solvents under identical experimental conditions was studied by comparing molecular weights, specific gravities, melting points, color and yields of polymers.

III—6

CONDENSATION OF *o*-AMINOPHENOL WITH PHYRIDINECARBONIC ACIDS

B. BASTIĆ and M. PILETIĆ

School of Technology, Institute for Organic Chemistry, Beograd

We earlier published the results of reactions between pyridinemonocarbonic acids and quinoline and cinchomeronic acid with *o*-aminothiophenol, in the presence of polyphosphoric acid.

In this work we condensed the same acids with o-aminophenol, in the presence of polyphosphoric acid as catalyst and solvent— without which the reaction will not go. The reaction products were the corresponding pyridyl-benzoxsazoles, some of them previously unknown. In some cases intermediaries, which indicate the course of the reaction were isolated.

III—7

SYNTHESIS OF BIS (2-CHLORETHYL) FORMAL

V. REKALIĆ, M. TENC-POPOVIĆ and S. RADOSAVLJEVIĆ

Institute of Inorganic Chemistry, School of Technology and Institute for Chemistry, Technology and Metallurgy, Beograd

The synthesis of bis (2-chlorethyl) formal with and without addition of catalysts is reported. Calcium chloride and sulfuric and hydrochloric acid were used as catalysts. The following conditions were determined: quantities of catalysts, reaction time and temperature.

III—8

REACTIVITY OF PYRIDINE-2-CARBOXYLIC ACIDS 1-OXIDES IN THEIR REACTION WITH DIPHENYLDIAZOMETHANE

Đ. DIMITRIJEVIĆ, Ž. TADIĆ and M. MIŠIĆ-VUKOVIĆ
Institute of Organic Chemistry, School of Technology Beograd

In previous papers we reported on studies of the reactivity of pyridine monocarboxylic acid-l-oxides with diphenyldiazomethane. The rate constants were compared with the corresponding ones for pyridinemonocarboxylic acids, and the exceptionally low reactivity of the 2-carboxylic group was observed. It was concluded that this fact cannot be explained only in terms of electron density effects due to the particular relative position of the carboxylic and the 1-oxide group.

To learn more about this phenomenon the reaction rate constants of monomenthylesters of pyridine carboxylic acid-1-oxides and of pyridine dicarboxylic acid-1-oxides with a 2 carboxylic group were investigated.

It was expected that determining the rate constants under suitable reaction conditions would give more information about the reactivity of the α-carboxylic group.

By comparing the rate constants obtained in this way and using data about the reaction products and the IR spectra, it was concluded that there is a hydrogen bond between the carboxylic group in position 2 and the $—N^{+}O^{-}$ group, which explains the low reactivity of this carboxylic group.

III – 9

MAXIMUM OVERLAP HYBRIDIZATION IN CYCLOPROPANE AND SOME RELATED MOLECULES

Z. MAKSIĆ and M. RANDIĆ

Ruđer Bošković Institute, Zagreb

The hybridization in cyclopropane, spiropentane, nortricyclene and 1,1-dimethyl cyclopropane is calculated on the criterion of maximum overlap. The s-p content in the general hybrids is found to be sensitive to changes in the interorbital angle Θ_{ij}. The results give information about the strain associated with bent bonds and its delocalization. The procedure also allows calculation of skeletal angles, such as $C_1 C_2 C_3$ in nortricyclene, which determine the geometry of the molecule.

III — 10

1, 4-DI-*n*-ALKYLBENZENES — DETERMINATION OF THEIR STRUCTURES BY PHYSICAL METHODS

J. JOVANOVIĆ

Petroleum Institute, Hanover and School of Technology — Beograd

A) Symmetrical 1,4-di-*n*-alkylbenzenes containing 16, 20, 24 and 26 C-atoms in primary *n*-alkyl chains were synthesized by the following reaction steps: alkanophenone, alkylbenzene, and*p*-alkyl alkanophenone.

B) Symmetrical 1,4-di-*n*-alkylbenzenes containing 16 and 30 C-atoms in secondary *n*-alkyl chains were synthesized by the following reaction steps: alkanophenone, dialkylphenyl carbinol, alkylbenzene, *p*-alkylalkanophenone and dialkyl-(*p*-alkyl)-phenyl carbinol.

Their stuctures were determined by means of infra-red spectra, gas chromatography and mass spectrometry.

III—11

THE EFFECT OF ALCOHOLS ON SOME PROPERTIES OF DODECYLBENZENE-SULFONATE SOLUTIONS

D. DŽOKIĆ

School of Technology, Beograd

Some properties of dodecylbenzenesulfonate solutions in the presence of methyl, ethyl, n-butyl, n-amyl and n-hexyl alcohol were investigated.

The wetting and foaming increase with increasing dodecylbenzenesulfonate and alcohol concentration in the following sequence: methyl — ethyl — n-butyl — n-amyl — n-hexyl.

The effect of alcohol on the surface tension of dodecylbenzene sulfonate was also determined.

III – 12

TEXTILE DYEING IN PRESENCE OF ORGANIC SOLVENTS

D. DŽOKIĆ and R. TRAJKOVIĆ
School of Technology, Beograd

The possibility of dyeing textiles in the presence of certain organic solvents was investigated. It was established that with small concentrations of certain solvents the exhaustion of dyes is improved. Under such conditions the time of half-dyeing is reduced and dyeing is possible at lower temperatures.

III—13

SAPONIFICATION OF PECTIN IN PLANT MATERIALS AND EXTRACTION OF SODIUM PECTATE

M. DŽAMIĆ and J. NEUKOM

Agriculturchemisches Institut ETH, Zürich and Agriculture School, Beograd

Conditions of saponification of pectic substances in apple pulp and extractions at different temperatures were studied.

It was found that by alkaline treatment and extraction at 0 °C, it is possible to get good yields of high molecular sodium pectate.

It also appears that there were some differences in properties of pectin obtained under different conditions.

III — 14

PREPARATION OF FODDER YEAST FROM FEEDS OBTAINED BY MILD HYDROLYSIS OF WHEAT HAY, SUNFLOWER HUSKS AND MAIZE EARS

V. KRAJOVAN, S. VESELINOVIĆ and B. GRUBNIĆ

School of Technology, Novi Sad

Hydrolysis of wheat hay, sunflower husks and maize ears was carried out at 125 °C for one hour. In case of hay and maize the hydromodule was 1 : 4 and in case of sunflower husks 1 : 7. Hydrolysis was effected with sulphuric acid whose concentration varied from 0.0 to 3.0 %. It was established that 3.92—43.56 % of the dry wheat hay material was hydrolyzed giving 3.29 to 24.16 % of reducing substances (calculated with respect to starting material). From 6.4 to 47.20 % of the dry maize ears material was hydrolyzed giving from 1.55 to 40.90 % of reducing substances (calculated with respect to starting material). With the sunflower husks, from 3.35 to 33.20 % of the dry material was hydrolyzed and from 0.45 to 13.55 % of reducing substances was obtained.

Yeast propagation from the wheat hay gave 56.5 % of dry yeast material calculated with respect to the reducing substances or 10.7 % when calculated with respect to hay. With sunflower husks a yield of 45 % of dry yeast material was obtained, with respect to reducing substances, or 8.56 % with respect to starting material. With maize ears a yield of 52.6 % of dry yeast material was obtained calculated with respect to reducing substances or 18.80 % when calculated with respect to starting material.

III — 15

ISOMERIZATION OF PRIMARY GASOLINES

R. VILENČIĆ

Zagreb, Miljacka 44/III

In order to establish whether ionic exchangers may be used as catalysts in the isomerization of hydrocarbons, a series of experiments were performed with primary gasolines from Stružec petroleum. Seven types of cationic exchangers were used.

The effect of γ -radiation on gasoline hydrocarbons was also investigated.

Isomerization reactions were followed by means of gas chromatography, infra-red spectra and octane ratings.

Cationic exchangers were found to produce considerable structural changes in fractions containing C_5- and C_6-hydrocarbons, less changes in fractions with C_7-hydrocarbons and only slight changes in fractions consisting of C_8—C_{10} hydrocarbons.

γ-radiation was also found to produce isomerization of primary gasolines.

Optimal duration of contact of the hydrocarbons with ionic exchangers in isomerization reactions was determined.

It was established that the capacity of dry exchanger considerably affects the isomerization process and the intensity of changes observed.

III — 16

SYNTHESIS OF POLYSULFIDE POLYMERS

M. TENC-POPOVIĆ, O. OLIĆ-LEKO, V. REKALIĆ and S. RADOSAVLJEVIĆ

Institute for Chemistry, Technology and Metallurgy and School of Technology, Beograd

Polysulfide polymers with formula $(— R\text{-}S_x —)_n$ can be prepared by reaction of alkyldihalides and alkali polysulfides.

The reaction conditions with 1,2-dichlorethane, bis (2-chlorethyl) ether and bis (2-chlorethyl) formal were investigated.

The quantities of the components and the dispersion agent, reaction time and temperature were varied.

III — 17

SEPARATION OF A MIXTURE OF TRIMER AND TETRAMER OF PHOSPHORNITRILE CHLORIDE

J. ŠAŠIĆ and S. RADOSAVLJEVIĆ

Institute for Chemistry, Technology and Metallurgy Beograd

According to the literature pure trimer is obtained by steam distillation whereas the tetramer is hydrolyzed to tetramethaphosphinic acid under these conditions. In the present paper it has been shown that the tetramer is not hydrolyzed under these conditions. Even on prolonged treatment with water at the same temperature only a small percentage of tetramer was found to be hydrolyzed. Thus, this method can be used for the separation of trimer and tetramer of phosphornitrile chloride.

III — 18

CONCERNING THE SYNTHESIS OF PHOSPHORNITRILE CHLORIDE

S. RADOSAVLJEVIĆ and J. ŠAŠIĆ

Institute for Chemistry, Technology and Metallurgy, Beograd

The effects of catalysts (ignited $MgCl_2.6H_2O$ and $TiCl_4$), molar ratio of reactants, and temperature of the yields of the crystalline fraction in the synthesis of phosphornitrile chloride of various polymerizations were investigated. The polymerization was carried out in monochlorobenzene as solvent. The following conditions were found to be optimal: $MgCl_2.6H_2O$ as catalyst, molar ratio of reactants $NH_4Cl : PCl_5 = 2 : 1$, and temperature 129—130 °C.

III – 19

ON THE ACTION OF METALLIC MAGNESIUM ON NITRIC ACID

(Preliminary communication)

A. M. LEKO and M. A. LEKO

Institute of Inorganic Chemistry — School of Technology and Institute for Chemistry, Technology and Metallurgy, Beograd

The action of metallic magnesium on nitric acid of different concentrations was investigated. The degree of reduction and the quantity of hydrogen evolved as function of the nitric acid concentration were determined. Of the products of reduction only the nitrous acid was determined, by dissolving magnesium in the presence of *m*-phenylenediamine.

III — 20

INCREASING THE UTILIZATION COEFFICIENT OF NaCl FROM SULPHATE TYPE BRINES

S. PRIBIĆEVIĆ

Institute for Mining, Technology and Chemistry, Tuzla

The changes of the NaCl utilization coefficient on evaporation of brines are surveyed. The utilization coefficient for Yugoslav brines has been found to be 0.45 to 0.83. A method for the evaporation of brines with soda factory waste water containing $CaCl_2$ is proposed. This would increase the utilization coefficient by at least 100/. Since in this way Na_2SO_4 is converted into NaCl, and the sewage from the factory contains sodium chloride, the theoretical utilization coefficient for Yugoslav brines would be augmented from 0.45 to 1.14 and from 0.83 to 1.04 (calculated with respect to sodium chloride present in brine).

Conditions for mixing brines and the waste water are described. The behavior of calcium sulphate in brine systems was investigated and a scheme for its removal is presented. Data on features of the use of soda factory waste water in the sodium chloride industry are given and four different technological schemes have been designed on the basis of these.

III—21

STUDY OF THE REACTIONS OF HEXANITROCOBALTATES (III) WITH AMINO ACIDS.

II. REACTIONS WITH DL-ALANINE, β-ALANINE, DL-α-AMINOBUTYRIC ACID AND DL-VALINE

M. B. ĆELAP, T. I. NIKOLIĆ, T. J. JANJIĆ and M. B. DIMITRIJEVIĆ

Institute of Chemistry, School of Sciences, University of Beograd and Institute of Chemistry, Technology and Metallurgy, Beograd

In an earlier paper we reported on the reaction of potassium and sodium hexanitrocobaltate (III) with glycine. Thereby we established that four nitro-groups in the complex ion are substituted by two glycine rests, i.e. that this amino acid behaves as a bidentate ligand forming two five-membered rings with the central cobalt atom. It was thus possible to prepare a new class of complex compounds: dinitrodiglycinatocobaltates (III), $M^{I}[Co(H_2N\cdot CH_2\,COO)_2(NO_2)_2]$.

Continuing our investigations, we examined the reactions of alkali hexanitrocobaltates (III) with DL-alanine. β-alanine, DL-α amino-butyric acid and DL-valine. We have established that these reactions take place in a way analogous to that described above, giving rise to four new classes of complex compounds of trivalent cobalt with amino acids:

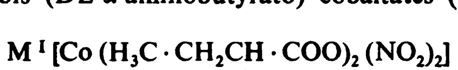
1. Dinitrobis (DL-alaninato) cobaltates (III),

$$M^{I}[Co\,(H_3C\cdot \underset{NH_2}{CH}\;COO)_2\,(NO_2)_2]$$

2. Dinitrobis (β-alaninato) cobaltates (III)

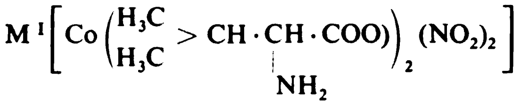
$$M^{I}[Co\,(H_2N\cdot CH_2CH_2COO)_2\,(NO_2)_2]$$

3. Dinitrobis (DL-α-aminobutyrato) cobaltates (III).



$$M^{I}[Co\,(H_3C\cdot CH_2\underset{NH_2}{CH}\cdot COO)_2\,(NO_2)_2]$$

4. Dinitrobis (DL-divalinato) cobaltates (III)



$$M^{I}\left[Co\left(\begin{matrix}H_3C\\H_3C\end{matrix} > CH\cdot\underset{NH_2}{CH}\cdot COO)\right)_2 (NO_2)_2\right]$$

The corresponding silver and mercurous salts were obtained by double decomposition of alkali salts of the compounds described with silver and mercurous nitrate, respectively.

In addition, these complex compounds were also synthesized by air oxidation of cobalt (II) to cobalt (III) in the presence of alkali nitrites and alkali salts of the corresponding amino acid.

III — 22

TECHNOLOGICAL SCHEME FOR THE PRODUCTION OF NaCl FROM SULPHATE TYPE BRINES

S. PRIBIĆEVIĆ

Institute for Mining, Technology and Chemistry, Tuzla

A technological scheme based on the removal of SO_4 ions by converting brines into an $NaCl$-$CaSO_4$-H_2O system is presented.

Precipitated gypsum is removed and the brine is treated with soda and converted into $NaCl$-Na_2SO_4-H_2O system whereby 78—95 % SO_4 ions are eliminated.

The effects of various factors on the process were investigated. Such as the effect of SO_4 ion concentration in the crude and concentrated brines, the concentration of $CaCl_2$ in waste brines, the effect of temperature, etc. Optimal conditions for the process were established.

III — 23

STUDY OF THE REACTIONS OF HEXANITROCOBALTATES (III) WITH AMINO ACIDS. III. DETERMINATION OF THE CONFIGURATION OF DINITRODIGLYCINATOCOBALTATES (III).

M. B. ĆELAP, D. J. RADANOVIĆ and T. J. JANJIĆ

Institute of Chemistry, School of Sciences, University of Beograd and Institute of Chemistry, Technology and Metallurgy, Beograd

In a recent paper we established that the action of glycine on hexanitrocobaltates (III) gives rise to a new class of complex compounds of tervalent cobalt with amino acids: dinitrodiglycinatocobaltates (III).

$$M^{I}[Co(H_2N, CH_2COO)_2(NO_2)_2]$$

Since the complex salts contain in complex ion two nitro groups and two glycyl rests as ligands, it might be expected on the basis of the Werner coordination theory, that they would give rise to five geometrical isomers. In two of them the nitro groups would be in the *trans* position, in the other three the nitro groups would be in the *cis* position. Therefore, the *cis* isomers ought to resolvable into optical antipodes, and the corresponding *trans* isomers should be symmetrical and optically inactive. To establish the position of the two nitro groups in the complex salts obtained, we attempted to resolve them into optical antipodes. By fractional crystallization of the d-cinchonine salt we obtained two diastereoisomers from which we prepared the optical antipodes in the form of the corresponding silver salts. Thus we proved that dinitrodiglycinatocobaltates (III) contain two nitro groups in the *cis* position.

This conclusion agrees with the fact that by the action of potassium glycocolate on potassium dinitrodiglycinato-cobaltate (III) β-triglycinatocobalt (III) is obtained, which is only possible if the nitro groups are in the *cis* position. In addition, this reaction indicates that both the carboxyl and the amino groups of the glycine rests are in the *cis* position. This finding was confirmed by the fact that by the action of potassium nitrite on β-isomer of triglycinatocobalt (III) a product identical with potassium dinitrodiglycinatocobaltate (III) was obtained.

In addition six new, in principle different procedures for the preparation of potassium dinitrodiglycinatocobaltate (III) were developed. In all cases the products were identical with potassium dinitrodiglycinatocobaltate (III) prepared by the action of potassium glycocollate on potassium hexanitrocobaltate (III). This was proved by ultraviolet, visible and infrared spectography, and paper chromatography. It can be concluded that the isomer obtained is the most stable form of dinitrodiglycinatocobaltate (III).

III — 24

REMOVAL OF CHROMIUM FROM RAW MATERIALS OF INDUSTRY

S. PRIBIČEVIĆ

Institute for Mining, Chemistry and Technology, Tuzla

Some of these raw materials contain CrO_4 ion. A method was developed for the removal of chromium consisting in the reduction of CrO_4 to Cr^{3+} ion through the presence of H_2S in the brine. Trivalent chromium was then precipitated in the form of $Cr(OH)_3$ and absorbed on $Fe(OH)_3$.

A system for the regeneration of Fe-ion by separating Fe and Cr on ion-exchange resins was developed.

III—25

BOD CONTRIBUTION OF HEAT STERILIZED ALGAE

M. MILOJEVIĆ

Civil Engineering School, Beograd

Algae may be found in effluents from sewage treatment plants, oxidation ponds and tertiary treatment plants, and in natural water bodies. When algae die they may contribute to the total BOD of these waters.

Mixed algae cultures, heat-sterilized for 1/2 an hour at 121 °C had a 5-day BOD approximately equal to one half the dry weight of algae cells present in the suspension. The rate of the biochemical oxygen uptake was somewhat greater than that generally accepted for average sewage.

IV – 1

SEPARATION OF CONDENSED PHOSPHATES ON A THIN LAYER OF STARCH

V. D. CANIĆ, M. N. TURČIĆ and S. M. PETROVIĆ
Institute of Chemistry, University of Novi Sad

Thin layer chromatography has not previously been applied for separating condensed phosphates. Investigations of starch as the adsorbent for thin layer chromatography indicate that corn starch can be used for separating condensed phosphates. Ascending and circular chromatography on a thin layer of starch were applied. Better separations may be obtained by the circular technique by which as many as 20 samples on a plate can be chromatographed. Destruction of the starch layer by the solvent mixture or the detection solutions was not observed, so the detected blue zones of heteropolymolybdophosphoric acid can easily be perceived on the white background. Besides linear chain polyphosphates, by using different solvents it is possible to separate the cyclic polyphosphates of linear chain polyphosphates. Polyphosphate preparations used in the food and other industries can be qualitatively analyzed quickly by this technique.

IV — 2

SEPARATION OF I, II, and IV CATION GROUP BY THIN-LAYER CHROMATOGRAPHY ON STARCH

V. D. CANIĆ, S. M. PETROVIĆ and A. K. BEM
Institute of Chemistry, University of Novi Sad

The separation of I, II and IV cation group was effected by thin-layer chromatography on maize starch.

The solvent for the separation of Pb^{2+}, Ag^{+} and Hg^{2+} was a mixture of acetone and 3 N HNO_3 (1 : 1), for the separation of Ba^{2+}, Ca^{2+}, Sr^{2+} and Mg^{2+} a mixture of acetone and 3 N HCl (2 : 3), and for II cation group a mixture of acetone and 3 N HCl (1 : 1).

Rf-values of cations are given in Tables.

IV—3

THE APPLICATION OF CORROSION POTENTIOMETRY IN ANALYTICAL DETERMINATIONS

A. DESPIĆ, K. POPOV-SINĐELIĆ and Z. LEVAKOV
School of Technology, Beograd

The use of corrosion current and corrosion potential for analytical purposes is considered theoretically.

Experiments were made on a system consisting of copper immersed in a deaerated $CH_3COOK+CH_3COOH$ solution as the corroding electrode, and silver ion solutions of various concentrations containing an inert electrode as the corroding agents. It was shown that at sufficiently low concentrations the corrosion current depends mainly on the diffusion conditions at the inert electrode and that in case this is well defined both the corrosion current and the corrosion potential can be used for determining the silver-ion concentration in the solution within the limits of accuracy characteristic for amperometric and potentiometric methods, respectively.

IV—4

APPLICATION OF RING COLORIMETRY TO THE DETERMINATION OF DYESTUFFS

M. B. ĆELAP, T. J. JANJIĆ and V. D. JEVTIĆ

Institute of Chemistry, School of Sciences, University of Beograd and Institute of Chemistry, Technology and Metallurgy, Beograd

The Weiss ring-colorimetry method was applied to the semiquantitative determination of the following dyestuffs: Indigo carmine, erythrosin A, amaranth O, new coccine, Victoria blue B, tartrazine, azorubin S, alizarine S, eosin, light green SF, Guinea green B, fuchsin, eriochrome black T, saphranine, ponceau 3R, cyanine, gelborange S, and methyl violet 6B.

The amount of dye required for one determination ranges from half a gamma to twenty gammas. The errors were a few percent.

The method was checked by determining azorubin S, methyl violet 6B, tartrazine, and amaranth O in various materials.

IV — 5

COULOMETRIC TITRATION OF PERMANGANATE AND DICHROMATE

S. MLADENOVIĆ

School of Technology, Beograd

The total amount of permanganate and dichromate can be quantitatively determined by coulometric titration with electrolytically-formed ferrous ions. In this titration the number of gram-equivalents of permanganate and dichromate is equal to the number of Faradays consumed.

Permanganate and dichromate can also be coulometrically determined from the amount of hydrogen ions, consumed in the reduction of permanganate and dichromate:

$$MnO_4^- + 4H^+ + 3e \rightarrow MnO_2 + 2H_2O$$

$$Cr_2O_7^{2-} + 14H \ + 6e \rightarrow Cr^{3+} + 7H_2O$$

In the reduction of one gram-equivalent of permanganate 4/3 gram-ions of hydrogen are consumed, and 4/3 Faradays are required for their reduction; in the reduction of one gram-equivalent of dichromate 7/3 gram-ions of hydrogen are consumed and 7/3 Faradays are required for their reduction. The total amount of permanganate and dichromate is determined on the basis of the decrease of the amount of acid in the electrolyte which is titrated coulometrically.

Since different amounts of electricity are consumed in coulometric titration of permanganate and dichromate with electrolytically-formed ferrous ions and hydrogen ions, it is possible to determine, on the basis of the amounts of electricity consumed in bot titrations, the individual quantities of permanganate and dichromate present.

IV—6

CONDUCTOMETRIC AND HIGH-FREQUENCY TITRATION OF BASES IN GLACIAL ACETIC ACID

V. VAJGAND and T. PASTOR

School of Sciences, Beograd

Conductometric titrations of tertiary amines and salts of organic acids in glacial acetic acid were performed in the presence of platinum and antimony electrodes by direct and indirect methods. The results show that a greater number of bases may be determined by the indirect method than by the direct method and that the former is more accurate. A large amount of acetic anhydride in the solvent mixture has an unfavorable effect on the titration accuracy and on the shape of the titration curve.

The same compounds were determined by high frequency titration. The results again showed that a large amount of acetic anhydride should be avoided.

IV—7

INTERFEROMETRIC TITRATION OF ACIDS AND BASES IN WATER AND GLACIAL ACETIC ACID

V. VAJGAND and T. TODOROVSKI

School of Sciences — Beograd

The conditions under which acids can be titrated with bases and vice versa by measuring slight changes of the refractive index caused by neutralisation were investigated. The equivalence point is found at the intersection of two straight lines, regardles of whether the titration is made in an aqueous medium or in glacial acetic acid. By this method it is possible to determine strong and weak acids and mixtures of them in water, and it is particularly promising foi determinations in nonaqueous media. Successful titrations were made of some weak bases in glacial acetic acid.

IV—8

POLAROGRAPHIC DETERMINATION OF VITAMIN K_3 IN MENADIONE BISULPHITE PREPARATIONS

V. VAJGAND and F. UVODIĆ

School of Sciences and Production Monitoring Laboratory of Galenika

Determination of vitamin K_3 in bisulphite preparations by the methods described in pharmacopoeias requires a considerable amount of the starting material and takes a long time because the addition compound has to be converted to pure menadione which is then extracted and determined by cerimetric titration.

Vitamin K_3 is polarographically determined in organic solvents, and therefore cannot be so determined in bisulphite preparations which are only water soluble. The polarographic methods for its determination in the latter described so far reduce to the mere comparison of waves of the sample and a standard solution whose vitamin K_3 content has to be determined by the methods mentioned above.

By investigating the behaviour of vitamin K_3 in different solvents and in the presence of varying amounts of sodium bisulphite, we found the conditions under which its direct polarographic determination in bisulphite preparations is possible.

IV — 9

COMBINED ELECTROLYTIC-SPECTROCHEMICAL METHOD FOR THE DETERMINATION OF RHODIUM AND INDIUM TRACES IN SOLUTIONS

V. VUKANOVIĆ, M. TODOROVIĆ, V. VAJGAND and N. SVILAR
School of Science, Beograd

This paper describes the principles of a method in which electrolytic separation and excitation in an intermittent arc take place simultaneously. Preliminary investigations with separation on a rotatory copper electrode have shown that this method is specially useful for elements having electrochemical potentials between +0.5 and —1 V. Rhodium and indium were chosen as representatives of this group of elements. We studied the conditions for the electrolytic separation of traçes of these elements and for their spectrochemical determination in the absence and presence of large quantities of other elements (Al and Pb).

IV – 10

A NEW METHOD FOR THE DETERMINATION OF MICRO QUANTITIES OF EASILY REDUCIBLE ELEMENTS BY RING COLORIMETRY

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

School of Sciences, University of Beograd

A new method is described for the determination of micro quantities of rhodium, tellurium, selenium, silver, mercury, paladium, platinum and gold.

A known volume of the solution to be analysed is washed out on a ring oven. Development is carried out with a convenient reducing reagent, whereby the elements appear in the form of coloured rings, which are then compared with the rings of a standard scale.

The quantities of individual elements necessary for one determination are only a few micrograms, and the average errors range from 1 % (for Pt) to 5.3 % (for Ag).

The above elements may be determined by this method in the presence of other elements which are not reduced under these conditions. The method has been used to determine the composition of various materials.

IV – 11

DETERMINATION OF MICRO QUANTITIES OF COPPER BY RING COLORIMETRY USING A *bis* (DIMETHYLGLYOXIMATO) — COPPER (II) COMPLEX STANDARD SCALE

T. J. JANJIĆ, Z. S. ČERVENJAK and M. B. ĆELAP

School of Sciences, University of Beograd and Institute for Nuclear Materials, Beograd

A new method for the determination of micro quantities of copper by ring colorimetry using a *bis* (dimethylglyoximato) — copper (II) complex standard scale is described.

Copper is washed on a ring oven with a 2% dimethylglyoxime solution in n-butanol saturated with 2N ammonia. Brown rings are formed, which can be directly compared with the rings of a standard scale. The determination is not affected by the presence of platinum (1 : 100 ratio), gold (1 : 100), silver (1 : 100), mercury (1 : 300), bismuth (1 : 300), cadmium (1 : 200), molybdenum (1 : 500), arsenic (1 : 100), antimony (1 : 50), tin (1 : 50), zinc (1 : 20), nickel (1 : 10), manganese (1 : 10) or iron (1 : 5).

The procedure requires only a few micrograms of copper so that it is very suitable for the analysis of traces in different materials.

The error of the method is on average 2% which corresponds to the errors of other micromethods.

The method may be succesfully applied for the determination of micro quantities of copper in different inorganic and organic materials, as was proved by the determination of copper in ores, alloys and some biological materials.

IV – 12

MAINTENANCE OF SWIMMING-POOL WATER

V. IVKOVIĆ, E. KROTIN and I. KOSTIĆ
School of Technology

The main properties of swimming-pool water required are that it be clear, bartericidal and of suitable temperature.

Most often water is clouded by algae; these can be killed by the addition of copper sulphate. The water can be cleared by aluminum sulphate and the bacteria destroyed by elementary chlorine.

The main difficulty encountered in maintenance is the problem of keeping the necessary amount of copper in solution, and simultaneously permitting the hydrolysis of aluminum sulphate, i.e. the formation of aluminum hydroxide.

A series of experiments were performed to study conditions for the formation of aluminum hydroxide, copper hydroxide and basic copper carbonate in dependance on the PH at various concentrations of aluminum and copper.

IV — 13

INDIRECT COULOMETRIC DETERMINATION OF CADMIUM

D. J. STOJKOVIĆ

School of Technology and Institute for Chemistry, Technology and Metallurgy, Beograd

Indirect coulometric determination of cadmium was effected in two phases. The first phase involved the electrolysis of aqueous Na_2SO_4 solution with platinum electrodes, the catholyte being separated from the anolyte. The cadmium ion in the catholyte was equilibrated with hydroxyl ions giving $Cd(OH)_2$. The current strength and the electrolysis time could be altered without restriction, provided the precipitation of cadmium was quantitative.

In the second phase, the catholyte for the new circuit of electrolysis was obtained by mixing the filtrate, after the separation of $Cd(OH)_2$, with the anolyte from the first phase and with the content of the electrolytic bridge. The anolyte consisted of a fresh solution of sodium sulphate. By using platinum electrodes and a constant current strength, a coulometric acidimetric determination of hydrogen ions in the catholyte was performed, that is determination of the acid formed in the anolyte in the first phase. This acid is equivalent to the amount of cadmium and it is not neutralized by the excess of hydroxyl ions formed in the catholyte in the first phase.

End-point determination was performed using tashiro indicator. The determination of other cations which exhibit a behavior similar to that of cadmium is under investigation.

IV — 14

POLAROGRAPHIC DETERMINATION OF THALLIUM IN AMMONIACAL SOLUTION OF TRILON B

S. MLADENOVIĆ

School of Technology — Beograd

In acid and ammoniacal solutions the ion of thallium is reduced at the mercury dropping electrode at potentials equal or very close to the reduction potentials of ions of lead, tin and cadmium.

However, in ammoniacal solution of trilon B, lead, tin and cadmium do not form polarographic waves while thallium does.

This method is suitable for the determination of thallium in the presence of cadmium, tin and other metals.

IV—15

DETERMINATION OF COPPER IN THE ELECTROLYTE FOR COPPER REFINING

S. ĐORĐEVIĆ and M. VOJNOVIĆ
School of Technology, Beograd

The method of electrogravimetric determination of copper in the presence of As and Sb was in proved by preliminary oxidation of As^{III} and Sb^{III} to As^{V} and Sb^{V} using 0.1 $KBrO_3$.

IV—16

NEW USES OF MUREXIDE IN CHELATOMETRY.
II. SIMULTANEOUS DETERMINATION OF SOME METALS

T. KIŠ

School of Technology, University of Novi Sad

With Murexide as the indicator, many simultaneous direct titrations of cadmium, zinc, manganese, bismuth and thorium with disodium ethylenediaminetetraacetate are possible, e.g. determination of copper and manganese, nickel and zinc, manganese, zinc and cobalt, copper and mercury.

The relative errors and standard deviations are within the limits of simultaneous chelatometric titrations.

VI—17

AMPEROMETRIC TITRATIONS WITH A SINGLE POLARIZED ELECTRODE. IODOMETRIC AND BROMATOMETRIC DEPOLARIZATION END POINT DETERMINATION OF HYDRAZINE

M. S. JOVANOVIĆ, N. TIJEGLIĆ, I. SELMIĆ and V. VUKOSAVLJEVIĆ

School of Technology, Beograd

Nernst's equation for the electrode potential cannot be applied for an electrode in the solution of an irreversible system. Coursier has called the potential observed in such cases an "irreversible potential". It does not depend much on the concentration of the electroactive ionic species. If an irreversible system is to be determined by means of a reversible system, the potential of the electrode will not change until the end point is reached. Then as depolarization of the electrode by the reversible titrant begins a sudden current jump occurs in the till then balanced circuit. The more irreversible the system to be determined, the higher the current jump and the easier detection of the end point. This was proved by determining strongly irreversible hydrazine with reversible iodine or bromate titrants.

IV—18

DEPOLARIZATION END-POINT ARGENTOMETRIC DETERMINATION OF CYANIDE

M. S. JOVANOVIĆ, M. M. MOJSILOVIĆ and F. D. SIGULINSKY

School of Technology, Beograd

It is shown that end-point depolarization of the electrode is applicable in argentometry if platinum is used for the electrode. According to Müller the responsibility of platinum to change of the *Ag* ion concentration is due to the presence of the reversible argento-argenti system at the end-point. According to Allen and Hickling it is due to alloying of platinum with silver after the platinum has been pretreated in some way. When cyanide is to be determined after Liebig, two succesive depolarizations of the electrode, i.e. two current jumps may be expected — the first when $Ag\,[Ag\,(Cn)_2]$ starts forming and the second when it stops. This was shown to be the case.

IV — 19

DEPOLARIZATION END-POINT ARGENTOMETRIC DETERMINATION OF IODIDE

M. S. JOVANOVIĆ and F. D. SIGULINSKY

School of Technology, Beograd

The depolarization end-point technique was applied for the determination of an irreversible system by means of a reversible one. In precipitation titrations, the degree of depolarization of the indicator electrode depends on the value of the corresponding solubility product. Thus the behaviour of the electrode is very similar to, when it is immersed in an irreversible system to which it does not correspond. At the end-point even a slight excess of the ions of the titrant will induce a relatively great depolarization of the electrode. The resulting current jump can be observed on a sensitive galvanometer.

IV—20

DEPOLARIZATION END-POINT PERMANGANATOMETRIC DETERMINATION OF MANGANESE

M. S. JOVANOVIĆ and D. M. PETROVIĆ
School of Technology, Beograd

In 1952 Coursier introduced the idea of an "irreversible potential". From this a method for end-point detection by observing the establishment of the reversible Nernst potential at the indicator electrode was developed. If an irreversible system is to be analysed by means of a reversible one, the electrode will begin to respond to changes of the concentration of the electroactive ionic species at the end-point. At the same time depolarization of the electrode begins, which is manifested as a sharp current jump at the e.p.

IV—21

ELECTROMETRIC DETERMINATION OF SULFITE IN SPENT AND COOKING LIQUOR IN PRODUCTION OF SEMI CHEMICAL PULP

LJ. VRHOVAC, L. PENZEŠ and M. JOVANOVIĆ
School of Technology, Beograd

The spent or black liquor which is obtained in semi-chemical pulp production (NSSC process) contains apart from lignosulfonic acids and destroyed polysaccharides, a certain amount of residual sulfite, which is the active chemical in the delignification of wood. Determination of this sulfite is very interesting from both the technological and economical point of view. Due to the very dark color of the liquor it is very difficult to determine the sulfite by the usual volumetric titration method, so the use of ordinary indicators is not possible.

Therefore the possibility of using two electrometric methods — the depolarization end-point and the dead-stop end-point methods — has been studied. In both cases a stabilized weakly acidified solution of the liquor was titrated with iodine until the sudden current jump due to depolarization of the electrode by the reversible iodine-iodide system. To check the methods sulfur dioxide was removed from the solution with a stream of nitrogen, oxidized in a closed system with hydrogen peroxide and gravimetrically determined as barium sulfate.

It has been shown that both methods can be used for spent and cooking liquors. This is particularly important for spent liquor since no other fast and precise method exists. The methods can be applied for the determination of sulfite in all other cases where the solution is dark colored as well.

IV—22

IODOMETRIC DETERMINATION OF SULFITE BY THE DEPOLARIZATION END POINT METHOD

LJ. VRHOVAC, M. JOVANOVIĆ and L. PENZEŠ

Faculty of Technology, Beograd

The titration end point of an irreversible system can be determined from the beginning of the electrode response to changes of concentration of the electroactive ionic species of the reversible titrant. This principle is used in the determination of the irreversible sulfite-sulfate system. The volumetric methods for the determination of sulfite involve titration of an acidified iodine solution with the sulfite solution being determined.

In this work it has been shown that this titration can be done in reverse, i.e. with the iodine solution as the titrant. To avoid concentration changes of the sulfite the solution was stabilized by addition of a small amount of EDTA. At the end point, due to establishment of the reversible potential of the indicator electrode, a sudden current jump appears. By this method it is possible to determine sulfite in cases where other indicators cannot be used.

IV—23

NEW USES OF MUREXIDE IN CHELATOMETRY I. DIRECT DETERMINATION OF CADMIUM, ZINC, MANGANESE, BISMUTH AND THORIUM

T. KIŠ

School of Technology, University of Novi Sad

Owing to the lability of metal-Murexide complexes, and the stability of ordinary auxiliary complexes, Murexide has only been used for titrating a few metals (calcium, nickel, cobalt and copper).

We have established that Murexide forms complexes with some other metals and that by using new labile auxiliary complexes these elements can also be titrated with disodium ethylenediaminetetraacetate: bismuth and thorium at pH 2 using nitrate to form the auxiliary complex; manganese and zinc at pH 10 using ammonia; cadmium at pH 5 also using nitrate, or sulfate or acetate. The errors and standard deviations in determination of macro and micro amounts of these metals were within the limits of direct complexometric titrations.

IV — 24

DIMETHYL PHTHALATE AND DIBUTYL PHTHALATE AS NEW STANDARDS FOR WATER TURBIDITY

S. JANKOVIĆ and M. MILOJEVIĆ

The stability of some emulsions prepared from dimethyl or dibutyl phthalate and mixtures of ethanol or methanol and water was investigated. It was established that some of these emulsions show such a stability that they can be proposed as standards for the determination of water turbidity below 10 mg/l (expressed as SiO_2); these findings are of special importance for waterworks practice.

IV—25

TOTAL BASE NUMBER OF MOTOR OILS

B. KNEŽEVIĆ

Kombinat nafte i plina — Zagreb
Rafinerija nafte — Rijeka

Motor oils often contain alkaline chemical additives which neutralize acid fuel combustion products (SO_2 and SO_3). These sulfur acids blow past into the crankcase and react with oil causing deposit-forming materials, and attacking metal parts causing corrosive wear. The alkaline value of these additives and the compounded oils is expressed as the "Total Base Number", TBN.

Many methods have been developed for testing the alkaline value of additives and finished oils. The most widely used methods for determination of TBN are the ASTM D-664 and a modified one with glacial acetic and perchloric acid. The choice of method depends on the type and chemical composition of the additives and how much of them there is in the oil.

Experimental data gotten with both methods are presented.

IV — 26

COULOMETRIC MERCUROMETRIC POTENTIOMETRIC DETERMINATION OF ANIONS

D. J. STOJKOVIĆ

School of Technology and Institute for Chemistry, Technology and Metallurgy, Beograd

Mercurous ions formed by anodic oxidation in the supporting electrolyte 0.2 M KNO_3 were used as the coulometric reagent for the determination of oxalate, chloride, bromide and iodide ion respectively. The end-point was determined potentiometrically with an indicator electrode at $I = O$. The indicator electrode in the determination of oxalate, chloride and bromide ion was a generator mercury electrode from the coulometric circuit, whereas the iodide ion was determined by means of a special indicator mercury electrode in the form of the letter "J". The determinations were performed at a constant current in the coulometric circuit. Diagrams of $EMF = f(t)$ and $mm = f(t)$ were recorded; diagrams of the first derivative of these two magnitudes are given as well. The method can be applied to the determination of micro and submicro quantities.

IV — 27

DETERMINATION OF RHENIUM IN SOME YUGOSLAV ORES

R. DIMITRIJEVIĆ and A. KOŠUTIĆ

Institute for Chemistry, Technology and Metallurgy, Beograd

The increasing importance of rhenium in the world and rapid growth of its production make it necessary to investigate rhenium content in some Yugoslav ores.

In order to determine rhenium content we developed a method suitable for our working conditions. The experimental conditions were such as to ensure full reproducibility of results.

The content of rhenium was determined in molybdenite concentrates from Majdanpek and Mačkatica as well as in ores from these areas.

It was found that the molybdenite concentrate from Majdanpek contains 0.17 % of rhenium. This is one of the largest rhenium concentrations found so far in the world. Molybdenite concentrates containing 0.03 % of rhenium are already used for the exploitation of rhenium.

V—1

EXPERIMENTAL STUDY AND CRITICAL SURVEY OF THE METHODS FOR SPECTROCHEMICAL DETECTION AND DOSAGE OF LITHIUM

A. ANTIĆ-JOVANOVIĆ

School of Science, Institute for Physical Chemistry, Beograd

A thorough and critical study of the published work on methods of spectrochemical detection and determination of lithium was made. The relatively simple spectrum of this element may be further simplified by appropriate choice of the method of excitation, which can increase selectivity in relation to other elements and possible interferences, especially from the very similar alkalis.

A comparative experimental study was made of the methods of arc, spark and flame excitation for this element, under well-defined conditions, which clearly proved that flame excitation is best. Various influences on *Li*-emission of different flame sources were investigated. The results were compared with data of other investigators and were critically examined with a view to better detectability and quantitative determination of this element.

V – 2

A MODIFICATION OF THE POROUS ELECTRODE METHOD FOR STEEL ANALYSIS

M. KLISKA and S. BLAŽIN

Boris Kidrič Institute of Nuclear Sciences, Vinča

A general survey of spectrochemical analysis of steel and the methods of solution analysis is made with particular reference to the spectrochemical analysis of steel solutions. The application of the porous electrode method for steel analysis is described. The technique developed allows analysis of steel of different compositions and in different forms with the following elements: Al (0.03 — 1.5 %), Cr (0.02 — 1 %), Mn (0.04 — 2 %), Mo (0.03 — 1.5 %), Ni (0.08 — 4 %) and V (0.012 — 0.6 %).

The precision of the method is 9 — 13 % for Cr, V 6 — 11 %, for Al, Mn, Mo and 5 % for Ni.

V—3

REACTION OF MOLYBDENUM WITH DIPHENYLCARBAZONE

V. ANTONIJEVIĆ and M. PRAVICA
Boris Kidrič Institute of Nuclear Sciences, Vinča

The dissociation of dyphenylcarbazone and conditions under which molybdenum complexes form in 10 % ethanol were studied spectrophotometricaly. The possibility of extracting molybdenum with diphenylcarbazone in chloroform was investigated and the optimal conditions determined. Conditions for direct spectrophotometric determination of molybdenum in uranium-molybdenum alloys and the interference of different cations and anions in the determination of 0.05 - 2 % molybdenum in alloys are presented.

V—4

REACTION OF ZIRCONIUM WITH ARSENAZO III IN STRONGLY ACID MEDIA

A. MUK

Boris Kidrič Institute of Nuclear Sciences, Vinča

The color reaction of zirconium with arsenazo III and the influence of the perchloric acid concentration on sensitivity in determining microquantities of zirconium was investigated. The mole ratios for zirconium and uranium complexes were determined. Beer's law was found to hold in the range 0.1-2.5μg and 0.04-1.0μg/25 ml for uranium and zirconium, respectively. The results suggest the possibility of their simultaneous determination.

V–5

SPECTROPHOTOMETRIC DETERMINATION OF NIOBIUM IN URANIUM ALLOYS WITH XYLENOL ORANGE

G. T. HAJDUKOVIĆ

Boris Kidrič Institute of Nuclear Sciences, Vinča

In slightly acid medium niobium reacts with xylenol orange giving an absorption maximum at 560 m μ

Beer's law holds in the range 10-60 μg of niobium in 50 ml, in the presence of twenty-fold ammonium oxalate and 1.0 ml 0.1 % xylenol orange.

The interference of other elements was investigated. Uranium does not interfere up to 10 mg.

V — 6

INVESTIGATION OF THE EFFECT OF pH ON ABSORPTION SPECTRA OF PELARGONIDOL, DELPHINIDOL and MALVIDOL

S. RISTIĆ and J. BARANAC

School of Science, Beograd

Absorption spectra of pelargonidol chloride, delphinidol chloride and malvidol chloride in a series of buffered solutions were investigated. Anthocyanidol solutions of 3 $\times 10^{-5}$ M were used and buffered solutions were prepared according to Sörensen.

It is known that, depending on the pH, anthocyanidols can exist in many different forms which, under certain conditions, have different equilibria. In this study an attempt was made to define the regions of existence of the two main ionic forms (the red cation and the blue anion). This was done by determining constants of the respective ionic equilibria, and study of the processes involved. Apart from tautomeric and ionic equilibria specific chemical and photochemical processes are involved, the role and importance of which are not yet completely understood.

Further investigations will involve other forms and their mutual relations.

V — 7

CONTRIBUTION TO GENERAL PHYSICO-CHEMICAL AND SPECTRAL PROPERTIES OF SYNTHETIC RUBY

M. JEREMIĆ

School of Science, Beograd

Physico-chemical properties, spectral characteristics and Cr^{3+} content of some samples of synthetic ruby obtained by the method of Verneuil were investigated.

Although the avaliable samples of synthetic ruby are not optically perfect, they show a number of characteristics which indicate that the defects may be ascribed rather to mechanical-technical imperfection of the production process than to essential features of the procedure.

Further improvements of the method are under investigation.

V — 8

DETERMINATION OF 3, 4-BENZOPYRENE CONTENT IN THE CONDENSATE OF CIGARETTE SMOKE

J. BABIN and Đ. POLIĆ

Laboratory for Experimental Oncology School of Medicine, Beograd

Analysis of the smoke condensate of Yugoslav cigarettes showed that the condensate of 100 cigarettes (without butts) contains 0.567 micrograms of 3, 4-benzopyrene.

Separation was effected by column and paper chromatography and the fractions were analyzed by means of absorption and fluorescence spectra.

V — 9

POSSIBILITY OF A MECHANICAL FRACTION COLLECTOR OF A NEW CONSTRUCTION

J. BABIN and Đ. POLIĆ

Laboratory for Experimental Oncology, School of Medicine — Beograd

On the basis of a recently published design* we developed a new construction for a device which may be used as a fraction collector. This device functions on the buoyancy principle and mechanically-produced rotation permitting automatic collection of chromatographic fractions. It may also be used for analogous automatic measuring of either equal volumes of liquids or of masses of different materials.

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*) Philips D. M. P. Nature 164.545-1949

V — 10

SPLITTING EFFECT AND SPECTRAL ANALYSIS OF TRACES IN DIRECT CURRENT ARC

D. VUKANOVIĆ

School of Technology — Beograd

The measured splitting effect of elements in the plasma of a direct current arc, perpendicular to its axis, was correlated with the duration of particles stay in the plasma as determined by other autors. The correlation confirmed that changes in the duration of particle stay in the plasma should be taken into consideration in explaining the mechanism of the effect of substances added to the plasma of arc (third partner effect).

VI – 1

QUANTITATIVE DETERMINATION OF G. P. ZONES IN *Al-Zn* ALLOYS

M. ROGULIĆ and R. NICHOLSON

School of Technology, Beograd

Small-angle X-ray scattering and electron-microscopy investigations have been made of Al-10 at. % Zn, Al-6.7 at. % Zn and Al - 4.5 at. % Zn. During the early stage of age-hardening G. P. zones precipitate but to a smaller extent than calculated from the miscibility gap in the phase diagram. Constant integrated intensity at small angles does not mean that precipitation has finished and the state of metastable equilibrium defined by the miscibility gap has been reached, but suggests a slowing down of the process, which seems to be influenced by kinematic and thermodynamic factors.

VI—2

AGE-HARDENING OF ALUMINUM-SILVER ALLOY

M. ROGULIĆ

School of Technology, Beograd

An aluminum - 5.9 at. % silver has been quantitative investigated by electron microscopy. The alloy was solution-treated at 520 °C and aged 3 days at 130 °C. Most zones observed on the electron micrographs were 20 Å whereas the volume fraction of the precipitated phase was $2.5 : 10^{-2}$. These data lead to the conclusion that the equilibrium state defined by the miscibility gap in the phase diagram has not been reached during this stage of precipitation.

VI – 3

THE INFLUENCE OF STRAIN AGEING ON THE ALTERNATE BENDING TEST ENDURANCE OF MILD STEEL

B. BOŽIĆ and D. MIHAJLOVIĆ

School of Technology, Beograd

The influence on strain ageing of 0.05 % C steel in the alternate bending test was studied. A high deformation-amplitude (bending angle ± 90°) method was used. The experiments were caried out at temperatures of 20, 90, 120 and 150° for different ageing times. It was established that in this strain range strain ageing lowers the endurance of the steel. The time taken to reach the minimum cycle number (N) is an exponential function of the ageing temperature in °K. The activation energy of the process corresponds to that of the carbon atom diffusion.

VI—4

THE ALTERNATE BENDING TEST BEHAVIOR OF CARBON STEEL AT TEMPERATURES UP TO 400°

B. BOŽIĆ and D. MIHAJLOVIĆ

School of Technology, Beograd

Carbon steels show increasing tensile strength and fatigue strength and decreasing ductility with increasing temperature above 100°, reaching turning values between 200-400°. Published results mostly refer to fatigue tests in the low stress high-endurance range. In the investigation presented here the following steels were tested by alternate bending in the low-endurance high-plastic-strain range: S 0145, S 1330, S 1430, S 1530 and S 1730. No. of cycles to fracture was minimum at 300-325 °C, regardless of the carbon content. These results support the hypothesis that this type of brittleness is produced by atmosphere locking of dislocations. It appears too, that at low endurances the fatigue life may be determined by the plastic strain.

VI—5

MARAGING OF NICKEL STEEL

N. VIDOJEVIĆ, N. NOVOVIĆ-SIMOVIĆ and J. POPOVIĆ
School of Technology, Beograd

Maraging improves the mechanical properties of structural steels and gives a good combination of strength and plasticity. The strength is increased by age-hardening of martensite, which has a high plasticity and low strength. The aim of this work was to produce a steel with such characterictics and to find the relation between heat treatment and the effects produced during age-hardening. A heat of 30 kgs was made. The steel was solution-treated at 820 °C for 20 min, air cooled to produce martensite and aged at between 250 °C and 600 °C for 1 min to 24 hours. Hardness measurements showed that the maximum effect is obtained by ageing at 450 °C. The maximum hardness was 50 HRC.

VI—6

A PROCESS FOR MANUFACTURING THIN HOMOGENEOUS POROUS BODIES

Č. B. PETROVIĆ, D. S. TRIFUNOVIĆ and M. B. JANČIĆ
Institute for Chemistry, Technology and Metallurgy, Beograd

A method of producing thin homogeneous porous bodies by sintering loose metal powder particles was investigated. The shape, size, size distribution, temperature and time of sintering were varied and their effects on the properties of sintered products were studied.

VI—7

INFLUENCE OF BETA GRAIN SIZE ON BETA-ALPHA TRANSFORMATION MECHANISM AND KINETICS IN URANIUM

Đ. DROBNJAK
Boris Kidrič Institute, Vinča

The influence of time and temperature in the beta-phase region on the alpha grain size and shape obtained on quenching was studied.

Increasing the duration or temperature of the beta-anneal before cooling coarsens the alpha grain size, and modifies the shape from equiaxed to irregular feathery and plate-like. These changes are attributed to the influence of the beta grain size on the beta-alpha transformation mechanism and kinetics.

VI—8

THE ISOTHERMAL DECOMPOSITION OF URANIUM - 2 WT. % NIOBIUM ALLOY

B. ĐURIĆ

Boris Kidrič Institute, Vinča

The isothermal decomposition of uranium-2 wt % niobium alloy quenched from the gamma phase field into the temperature range 350 - 685 °C was studied. It proceeds by three distinct transformation mechanisms: diffusion (640 - 685 °C), bainitic (570 - 600 °C), and martensitic (below 550 °C). In the diffusional range typical Widmanstätten precipitation of the beta or the alpha phase occurs.

VI—9

THE INFLUENCE OF COOLING RATE ON THE STRUCTURE OF U-0.65% Mo ALLOY

A. MIHAJLOVIĆ, M. KOSTIĆ and P. TEPAVAC

Boris Kidrič Institute, Vinča

Uranium alloys with low molybdenum additions are used as fuel for gas-graphite natural uranium reactors. The molybdenum increases the thermal and radiation stability by increasing the strength and fineness of the alpha grain structure.

The influence of the cooling rate on the beta-alpha transformation temperature was studied and the correlation between the transformation temperature and the alpha-grain size was determined. From the continuous-cooling diagram and the change in the microstructure with the cooling rate it was concluded that at a cooling rate of 10°/s the beta-alpha transformation mechanism changes. The optimal cooling rate from beta temperature range for getting fine polygonal alpha grains was determined.

VI – 10

MAGNETIZING ROASTING OF LIMONITIC IRON ORE

V. LOGOMERAC

Zagreb University School of Technology, Sisak

One of the most promising processes for the enrichment of indigenous limonitic iron ore is magnetizing roasting followed by magnetic separation. Work done to date is outlined, and conditions for getting concentrates containing 57 - 61 % Fe and less than 8 % SiO_2 are presented. These results provide the basis for industrial application of the prosess, thereby making it possible for the Yugoslav iron and steel industry too to exploit ores of a quality now normaly being used abroad.

VI—11

SUBSTITUTION OF IMPORTED ORE FOR STEEL BY INDIGENOUS RAW MATERIAL

V. LOGOMERAC

Zagreb University School of Technology, Sisak

Yugoslav steel works today use exclusively imported hematite for steel refining. However, our country has a number of raw materials which with proper pretreatment and processing, could completely cover the total ore needs for refining. One of these is concentrate obtained from blast furnace flue dust. With this in view systematic experiments have been done in one of our steel plants. The results confirm that pelletized blast furnace flue dust concentrate is completely satisfactory for refining.

VI – 12

REGENERATION OF WASTE MATERIAL IN PRODUCTION OF SEMICONDUCTING ELEMENTS

B. ĐURKOVIĆ, Z. POPOVIĆ and D. SINADINOVIĆ
School of Technology, Beograd

In the production of semiconducting elements the utilisation of germanium is 20 - 30 % while the rest is waste. Depending on the technique the remaining germanium appears mostly in the form of small plates or sawdust-powder, mixed with waste-material from the saw and other dirt. A smaller fraction is lost in the form of a solution or in various evaporation compounds etc.

Regeneration of germanium from waste material in the shape of small plates and powder is of special interest. The conditions for regeneration, its problems, and results particularly with regard to utilisation of metal and purity of the product are presented.

VI—13

ON THE CYANIDATION OF GOLD FROM THE GOLDEN-BEARING PYRITE OF LECE MINE

M. SPASIĆ, B. ĐURKOVIĆ and D. SINADINOVIĆ
School of Technology, Beograd

One of the problems in the gold-cyanidation of gold-bearing pyrite is the relatively low leaching of gold, and the great consumption of cyanide at leaching.

The results of metallurgical preparation of pyrite to increase the utilisation of gold and decrease the consumption of cyanide are presented.

The preparation included pyrometallurgical, hydrometallurgical and mechanical treatment of concentrate, under various conditions. The results indicate that considerable improvement of the gold cyanidation process could be obtained if the raw material was metallurgically treated first.

VI – 14

THE BEHAVIOR OF ARSENIC, ANTIMONY AND BISMUTH IN THE ELECTROLYTE FOR COPPER REFINING

S. ĐORĐEVIĆ, O. TATIĆ-JANJIĆ and J. TARABIĆ

School of Technology and Institute for Chemistry, Technology and Metallurgy, Beograd

There is not enough data about the valency states of arsenic, antimony and bismuth in the electrolyte during the process of copper refining, or about the nature of various precipitates of them which are formed in the electrolyte.

The behavior of trivalent antimony in the presence of pentavalent arsenic in the electrolyte for copper refining was studied. AsV forms precipitates with Sb III with the atomic ratio As : Sb = 1. The solubility of this precipitate was determined at several temperatures and at various sulfuric acid concentrations.

The rate of precipitate formation in the presence of pentavalent arsenic and trivalent bismuth in the electrolyte was measured. The solubility of bismuth arsenate in sulfuric acid was determined.

VI – 15

A LABORATORY PROCEDURE FOR ELECTROLYTIC COPPER REFINING

S. ĐORĐEVIĆ and M. HALAI

School of Technology and Institute for Chemistry, Technology and Metallurgy,
Beograd

A laboratory scale apparatus for electrolytic copper refining was developed to allow electrolytic copper refining under conditions identical to those in an industrial plant.

The following basic factors were observed: current density, electrolyte composition regarding basic components, electrode materials, electrode spacing, electrolyte composition regarding impurities, operating temperature, electrolyte circulation, concentration of addition agents, and continual operation.

The apparatus was tested in a series of experiments.

VI – 16

SOME CHARACTERISTICS OF COLD DRAWN OFHC COPPER WIRE WITH LARGE DRAFTS

V. MILENKOVIĆ, S. TODOROVIĆ and D. CVETKOVIĆ

School of Technology Beograd, Cable factory Svetozarevo

The possibility of cold drawing OFHC copper wire in large drafts is dealt with. The suitability of the wire for cold drawing was examined in terms of the mechanical and physical properties. Cold drawing was done in two ways, one to study the characteristics of drawing machines the other to study the suitability of the metal for deformation by cold drawing.

The results show that the construction of drawing machines does not correspond to the metallurgical aspects of cold drawing, which is of great importance in practice.

VII—1

CALCULATION OF ENTHALPY CHANGES OF TWO-STAGE OXIDATION OF URANIUM DIOXIDE

I. G. STAMENKOVIĆ and R. KUBAT

Boris Kidrič Institute, Laboratory for reactor materials, Vinča

The reaction heat of the first and second oxidation stages of stoichiometric uranium dioxide has been determined by differential thermal analysis (DTA) at a heating rate of 4 °C/min under atmospheric pressure. Both calibration materials and uranium dioxide powder were examined in mixtures with Al_2O_3.

The paper also describes the possibilities of determining enthalpy changes of the separate oxidation stages of uranium dioxide and the enthalpy change of the formation of the intermediate oxide U_3O_7.

VII—2

GENERAL KINETIC EQUATION OF ZINC OXIDE SINTERING

B. ŽIVANOVIĆ and M. RISTIĆ

Boris Kidrič Institute, Laboratory for reactor materials, Vinča

Zinc oxide was studied with a view to more accurate definition of the kinetics of oxide material sintering. Particular attention was paid to volume shrinkage of pressed samples in the temperature range 700 - 1200 °C in 0 - 4 hours. The results show that the equations of Kingery, Fedorchenko, Burke and Pines cannot be used to describe the process studied. Under the above conditions the equation $\Delta V/V = kt$ where k and n are functions of temperature is valid.

VII—3

CRITICAL ANALYSIS OF KINETICS OF UO_{2+x} SINTERING PROCESS

D. DELIĆ, R. DELETIĆ, E. KOSTIĆ and M. RISTIĆ

Boris Kidrič Institute, Laboratory for reactor materials, Vinča

Analysis of the sintering kinetics of UO_{2+x} powders has shown that neither Fedorchenko's equation for shrinkage of pressed samples in the early stages of sintering, nor Pines' equation for its later stages can be applied. Shrinkage of sintered plates goes as $\Delta V/V = kt^n$. A detailed analysis of the mechanism of sintering and of a number of other processes taking place simultaneously provides an explanation of the discrepancy between our kinetic equation and the relations of Fedorchenko and Pines.

VII—4

COMPARATIVE MICROSTRUCTURAL ANALYSIS OF POWDERS OF SINTERED UO_{2+x}

V. PETROVIĆ, E. KOSTIĆ, R. DELETIĆ and M. RISTIĆ

Boris Kidrič Institute, Laboratory for reactor materials, Vinča

Detailed microstructural analysis of sintered UO_{2+x} powders clearly shows that sintering proceeds in two stages. Investigation of pore size during heating gave the following results: in the first stage of sintering the pore size growth rate is fairly slow, whereas after 1000° it becomes much faster. Study of changes occurring in the grain size of sintered pallets yielded various equations for grain growth in the first and second stages of sintering.

VII–5

A CRITICAL SURVEY OF METHODS FOR MEASURING DENSITY OF SINTERED MATERIALS

F. SIGULINSKI and M. STEVANOVIĆ

Boris Kidrič Institute, Laboratory for reactor materials, Vinča

Methods for measuring the density of sintered materials are surveyed. Experimental results, accuracy and factors affecting the accuracy are analysed. Particular attention is paid to sources of error.

VII—6

REACTION KINETICS IN SOLID STATE OF THE SYSTEM UO_2 - Al

S. KIŠ and M. M. RISTIĆ

Boris Kidrič Institute, Laboratory for reactor materials, Vinča

The paper presents results of a reaction kinetics study in the polydispersed UO_2 - Al system, with molar ratio 3 : 13, in the temperature range 600 - 760°. It also points out the possibility of applying modified equations to reaction kinetics in monodispersed systems. The activation energy of the reaction between uranium dioxide and aluminum with the temperature range under examination was found to be 30.5 kcal/mol. In addition, an essential relationship was found between the size distribution of uranium dioxide powder and kinetic parameters of the reaction.

VII—7

MEASURING OF THERMAL CONDUCTIVITY OF CERAMICS AT TEMPERATURES FROM 20° TO 200°C

J. KATANIĆ

Boris Kidrič Institute, Laboratory for reactor materials, Vinča

Thermal conductivities of ceramics in the temperature range 20 - 200 °C were measured by Schröder's absolute method. The construction and principles of the apparatus are described. The measuring of heat flux and temperature is not necessary — by means of two boiling liquids a constant temperature drop across the sample (10 - 20 °C) is maintained. The time necessary for a certain quantity of the distillate to accumulate is measured. The advantages of this apparatus are pointed out. The estimated error does not exceed ± 5 % for heat conductivities below 0.2 cal/cm sec 0 °C. Heat conductivity measurements of glass, sintered ZnO, TiO_2, UO_2 etc at 40.5 °C are given. In case of ceramics the results have been reduced to theoretical density.

VII—8

EFFECT OF FAST NEUTRON IRRADIATION ON MECHANICAL PROPERTIES OF REFRACTORY OXIDES

M. STEVANOVIĆ

Boris Kidrič Institute, Laboratory for reactor materials, Vinča

The study deals with effect of fast neutron irradiation of an integral flux of the order of 10^{20} n_r /cm^2 upon the elastic constants, microhardness and mechanical properties of monocrystals and sintered samples of Al_2O_3 and MgO. On the basis of the results the mechanism of the primary and secondary effects of irradiation upon the mechanical properties of oxides are discussed. A hypothesis is proposed concerning the mechanism of elasticity modulus changes of sintered samples.

VII — 9

SPONTANEOUS DECOMPOSITION OF AGATE

O. LJ. ĆUKOVIĆ

School of Technology — Beograd

Spontaneous decomposition of agate on a piece of a laboratory mortar was followed over a period of 18 months. Spectral analysis of material taken from the decomposed surfaces of the piece was performed. The material was photographed both at the beginning of the experiment and after 18 months. Keeping the agate at a constant 100 °C for one month brougth no increase of the decomposition rate.

VII–10

HYDRATATION OF (*Ca*, *K*) MONTMORILLONITE.
II. ADSORPTION ISOTHERMS

D. DELIĆ and M. TECILAZIĆ-STEVANOVIĆ

Institute for Inorganic Chemistry, School of Technology, Beograd

By an isopiezometric method, adsorption isotherms for (Ca, K) montmorillonite have been determined at 20 and 35 °C. Calcium and potassium isoeletronic ions were chosen as complementary cations, because of theoretical and practical knowledge of the behaviour of (Ca, K) montmorillonite. Hydratation was studied with the hope that detailed knowledge of the thermodynamic state of the adsorbed water would give data not only about the adsorbed phase, but also about the nature of the mineral surface involved in the process of adsorption too.

From the experimental results (isotherms), the differential heats and the differential entropies of water adsorption on (Ca, K) montmorillonite were determined. The starting material was montmorillonite mineral separated from Wyoming bentonite.

VII – 11

POSSIBILITY OF MANUFACTURE OF FINE PORCELAIN WITHOUT FELDSPAR FROM YUGOSLAV RAW MATERIALS

J. ZLATANOVIĆ

University of Skopje

A test was made to examine the possibility of making fine porcelain from raw materials from the area of Bujanovac without adding feldspar. The experiments were carried out under industrial conditions at the Boris Kidrič works, Titov Veles. The raw materials from the Bujanovac area contain, besides kaolin and feldspar, the products of feldspar decomposition kaolin aluminum oxide and free silicic acid. These enable the quartz sand mixtures to retain material plasticity, even with up to 50 % sand. The results of the test are satisfactory.

VII — 12

THE POSSIBILITY OF INDUSTRIAL APPLICATION OF BENTONITE FROM THE SURROUNDINGS OF NIŠ

M. TECILAZIĆ-STEVANOVIĆ, T. JANAĆKOVIĆ and V. KOVAČEVIĆ
Institute for Inorganic Chemical Technology, School of Technology, Beograd

Bentonite reserves from places near Niš — Zavidince, Mečiji Do and Jelenkovac — are of unequal quality and quantity. One possible way of solving the exploitation problem as well as the problem of the wider industrial application of bentonite from the area is to produce commercial bentonite, starting with a mixture of bentonite clays from the three places mentioned.

This was the main subject of this study. By alkali treatment of manufactured mixtures (three components), a commercial bentonite was manufactured which proved good for casting and ground injection. In suspensions of more than 6 % these bentonites could also be used for drilling fluid. Theoretical considerations of the geological properties of dispersed bentonite-water systems as a function of bentonite concentration are also given.

VII — 13

CONTRIBUTION TO THE STUDY OF VOLCANIC GLASS FROM THE KRATOVO AREA

M. DIMITROVSKI

University of Skopje

The large reserves of volcanic glass-opcidiane discovered on the slopes of the mountain Crni Vrh, have attracted the attention of the construction industry, as a possible new raw material for the manufacture of light concretes. The author has studied the composition and physico-chemical properties of this glass when heated to different temperatures. The chemical composition and ignition loss do not differ from those of glasses currently used in production in e.g. Hungary, Bulgaria and Russia. The experiments, carried out on laboratory scale did not give the optimum results citied in the literature. The raw material has desirable properties, since it maximally expands at between 800 - 900 °C. The expansion experiments were carried out with other raw materials of volcanic origin too, for example tuffs, but the results were unsatisfactorily low.

VII — 14

CONTRIBUTION TO THE STUDY OF RING FORMATION IN ROTARY CEMENT KILNS

J. ZLATANOVIĆ, M. MATKALIJEVA and M. DIMITROVSKI
University of Skopje

The reasons for ring formation in rotary kilns for clinker firing have been examined over a long period of time. The authors conclude that ashes from the coal used to heat the kiln are one of the main factors. By using different coal (containing less ash) it was possible to eliminate ring formation almost completely.

With some coal, e.g. from Aleksinac, a ring formed after 7 days, when the kiln had to be shut down so that the ring could be removed. With Soko coal this period was prolonged and by use of a suitable process technique, ring formation was almost eliminated.

VIII — 1

PHOTO-NUCLEAR DETERMINATION OF URANIUM AND THORIUM IN SOME YUGOSLAV ROCKS

B. PAVLOVIĆ and D. PETROVIĆ

School of Technology, Beograd

Determination of uranium and thorium in some rocks by observing alpha-particle tracks in photo-nuclear emulsions gives results that do not always agree with those gotten by uranium fluorimetry and thorium emanometry. Those deviations are particularly great in the results for uranium concentrations in travertines.

Analyzing the origin of these deviations we come to the conclusion that they are a consequence of radioactive disequilibrium between some elements of the radioactive series in the rocks. Thus Coppen's formula which we used to calculate the uranium and thorium concentrations in the photo-nuclear method may only be applied in case these elements are in radioactive equilibrium with their disintegration products.

VIII—2

ISOTOPE ANALYSIS OF URANIUM SAMPLES BY ALPHA SPECTOMETRY

D. CVJETIČANIN, V. BULOVIĆ and K. ZMBOV

Boris Kidrič Institute, Hot-Laboratory Department and Analysis and Measurement Department, Vinča

The isotopic ratios $^{234}U/^{238}U$ and $^{235}U/^{238}U$ in depleted, natural and slightly enriched (up to 2 wt. % ^{235}U) uranium samples were determined by alpha spectrometry using a Frisch-type ionization chamber. The results were compared with the ^{235}U content determined by mass spectrometry.

The $^{234}U/^{238}U$ and $^{235}U/^{238}U$ alpha activity ratios in the samples investigated were within (0.163 ± 0.05)— (2.98 ± 0.03) and (0.018 ± 0.002) — (0.125 ± 0.002), respectively.

The data obtained for our samples show a definite dependence of the $^{234}U/^{235}U$ isotopic ratio on the ^{235}U content.

VIII – 3

THE RADIOACTIVITY OF K^{40} IN RAINWATER AND FRESHWATER IN THE ENVIRONMENT OF VINČA

R. RADOSAVLJEVIĆ, M. KOVAČEVIĆ, V. VUJOVIĆ, D. ĐORĐEVIĆ

Boris Kidrič Institute, Department of Radiological Protection, Vinča

The natural background in the biosphere originates mostly from potassium-40 (85 %). At the Institute of Nuclear Science at Vinča the content of potassium is systematically determined in various biomaterials—rainwater, freshwater and soil. Determination of the potassium contained in the rainwater which is sampled at ground level shows considerable deviation from seasonal variations. Also, it is found that the content of potassium depends on the quantity of rainwater.

The potassium content was measured over a long period in the water of the Danube, in drinking water prepared from the Danube water, in the stream Mlaka and in the river Boletica.

VIII—4

RADIONUCLIDE DISTRIBUTION IN A HETEROGENEOUS SYSTEM

R. DESPOTOVIĆ

Laboratory of Radiochemistry, Department of Physical Chemistry, Ruđer Bošković Institute, Zagreb

In a two-phase solid-liquid system the mechanism of migration of radionuclides from the liquid to the solid phase depends on the genotypic and phenotypic properties of the system.

The process of heterogeneous exchange in solid-liquid model systems was investigated and the influence of genotypic and phenotypic properties on the kinetics and nature of the mechanism is analyzed.

The radionuclide distribution in the two-phase systems considered indicates that the crystallization-dissolution equilibrium and ion self-diffusion in the crystal lattice are dominant factors.

VIII—5

SEPARATION OF AMERICIUM FROM PLUTONIUM BY ANION EXCHANGE

D. CVJETIČANIN and S. RATKOVIĆ

Boris Kidrič Institute, Hot-Laboratory Department, Vinča

A method for the separation of Am^{3+} from Pu^{4+} by anion exchange on Dowex 1, X4, at 50 °C is described. The procedure allows quantitative seperation of small amounts of americium from plutonium in one run.

The method was used for the determination of ^{241}Am, ^{241}Pu (by measuring the alpha activity of ^{241}Am built-up from ^{241}Pu) and ^{233}Pu in plutonium samples, using alpha spectrometry.

VIII—6

THE EXTRACTION OF PLUTONIUM WITH SOME NITRO-COMPOUNDS

N. MILIĆ

Boris Kidrič Institute, Hot-Laboratory Department, Vinča

The extraction of Pu^{4+} and PuO_2^{2+} from aqueous solutions of nitric acid using nitromethane, nitrobenzene, and a mixture of them and a mixture of nitromethane and thenoyltrifluoroacetone was studied.

The dependence of the extraction coefficients of Pu on the initial aqueous HNO_3 concentration and on the extractant concentration in the organic phase was determined.

VIII—7

SYNTHESIS OF SOME ORGANIC PHOSPHORUS INSECTICIDES LABELED WITH PHOSPHORUS-^{32}P AND SULPHUR-^{35}S

V. JEZDIĆ, M. SKAKUN and S. KONSTANTINOVIĆ

Boris Kidrič Institute, Hot-Laboratory Department, Vinča

Malathion (0,0-dimethyl dithiophosphate of diethyl mercaptosuccinate) and dipterex (0.0-dimethyl-2,2,2-trichloro-1-hydroxyethyl phosphate) belong to a group of organic phosphorous compounds which have been widely applied in agriculture as powerful insecticides. To study their insecticidal effect, methods have been developed of synthezing these compounds labeled with radioactive isotopes ^{32}P and ^{35}S.

This paper describes a procedure for the synthesis of malathion-^{35}S starting from sulfuric acid-^{35}S, and of malathion-^{32}P, starting from red phosphorus ^{32}P. This procedure is simpler and has a higher yield than procedures previously described. It can be used within the range 10 to 40 mmoles.

The method for dipterex-^{32}P is very simple. It has been developed for 1 to 5 mmoles.

VIII–8

DETERMINATION OF THE DETECTION ENERGY THRESHOLD OF THE 4–π LIQUID SCINTILLATION COUNTER

D. PALIGORIĆ and LJ. DOBRILOVIĆ

Boris Kidrič Institute, Department of Analysis and Measurement Metrology, Vinča

A method of determining the detection energy threshold of the 4–π liquid scintillation coincidence spectrometer for pure β-emitters is described.

The threshold was determined at the maximum energy of ^3H in integral spectra, recorded with two photomultipliers, singly and in coincidence.

The position of the energy maximum of ^3H was obtained from the cross-section of the integral spectra of ^{35}S and $^{35}S+{}^3H$.

VIII — 9

DEPENDENCE OF COUNTING EFFICIENCY OF THE 4-π LIQUID SCINTILLATION COUNTER ON SOURCE HEIGHT

Đ. BEK-UZAROV, LJ. DOBRILOVIĆ and D. PALIGORIĆ

Boris Kidrič Institute, Department of Analysis and Measurement, Vinča

It has been found that the source height has different effects on the counting efficiency of the 4-π scintillation counter for pure beta emitters with different energy maxima.

This dependence was investigated with the following isotopes: ^{3}H, ^{35}S, ^{204}Tl, and ^{32}P for sources with different flask diameters from 10-42 mm, corresponding to weights of 0.3-32 g.

VIII — 10

GAMMA RADIATION DOSE MEASUREMENT WITH AN AIR-EQUIVALENT IONIZATION CHAMBER

D. NOVKOVIĆ and Đ. BEK-UZAROV

Boris Kidrič Institute, Department of Analysis and Measurement, Vinča

Calculation of an air-equivalent material is given. One of the air-equivalent materials for making an ionization chamber is described.

The calculations were checked by measuring the X-radiation of the material over a wide range of energies.

VIII—11

POSITION OF MAXIMUM AND HALFWIDTH OF AN ALPHA PARTICLE SPECTRAL LINE AS A FUNCTION OF SOURCE THICKNESS

LJ. DOBRILOVIĆ

Boris Kidrič Institute, Department of Analysis and Metrology, Vinča

Our experimental results confirm the theoretical analytical expression for the final shape of an alpha spectrum line (Kocharov and Korovlev). With increasing source thickness the position of the maximum shifts to lower energy and its halfwidth increases.

The dependence was investigated on ^{421}Am sources in the range 5.3×10^{-6} to 8.4×10^{-2} h/Ro (h = source thickness, Ro = range of alpha particle of given energy in source material).

IX – 1

MIXED PILE RADIATIONS IN AQUEOUS RADIOCHEMISTRY

I. DRAGANIĆ, B. RADAK and V. MARKOVIĆ
Boris Kidrič Institute, Department of Radiochemistry, Vinča

The application of mixed pile radiation in aqueous radiochemistry is discussed from the aspect of dosimetry and experimental techniques.

Two dosimetric methods are considered in detail — the calorimetric and the chemical method.

A differential calorimeter is described. It is constructed so as to permit simultaneous measurement of energy absorption in liquid and solid samples. Gamma and neutron contributions can be derived from energy absorption measurements in different materials. The possibility of putting liquid samples in the calorimeter make it very useful for radiochemistry studies.

The chemical system uses oxalic acid decomposition in light and heavy water solutions. It allows determination of gamma and neutron contributions to total absorbed doses in a similar way to the calorimetrical method. Different G-values for oxalic acid decomposition induced by gammas and pile protons or deuterons are presented.

IX — 2

RADIOLYSIS OF AQUEOUS ALKALINE SOLUTIONS OF OXALATES IN PRESENCE OF OXYGEN

Z. DRAGANIĆ, M. KOSANIĆ, M. TONIĆ, D. OVCIN and I. DRAGANIĆ
Boris Kidrič Institute, Department of Radiochemistry, Vinča

Radiation yields of CO_2, H_2 and H_2O_2 were measured at 50 mM oxalate and 0.6 mM oxygen concentration. The initial pH was varied from 9.5-13. In some cases the consumption of O_2 was followed polarographically ($[O_2]$ — 0.3 mM.) Using ^{14}C as a radioactive indicator the possibility of oxalic acid reforming by recombination of carboxylic radicals was studied. The results show that in the presence of O_2 reformation of oxalic acid is not possible and that the sharp decrease of oxalic ion decomposition with increasing pH is due to a change in the nature of the hydroxyl radicals. Reactions of O^- ion radicals with oxalic acid, hydrogen peroxide and oxygen are discussed. The reaction scheme allows calculation of the primary molecular hydrogen yields and short-lived reducing species. Some observations concerning the primary oxidizing species of water radiolysis are made.

IX — 3

THE POSSIBILITY OF INDUCING SYNTHESIS OF LABELED OXALIC ACID WITH $^{60}C_o$ GAMMA RAYS

M. TONIĆ and Z. DRAGANIĆ

Boris Kidrič Institute, Department of Radiochemistry, Vinča

The possibility of inducing synthesis of ^{14}C-labelled oxalic acid with radiation has been studied. Aqueous solutions of potassium oxalate (1.10^{-2} and 5.10^{-2}M, pH 7.0-13) in the presence of $NaH^{14}CO_3$ (5.10^{-4}) or $H^{14}COONa$ (1.10^{-2}M) were investigated. Experiments were made in the presence and absence of oxygen.

The mechanism of formation of labelled oxalic acid and the inhibitory action of oxygen are discussed.

IX—4

CHEMICAL DETERMINATION OF RADIOLYSIS PRODUCTS IN SOLID SYSTEMS

LJ. JOSIMOVIĆ and O. GAL

Boris Kidrič Institute, Department of Radiochemistry, Vinča

The observation of the effect of radiation on solid oxalic acid and ammonium oxalates requires determination of the final, stable radiolysis products. To do this we used the method of chemical analysis of irradiated samples dissolved in water. Since radiolysis of a system produces related chemical compounds, the analysis of an aqueous solution of the irradiated system is a rather complex problem i.e. the identification and quantitative determination of some compounds require a method which is both selective and very sensitive. Qualitative analysis (spot reactions and paper chromatography) were made for a series of compounds expected. Quantitative specific spectrophotometric measurements of the total extinction of aqueous solutions of irradiated samples were also made. Comparison was made with pure compounds. The results provide data on the nature of the products. By spectrophotometric methods with 2,7 dihydroxynaphthalene and phenylhydrazinchlorhydrate the dependence of the total measured amounts of products on the absorbed dose was found for both gamma and reactor radiation.

IX–5

LUMINESCENCE IN SOME SOLID OXALATES IRRADIATED WITH HIGH DOSES OF REACTOR AND ^{60}Co GAMMA RADIATION

O. GAL and J. PATKO

Boris Kidrič Institute, Department of Radiochemistry and Institute of Applied Physics, Kossuth Lajos University, Debrecen

Some general observation on the luminescence phenomena induced by high doses of ionizing radiation are presented. Results of fluorescence measurements of different oxalic acid and ammonium oxalate samples exposed to high doses of mixed pile and ^{60}Co gamma radiation are given. The causes of these phenomena are considered.

IX—6

CONTRIBUTION ON PROTECTION OF LIVING ORGANISMS AFTER THE ACTION OF IONIZING RADIATION

A. STEINER, E. MOHOROVIČIĆ, M. KIRIGIN and E. CERKOVNIKOV

Institute of Physics and Institute of Chemistry and Biochemistry, University of Zagreb, Medical School, Rijeka

The influence of dosage X-ray tube voltage and some biocatalysators on germination of wheat seeds.

It was earlier shown in laboratory and field experiments that some bio-catalysators to some extent inhibit the action of X and gamma rays on the germination and yield of corn and soya beans (Biochimica e biologia sperimentale II (1963) 158; Acta Pharm. Iug. XIV (1964) 1; IV Kongres farm. Jug. X. 1964 — Opatija).

Continuing this work, we studied influence of the X-ray tube voltage on irradiated wheat germination.

The experiments were made with "Mara" wheat from Cepić 1963 harvest. In each experiment 200 grains were X-rradiated. They were then put 30 minutes in a solution of calcium hydroxide, washed in distilled water, and put in Petri dishes containing sterilized sand (about 90 g) mixed with 50% of Shive nutrient solution (Macht, J. Lab. Clin. Med. 26 (1941, 957), dilluted with water or some plant hormones solution. The grains germinated in a dark hot-bed at a temperature of 28°C. Every third day 5 ml of dist. water was added. After 8 days the lengths of shoots were measured. Each experiment was repeated 3 times. The results were statistically treated and compared.

Group 1. The experiments were divided in two groups. The dosage was constant — 2 kr, and the tube voltage was 85, 115 or 145 KV. The wheat only grew on nutrient substrate: the results were compared with analogous experiments where to the nutrient solution was added some MCPA (4 chlor-2 methylphenoxy acetic acid), 2,4-D (2,4-dichlorphenoxy acetic acid) or PMCA (phenilmercopto acetic acid). In all these experiments the smallest shoot length was for 85 KV, and the largest with 115 KV radiation.

Group 2: At 100 KV doses 4 and 20 kr were given. The shoots for 20 kr were much bigger than at 4 kr, but still less than for nonirridiated wheat. At 4 kr the biggest inhibition was obtained without hormones, with 100 mg/grain with 2,4-D and 1000 mg/grain with PMOA. At 20 kr the best results were with 10 mg/grain MCPA and poorest without hormones and with 1000 mg/grain PMCA.

Hence a) Laboratory in experiments the shoot length depends not only on the dose but also on the X-ray tube voltage.

b) By adding bio-catalysators it is possible to reduce the inhibitory action of X-rays.

IX — 7

THE EFFECT OF IONIZING RADIATION ON PECTIN, II

M. DŽAMIĆ, B. JANKOVIĆ and S. VELJKOVIĆ

Institute for the Application of Nuclear Energy in Agriculture, Veterinary Science and Forestry Beograd (Zemun) and School of Agriculture, Beograd

Some effects of gamma-rays on apple pectin under different conditions were studied. The following doses were used: 0.02, 0.05, 0.1, 1.0 and 2.0 Mrad.

The following properties and changes were determined: Specific viscosity, degree of esterification, thermal degradation activation energies, rate constants, the influence of some electrolytes in pectin solutions.

Further research is under way.

Izdavač

IZDAVAČKO PREDUZEĆE "NOLIT", BEOGRAD, TERAZIJE 27

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