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SPECTROPHOTOMETRIC DETERMINATION OF TWO-COMPONENT SYSTEM Co(II) — Ni(II)

by

J. MIŠOVIĆ, M. JOVANOVIĆ and LJ. FOTIĆ

The two-component Co-Ni system has been investigated by a number of authors (1,2,3,4,5,6) by the spectrophotometric method using different organic reagents. All these determinations were mostly carried out in organic solvents and are rather complicated in comparison with ours, which are more advantageous because they are much simpler.

The present paper describes the simultaneous determination of Co(II) and Ni(II) by a spectrophotometric method in which cobalt and nickel are converted into colored compounds using EDTA in aqueous solutions. For the simultaneous determination of Co and Ni, light absorptions were measured at 520 nm and 600 nm. These wavelengths fulfil the conditions given by Mellon(7), that is, they represent wavelengths at which the absorptivity relation of the two components is minimal and maximal, i.e., the light absorption of both components is one additive value(8). The concentrations were calculated from the absorptions measured at the above wavelengths by solving two additive absorption equations. The results are given in the experimental part. All measurements were made at pH 4.6 and the concentration range investigated was 20—60 mg Co/100 ml and 40—80 mg Ni/100 ml. The absorption of cobalt changes with the changing pH of the solution. In the case of nickel it is constant to pH = 5. The color of the complexes formed is stable and they are subject to Beer's law in the given concentration range.

The formation of complex compounds between EDTA and Co(III) and Ni(II) has been studied by Přibil and Malík(9) and others(10), and Nielsch and Böltz(12), who found that Co(III)-EDTA yields a water soluble reddish-violet colored complex compound and Ni(II)-EDTA gives a blue colored compound.

EXPERIMENTAL PROCEDURE

Apparatus: Spectral curves were determined on a UNICAM SP 600 spectrophotometer in 2-cm cells. The pH values of the solution were measured on a Radiometer-Copenhagen Type PHM pH-meter of 22 r.

Reagents

Standard nickel solution: A $NiSO_4$ solution was prepared with 0.004 g Ni/ml. The solution was standardized by the gravimetric procedure by precipitating nickel in the form of Ni-dimethylglyoxime.

Standard cobalt solution: A $Co(NO_3)_2$ solution was prepared with 0.006 g Co/ml. The solution was standardized by the gravimetric procedure as cobalt pyrophosphate.

EDTA solution: A 0.1 M solution of EDTA was prepared. This solution was used to develop a stable color in the Co and Ni complex.

Buffer solution: 238 g of Na-acetate were dissolved in 500 ml of water, 102 ml of glacial acetic acid were added and the solution was made up to one liter. If 5 ml of this solution are diluted to 25 ml, the pH value of the solution obtained is 4.6. The pH values were checked with a pH-meter.

The procedure of determination: Corresponding concentrations of the Co and Ni solution, 30 ml of 0.1 M EDTA and 20 ml of the buffer solution were put in a 100 ml measuring flask. The content was diluted to 100 ml with distilled water. For the blank test we only used distilled water, since, as is known, the EDTA solution is colorless and the Co(II) and Ni(II) solution in the concentrations investigated do not have noticeable color.

Absorption spectra of the Co-EDTA and complexes

In order to determine the experimental wavelengths we determined the following absorption spectra:

- absorption spectrum of the Co(II) — EDTA complex
- absorption spectrum of the Ni(II) — EDTA complex
- absorption spectrum of a mixture of the Co-EDTA and Ni-EDTA complexes.

The absorption spectrum of the Co(II)-EDTA complex was obtained by diluting the standard solution of cobalt and taking the mean concentration value (40.15 mg Co/100 ml) of the range of concentrations determined, and preparing a solution for investigation in the above described way with 10 ml of the EDTA solution. The results obtained in determining the absorption curve $\lambda = 380$ nm to 1000 nm are shown in Table 1. It can be seen that the maximal absorption of the CO(II)-EDTA complex is at 520 nm.

To determine the absorption spectrum of the Ni(II)-EDTA complex we carried out the same procedure as for cobalt, with the exception that the mean concentration value was 60.75 mg Ni/100 ml and 20 ml of 0.1 M EDTA was added to 100 ml of the solution investigated. The results are shown in Table 2. The maximal absorption of the Ni-EDTA complex is at the wavelength of 600 nm.

The absorption spectrum of the two-component Co(II)-EDTA and Ni(II)-EDTA system was obtained in a similar way. The color of the solution was violet-blue. The results of measurement of the absorption at various wavelengths are shown in Table 3. It can be seen that the maximum absorption is also at wavelengths from 520 nm to 600 nm. We have seen above that at these wavelengths the components from the investigated system undergo maximal absorption under the same conditions when they are separate. This indicates that the light-absorption of one component does not influence the light-absorption of the other. This was also confirmed by comparison with a theoretical diagram of the investigated system.

Influence of the pH of the solution on the absorption of the Co(II)-EDTA and Ni(II)-EDTA complexes

Prior to determining the two-component system, the influence of the pH of the solution on the absorption of the investigated complex compounds had been investigated.

TABLE 1
Absorption spectrum of Co(II)-EDTA solution, conc. 40.15 mg *Co*/100 *ml*

TABLE 2
Absorption spectrum of Ni(II)-EDTA solution conc. 60.75 mg *Ni*/100 ml.

TABLE 3
*Absorption spectrum of Co(II)-EDTA and Ni(II)-EDTA solution, conc. 40.15 mg Co/*100 *ml.* and *60.75 mg. Ni/*100 *ml.*

No.	λ *nm*	*T*%	*A*	*T*%	*A*	*T* %	*A*
1	380	99.4	0.003	—	—	51.1	0.292
2	400	99.8	0.001	60.6	0.217	59.1	0.229
3	420	98.2	0.008	84.4	0.073	77.1	0.113
4	440	90.5	0.044	93.0	0.031	76.6	0.116
5	460	73.6	0.133	91.5	0.039	63.2	0.199
6	480	63.6	0.200	95.5	0.020	64.2	0.192
7	500	63.0	0.201	95.0	0.022	63.0	0.201
8	520	62.4	0.205	92.0	0.036	62.4	0.204
9	540	70.6	0.151	85.8	0.067	64.0	0.194
10	560	82.2	0.085	77.6	0.112	65.0	0.187
11	580	89.1	0.050	68.0	0.167	62.9	0.201
12	600	91.6	0.038	63.2	0.199	61.2	0.213
13	625	93.3	0.030	66.5	0.177	64.8	0.188
14	650	95.2	0.021	75.1	0.124	71.4	0.146
15	700	98.0	0.009	85.4	0.068	84.5	0.073
16	750	99.1	0.004	91.0	0.040	88.1	0.055
17	800	99.1	0.004	84.0	0.076	75.0	0.118
18	850	98.5	0.007	77.0	0.134	66.0	0.185
19	900	98.5	0.007	60.2	0.220	45.8	0.339
20	950	—	—	43.9	0.358	27.0	0.569
21	1000	88.8	0.052	34.1	0.467	21.0	0.678

TABLE 4
Absorption of Co-EDTA solution against the pH value

TABLE 5
Absorption of the Ni-EDTA solution against the pH value

No.	pH	*T*%	*A*	pH	*T*%	*A*
		λ=520 nm			λ=600 nm	
1	2.50	62.1	0.207	2.62	63.2	0.193
2	2.80	69.1	0.161	2.90	65.0	0.187
3	3.25	63.4	0.198	3.00	65.0	0.187
4	3.50	64.5	0.190	3.60	65.0	0.187
5	4.45	66.5	0.177	4.00	65.0	0.187
6	5.00	67.7	0.172	4.90	65.0	0.187
7	5.60	66.7	0.175	5.87	65.5	0.184
8	6.60	66.9	0.174	6.40	65.0	0.193
9	7.70	66.5	0.177	7.60	64.8	0.188
10	8.70	67.2	0.173	8.50	63.0	0.201
11	9.40	62.9	0.201	9.20	73.0	0.137
12	10.05	58.2	0.235	9.50	61.4	0.212

Absorption were measured at wavelengths corresponding to maximum absorptions of the solution. The results for Co-EDTA are shown in Table 4 and for Ni-EDTA in Table 5. As is seen, the pH of the solution exerts influence on the absorption of Co-EDTA, while in the case of Ni-EDTA there is no influence up to pH=5. Therefore, all measurements were made at constant pH of the solution, the optimal value being pH 4.6.

Simultaneous determination of cobalt and nickel

In order to determine the f-values necessary for the determination of unknown concentrations of cobalt and nickel, it was necessary to have Beer's diagrams for each component in the system. From Beer's diagram, if absorption is plotted on the ordinate and known concentrations on the abscissa, one can determine the slope of the straight line as the ratio $A : c$ with chosen wavelengths. The diagrams were determined for the concentration ranges 20—60 mg Co/100 ml and 40—80 mg Ni/100 ml, since they were proved to obey Beer's law.

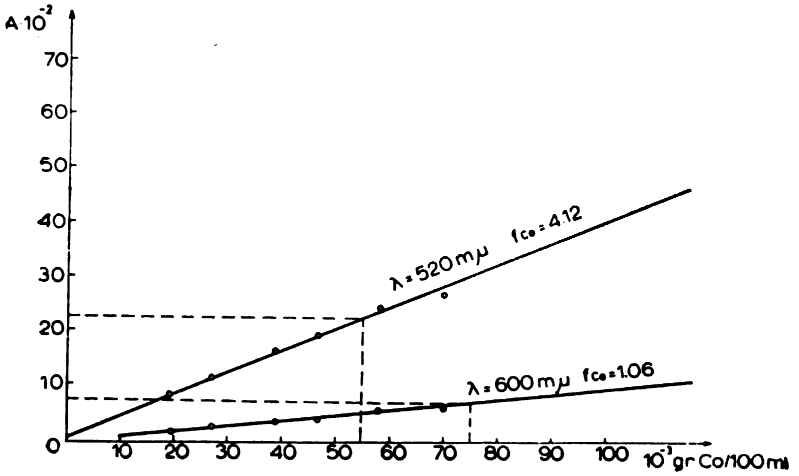

Fig. 1
Beer's diagram for *Co*-EDTA, used for calculations of *f*-value

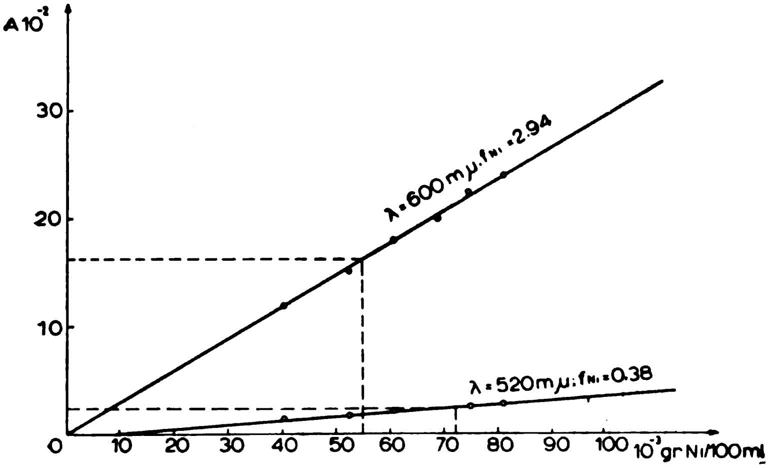

Fig. 2
Beer's diagram for *Ni*-EDTA, used for calculations of *f*-value

The solutions were prepared in the above mentioned way. The results for Co-EDTA are shown in Fig. 1 and for Ni-EDTA in Fig. 2. The *f*-values calculated for these diagrams are: $f_{Co,520}=4.12$; $f_{Co,600}=1.06$; $f_{Ni,520}=0.38$ and $f_{Ni,600}=2.94$.

By measuring the absorptions of Co and Ni solutions of various concentrations with two wavelengths and solving the equations of additive absorptions into which the calculated *f*-values and measured absorptions were introduced, we obtained Table 6. It can be seen from the table that the results vary within the permissible range of error.

TABLE 6

Results of simultaneous spectrophotometric determinations of cobalt and nickel

No.	Taken *mg Co*/100 *ml*	Taken *mg Ni*/100 *ml*	*A* = 520 *nm*	*A* = 600 *nm*	Found *mg Co* /100 *ml*	Found *mg Ni* /100 *ml*	Relativ. error *Co* %	*Ni* %
1	27.23	48.60	0.129	0.171	26.85	48.38	—1.49	—0.45
2	38.90	64.80	0.186	0.233	29.24	65.05	+0.87	+0.38
3	54.46	50.63	0.240	0.206	53.91	50.76	—1.01	+0.25
4	27.23	44.55	0.128	0.162	26.98	45.30	—.092	+1.68
5	31.12	52.65	0.148	0.190	30.81	53.45	—0.99	+1.55
6	42.79	72.90	0.202	0.260	42.30	73.06	—1.14	+0.22
7	23.34	81.00	0.125	0.263	22.83	81.15	—0.22	+0.18
8	38.90	60.75	0.184	0.219	38.59	60.56	—0.79	—0.31

DISCUSSION

From the above measurements it may be concluded that the spectrophotometric determination of cobalt and nickel as a two-component system is possible in the concentration ranges 20—60 mgCo/100 ml and 40—80 mgNi/100 ml. The obtained values vary within the permissible range of error and the results are reproducible.

Investigation of foreign ions was not done, since it is known which ions give colored compounds with EDTA (e.g., Cu^{2+}, Ca^{2+}, Mg^{2+}, etc.) and hence may interfere with the determinations and consequently must be first removed. The above investigations offer the possibility of determining two-component or three-component systems containing, besides Co and Ni, also ions which give colored compounds with EDTA.

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OSCILLOMETRIC TITRATIONS OF TERTIARY AMINES AND SALTS OF ORGANIC ACIDS IN GLACIAL ACETIC ACID

by

VILIM J. VAJGAND and TIBOR J. PASTOR

Recently oscilometric titrations have become more and more used in analytical chemistry because they are simple and rapid. The basic advantage of oscillometry over other electrochemical methods is that there is no direct contact between the electrodes and the solution investigated, by which all changes caused by reactions on the electrodes during measurements are avoided. Although this method is not specific, because the changes originating from all components of the test solution are measured during titration, yet it is suitable for the determination of a series of inorganic and organic compounds.

Glacial acetic acid is most often used as a solvent in determining weak organic bases, because of its strongly pronounced leveling effect. Very weak organic bases can also be determined in it by various electrochemical methods, which has also enabled the development of methods for determining bases of various intensities by the osicllometric (high-frequency) method(1,6). Hara and West(7), and Masui *et.al*(8). determined alkaloids, while Oehme(9) and Masui(10) titrated amino acids. The determination of some antibiotics as bases(11) and some other important products of the pharmaceutical industry(12,13) has been investigated. In addition, components of binary mixtures of inorganic acids in acetic acid(14,15) have also been successfully titrated.

The present work is a continuation of our earlier investigations in glacial acetic acid(16—19) and it determines tertiary amines and salts of organic acids also by oscillometric titration. Here we undertook to develop and compare direct and indirect methods of determining the bases, to investigate the conditions for the determination of hydrochlorides of some bases and to observe the influence of acetic acid anhydrides on the shape of the titration curves.

EXPERIMENTAL

The titrations were performed with a "Radelkis OK 302 system Dr. E. Punger" oscillometer operating at 130 Mc/s. As the smallest electrode of the commercial apparatus was designed for vessels of 100 ml, we made smaller electrodes (interrings) to save chemicals. For the titration cell we used 40-ml cylindric colorimetric cells 10 cm high. Because of the small diameter of the vessel, the solution was mixed with a magnetic mixer instead of the original vibration mixer. The disturbances caused by the magnetic field of the mixer were eliminated by placing a silver plate 0.5 mm thick under the titration vessel. The solvent was glacial acetic acid p.a. "Kemika" or "C. Erba" and once redistilled nonaqueous acetic acid.

The titrations were performed with 0.1 N solutions of perchloric acid or sodium acetate in nonaqueous acetic acid prepared by standard procedures(17).

Before titration started, the volume of the test solution was 30 ml. The titrated bases were mostly pharmaceutic products which had not been previously purified.

The oscillometric determinations were performed by direct titration and retitration. The former method gives good results in titrating about 10^{-2} normal solution of strong organic bases in acetic acid using a 0.1 N perchloric acid solution. Solutions of this concentration were prepared by dissolving 2.5×10^{-4} to 4×10^{-4} equivalents of substances in 30 ml solvent. Although when using acetic acid, the oscillometer still does not show maximum sensitivity in this concentration range (Fig. 1), we chose it because most of the titrated substances dissolve under the above conditions. Besides, the sensitivity of the apparatus is sufficient to obtain clearly expressed titration curves when changes read on the scale of the apparatus are plotted against the quantity of titration medium added, in which case the

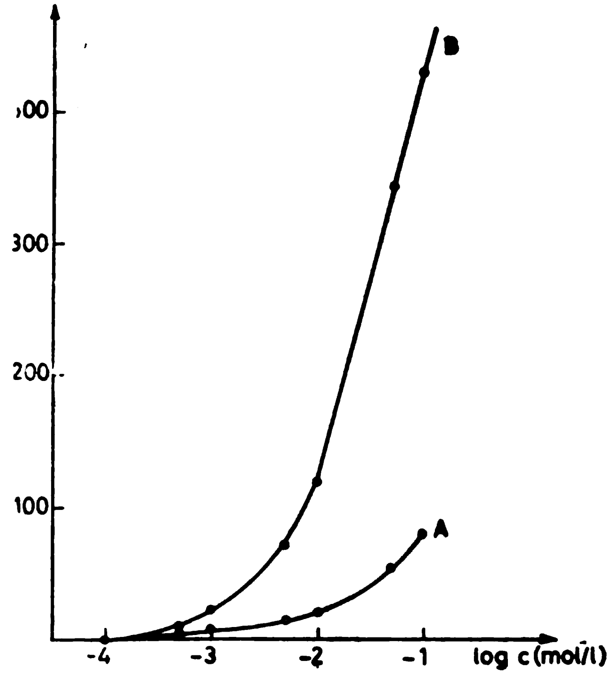

Fig. 1

Sensibility of the apparatus (Q-quality factor) as function of log C, when measured in glacial acetic acid (switch on "increasing")

A) in the presence of sodium acetate

B) in the presence of perchloric acid

titration end-point is accurately determined even without the use of a correction factor for volume increase. Maximum deviation from the mean value in each determination was ±1%. The typical shape of the curve obtained by titrating these bases is seen in Fig. 2. Only in determining potassium acetate, which was treated under the same conditions as the other bases, the direction and angle of intersection of the straight lines vary because of the forming of a precipitate of potassium perchlorate (Fig. 3).

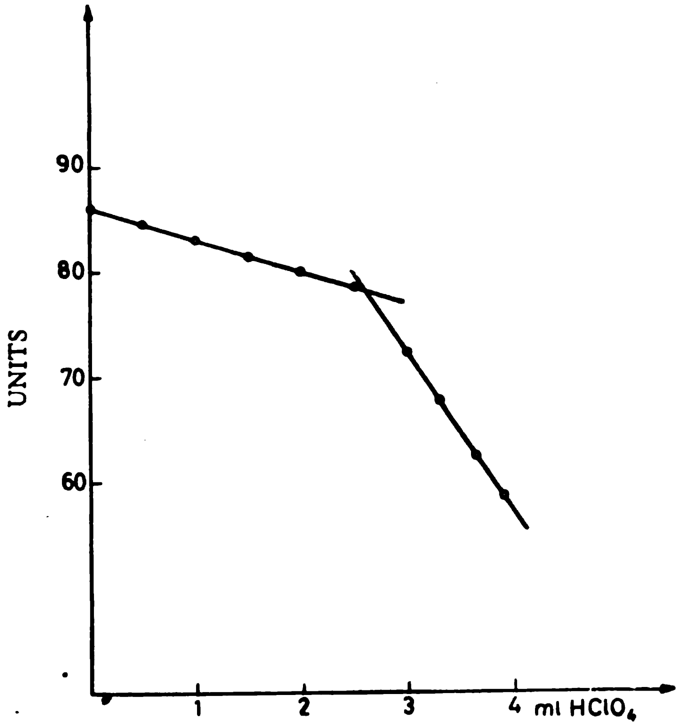

Fig. 2

Direct titration of $10^{-2}N$ solution of narcotine (switct on "decreasing")

The apparatus shows maximum sensitivity at resonance frequency, which is obtained by a corresponding choice of position for the variable condenser for adjusting to resonance (coupling). The sensitivity also depends on the position of the switch for direction change (increase and decrease). When a system whose conductivity increases with the addition of titrating medium is titrated, the switch should be positioned to increase and vice versa.

Besides the above apparatus on which measurements are made by the deflection method in which the change due to conductance is measured during titration, a high-frequency HFT 30 C titrimeter was also used. This equipment enables special observation of the changes of conductance or susceptance of the solution during titration. However, because of the poor sensitivity of the apparatus, we did not obtain clearly expressed curves or satisfactory results.

Good results were not obtained by direct titration in working with weak bases or with systems in which the precipitate appears near the end-point of the titration. Precipitation causes great changes in the conductivity of titrated systems and consequently the conductivity no longer changes linearly with the addition of titration medium. In these cases the retitration method can be successfully employed. An excess of about 3 × 10^{-4} mole perchloric acid was added to the base solution, which was then retitrated with a 0.1 N solution of sodium acetate. By the same method we also determined novalgin in order to compare the shape of the curve and the results obtained oscillometrically with those obtained conductometrically(19). The titration curve for novalgin is shown in Fig. 4; its rising part is not so conspicuous as in the case of the conductometric titration.

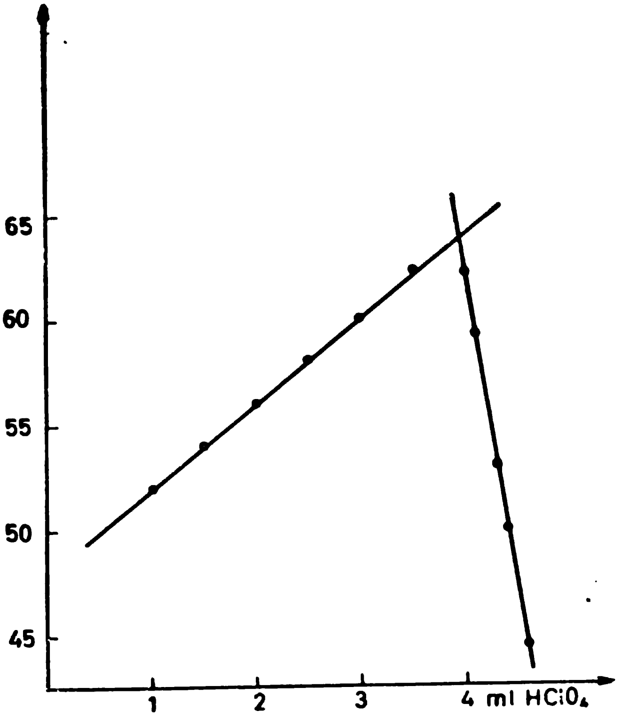

Fig. 3

Direct titration of $10^{-2}N$ solution of potassium acetate (switch on "decreasing")

In oscillometric determination of hydrochlorides of bases, to their solutions were added variable amounts of a 3% solution of mercuric acetate whose excess was changed up to double molar concentration in relation to the base determined. Due to chemical reaction, the base is liberated and undissociated mercuric chloride forms. As the presence of foreign salts is disadvantageous because it decreases tha sensitivity of this method(20), care should be taken that the smallest possible quantity of mercuric acetate is added. Good results were obtained by the method described above only in the titration of procaine and pyridoxine hydrochloride, while the hydrochlorides of other bases do not give reproducible results.

In investigating the optimal conditions of titration, we studied the shape of the titration curves in pure acetic acid and after the addition of variable quantities of acetic acid anhydrides or water. As Fig. 3 shows. large quantities of acetic acid anydrides in the solvent cause bending of the titration curves, which renders difficult or impossible the determination of the end-point of titration. On the contrary, small quantities of acetic acid anhydrides are not damaging. The end-point of titration is obtained from the intersection of the two straight lines, which enclose an angle whose size also depends on the degree of amplification. This offers the possibility of titrating systems which contain a mixture of tertiary and primary or tertiary and secondary amines. Consistent with the results obtained by Zarinski[1] and Gurjev(21), we found that small quantities of water do not interfere with the oscillometric determination of strong bases in acetic acid. Similar effects were also observed in conductometry when investigating the effect of acetic acid anhydrides and water on the shape of the titration curves and the accuracy of the results.

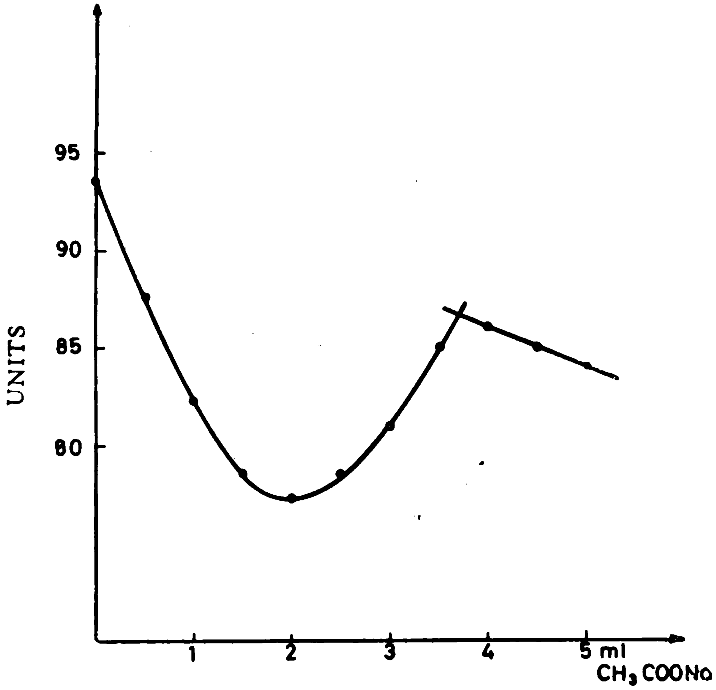

Fig. 4

Retitration of novalgine (switch on "increasing")

The titrated substances and results are shown in Table 1.

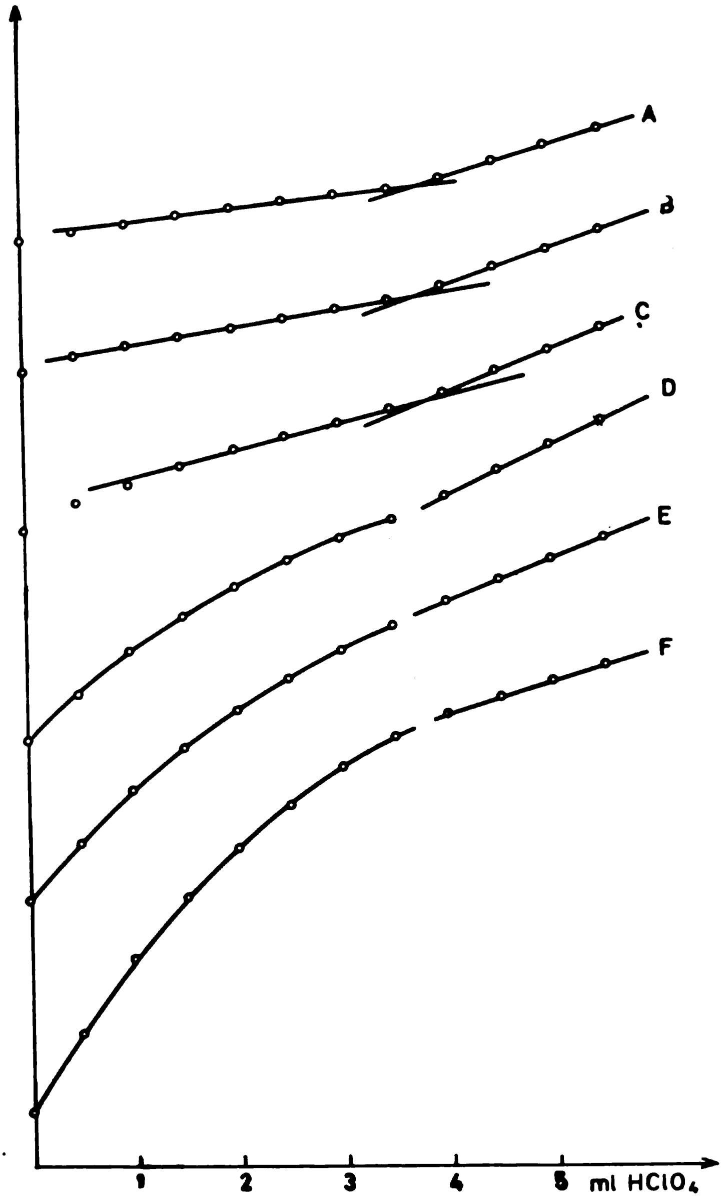

Fig. 5*

Titration curves of sodium acetate:

A, in pure glacial acetic acid

B, C, D, E, and F, in mixtures of glacial acetic acid and acetic anhydryde in rations 9:1 8:2, 6:4, 4:6, and 1:9 respectively

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* 1 cm on the Y axis coresponds to 10 scale units

TABLE 1

Titrated substance	*Taken mg*	*Found by potent. titr. %*	*Direct titration*		*Indirect titration*	
			No. of titr.	*Found %*	*No. of titr.*	*Found %*
Sodium acetate	31.1	100.00	8	100.44±0.49		
Potassium acetate	39.2	99.74	8	99.80±0.35		
Sodium benzoate	60.0	98.41	7	99.05±0.45	5	98.59±0.27
Sodium salicylate	60.0	98.62	7	99.25±0.64	5	98.61±0.23
Sodium *p*-amino salicylate	70.0	99.25			5	99.79±0.33
Cinchonine	60.0	94.72	5	94.54±0.25	4	94.66±0.28
Nicotine	30.4	98.03	7	98.33±0.24	7	98.56±0.41
Narcotine	110.0	98.80	5	99.14±0.66	5	98.92±0.20
Strychnine nitrate	130.0	99.31	8	99.58±0.30		
Nicotinamide	60.0	99.72			8	99.53±0.43
Isoniazide	60.0	99.69	8	99.65±0.40	5	99.77±0.40
Promethazine	100.0	99.87	9	99.44±0.45	6	99.60±0.37
Procaine-HCl	100.0	99.26	5	99.64±0.21		
Pyridoxine-HCl	70.0	99.77	5	99.79±0.38	4	100.32±0.47

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SOME COMPOUNDS OF *N*-METHYLPYRROLIDINE WITH ORGANIC ACIDS

by

MLADEN DEŽELIĆ and BRANKO NIKOLIN

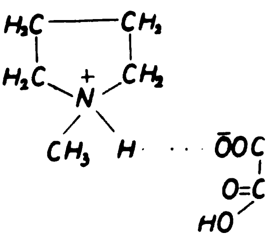
In many physiologically and pharmacologically active substances appears an N-methylpyrrolidine nucleus. It is found in nicotine, cocaine, atropine, and other important substances. N-methylpyrrolidine itself is found in the leaves of belladonna (Atropa belladona)$^{(1)}$ and in tobacco (Nicotiana tabacum). Späth and Biniecki$^{(2)}$ have isolated it from tobacco by building up the picrate, trinitro-m-cresolate and chloraurate. Synthetically N-methylpyrolidine can be obtained in several ways: from 1,4—dibrombutane and methylamine in alcohol$^{(3)}$ and by methylating pyrrolidine with formaldehyde and formic acid$^{(4)}$.

As a tertiary base N-methylpyrrolidine possesses a free electron pair on the nitrogen atom. Hence, it can form salts with inorganic and organic acids, nitrophenoline and metallic salts.

The basicity constant of N-methylpyrrolidine is $K = 1.5 \times 10^{-4}$ $^{(5)}$, i.e., it has a slightly smaller basicity than pyrrolidine which has $K = 1.3 \times 10^{-3}$ at 25°$^{(6)}$. This is understandable, because the CH_3-group which repels electrons is bound to the nitrogen atom of the N-methylpyrrolidine nucleus, and due to this, the possibility of protonation is reduced and consequently the basicity in relation to pyrrolidine is also slightly reduced.

The following crystallized salts of N-methylpyrrolidine with organic substances are known from the literature: N-methylpyrrolidine pictrate$^{(7)}$ and N-methylpyrrolidine-trinitro-m-cresolate$^{(8)}$. All salts are of an equimolecular composition. The present work is an approach to the synthesis of new crystallized salts of N-methylpyrrolidine with organic acids. The composition of all the new compounds and the structure of some of them have been determined.

With oxalic acid, N-methylpyrrolidine built up in an alcoholic medium a finely crystallized long-needle-shaped salt, N-methylpyrrolidine oxalate. The composition of this substance was determined from the results of the elementary analysis, while infra-red spectra showed that a salt of the type of ammonium or amino salts was formed (I).



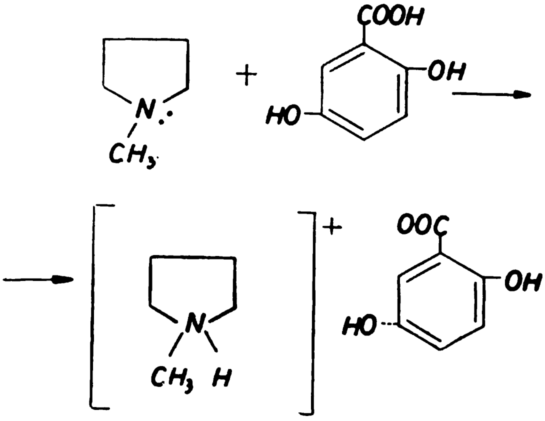
I

Dicarbonic aromatic acid, phthalic acid, also formed a crystalized compound with N-methylpyrrolidine, which crystallized in the form of transparent plates.

With aromatic hydroxy-acids, such as gallic, gentisic, and salicylic acids, N-methylpyrrolidine gives well crystallized salts from ethanol solutions.

With gallic acid (3,4,5-hydroxy-benzoic acid) a well crystallized compound in the form of groups of rhombohedra was formed.

With gentisic acid a cubic crystallized compound was obtained. The type of chemical bonds in this compound could be determined by infra-red analysis. Therefore, the course of the reaction between N-methylpyrrolidine and gentisic acid can be schematically shown (II).



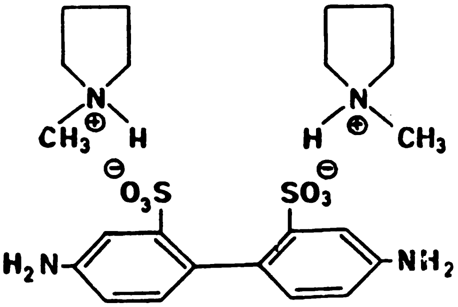
II

Salicylic acid and acetylsalicylic acid formed the same compound with N-methylpyrrolidine, N-methylpyrrolidine-salicylate, which was confirmed microanalytically and by the boiling point of their mixture, which does not show depression. Basic N-methylpyrrolidine saponified the acetyl residue, which was also noticed by the intense odor of ethyl acetate after work in the ethanol medium.

With p-aminosalicylic acid it was not possible to make a crystallized compound. N-acetyl-p-amino salicylic acid forms with N-methylpyrrolidine a crystallized compound in the form of rectangular plates.

Dicarbonic and hydroxy-monocarbonic acids form salts of equimolar compositon with N-methylpyrrolidine.

Some aromatic sulfonic acids also form crystallized compounds with N-methylpyrrolidine, i.e., sulfanilic, sulfo-salicylic and benzidine--2-2'-disulfonic acids. The compound with sulfanilic acid crystallizes in the form of groups of long needles and its composition is equimolar. With sulfo-salicylic acid it crystallizes in the form of fine needles and its composition is also equimolar. Because of the presence of 2 sulfonic groups, benzidine-2-2'-disulfonic acid behaves like a dibasic acid and with N-methylpyrrolidine it forms a compound whose composition is two moles of N-methylpyrrolidine to one mole of acid. The compound crystallizes in the form of plates whose structure can be represented by formula III.



III

Compounds of N-methylpyrrolidine were then synthesized with the following nitro-acids: p-nitrobenzoic acid, m-nitrosalicylic acid, 5-nitrosalicylic acid, 2,4-dinitrophenylacetic acid, 4-nitro-antranilic acid and N-acetyl-4-nitroantranilic acid.

By the methods of other authors we first synthesized 4-nitroantranilic acid, N-acetyl-nitroantranilic acid(9) and 2,4-dinitrophenylacetic acid(10).

The compound with p-nitrobenzoic acid and 3,5-dinitrobenzoic acid is of equimolar composition while the other compounds are composed of 1 mole N-methylpyrrolidine and 2 moles of acid. This composition was confirmed by elementary analysis.

To determine the structure of synthesized salts — both those of equimolar composition and those composed of 1 mole N-methylpyr-

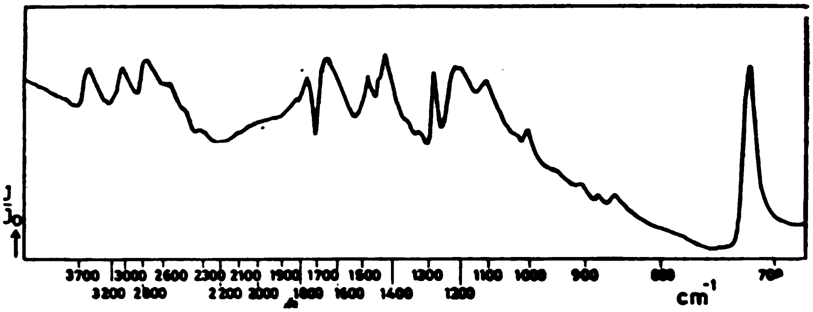


Fig. 1
Infrared spectrum of N-methylpyrrolidine-oxalate

rolidine to 2 moles of acid — we spectrographed the following compounds in the infra-red region: N-methylpyrrolidine-oxalate, N-methylpyrrolidine-gentisinate and N-methylpyrroldine -m-nitrobenzoate.

On the above spectrum one can see two carboxylate bands at 1625 cm^{-1} and 1404 cm^{-1} and a carbonyl band at 1720 cm^{-1}. The presence of carboxylate bands is a proof that a compound of the ammonium salt type is formed, i.e., the nitrogen atom of the N-methylpyrrolidine nucleus is protonized. The carbonylic band indicates the presence of another free carboxylic group. Therefore, the structure of this salt is as shown above (I).

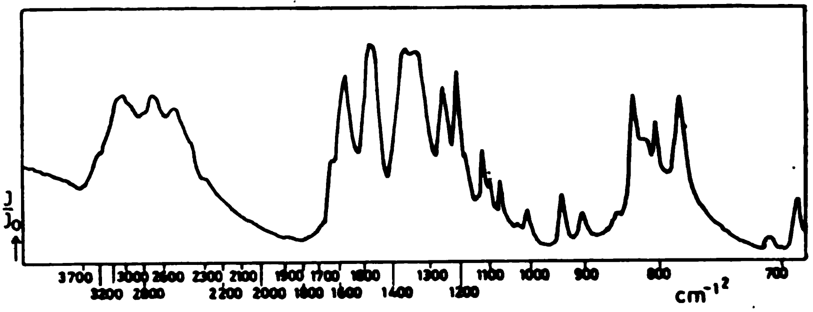
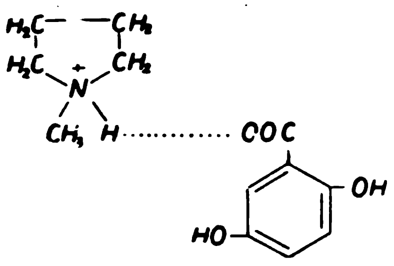


Fig. 2
Infrared spectrum of N-methylpyrrolidine — gentisinate

This spectrum shows a pronounced carboxylate band at 1577 cm^{-1}, while the band of the carbonylic group at 1680 cm^{-1} is absent. This leads us to the conclusion that a typical salt was formed — in between a base and an acid.

Therefore the structure of this compound can be expressed by formula IV.



IV

In compounds with a composition of 1 mole of N-methylpyrrolidine to 2 moles of acid we assumed that the acid component was probably bound in the form of a dimer. To confirm this assumption we spectrographed the compound N-methylpyrrolidine-m-nitrobenzoate in the infrared region.

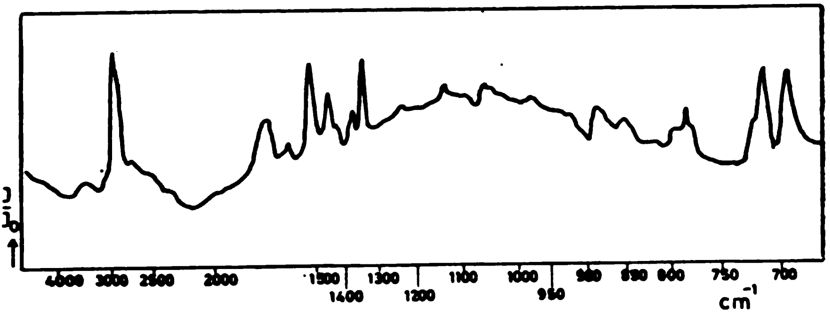


Fig. 3
Infrared spectrum of N-methyl-pyrrolidine-m-nitrobenzoate

Two bands of the nitro-group at 1350 cm^{-1} and 1550 cm^{-1} and a weak carbonyl band at 1720 cm^{-1} are clearly seen on the spectrum. Bands of the OH-group are weak, while, in view of the assumed structure of this compound, a stronger intensity was expected.

Our pharmacological investigations of the prepared crystallized salts of N-methylpyrrolidine showed that these compounds have a nicotinolytic action(11).

EXPERIMENTAL

The N-methylpyrrolidine which we used was a product of the Fluka company. After several distillations a pure product with a boiling point of 80° was obtained. All the acids used were recrystallized several times to a constant, melting point. All the melting points were determined on a Kofler microscope. For analysis all the substances were dried in vacuum at room temperature with silica gel.

The new compounds were prepared in the following five ways:

a) A volume of 0.01 mole N-methylpyrrolidine is added to a solution or suspension of 0.01 mole acid in 5 ml ethanol. After a short time the reaction mixture gets warm by itself. After standing and cooling, the salt crystallizes in colorless crystals.

b) A volume of 0.01 mole N-methylpyrrolidine is added to a solution of 0.01 mole acid in acetone. The mixture heats up spontaneously. After cooling, a colorless salt crystallizes.

c) A mixture of 0.01 mole acid and 0.02 mole N-methylpyrrolidine heats up spontaneously. After adding 5 ml water and heating over a water bath for 10 min, the whole mixture dissolves. After standing on ice for a long time, a salt crystallizes.

d) A volume of 0.01 mole N-methylpyrrolidine is added to a suspension of 0.01 mole acid in ethylacetate. Upon heating over a water bath, the mixture dissolves. Cooling crystallizes a colorless salt.

e) A volume of 0.01 mole N-methylpyrrolidine is added to a solution of 0.02 mole acid in absolute ethanol or acetone. The mixture becomes spontaneously warm, and then is heated for another 10—15 minutes over a water bath. Cooling crystallizes a salt.

By method a) the following salts were prepared:

N-methylpyrrolidine-oxalate was recrystallized from acetone in long needle-like crystals, m.p. 104—105°. Yield 80%. Soluble in water and acetone.

$C_5H_{11}N.C_2H_2O_4$ (175.17) Calc.: C 48.04%, H 7.49%, N 8.00%
Found: C 48.10%, H 7.14%, N 7.84%

N-methylpyrrolidine-galate crystallizes from water in rhombic crystals, m.p. 196°. Yield 88%. Soluble in water, hardly soluble in ethanol, acetone and ether.

$C_5H_{11}N.C_7H_6O_5$ (255.28) Calc.: C 56.52%, H 6.72%, N 5.49%
Found: C 56.50%, H 6.89%, N 5.78%

N-methylpyrrolidine-gentisinate crystallizes from ethanol in cubic crystals, m.p. 154°. Yield 73%. Soluble in water, ethanol and acetone; insoluble in ether.

$C_5H_{11}N.C_7H_6O_4$ (239.24) Calc.: C 60.21%, H 7.16%, N 5.86%
Found: C 59.88%, H 7.43%, N 6.02%

N-methylpyrrolidine-salicylate crystallizes from ethanol in the form of plates, m.p. 103°. Yield 95%. Soluble in water, ethanol, acetone and ethylacetate. Insoluble in ether. An identical compound is obtained from acetylsalicylic acid and N-methylpyrrolidine when their solution in absolute ethanol is boiled over a water bath for 10 min, because in this reaction the acetyl group is saponified.

$C_5H_{11}N.C_7H_6O_3$ (223.24) Calc.: C 64.63%, H 7.68%, N 6.28%
Found: C 64.40%, H 7.89%, N 6.56%

N-Methylpyrrolidine-N-acetyl-p-aminosalicylate crystallizes from acetone in the form of plates, m.p. 143°. Yield 75%. Soluble in acetone and ethanol; insoluble in ether.

$C_5H_{11}N.C_9H_9O_4N$ (280.29) Calc.: C 60.05%, H 7.20%, N 10.02%
Found: C 60.24%, H 7.41%, N 10.30%

N-methylpyrrolidine-sulfanilate crystallizes from absolute ethanol in the form of needles, m.p. 163°. Yield 60%. Easily soluble in water and ethanol. Insoluble in acetone and ether.

$C_5H_{11}N.C_6H_7O_3NS$ (258.30) Calc.: C 51.21%, H 7.03%, N 10.86%

Found: C 51.22%, H 7.01%, N 10.84%

N-methylpyrrolidine-sulfosalicylate crystallizes from ethanol in long prismatic assemblages. M.p. 156—157°. Yield 82%. Soluble in ethanol: slightly soluble in water; insoluble in acetone and ether.

$C_5H_{11}N.C_7H_6O_6S.2H_2O$(339.30) Calc.: C 42.51%, H 5.05%, N 4.13%

Found: C 42.77%, H 5.59%, N 3.93%

N-methylpyrrolidine-3, 5-*dinitrobenzoate* crystallizes from ethanol in needles, m.p. 174°. Yield 89%. Soluble in ethanol; slightly soluble in water.

$C_5H_{11}N.C_7H_4O_6N_2$ (297.24) Calc.: C 48.53%, H 5.09%, N 14.15%

Found: C 48.66%, H 4.92%, N 14.37%

The following salt was prepared by method b):

N-methylpyrrolidine-phthalate crystallizes from acetone in the form of plates M.p. 119°. Yield 73%. Soluble in water, acetone and chloroform; insoluble in ether.

$C_5H_{11}N.C_8H_6O_4$ (251.25) Calc.: C 62.20%, H 6.83%, N 5.58%

Found: C 61.98%, H 6.50%, N 5.55%

The following salt was prepared by method c):

N-methylpyrrolidine-2, 2′-*benzidine-disulfonate* upon purification with activated charcoal crystallizes from water and plates, m.p. 290°. Yield 73%. Soluble in water; slightly soluble in ethanol.

$2C_5H_{11}N.C_{12}O_6N_2S_2$ (514.61) Calc.: C 51.40%, H 6.67%, N 10.90%

Found: C 51.31%, H 6.61%, N 10.87%

By method d) the following salt is prepared:

N-methylpyrrolidine-p-nitrobenzoate crystallizes from absolute ethanol in the form of needles, m.p. 156°. Yield 96%. Soluble in ethanol and warm acetone; insoluble in water and ether.

$C_5H_{11}N.C_7O_4N$ (252.24) Calc.: C 57.19%, H 6.40%, N 11.12%

Found: C 57.17%, H 6.28%, N 11.20%

By method e) the following salts were prepared:

N-methylpyrrolidine-2, 4-*dinitrophenylacetate* crystalizes from ethanol in needle form. M.p. 70°. Yield 68%. Soluble in alcohol, acetone and chloroform; moderately soluble in ether; insoluble in water.

$C_5H_{11}N.2C_8H_6O_6N_2$ (537.39) Calc.: C 46.97%, H 4.32%, N 13.04%

Found: C 46.91%, H 4.02%, N 13.25%

N-methylpyrrolidine-5-nitrosalicylate crystallizes from ethanol in the form of plates, m.p. 170—171°. Yield 81%. Soluble in ethanol and hot water.

$C_5H_{11}N.2C_7H_5O_5N$ (451.35) Calc.: C 50.60%, H 4.69%, N 9.32%

Found: C 50.54%, H 5.16%, N 9.25%

N-methylpyrrolidine-m-nitrobenzoate crystallizes from acetone in the form of rectangular plates, m.p. 103°. Yield 71%. Soluble in ethanol, acetone, chloroform and hot water; insoluble in ether.

$C_5H_{11}N.2C_7H_5O_4N$ (419.35) Calc.: C 54.46%, H 5.05%, N 10.03%
Found: C 54.04%, H 4.68%, N 9.74%

N-methylpyrrolidine-4-nitroanthranilate crystallizes from ethanol in the form of orange needles, m.p. 198—200°. Yield 68%. Soluble in ethanol and acetone; insoluble in water.

$C_5H_{11}N.2C_7H_6O_4N_2$ (449.37) Calc.: C 50.82%. H 5.16%, N 15.59%
Found: C 51.45%, H 5.28%, N 15.60%

N-methylpyrrolidine-N-acetyl-4-nitroanthranilate crystallizes from ethanol in the form of needles, m.p. 189°. Yield 61%. Soluble in ethanol, acetone and ether.

$C_5H_{11}N.2C_9H_8O_5N_2$ (533.45) Calc.: C 51.83%, H 5.11%, N 13.14%
Found: C 51.91%, H 4.83%, N 13.31%

N-methylpyrrolidine-3-*nitrosalicylate* crystallizes from acetone in the form of yellow plates. M.p. 170—171°. Yield 72%. Soluble in acetone; moderately soluble in ethanol; slightly soluble in water and chloroform.

$C_5H_{11}N.2C_7H_5O_5N$ (451.35) Calc.: C 50.60%, H 5.16%, N 9.32%
Found: C 50.29%, H 4.90%, N 9.45%

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QUANTITATIVE EVALUATION OF AGEING OF AN ALUMINUM — 5.9 at.% SILVER ALLOY

by

MILEVA J. ROGULIĆ

INTRODUCTION

The decomposition of a supersaturated solid solution at room or elevated temperature brings about the segregation of interequilibrated precipitatiants which have often been the subject of very detailed investigations. In recent times electron microscopy has contributed a lot to the understanding of hardening process kinetics and to quantitative evaluation of ageing process.

Investigations of spherical Quinier-Preston zones (or QP zones) in aluminum-silver alloy have been carried out by means of different physical and mechanical methods. However, the problem of quantitative evaluation of amounts segregated and the problem of zone structure have not been solved. The investigations performed so far show discrepencies between the results of electron microscopy and those of small-angle X-ray scattering. Bauer and Gerold(1) studied a series of aluminum-silver alloys by small-angle X-ray scattering and found that the total integrated intensity A_0 remains unchanged in the course of QP-zone growth. They hypothesize that the magnitude of the integrated intensity is determined by the metastable nonmiscibility gap in the equilibrium diagram, and on the basis of this they calculated the concentration of silver (m_1) in QP-zones and the concentration of silver (M_2) in the residual solid solution. To make the evaluation the intergrated intensity was measured in absolute units.

On the basis of the data obtained they concluded that after quenching equilibrium is established rapidly, and that the further, course of ageing depends exclusively on the growth of the zones, i.e. larger zones grow at the expense of smaller ones. Accordingly the magnitude of the constant integral intensity corresponds to the total volume participation of QP-zones, which can be determined from the state diagram metastable nonmiscibility gap. It was found that the integral intensity decreases with increasing temperature of ageing, as this predicted from the state diagram.

First quantitative investigations by means of electron microscopy were carried out by Friese, Kelly and Nicholson(2). They compared the results obtained by electron miscroscopy with those achieved by small-angle X-ray scattering and established that the radii determined by means of X-rays were larger than those determined by electron microscopy. These discrepencies are probably due to the fact that the small-angle diffraction intensity is proportional to the six power of the zone radii, so that small zones contribute very little to the diffracted intensity, whereas electron microscopy measurements yield an average value of zone size.

Friese *et al.* studied an aluminum-4.4 at% silver alloy which was aged at 125°C for 66 hours. The radius of QP-zones determined be the X-ray method was 28 Å, and by electron microscopy 15 Å; accordingly, the zone size determined by the former method was larger by almost a factor of two. Since the number of zones ($N_z = 2.4 \times 10^{-17}$) was determined, the volume fraction of zones in the ageing process was 4×10^{-8} when constancy of integral intensity was reached. Despite many errors which can creep in in such measurements, the given data show that the maximum segregation in the alloy was not reached and that the solid solution was still in metastable equilibrium with respect to the silver percentage.

In the present work we wanted to determine the degree of QP-zone segregation in the course of ageing in order to explain the dependence of integral intensity upon ageing. It was also of interest to establish whether the constant integral intensity represents maximum segregation of the alloying element in QP-zones, deduced from the state diagram.

EXPERIMENTAL

The investigations were carried out on an silver alloy of the following composition: 19.8 w.% Ag. 0.004 w.% Fe, 0.003 w,% Si, 0.001 w.% Cu and aluminium. The alloy was in a sheet of about 1 mm thickness; by cold rolling the thickenss was reduced to 125 μ. Sheet samples were cut and treated thermally by heating for 6 hrs at 520°C; then they were quenched in $CaCl_2$ solution at —4°C and aged for 3 days at 130°C. Thin foils for electron microscope studies were prepared by the electropolishing technique, carried out by the frame method at 70°C, in Lenoir solution of the following composition: 617 ml of orthophosphoric acid (sp.g. 1.75), 134 ml of sulphuric acid (sp.g. 1.84), 156 ml of chromic acid and 240 ml of water. The cathode was of stainless steel. When taking the samples out of the polishing solution, the formation of an oxide film was observed on the sample surface, and therefore specimens were further purified by dipping for 10 to 30 min in a solution of orthophosphoric acid (350 ml), chromic acid (100 g) and water (500 ml) at room temperature. They were then left in ethanol and thin foils for electron microscopy studies were cut out.

Investigations were carried out with a Siemens Elmiskop I electron microscope at 100 kv and about 30 μA. To achieve good contrast a stereo supporter was used. The orientation of the crystal lattice was determined by means of the system for selective choice of diffraction points.

X-ray studies were performed with a Siemens Kristalloflex IV apparatus which was set for small angles. Nickel and cobalt balance filters were used in order to obtain monochromatic CuK_α radiations. A copper foil about 1 mm thick was placed between the sample and the counter for the detection of X-ray scattering in the air. Measurements were carried out with a scintillation counter.

RESULTS AND DISCUSSION

Quantitative investigations of QP-zone segregation in the course of hardening by precipitation have been limited exclusively to the segregation period characterized by the constancy of integral intensity at a given segregation temperature.

For the quantitative evaluation of the volume fraction of Q.P zones per unit per volume, it is essential to determine precisely the thickness of the foil in the area of zone counting and sizing. The foil thickness was determined from the projected width of the trace of dislocation movement and the known foil orientation. The latter was determined from the electron diffraction pattern. This method of measuring the foil thickness is considered to be the most accurate. Therefore, all measurements were performed only at places where dislocation movement could be produced.

On account of appreciable differencies in the factor of scattering between atoms of aluminum and silver, a good contrast between QP-zones and the background was achieved (Fig. 1). The size of zones was measured from electron-micrographs at a magnification of 300.000.

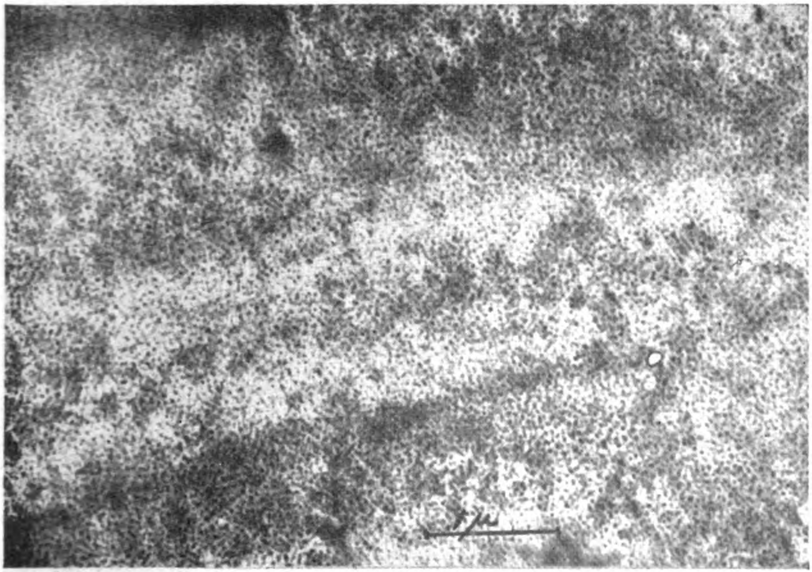
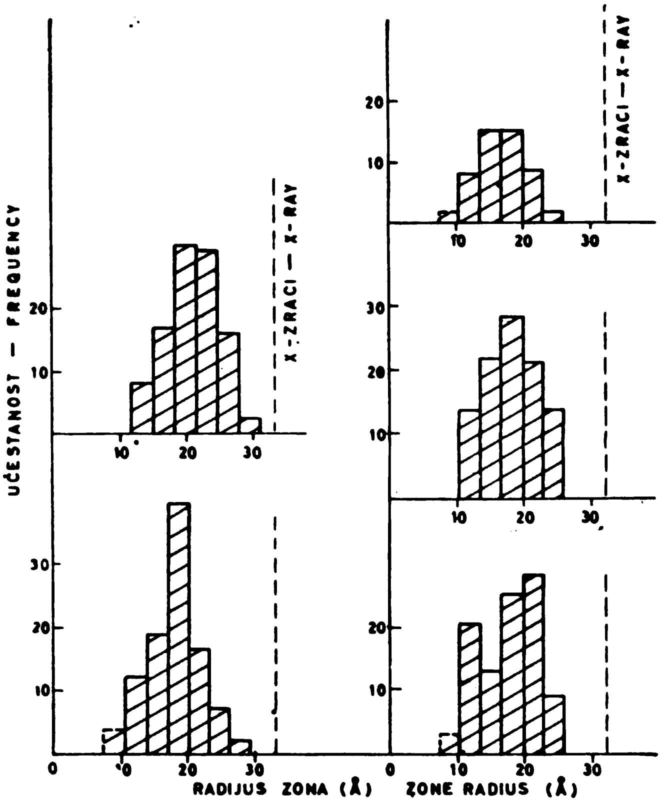


Fig. 1

Histogram is showing the distribution of zone sizes in the investigated *Al* —5.9 at% *Ag* alloy

The frequency of distribution of zone size is given in Graph I. For comparison, the graph also shows the zone size determined by small-angle X-ray scattering. The most common size is about 20 Å.



Graph 1
Histogram is showing the distribution of zone sizes in the investigated *Al* —5.9 at% *Ag* alloy

The area on the histograms is not always the same, since the number of zones was not always measured on an area of the same size; this was dictated by the size of the field exhibiting a good contrast between zones and background. The mean zone volume fraction was $2 \times 5 \times 10^{-2}$ and the mean zone density per unit volume 0.71×10^{18} zones per cm^2. Due to small zone size, considerable overlapping might be expected, and, in quantitative determinations, it should be taken into consideration. However, it is evident that the overlapping depends on the sample thickness. In the determination of the number of zones per unit volume, correction for zone overlapping was made by the method of Hillard(3).

RESULTS

If the Quinier(4) method for the calculation of particle size is used, the slope of the curve of log I(h) against ε^2 (if the tangent is drawn to the curve immediately below its maximum) only allows the sizing of larger particles, i.e. QP-zones in this case. The identification of smaller zones is possible by graphical analysis of the curves(5). However, there is a danger that by this method the tangent drawn to the curve at slightly larger angles will not present the actual state, since this part of the diffraction intensity is affected by interference between particles, and which, in case of solid state, has not yet been thoroughly studied. Accordingly, this method of graphical analysis might lead to confusion in the sizing of QP-zones. Weissmann and Wird(6) used another method of graphical analysis of the diffraction intensity curve and by applying it to the results of Friese *et al.*(3), they established that the contribution of small particles is very large, and that the results observed are in good agreement with histograms obtained by transmission electron microscopy.

From the histograms in Graph I it is seen that the size of GP-zones ranges between 10 Å and 30 Å, whereas the size determined by the X-ray method is 33 Å, which is very close to the upper limit of zone size determined by electron microscopy.

In view of the fact that the foil thickness in the areas of zone counting and sizing was about 300 Å, no considerable overlapping was expected to occur. Chute *et al.* (7) have given a method for the calculation of overlapping for zone sizes between 30 and 60 Å. This method gives a good correction for larger foil thickness, but in our case the correction was nearly zero. On account of limited resolution power of the electron microscope and contrast conditions, particles smaller than 8 Å were mostly left unobserved, and also quite a lot of smaller particles were unobservable on account of overlapping. In the investigated stage of ageing, very small zones have no considerable effect on the volume fraction of QP-zones, but considerable error can arise when several small zones are measured as a large one.

In X-ray studies Bauer and Gerold(1) assumed that constant integral intensity represents the maximum degree of segregation as determined from the state diagram. According to the phase diagram and the metastable nonmiscibility gap it follows that QP-zones segregated in the course of thermal precipitation at 130°C contain 55 at.% silver, whereas the solid solution contains only 0.7 at.%. Consequently, if the alloy reaches the equilibrium state defined by the limit of the metastable nonmiscibility gap, then 5.2 at% silver should be segregated from our alloy, corresponding to a volume fraction of QP-zones of 9.42×10^{-2}.

Since the volume fraction of QP-zones determined by electron microscopy is smaller than the value expected from the state diagram by a factor of about 3.5, it seems probable that the excess of silver atoms dissolved in the solid solution is not segregated in the first stage of hardening by precipitation, i.e. in the course of QP-zone formation.

Recent investigations of Bauer and Gerold(8) of an aluminum--4 at.% silver alloy aged for 12 hours at 145°C, indicate that the volume fraction of QP-zones, determined by electron microscopy, is about 40% smaller than the value obtained from the state diagram, i.e. by means of small-angle X-ray scattering.

The above given data show that the volume fraction of QP-zones determined in our study is smaller than that obtained by Bauer *et al.* by a factor of two (both values were obtained by electron microscopy). This discrepancy might be due to inncorrect or approximate determination of foil thickness, or if the foil thickness was not determined in the area of zone sizing. An other factor which increases the volume fraction of QP-zones is the possibility of measuring two or more zones as only one; this is caused by small resolution. The latter error is made in case of thick foils. Hence it is very difficult to decide what is the real reason for the above discrepencies. However, it may be undoubtedly concluded that the segregation of silver from supersaturated solid solution is not completed during the stage of QP-zone formation, and that constancy of integrated intensity does not mean the end of the precipitation process but only indicates a great slowing up.

The size of QP-zones at any moment of segregation is not uniform but there is a range of sizes, as shown in the histograms.

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CONTENTS

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METHODOLOGICAL ASPECTS OF THE STUDY OF COMPLEX CHEMICAL REACTIONS.

II. GENERATION OF REACTION MECHANISM MODELS

by

ALEKSANDAR R. DESPIĆ

I. INTRODUCTION

Difficulties inherent in the present method of assessing reaction mechanisms were outlined in an earlier paper$^{(1)}$. Here, detailed consideration will be given to the problem of modeling *all possible* reaction paths for a given overall reaction in a complex system, *when it is known* that the latter consists of M stable chemical species and I unstable ones.

II. PRIOR ART

It was shown$^{(1)}$ that in this case, using a proposed formal method, it is possible to devise a number (S) of plausible unit steps as potential participants in a reaction mechanism.

Horiuti and Nakamura$^{(2)}$ were the first to consider the problem of the relation between the numbers S and I and the number of possible reaction paths N describing reaction mechanisms which, in general, lead to P different overall reactions. They have shown that each reaction path may be described by one set of "stoichiometric numbers"

$$N^{(p)} = (\nu_1^{(p)},\ \nu_2^{(p)},\ \dots\ \nu_s^{(p)},\ \dots\ \nu_S^{(p)}) \tag{1}$$

where $\nu_s^{(p)}$ represents the number of occurences of the unit step s for each act of the overall reaction p. For obvious stoichiometric reasons the set (1) must satisfy two sets of linear equations, one set of the type

$$f_{is} = \sum_{s=1}^{S} b_{is}\, \nu_s^{(p)} = 0 \qquad i = 1, 2, \dots\ \mathrm{I} \tag{2}$$

where b_{is} is the stoichiometric factor with which each particular intermediate i participates in the s-th unit step, and the other

$$f_{ms} = \sum_{s=1}^{S} b_{ms}\, \nu_s^{(p)} = B_m^{(p)} \qquad m = 1, 2, \dots\ M \tag{3}$$

where b_{ms} and $B_{ms}^{(p)}$ are the stoichiometric factors for the participation of the reactant (stable species) m in the s-th unit step and the overall reaction p respectively.

If it is required that *all* the stable species, intermediates and possible unit steps take part in a reaction path, i.e. that all the $\nu_s^{(p)} \neq 0$, each reaction path must determine a different overall reaction. Horiuti and Nakamura have shown that the number of linearly independent sets of stoichiometric numbers $N^{(p)}$, and hence the number of possible overall reactions P is given by

$$P = S - I \tag{4}$$

However, equation (4) does not answer the basic question of possible reaction paths in a given system, since it is obvious that a reaction path need not include all the unit steps which can be theoretically postulated as possible between the stable species and intermediates in the system. Hence, if it is allowed that some stoichiometric numbers may be zero, within one and the same overall reaction p there may be a number of sets $N_j^{(p)}$ $(j = 1, 2, \ldots J)$ satisfying equations (2) and (3).

This problem was recently considered by Milner$^{(3)}$, who tried to devise a formal method for obtaining the list of all reaction paths which colud lead to *a single overall reaction*, each path being unique in that it cannot be obtained by superposition of any others on the list. Milner's conclusions result from an analysis similar to that of Horiuti and Nakamura. For, if equation (4) is correct, then it is obvious that the number of unit steps S' required for describing a reaction path within a single given overall reaction $(P = 1)$ must be

$$S' = I + 1 \tag{5}$$

Milner concludes that in a system containing I intermediates and S possible unit steps, the maximum number of conceivable independent reaction paths must be

$$J_{max} = \binom{S}{S'} = \binom{S}{I+1} \tag{6}$$

This number of combinations is actually equal to the number of determinants of the $(I+1)$-th order which can be formed from a matrix of the type

$$\begin{array}{cccccccc}
b_{11} & b_{12} & b_{13} & \cdots\cdots & b_{1I} & b_{1(I+1)} & \cdots\cdots & b_{1S} \\
b_{21} & b_{22} & b_{23} & \cdots\cdots & b_{2I} & b_{2(I+1)} & \cdots\cdots & b_{2S} \\
\vdots & \vdots & \vdots & & \vdots & \vdots & & \vdots \\
b_{I1} & b_{I2} & b_{I3} & \cdots\cdots & b_{II} & b_{I(I+1)} & \cdots\cdots & b_{IS} \\
b_{R1} & b_{R2} & b_{R3} & \cdots\cdots & b_{RI} & b_{R(I+1)} & \cdots\cdots & b_{RS}
\end{array} \tag{7}$$

corresponding to the set of linear equations (2) and one equation from set (3) describing the system. Milner points out that each determinant may render a set $N_j^{(p)}$ as a solution, but that not all of them need do so, since some may vanish or duplicate a result already obtained.

He therefore concludes that this is the upper limit to the number of possible independent reaction paths.

III. FURTHER DEVELOPMENT

By setting out to investigate only determinants of the $(I+1)$-th order, Milner limited his method to the analysis of only those reaction paths which inovlve *all* the intermediates potentiallly present in the system. Obviously, in reality many mechanisms may be of interest which do not satisfy this condition. Even if all the intermediates are actually experimentally detected, they can be formed as participants of different reaction paths which may occur simultaneously, each containing a smaller number of intermediates and leading to the same or a different overall reaction.

Milner's system of generation itself may yield some reaction paths which do not involve some intermediates as a natural result of solving a given determinant. In fact, this must always be the case when the number of stoichiometric numbers in any row which remains outside the determinant is greater than or equal to the number of unit steps involving a certain intermediate. In that case there must exist one or more situations in which all these unit steps are left out (assigned zero stoichiometric numbers) and hence the solution of the remaining system of equations must yield direct paths not involving that intermediate.

In general, if a given choice of unit steps yields a vanishing determinant of the $(I+1)$-th order, lower order determinants obtained by leaving out some intermediates may non-vanishing, and their solution may yield direct paths consisting of fewer unit steps and intermediates.

An example of such a situation may be found in the hypothetical action of water on an ester of an unsaturated acid

$$\underset{(A)}{\text{R-CH}_2\text{CHCOOCH}_3} + \underset{(B)}{\text{H}_2\text{O}} \rightarrow \underset{(C)}{\text{R-CH}_2(\text{CH}_3)\text{CH(OH)COOH}}$$

involving hydrolysis of the ester and addition of the alcohol onto the double bond. This process may be postulated as involving the following intermediates:

$R-CH_2=CHCOOH$	(*R*)
CH_3OH	(*S*)
CH_3	(*T*)
OH	(*Q*)
$R-CH_2(CH_3)CHCOOH$	(*P*)
$R-CH_2(OH)COOH$	(*V*)

In this case the following unit steps can be envisaged:

1. $A+B=R+S$
2. $R+S=C$
3. $R+T=P$
4. $R+Q=V$
5. $S=T+Q$
6. $T+V=C$
7. $Q+P=C$

With the seven unit steps and seven intermediates equation (6) would indicate a single combination to check for a direct path but the corresponding determinant of the $(I+1)$-th order yields no solution. However, in analyzing the set of unit steps it is immediately clear that at least three feasible direct paths can be found, i.e.

$N_1=(1,1,0,0,0,0,0)$
$N_2=(1,0,1,0,1,0,1)$
$N_3=(1,0,0,1,1,1,0)$

and they can be obtained mathematically by solving determinants of lower order than $(I+1)$-th.

As Milner himself observes that kinetically and with respect to physical reality no mechanism containing a given unit step can be equivalent to another which does not contain it, the non-vanishing determinants must also be considered.

On this ground it appears that to obtain a complete list of possible direct paths it is necessary to solve all the determinants existing in the matrix, the number of which is larger than that predicted by equation (6) by a factor of $(I+1)!$. However, a closer inspection of the matrix problem reveals that some of the determinants may be discarded as obviously unable to yield a reaction mechanism, viz:

(*a*) there is a *lowest possible order* of determinant that can be of interest, and this is determined by the shortest possible way of performing the overall reaction. This depends on the features of the system and on certain assumptions made in making up the list of plausible unit steps (e.g. improbability of multi-molecular collisions, single electron exchange in redox or electrochemical reactions, etc.).

(*b*) Only those determinants can render direct paths which contain at least one non-zero element in the row pertaining to the reactant in the matrix (last row in (7)).

Hence, the number of determinants to be tested can be found by the following reasoning: all the unit steps are divided into those containing and those not containing the particular reactant in the matrix. Then the usual methods of combinatorial analysis are employed. Determinants of a given order Q can be made by combining p columns of the first group with $(Q-p)$ columns of the second. Since in R columns of the first group there are $\left(\frac{R}{p}\right)$ combinations and in $(S-R)$ columns of the second group $\left(\frac{S}{Q}-\frac{R}{p}\right)$ combinations, the product of these two summed over all values of p from 1 to Q gives the number of different chioces of columns for the determinant. Multiplying this by $\binom{I}{Q-1}$ for the number of row combinations in which the row of the reactants is always present, we obtain

$$D_{\text{test}} = \sum_{Q=m}^{I+1} \binom{I}{Q-1} \left\{ \sum_{p=1}^{Q} \binom{R}{p} \binom{S-R}{Q-p} \right\} \tag{8}$$

where m is the lowest order to be tested.

Because of the limitation (*b*) Milner's number (of the highest order determinants only) comes out somewhat less than calculated by his original formula. Thus, in the case of his example of the reduction of oxygen, instead of 8568 combinations, equation (8) gives 8512 combinations when OH^- is taken as the reactant for which the matrix is set up ($R=10$). However, the total number of determinants of all orders above the third comes out to be considerably larger.

Even though they satisfy the above conditions, some determinants when set up give obvious indications that no real solution can be expected, which further limits the number of determinants to be solved. Thus,

(*c*) no determinant need be considered in which one row or column consists of all zero elements (incomplete determinant).

(*d*) Only those determinants can yield direct paths summing up to the given overall reaction in which the sum of the stoichiometric numbers of intermediates in each row which is left out is zero for the columns composing the determinant. In most cases in practice this reduces to inspecting to see that no column participating in the determinant contains a non-zero stoichiometric factor outside of the determinant.

Condition (*d*) immediately implies that in each set of columns at most one set of rows can give a determinant worth solving. This is an accordance with the fact that a combination of columns can represent at most one reaction mechanism of the given order. Hence, rows should be tested to see if they can give a determinant worth solving; the first combination which does so should be solved and further investigation of that combination of columns abandoned. Therefore, D_{test} actually represents the upper limit of the number of combinations to be tested and it is probable that the actual number will be considerably less. In any case, the number of determinants whose solution should be attempted will be even less since one determinant per combination of columns is sufficient. This, at the same time is the maximum number of direct paths to be expected.

Thus,

$$D_{\text{solve}} = J_{\max} = \sum_{Q=m}^{I+1} \sum_{p=1}^{Q} \binom{R}{p} \binom{S-R}{Q-p} \tag{9}$$

The actual number J will be considerably less since many determinants within the number resulting from equation (9) will drop out because of conditions (*c*) and (*d*), or because they do not yield real solutions. However, it appears that this cannot be taken into account in any general way, so that all the D_{solve} determinants have to be investigated.

IV. TEST OF THE MODIFIED MILNER SYSTEM

To test the system with the new considerations taken into account a programme was set up for the ZUSE Z-23 digital computer with automatic checking of all the combinations given by equation (8) and exclusion from further treatment those not satisfying (*c*) and (*d*).

The example used was the electrooxidation of ammonia, for which a systematic analysis of intermediates and possible unit steps was made earlier (1). The very numerous possible combinations in the system with all 10 intermediates and 75 potential unit steps, of which 23 contain ammonia as one of the reactants, would prove a long task even for the fastest computers available. Hence, the analysis was restricted to a simpler system with 5 intermediates, without which the reaction in alkaline solution is hard to conceive — NH_2, NH, N, H, H_2.

The number of potential unit steps is thus reduced to 21, so that with ammonia as the reactant in the matrix, a matrix of two blocks 6 x 6 and 6 x 15 is obtained, as shown in fig. 1.

		2	27	28	33	35	38	10	17	21	24	48	49	53	54	56	64	65	66	67	70	71
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21
NH_3	1	1	1	1	1	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
NH_2	2	-1	-1	0	-2	-1	-1	1	0	0	0	1	1	1	1	1	0	0	0	0	0	0
NH	3	0	0	-1	1	-1	0	-1	1	0	0	-1	0	-2	0	-1	1	2	1	1	0	0
N	4	0	0	0	0	1	0	0	-1	0	0	0	-1	1	1	0	-1	0	1	-1	2	0
H	5	0	-1	0	0	0	1	0	0	1	-1	-1	0	0	0	1	-1	0	-1	1	0	2
H_2	6	0	0	-1	0	0	-1	0	0	0	1	0	-1	0	-1	-1	0	-1	0	-1	0	-1

Figure 1. Matrix describing possible reaction paths in electrooxidation of ammonia

The overall reaction $2NH_3+6OH^-=N_2+6H_2O+6e$ cannot be performed in less than 4 unit steps under the assumptions used in (1), and therefore according to equation (9) a total of 71,042 determinants of 4th to 6th order may potentially yield the reaction mechanism.

All the determinants of the 4th order were tested and solved on the computer. Out of the 4370 combinations indicated by equation (9) only 23 or 0.5% rendered a solution, most of them being discarded as failing to satisfy (*d*). 10 of the solutions contained both positive and negative stoichiometric numbers for the unit steps in the first block, implying that in the mechanisms they describe ammonia appears both as reactant and reaction product.

A check on the rate of progress of the computer indicated that in the case of determinants of higher order, a long time would be required for the complete operation. Since the usefulness of the long list of direct paths is in any case highly questionable, it was decided to limit the investigation to a 5 hour test.

Of the 5th order determinants the computer tested 900, or 5% of the total number of 17,356 indicated by equation (9). 22 solutions were obtained. However, 6 of those had already been obtained as solutions of the 4th order. Hence, 16 solutions (1.8%) of the 5th order were recorded. All solutions had positive and negative stoichiometric numbres for columns of the first block, the latter due to the fact that all the determinants tested contained more than one column of the first block. In such a case, if there is a solution, the stoichiometric numbers for these columns must be such that equation (3) is satisfied, which for the majority of cases means that they must have opposing signs.

The determinants of the 6th order were investigated in three sets. In the first set three columns of the first block (1, 3 and 5) were combined with the columns of the second block. All of the existing 455 combinations were tested and 150 of them gave useful solutions. However, only 64 of those were really of the 6th order, while 59 and 27 gave solutions with 5 and 4 non-zero stoichiometric numbers respectively.

Moreover, the 59 solutions represented only 25 different reaction paths, some being repeated several times. Similarly the 27 solutions of the 4th order represented only 6 different reaction paths, all of which had already been recorded in the 23 solutions of the 4th order mentioned earlier. All solutions, except two of the 4th order, contained both positive and negative stoichiometric factors for the reactant.

In the second set two columns of the first block were combined systematically with the columns of the second block, and 378 determinants were tested. Althoug 180 solutions were obtained, only 39 were of the 6th order, while in the 67 solutions of the 5th order there were 23 different reaction paths and in the 74 of the 4th order only 4 different reaction paths. Only one solution had positive signs for both stoichiometric numbers of the steps in thet firs block, there were 3 solutions with a positive and a zero stoichiometric number and 146 with positive and negative stoichiometric numbers for the two columns.

In the third set only one column of the first block was combined with the columns of the second block in 426 combinations. This gave 162 solutions, 44 of which were of the 6th order, 73 of the 5th order (28 different reaction paths) and 45 of the 4th order (2 different reaction paths). All solutions had a positive sign for the stoichiometric number of the unit step involving the reactant.

Summarizing, of the total of 49,316 combinations of the 6th order 1259 determinants were tested (2.5%). There were 147 or 11.7% solutions of the 6th order.

V. DISCUSSION

The test indicates that by further developing Milner's system satisfactory method is obtained for quantitatively assessing the maximum number of possible reaction mechanisms and for establishing a complete list of these, once the overall reaction and the intermediates existing in the system are known.

The digital computer programme made according to the derived premises and proven successful, need be further modified only so far as to avoid recording solutions containing some zero stoichiometric numbers and hence to avoid the repetition of solutions obtained when determinants of lower order are solved.

A few interesting conclusions can be reached by inspecting the partial list of direct paths obtained for the above example:

(*a*) Mechanisms of the type usually postulated, in which the reactants appear on the left side of the unit step equations only, are not so numerous and are obtained, with very few exceptions, when one unit step from the first block of the matrix is combined with the unit steps in the second block.

(*b*) Chain reactions are indicated by a particular location in the matrix when a second order symmetrical element of the type

$$\begin{array}{cccccc} & \vdots & \vdots & \vdots & \vdots & \\ \cdots & \cdot & 1 & -1 & \cdot & \cdots \\ & \vdots & \vdots & \vdots & \vdots & \\ \cdots & \cdot & -1 & 1 & \cdot & \cdots \\ & \vdots & \vdots & \vdots & \vdots & \end{array}$$

which contains factors of opposite sign is taken for the determinant. Since the method can yield only those solutions summing up to the overall reaction, only the "main flow" of any chain reaction can be obtained, initiation and termination reactions excluded unless they are needed to complete the overall reaction. Thus in the case of ammonia oxidation examples can be found of the type

$$\begin{array}{ll} N_j=(0,0,0,0,2,0,2,4,0,0,0,0,0,0,0,0,0,0,0,1,0) & \\ \quad NH_3+N=NH_2+NH & (\times 2) \\ \quad NH_2+OH^-=NH+H_2O+e & (\times 2) \\ \quad NH+OH^-=N+H_2O+e & (\times 4) \\ \quad 2N=N_2 & (\times 1) \end{array}$$

where the chain carriers are N and NH and must be formed by some initiation reaction outside the mechanism, e.g.

$$NH_3=NH+H_2$$

While the initiation reaction takes no part in the stoichiometry of the overall reaction, it may be seen that the termination reaction in this example does so. Also, this is an electrochemical chain reaction, since its propagation involves electron exchange and hence must be potential-dependent.

(*c*) A new class of reaction mechanisms seems to be indicated in most of the solutions containing negative stoichiometric numbers for unit steps involving reactants. Besides some chain reaction in which such a case is known to appear (usually termination), here mechanisms are obtained having a normal course up to a point where the accumulation of some intermediates is resolved by some additional unit step returning them to the initial state. E.g.

$N_j=(6,-4,0,0,0,0,0,0,0,0,2,0,0,0,0,1,0,1,0,0,0)$

$NH_3+OH^-=NH_2+H_2O+e$ (×6)

$NH_2=NH+H$ (×2)

$NH=N+H$ (×1)

$NH+N=N_2+H$ (×1)

$H+NH_2=NH_3$ (×4)

where obviously the last reaction is one from the first block but with a negative stoichiometric number indicating reversal.

(*d*) Mechanisms with fractional stoichiometric numbers are found, as e.g.

$N_j=(3.5,0,-1.5,0,0,0,2.5,0,0,0,0,0,0,1,0,0,0,0,1,0,-0.5)$

$NH_3+OH^-=NH_2+H_2O+e$ (×3.5)

$NH_2+OH^-=NH+H_2O+e$ (×2.5)

$NH+H=N+H_2$ (×1)

$NH_2+N=N_2+H_2$ (×1)

$H_2=2H$ (×0.5)

$NH+H_2=NH_3$ (×1.5)

which, however improbable, could occur if the 3rd and 4th unit steps were for some reason very fast. In such cases two acts of the overall reaction are needed for whole numbers of unit steps to take place.

Finally, looking at the result as a whole, althoug no quantitative generalizations can be made on the basis of this or any other example, sufficient qualitative evidence is given that even the relatively very simple reactions have extremely large numbers of possible reaction paths, so that the value of making a complete list of them is questionable. Morever, any speculation concerning reaction mechanisms which is based on limited experimental evidence is of highly doubtful value.

The only acceptable approach seems to be to set up the list of intermediates, unit steps, for the matrix and then use experimental evidence to simplify it (i.e. eliminate intermediates and unit steps). Then, a look at the matrix at any stage will give an indication of the progress made in elucidating the reaction mechanism. It is difficult, however, to expect this to be so rapid as to readily reduce the picture to a single determinant.

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POTENTIOGRAPHIC REGISTRATION OF THE ELECTROLYSIS OF POTASSIUM MANGANATE SOLUTION*

by

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Registration of the electrolysis process in the production of potassium permanganate by the electrochemical oxidation of alkaline potassium mangante solution is a particular problem because of difficulties in following, rapidly and precisely, the changes of manganate and permanganate concentrations in the electrolyte.

A great number of methods for the determination of the concentrations of manganate and permanganate simultaneously present in the solution are reported in the literature(1–12); this fact indicates that there is no adequate method, and that there is a trend to develop methods better than those used so far. The main difficulty in a simultaneous determination of manganate and permanganate arises from the fact that the chemical behavior of both ions is very similar, and that both ions are relatively unstable in solution. The existing analytical methods involve two determinations. In most methods the total amount of manganate and permanganate is first titrated by suitable reducing agents (usually iodometrically). Differences between individual methods appear in the second determination procedure, in which various procedures are used to convert permanganate into manganate, and finally, the total manganese is determined as manganate.

The common disadvantages of the mentioned methods, from the standpoint of monitoring the electrolysis of alkaline potassium manganate solutions, are a slow working rate, little precision at low permanganate concentrations (satisfactory precision is achieved only when molar ratio of manganate to permanganate is 1 : 10, whereas the maximal value of this ratio in the course of electrolysis is 1 : 5), and the fact that the automatic recording and automatization of the process are not possible.

In addition to chemical methods, in recent times some new physico-chemical methods (spectrophotometric, polarographic) for the determination of manganate and permanganate have been deve-

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loped, but, on account of complicated experimental procedures and apparata required, it seems likely that they would not be widely applied.

In the course of our investigations of the process of the electrochemical oxidation of potassium manganate(13), we have come to think that the course of the electrolysis, and the time required for its completion, might be arrived at by measuring the variations of the potential of an inert metal electrode immersed into the electrolyte. Such an indicator electrode, independent of the electrolysis circuit, would be connected with a convenient reference electrode, and the electromotive force of this circuit would reflect the variations of the potential of the indicator electrode with time; these variations might be registered continuously during the electrolysis.

This way of registering the electrochemical oxidation of potassium manganate was checked in a series of experiments, and it was established that, by interpreting correctly the variations of the indicator electrode potentials, the registration of the electrolysis may be carried out with approximately the same accuracy as with chemical methods, the other disadvantages of the chemical methods being thus avoided.

In this paper we discuss and describe in detail the proposed method in order to make its practical possibilities more apparent.

THEORETICAL TREATMENT

(1) In the electrolysis of alkaline potassium manganate solutions, under the given experimental conditions(13) the main process taking place at the inert anode is the oxidation of manganate ions:

$$MnO_4^{--} \rightarrow MnO_4^{-} + e; \quad e_0 = +0.564\ V$$

whereas at the cathode hydrogen is evolved:

$$H_2O + e \rightarrow OH^- + {}^1/_2\,H_2; \quad e_0 = -0.828\ V$$

Apart from these main electrochemical processes, some undesirable electrochemical reactions take place at the electrodes. At the anode oxygen is evolved:

$$2OH^- \rightarrow H_2O + {}^1/_2 O_2 + 2e; \quad e_0 = +0.401\ V$$

whereas at the cathode the reduction of oxy-manganese ions occurs:

$$\begin{array}{lll} MnO_4^- & + e \rightarrow MnO_4^{--} & e_0 = 0.564\ V \\ MnO_4^{--} & + e \rightarrow MnO_4^{---} & e_0 = +0.285\ V \\ MnO_4^{--} & + 2H_2O + 2e \rightarrow MnO_2 + 4OH^- & e_0 = +0.600\ V \\ MnO_4^{---} & + 2H_2O + e \rightarrow MnO_2 + 4OH^- & e_0 = +0.914\ V \end{array}$$

In adddition to these undesirable electrochemical processes, undesirable chemical processes(11,12) take place in the electrolyte as well: (*a*) the degradation of permanganate ion

$$4MnO_4^- + 4OH^- \rightarrow 4MnO_4^{--} + 2H_2O + O_2$$

and (*b*) the disproportionation of the manganate ion

$$2MnO_4^{--} + 2H_2O \rightarrow MnO_4^- + MnO_2 + 4OH^-$$

Undesirable electrochemical and chemical processes bring about a decrease in the current utilization, and lead to irreversible losses of manganate, so that in practice the utilization of the electrical currents amounts to only 50%.

As it might be seen, the process of electrochemical oxidation of potassium manganate is very complex, so that continuous recording of the process is required. The recording should answer to two questions: (*a*) whether the process of the electrolysis is developing in the desired direction with satisfactory current utilization and (*b*) when it should be interrupted.

(2) In accordance with the main electrochemical processes, the oxidation of potassium manganate may be represented by the following summary reaction scheme:

$$(2K^+ + MnO_4^{--}) + H_2O \xrightarrow{+1F} (K^+ + MnO_4^-) + (K^+ + OH^-) + {}^1/_2\,H_2$$

from which it follows that the decrease of the molar potassium manganate concentration in the electrolyte, in the course of the electrolysis, is equal to the increase of the molar concentration of potassium permanganate.

Assuming that all processes which lead to irreversible losses of manganate might be neglected (this can be achieved by means of well chosen electrolysis conditions), the molar concentrations of permanganate and manganate may be written as:

$$\begin{aligned} C_{KMnO_4} &= a + y \\ C_{K_2MnO_4} &= b - y \end{aligned} \qquad (1)$$

where a and b are the initial permanganate and manganate concentrations, and $y = y(t)$ is the increase of the molar permanganate concentration, i.e., the decrease of the molar manganate concentration from the beginning of the electrolysis till the moment t. The latter value represents a complex time function of the electrolysis, which also reflects the unfavorable effects of the electrochemical and chemical degradation of permanganate into manganate.

The following term may be obtained from Faraday's law, after some elementary transformations:

$$y = y(t) = \alpha\eta t \qquad (2)$$

t is the time of the electrolysis, $\eta = \eta(t)$ the utilization of the current, and α the intensity of the electrolysis process. This magnitude is defined by the equation:

$$\alpha = \frac{i}{F \cdot V} = \frac{C_i}{F} \qquad (3)$$

in which i is the current strength, V the volume of the electrolyte, F Faraday's constant, and C_i the current concentration.

(3) If an inert metal electrode, independent of the electrolysis circuit, is immersed into the electrolyte during electrolysis, its potential is the following:

$$e = e_0 + \frac{RT}{F} \ln \frac{a_{MnO_4^-}}{a_{MnO_4^{--}}} \tag{4}$$

The values of $a_{MnO_4^-}$ and $a_{MnO_4^{--}}$ represent the activities of permanganate and manganate ions, e_0 is the standard potential, and other symbols have their usual meanings.

The equation (4) may be writen in the form:

$$e = e_0 + \frac{RT}{F} \ln \frac{f_{MnO_4^-} \cdot c_{MnO_4^-}}{f_{MnO_4^{--}} \cdot c_{MnO_4^{--}}} \tag{5}$$

where $C_{MnO_4^-}$ and $C_{MnO_4^{--}}$ represent the concentrations, and $f_{MnO_4^-}$ and $f_{MnO_4^{--}}$ the activity coefficients of permanganate and manganate ions, respectively. From the equation (5) it follows that:

$$e = e_0 + \frac{RT}{F} \ln \frac{f_{MnO_4^-}}{f_{MnO_4^{--}}} + \frac{RT}{F} \ln \frac{c_{MnO_4^-}}{c_{MnO_4^{--}}} \tag{6}$$

The magnitude:

$$e_f = e_0 + \frac{RT}{F} \ln \frac{f_{MnO_4^-}}{f_{MnO_4^{--}}} \tag{7}$$

represents some formal potential which is a function of the ionic force of the electrolyte, since this force determines the values of activity coefficients. In the case of dilute electrolytes, by substituting the approximate term for activity coefficients according to the Debye--Huckel law, it might be seen that e_f is the function of the square root of the electrolytes ionic strength. However, for electrolytes of practical interest this approximation is not valid$^{(14)}$, but anyway, e_f might be taken as a constant, since the electrolyte's ionic force is only slightly changed during electrolysis. Then:

$$e = e_f + \frac{RT}{F} \ln \frac{C_{MnO_4^-}}{C_{MnO_4^{--}}} \tag{8}$$

or

$$e = e_f + \frac{RT}{F} \ln \frac{C_{KMnO_4}}{C_{K_2MnO_4}} \tag{9}$$

By substituting (1) in (9)

$$e = e(t) = e_f + \frac{RT}{F} \ln \frac{a + y(t)}{b - y(t)} \tag{10}$$

is obtained.

(4) If we want to follow the variations of the potential of an inert metal electrode immersed into the electrolyte in the course of electrolysis, it is necessary to connect it with an identical electrode immersed into the electrolyte of initial composition ($y=0$), and to register the EMF of this system in the course of the electrolysis. Since e_f is considered as a constant, the EMF is given by the following term:

$$E=E(t)=\frac{RT}{F}\ln\frac{b[a+y(t)]}{a[b-y(t)]} \tag{11}$$

or

$$E=E(t)=\frac{RT}{F}\ln\frac{b[a+\alpha\eta(t)\cdot t]}{a[b-\alpha\eta(t)\cdot t]} \tag{12}$$

(5) From the above equations it is possible to calculate $y(t)$ and $\eta(t)$ from the measured values of E and the known initial composition of the electrolyte. However, even if the given assumptions are valid, these calculations can only be approximative on account of the logarithmic form of the equations (11) and (12), so that small errors in the determination of E would cause great errors in calculated values. To avoid these difficulties one should not operate with the function $E(t)$, but with its derivative:

$$E'(t)=\frac{RT}{F}(a+b)\frac{y'(t)}{[a+y(t)]\,[b-y(t)]}=$$

$$=\frac{RT}{F}(a+b)\frac{\eta(t)+t\eta'(t)}{[a+\alpha\eta(t)t]\,[b-\alpha\eta(t)t]} \tag{13}$$

However, this leads to some mathematical difficulties which arise from the fact that the form of the function $\eta(t)$, and with this $y(t)$, is not precisely known. Namely, this is the case when the changes of the potential of the indicator electrode in the course of the electrolysis are registered as the experimental curve $E=f(t)$ and its differential curve $E'=f(t)$, then, provided the equation (12) mathematically represents the experimental curve, $E'(t)=f'(t)$, i.e.:

$$\frac{RT}{F}(a+b)\frac{y'(t)}{[a+y(t)]\,[b-y(t)]}=f'(t) \tag{14}$$

or

$$y'(t)=kf'(t)\,[a+y(t)]\,[b-y(t)] \tag{15}$$

where

$$k=\frac{F}{RT(a+b)} \tag{16}$$

is constant for the given electrolysis conditions.

The equation (15) denotes a differential equation in which $f'(t)$ is a variable parameter which is registered experimentally under the given conditions. This equation cannot be solved analytically except in some specific cases which will be considered briefly.

(*a*) Let us assume that $f'(t)=0$; this is equivalent to the assertion that the experimental curve $E=f(t)$ is a straight line parallel to the axis of time, and this might be correct only for a limited part of the curve at the end of the electrolysis. The solution of the equation (15) is then very simple:

$$y=\text{const}=b \tag{17}$$

i.e.

$$\eta=\frac{b}{\alpha t} \tag{18}$$

(*b*) Let us assume that $f'(t)=\text{const}\neq 0$; this is equivalent to the assertion that the experimental curve $E=f(t)$ represents a straight line whose direction coefficient is different from zero, and this might be only approximatively correct for particular parts of the curve. This assumption reduces the equation (15) to:

$$y'(t)=k'[a+y(t)]\,[b-y(t)] \tag{19}$$

where $k'=kf'(t)=\text{const}$.

The equation (19) permits separation of the variables so that the solution (provided $y=0$ for $t=0$) is:

$$y=ab\frac{\exp\,[k'(a+b)t]-1}{a\exp\,[k'(a+b)t]+b} \tag{20}$$

It might be seen that the solution (20) gives a good qualitative description of the process since $y\to b$ when $t\to\infty$ and $y\to 0$ when $t\to 0$.

With some approximations the solution (20) can be obtained in a more simple form. For very short electrolysis time periods $b\gg a>y(t)$, and is approximately:

$$y'(t)=k'ab \tag{21}$$

The solution of this equation (provided $y=0$ for $t=0$) is simple:

$$y=k'\,abt \tag{22}$$

From the above equation:

$$\eta=\frac{k'ab}{\alpha} \tag{23}$$

It might be seen that in this case the current utilization is constant.

If $b\gg y$ for short electrolysis time periods, the equation (19) asquires the form of:

$$y'(t)=k'[a+y(t)]b \tag{24}$$

This equation permits the separation of variable, and the solution is simple (provided $y=0$ for $t=0$):

$$y(t)=a[\exp(k'bt)-1] \tag{25}$$

i.e.,

$$(t)=\frac{a}{\alpha t}[\exp(k'bt)-1] \tag{26}$$

The solution (25) is defined only for electrolysis periods up to:

$$t=\frac{1}{k'b}\ln\frac{a+b}{a} \tag{27}$$

(c) Except in special cases given above which are of interest only for particular electrolysis time periods, it is not possible to solve the equation (15) analytically. However, the solution for each experimental curve $E=f(t)$ can be obtained on an analog computer. This way of solving the assigned problem involves the following: by means of a function generator in an analog computer the curve $E=f(t)$ is generated according to experimental points, and its differentiation gives the curve $E'=f'(t)$. Then, by means of an analog circuit there is generated the function $y(t)$ which satisfies the equality $E'(t)=f'(t)$, i.e., the equation (15) for the condition $y(t)=0$ for $t=0$.

The solving of the equation (15) by means of analog computer for each experimental curve is not performed in practice. However, the knowledge of a general solution $y(t)$ makes it possible to compare the values given by this function with those obtained by chemical methods. By means of such a comparison one can estimate the reality of assumptions on which the equations from (11) to (27) are based. This estimation may offer the basis for the consideration of the possibility to arrive, by the correct interpretation of results, at a method of recording in which the above mentioned mathematical difficulties would be avoided.

EXPERIMENTAL

The scheme of the apparatus used is given in Fig.1. It consits of an electric electrolysis circuit with the usual components: current source (U), rheostat (R), switch (K), amp-hourmeter (Ah), ampmeter (A), voltmeter (V), and the cell for the electrolysis (E). The electrolysis cell of 1 *l* capacity was placed in a thermostat (not shown in Fig. 1) with which the temperature of the electrolyte was kept constant at 60°C with an accuracy of ±0.1°C. The electrodes were coaxial cylinders of nickelfoil, the surface of the anode being ten times that of the cathode. The experiments were carried out with 80—150 A/m^2 anodic current densities. The electrolyte was prepared by leaching manganate with sodium hydroxide solution(13, 15).

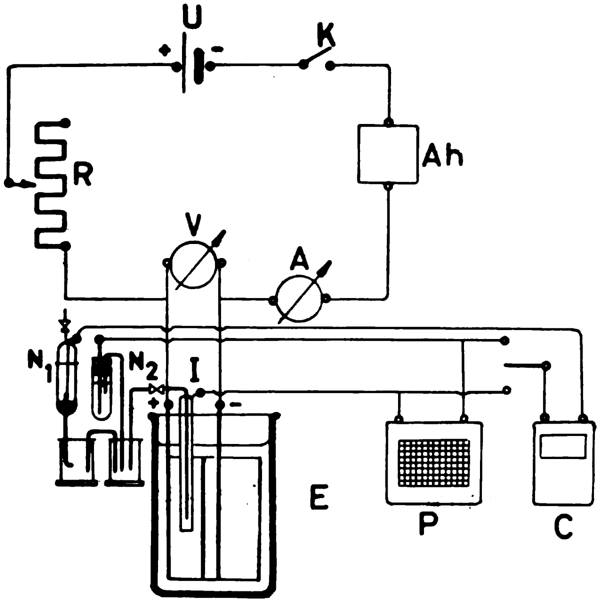

Figure 1
Apparatus for electrolysis

The indicator electrode (I) in the form of a platinum foil cylinder of 25 cm^2 surface was placed in a glass vessel dipped into the electrolyte, and was connected with the reference electrode. The reference electrode (N_2) was a platinum foil cylinder of 25 cm^2 surface immersed into 50 ml of the electrolyte of initial composition which was placed in a separate vessel and put into the thermostat. EMF of the indicator-reference electrode system was registered continuously in the course of the electrolysis by means of a potentiograph (P), type "Bristol", at 0–100 and 0–200 mV with an accuracy of ±1 mV. To check continuously the reading of the potentiograph and to check whether the potential of the reference electrode was altered, at longer time intervals the potentials of both electrodes were measured with respect to a standard Hg/HgO 4 N KOH electrode (N_1) be means of an Hewlet-Packard electronic millivoltmeter (C). It was established that the potential of the reference electrode in the course of several hours did not change more than ±2 mV. The registered values of EMF were corrected for these changes of EMF.

RESULTS AND DISCUSSION

In the present work a series of curves for various *a*, *b*, and *α* values was obtained. The curves were found to possess specific forms. In the beginning of the electrolysis the potential of the indicator electrode was found to augment rapidly towards more positive values;

then, the increase was established to take place more slowly; and at the end, a tendency toward a constant potential value was observed. Parallel chemical analyses of the electrolyte, carried out in the course of the electrolysis as described in the literature(11), showed that in the period just before the achievement of a constant potential, i.e., for $f'(t)=0$, the concentration of permanganate in the electrolyte was only slightly increased, whereas the current utilization fell below the value of 20—25%, which is known in the literature as the lowest limit of an economic process(15). Time required for the achievement of an approximatively constant potential and the total change of the potential depended on the values of *a*, *b*, and α, for all curves investigated.

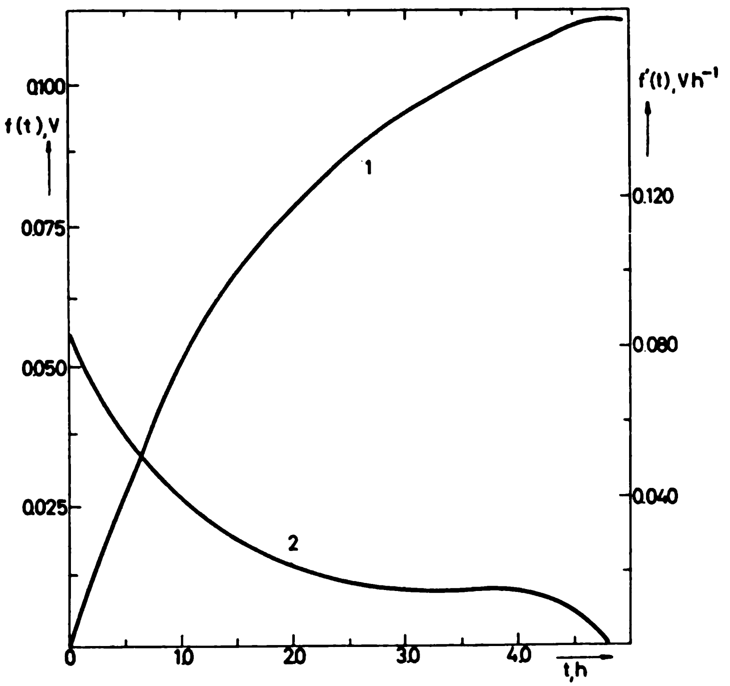

Figure 2

(1) Function $E=f(t)$ for $a=0{,}04$ and $b=0{,}485$ $mol \cdot lit^{-1}$ $\alpha=0{,}2$ $mol \cdot lit^{-1}h^{-1}$.
(2) Function $E'=f'(t)$

The time and the total change of the potential, when calculated according to equation (12) (with an approximative value of η), were qualitatively in agreement with the measured values. Since the form of the function $\eta(t)$ and the logarithmic form of the equation (12) are not known, these calculations are only roughly approximative.

In Fig. 2 a typical curve $E=f(t)$ (curve 1), chosen for mathematical analysis, and its differential curve $E'=f'(t)$ (curve 2), are shown.

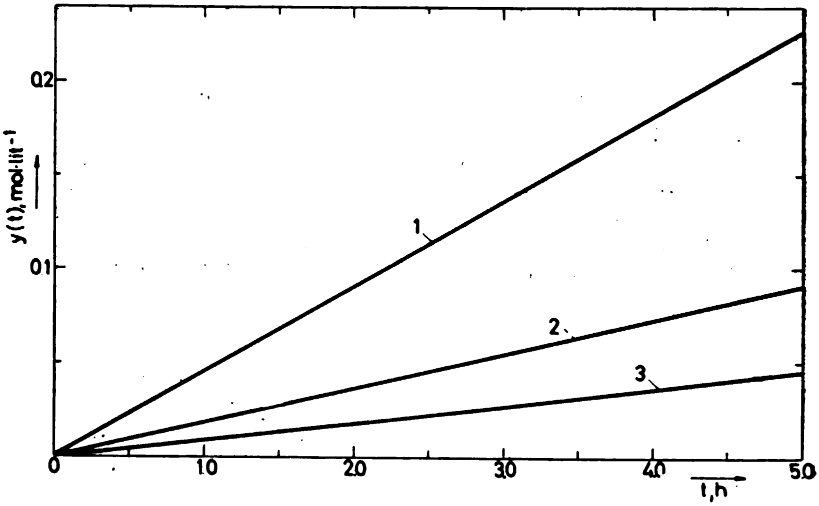

Figure 3
Solutions of equation (21)
(1) $f'(t)=0.085\ Vh^{-1}$, (2) $f'(t)=0.034\ Vh^{-1}$, (3) $f'(t)=0.017\ Vh^{-1}$.

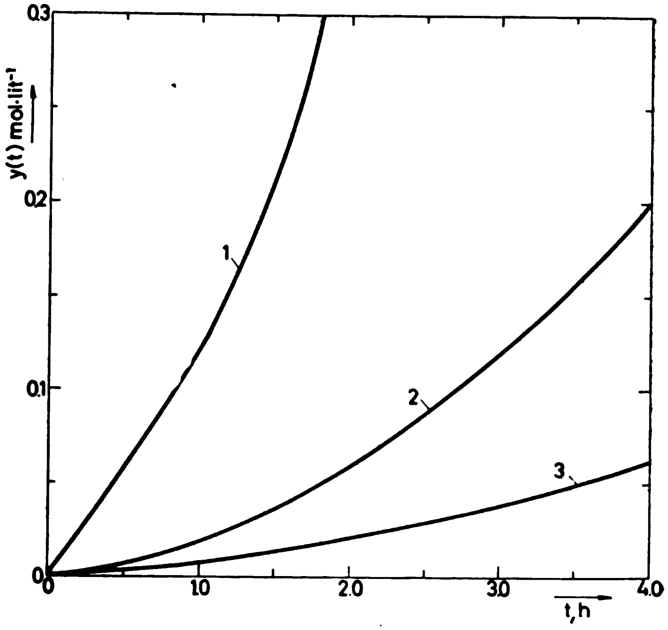

Figure 4
Solutions of equation (24)
(1) $f'(t)=0.085\ Vh^{-1}$, (2) $f'(t)=0.034\ Vh^{-1}$, (3) $f'(t)=0.017\ Vh^{-1}$.

On the curve $E=f(t)$ one might observe the characteristic parts corresponding to periods of rapid and slow increase of potential, and to the tendency of achievement of a constant potential. The increase of the potential at the end of the electrolysis is for a rather long time-period linear, and this is apparent from the differential curve, $E'=f'(t)$.

The solutions of equations (21) and (24) for this experimental curve (curve 1; Fig 2) are given in Figs. 3 and 4. These curves should represent approximatively the increase of the concentration of permanganate in the electrolyte for various values of $f'(t)$. However, it might be seen that these approximative functions tdo not correspond qualitatively to the course of the process, since they show the tendency for unlimited increase, whereas the function $y(t)$ should be limited to the value $y(t)=b$.

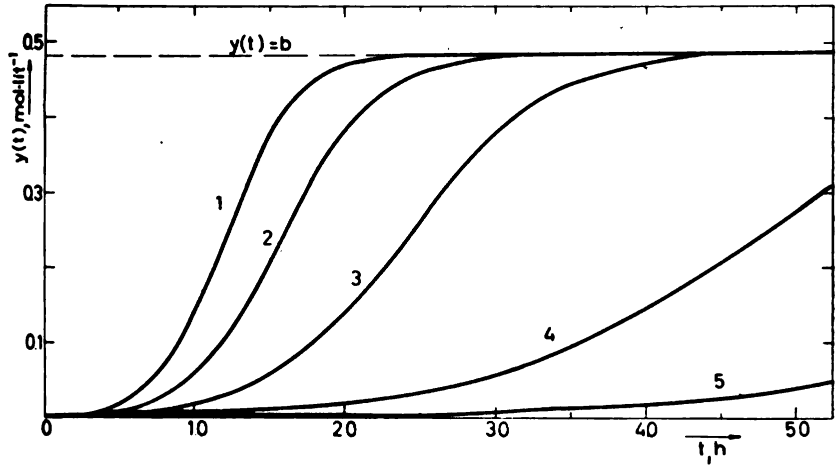

Figure 5

Solutions of equation (19)
(1) $f'(t)=0.034\ Vh^{-1}$, (2) $f'(t)=0.0255\ Vh^{-1}$ (3) $f'(t)=0.017\ Vh^{-1}$,
(4) $f'(t)=0.0085\ Vh^{-1}$ (5) $f'(t)=0.0034\ Vh^{-1}$.

Graphic solution of equation (19) is shown in Fig. 5. The given curves reflect qualitatively the course of the increase of the permanganate concentration in the electrolyte and the dependence of this increase rate on $f'(t)$. However, in view of the assumption that $f'(t)=$ const., it should not be expected that these curves correspond to the actual curve $y(t)$, except for very narrow time intervals.

The solution of equation (15) for the given experimental curve is shown in Fig. 6. (curve 1). Figure 6 also contains the values for the increase of permanganate concentration, obtained by chemical analyses (dotted line). It might be seen that there is a good consistency between the obtained function and the actual process (difference between final concentrations amounts to about 4%). Higher values which give the function $y(t)$ are probably due to disproportionating of manganate, which was not taken into the above considerations. In the beginning of the electrolysis the rate of the increase of the permanganate concentration is somewhat low (on account of chemical degradation of permanganate which is known to take place at low permanganate concentration), then it rapidly augments and after a time interval it is constant until the end when it reaches zero value.

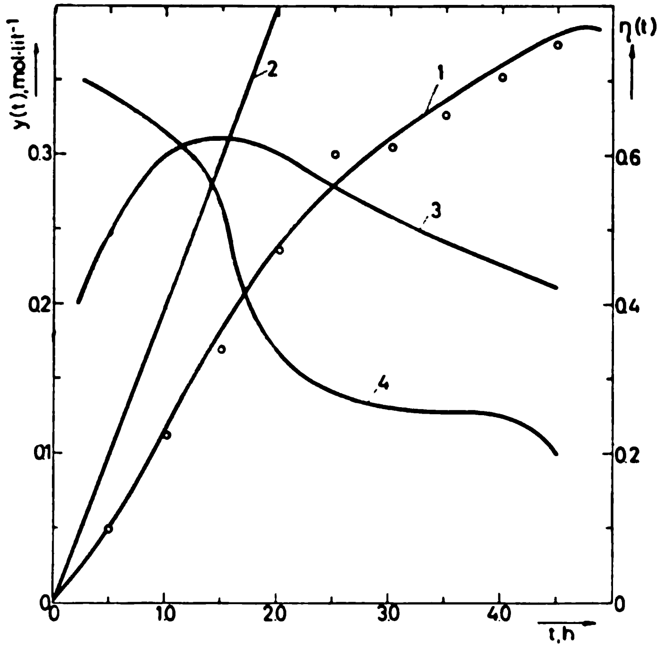

Figure 6

(1) Function $y(t)=\alpha\eta(t)\cdot t$ — exact solution
(2) Function $y(t)=\alpha\cdot t$
(3) Function $\eta_S(t)$
(4) Function $\eta(t)$

The function $\eta(t)$, i.e., the dependence of current utilization on time, can be obtained from the function $y(t)$ in two ways. The function $y(t)=\alpha\eta(t).t$ may be divided by the function $y(t)=\alpha t$ (curve 2), which represents Faraday's. Law for the ideal case $\eta(t)=1$, giving the curve $\eta_s(t)$ (curve 3), which shows the dependence of the average current utilization (for the interval $0-t$ observed) on time.

On the other hand, graphical differentiation of the curve $y(t)=\alpha\eta(t)\,.\,t$, followed by division with α, achieves the curve $\eta(t)$ (curve 4), which represents the dependence of actual current utilization (for short time periods) on time. It is evident that:

$$\eta_s(t)=\int_0^t \eta(t)dt$$

From the curve $\eta_s(t)$ it might be seen that the average value of the current utilization for $t=4.5$ hrs is $\eta_s=0.42$, whereas from curve $\eta(t)$ the graphical interpolation yields the value of η_s 0.40. The value obtained by chemical analysis is η_s 0.32. The actual value of current utilization of the period of about 4.5 hrs is $\eta=0.20$ from curve $\eta(t)$ and $\eta=0.16$ from the data of chemical analysis.

On the basis of all said afore it might be concluded that the potential of an inert electrode immersed into the electrolyte in the course of the electrolysis is a relatively well defined function of the electrolyte composition (a, b), current utilization (η), electrolysis intensity (α), and time (t). From the measured values of this potential it is possible, be means of a mathematical procedure, to obtain approximately accurate dependence of the increase of the permanganate concentration and of current utilization on electrolysis time.

The mathematical procedure which leads to these dependences is rather complex and it may be simplified by employing the results of mathematical analyses performed. In practice, the current utilization is a criterion for the efficiency of the electrolysis. However, accurate solution of the equation (15) has confirmed the fact, indicated by orientation calculations, that just before the achievement of a constant indicator electrode potential, the current utilization falls below the lowest limit permitted for an economical process. Accordingly, the registration of the differential curve of the indicator electrode potential under given electrolysis conditions may be a good method of recording.

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STANDARD FREE ENERGY OF FORMATION OF AMMINE-COPPER COMPLEX IONS

by

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INTRODUCTION

This paper deals with the standard free energy of ammine-copper complex formation, ΔF°, i.e., with the dependence of this magnitude on the number of ammonia molecules present in the inner sphere of the complex ions. In the thermodynamic treatment of the process of polyvalent metal ions hydrolysis, a very approximate linear dependence of standard free energies of hydrolysis products on the number of linked hydroxyl group was established, starting from the value of the standard free energy of formation of the free ion in aqueous solution, till the final hydrolysis product, i.e., metal hydroxide(1, 2).

On these bases it was possible to predict graphically the most probable approximate value of the standard free energy of formation for those hydrolytic products for which the values of ΔF° were not known. Graphically predicted values of standard free energies of formation for simple and polynuclear products were in good agreement with ΔF°-values calculated from experimentally obtained hydrolysis constants(3).

Very few data on standard free energies of formation ΔF° of ammine-copper complexes are reported in the literature. Therefore, in the treatment of standard free energies of formation, the values of equilibrium constants for completely ionized complex ions were used.

The values of the standard free energies of formation of ammine-copper complexes were calculated from the known instability constants, by using the known values of the standard free energies of formation of mono- and bivalent copper ions and ammonia in aqueous solution.(4)

The dependence of the thermodymanic value ΔF° *(kcal/mol) on the number of ligands for mono- and di-ammine-Cu(I)-ions.*

M. W. Latimer⁽³⁾ cited the following values of standard free formation energies, ΔF°, for mono-, and di-ammine-Cu(I)-ions, and for Cu^+ ion:

$$\Delta F^\circ_{Cu^+} = +12 \ kcal/mol$$

$$\Delta F^\circ_{Cu(NH_3)^+} = -\ 2.8 \ kcal/mol$$

$$\Delta F^\circ_{Cu(NH_3)_2^+} = -15.6 \ kcal/mol$$

These ΔF°-values were applied to the construction of the diagram of $\Delta F^\circ - n\ NH_3$, where the ordinate represents the values of standard

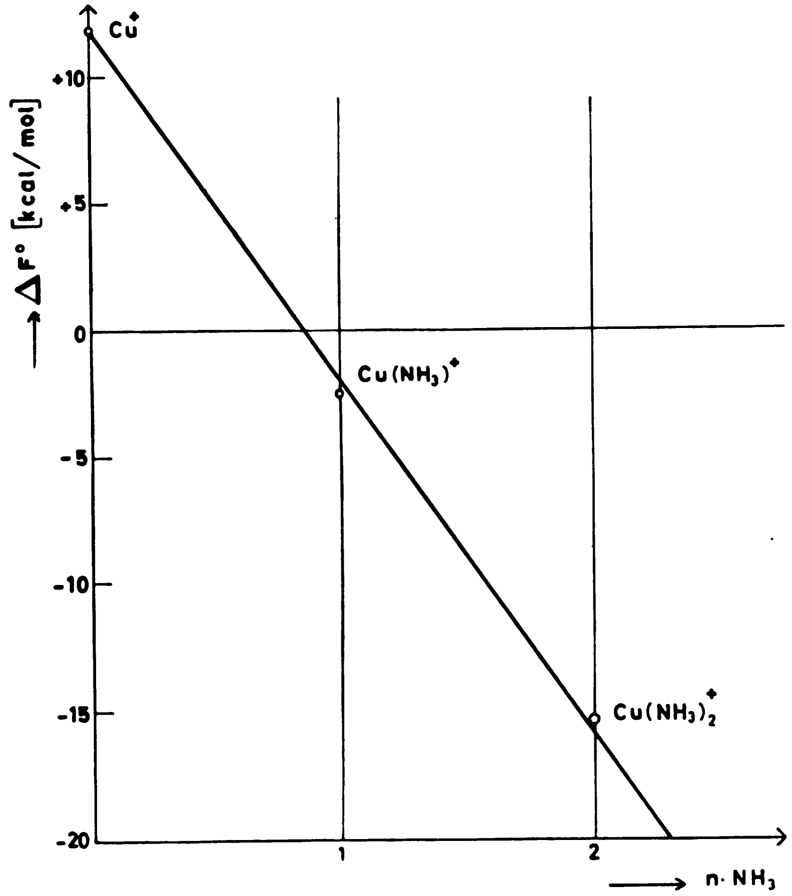

Fig. 1 Diagram of ΔF° (kcal/mol) — $n \cdot NH_3$ for mono- and di-ammine-Cu (I) complex ions.

free energies of formation of given ions, and the abscissa the number of ammonium molecules in the complex ions (Fig. 1). In addition to these ΔF°-values (in diagram denoted by circles), the diagram also contains ΔF°-values calculated from instability constants of these ions, according to G. Charlot⁽⁵⁾ (in diagram denoted by circles).

From the diagrama in Fig. 1 it might be assumed that there is a linear dependence of the standard free energy of formation, ΔF°, on the number of ammonium molecules present in mono-and di-ammine-Cu(I) ions.

Standard free energy of formation, ΔF°, for mono-, di-, tri-, and tetra-ammine-Cu(II) ions

M. W. Latimer cited only the value of the standard free energy for tetra-ammine-Cu(II) ion:

$$\Delta F^\circ_{Cu(NH_3)_4}{}^{2+} = -40.8 \; kcal/mol$$

The values of ΔF° for the study of the dependence of the standard free energies of formation of mono-, di-, tri-, and tetra-ammine-Cu(II) ions on the number of ammonium molecules present in the inner sphere of complex ions, were calculated from the instability constants of the studied complex ions according to the known relation:

$$\Delta F^\circ_R = -RT \ln K$$

i.e., at 25°

$$\Delta F^\circ_R = 1.3643 \; pK$$

where ΔF°_R represents the difference between the sum of the standard free energies of formation of products, and the sum of the standard free energies of reactants of the chemical reaction involved. In these calculations the data given be M. W. Latimer were used:

$$\Delta F^\circ_{Cu}{}^{2+} = +15.53 \; kcal/mol$$

$$\Delta F^\circ_{NH_3aq} = - \; 6.36 \; kcal/mol$$

From the reaction

$$Cu(NH_3)^2 \rightleftarrows Cu^{2+} + NH_3 \; aq \qquad (1)$$

and the value of the instability constant⁽⁵⁾

$$pK_1 = 4.15$$

the following standard energy of mono-ammine-Cu(I) ion was obtained

$$\Delta F^\circ_{Cu(NH_3)}{}^{+} = + \; 3.52 \; kcal/mol$$

In the same way, from the value $pK_2=7.65^{(5)}$, in case of the reaction

$$Cu(NH_3)_2^{2+} \rightleftarrows Cu^{2+}+2NH_3\ aq \qquad (2)$$

it was obtained that

$$\Delta F^\circ_{Cu(NH_3)_2^{2+}} = -7.62\ kcal/mol$$

From the reaction

$$Cu(NH_3)_3^{2+} \rightleftarrows Cu^{2+}+3\ NH_3 aq \qquad (3)$$

and the equilibrium constant$^{(5)}$, i.e.,

$$pK_3=10.54$$

the standard free energy of the tri-ammine-Cu(II) ion was calculated to be

$$\Delta F^\circ_{Cu(NH_3)_3^{2+}} = -17.9\ kcal/mol.$$

For the reaction

$$Cu(NH_3)_4^{2+} \rightleftarrows Cu^{2+}\ +4\ NH_3 aq \qquad (4)$$

G. Charlot$^{(5)}$ gave the value of $pK_4=12.67$, wherefrom it was obtained that

$$\Delta F^\circ_{Cu(NH_3)_4^{2+}} = -27.7\ kcal/mol$$

This value of the standard free energy of formation of tetra-ammine--Cu(II) complex is very much different from the value given by M. W. Latimer. Therefore, the equilibrium constants of the reaction (4) given by other authors were taken into consideration. They were slightly different, depending on the experimental methods used for their determination. By calculation, the following ΔF°-values for the tetra-ammine-Cu(II) complex were obtained:

$$\Delta F^\circ = -29.54\ \text{kcal/mol}^{(4)}$$

$$\Delta F^\circ = -28.14\ \text{kcal/mol}^{(7,\ 8)}$$

When all the above mentioned values of ΔF° are drawn into the diagram $\Delta F^\circ - n\,NH_3$ (Fig. 2), it might be seen that there is an approximate linear dependence of the standard free energies of these complex ions on the number of ligands present in their inner spheres. However, this approximate linear relationship is valid only if the calculated values of ΔF° for $Cu(NH_3)_4^{2+}$ ions are taken into consideration.

The ΔF°-value (kcal/mol) for the tetra-ammine-Cu(II) complex given by M. W. Latimer differs by about 12 kcal/mol from the ΔF°--value calculated from instability constants. Therefore, it might be taken for certain that the ΔF°-value given by M. W. Latimer should be corrected.

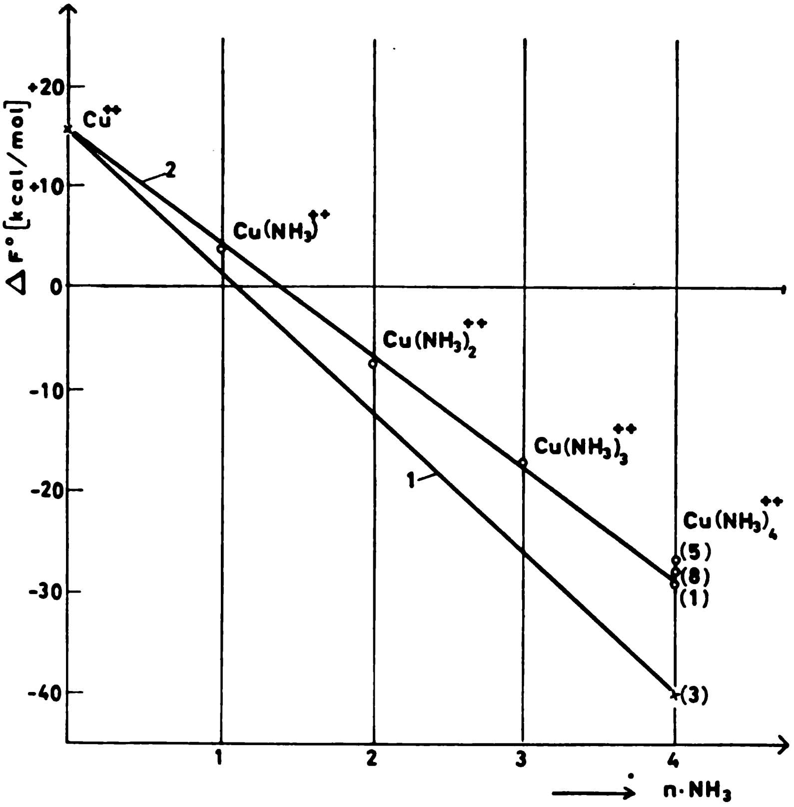

Fig. 2 The dependence of the standard free energy of formation, ΔF°, of mono-, di-, tri-, and tetra-ammine-Cu(II) complex ions on the number of ammonium molecules.

Then, it might be assumed that the linear relationship between the standard free energy of formation, ΔF°, of mono-, di-, tri-, and tetra-ammine-Cu(II) complex and the number of ammonium molecules in the inner spheres of complex ions, is valid in this case as well.

Standard free energy of formation, ΔF°, for penta- and hexa-ammine-Cu(II) ions

Data in the literature on the equilibrium constant in the case of complete ionization of penta- and hexa-ammine-Cu(II) ions are very scarce. Therefore, in the thermodynamic treatment of these complex ions, data given by G. Charlot$^{(5)}$ for the reaction:

$$Cu(NH_3)_5^{2+} \rightleftarrows Cu^{2+} + 5NH_3\ aq \qquad (5)$$

$$pK = 12{,}2$$

were used. From this reaction, by using the proper values of ΔF° for Gu^{2+}-ion and NH_3 *aq*, it was possible to calculate the standard free energy of formation, ΔF°, for Cu $(NH_3)_5{}^{2+}$, which was found to be:

$$\Delta F^\circ_{Cu(NH_3)_5}{}^{2+} = -31.84 \text{ kcal/mol}$$

M. W. Latimer's data for the reaction,

$$Cu(NH_3)_5{}^{2+} \rightleftarrows Cu(NH_3)_4{}^{2+} + NH_3\ aq$$

$$pK = -0.5$$

on account of different ΔF°-values for Cu $(NH_3)_4{}^{2+}$,were not convenient for these investigations.

For the calculation of the standard free energy of formation, ΔF°, for hexa-ammine-Cu(II) complex, the following data(5) were available:

$$Cu(NH_3)_6{}^{2+} \rightleftarrows Cu(NH_3)_5{}^{2+} + NH_3\ aq \qquad (6)$$

$$pK = 2.5$$

from which we obtained the value of ΔF°

$$\Delta F^\circ_{Cu(NH_3)_6}{}^{2+} = -34.8 \text{ kcal/mol}$$

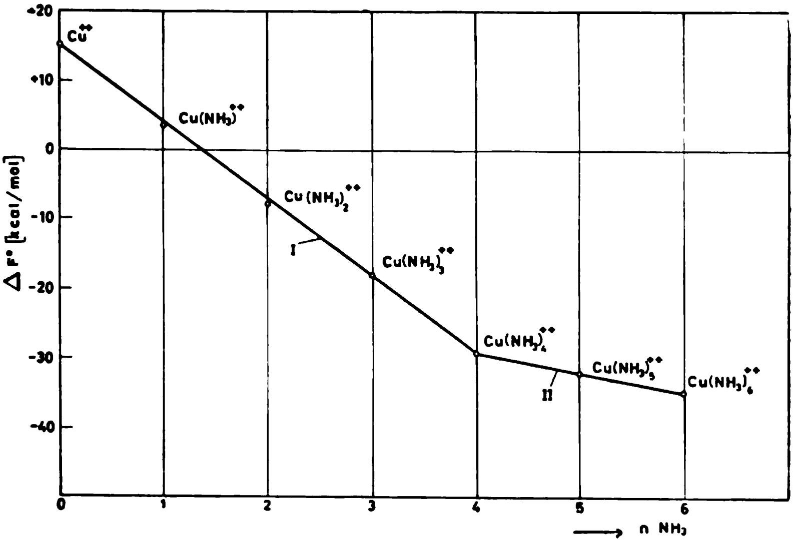

Fig. 3 Diagram of ΔF°(kcal/mol) — $n.NH_3$ for ammine Cu(II) complex ions

The diagram $\Delta F^\circ - n\,NH_3$ in Fig. 3 contains the values of calculated standard free energies of formation for all the above mentioned complex ions.

The point of the intersection of the line (1) representing the most approximate linear relationship between the free energies of formation for mono-, di-, and tri-ammine-Cu(II) complex ions, and the line (2) drawn through the points for penta-and hexa-ammine-Cu(II) complex ions, might denote the most probable value of the standard free energy of formation for the $Cu(NH_3)_4^{2+}$ – ion, i.e.,

$$\Delta F^\circ_{Cu(NH_3)_4^{2+}} = -28.8 \text{ kcal/mol}$$

This value of the standrd free energy of the tetra-ammine-Cu(II) ion is in fact the mean value of ΔF°-values calculated from instability constants by M. W. Latimer(3) and B. N. Alekseev(7).

CONCLUSION

On the basis of the given thermodynamic treatment of ammine--copper(II) complex ions, the following might be assumed:

1. One, two, three, or four ammonium molecules are linked to Cu^{2+} ion by coordinative bond, whereby an inner sphere of the complex ion is formed. This is consistent with the known fact that the coordination number of the Cu^{2+}-ion is four.

2. The linking of more than four ammonium molecules, i.e., the formation of penta- and hexa-ammine-Cu(II) ions, takes place with the change of the standard free energy of the reaction, which is different from the change observed in the linking of the first four ligand molecules. This leads to the assumption that the linking of the fifth and the sixth ammonium molecules takes place in a different way.

3. Since the instability constants determined by different authors are different, and consequently the values of ΔF° for tetra-ammine-Cu(II) ion are also different, we assume that the value of

$$\Delta F^\circ_{Cu(NH_3)_4^{2+}} = -28.8 \; kcal/mol$$

determined graphically might be taken as very probable.

4. Since the value of ΔF° for $Cu(NH_3)_4^{2+}$ given by Latimer is very much different from the values obtained by calculation from different instability constants, it might be concluded that this value, $\Delta F^\circ_{Cu(NH_3)_4^{2+}} = -40.8$ kcal/mol, should be corrected.

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DETERMINATION OF RHODIUM IN SOLUTIONS BY A COMBINED ELECTROLYTIC SPECTROCHEMICAL METHOD

by

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VILIM J. VAJGAND and NEVENKA M. SVILAR

INTRODUCTION

The methods which are most often used for the spectrochemical analysis of solutions are those with rotatory electrodes, whereby electrodes of graphite or copper disks are utilized. Detailed reviews of the application of these methods in the analytical practice are reported by M. Matherney(1), T. H. Zink(2), O. Szakács(3), and W. K. Baer and E. S. Hodge(4). The advantages of these methods reside in the possibility of direct analysis of solutions and in an easy preparation of reliable standards. However, these methods do not represent the most sensitive standards.

To increase the sensitivity of the determination we have combined the process of electrolytic separation of elements with simultaneous spectrochemical excitation.

The processes of previous electrolytic separations have been described by many authors(5,6,7,8). The application of electrolytic separations was thoroughly studied by A. Schleiher(9). However, all these methods have not been widely applied in spectrochemical analytical practice either on account of complicated procedures or due to a long time period required for the electrolysis. We wanted to develop a sensitive method for the analysis of solutions, a method which would be experimentally simple and thus applicable in analytical practice.

In a preliminary communication(10) we have described a combined electrolytic spectrochemical method for the analysis of solutions. Applying this method to the analysis of rhodium solutions we wanted to show its advantages.

Rhodium content in noble metals, in concentrations ranging from 0.001% to 1%, has been mostly determined spectrochemically(11,12,13,14). The best sensitivities were achieved by means of ion-exchange enrichment, using the copper spark method(14)

(0.2 ppm), and by means of atomic absorptions(15) (0.2 ppm with an error of 10%). The method of A. Bardocz and F. Varsanyi(16) is also worth mentioning: rhodium solutions were analyzed by means of four rotatory electrodes whose upper parts during rotation entered into rhodium solution, thus carrying rhodium into spark plasma. By this method the authors obtained a relatively high reproductivity with an error of only some percent, but only for concentrations ranging from 1 to 25%.

EXPERIMENTAL

The scheme of the apparatus used is given in Fig. 1, which shows that there are two electrical circuits: the circuit for the electrolysis and the circuit for the excitation. The common point of both circuits is the rotatory copper electrode disc which is 1.5 mm thick and has a diameter of 2 cm. The sides of disks are covered with an insulator layer in order that the electrolysis takes place only at the border of the disk dipped about 2 mm into the solution.

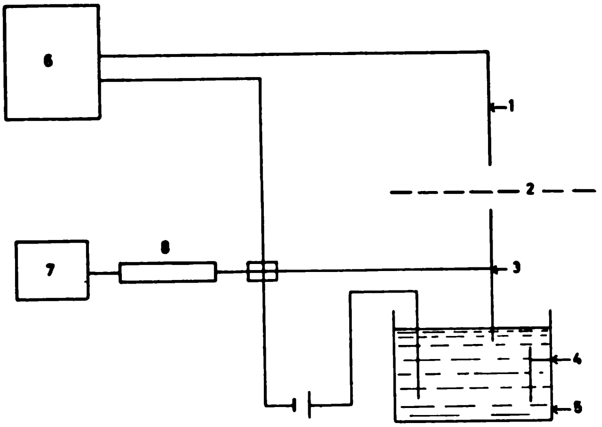

Figure 1

1-Upper electrode, 2-Optical axis, 3-Lower electrode-rotating Cu disk, 4-Ag anode, 5-Solution, 6-Excitator, 7-Motor rotating the electrode, 8-Isolation

Electrolysis circuit: the current varied about 0.8 mA with an initial potential of 1 V. A ring of silver foil was used as the anode and the electrolyte was a 0.3 N potassium chloride solution. Sample volume was 3 ml.

Excitation circuit: the generator was an interrupted arc according to Bardocz, type BIG-100. The current strength was 3.6 A with ten interruptions per second. The upper part of the electrode was made of sharp pieces of copper foil (the same was used for the copper disks).

Photographing conditions: quartz spectrograph *Q*-24 was used, exposure time was 10 minutes, and ordinary Ilford N 30 plates were utilized. Rhodium line at 3434.9 A was observed.

Duration of exposure was determined by preliminary investigations which had shown that the separation of rhodium, for the range of concentrations studied, was highest within the first ten minutes.

The rhodium solution for the preparation of standard solutions was made by fusing metallic rhodium with an approximately sixfold amount of potassium bisulfate in a porcelain basin.

RESULTS

Figure 2 shows the dependence of *S* on the log *C* of rhodium. The standard error of individual measurements amounted to 10%.

The sensitivity was determined according to the equation given by A. H. Zejdel(17); for noncontaminated rhodium solutions it amounted to 0.08 ppm, which represents an absolute sensitivity of 2.4x10^{-7} g of rhodium under given experimental conditions.

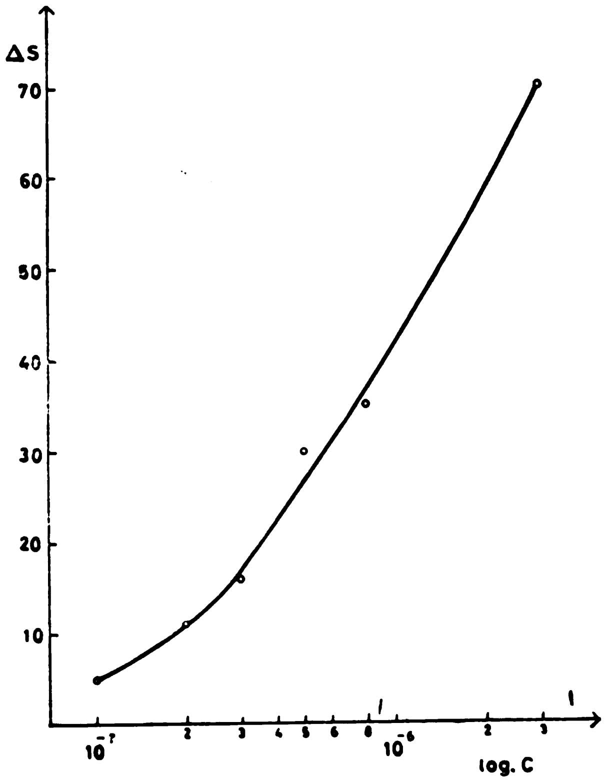

Figure 2

Dependence of *S* on log *C* of Rhodium

By comparing these results with those published in the literature it might be seen that the combination method falls among the most sensitive methods for the determination of rhodium.

The interfering effect of other elements upon the determination of rhodium by means of this method has not been investigated.

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RECOVERY OF GERMANIUM FROM WASTES OBTAINED IN THE PRODUCTION OF SEMICONDUCTOR ELEMENTS

by

BRATIMIR B. ĐURKOVIĆ, DRAGAN S. SINADINOVIĆ
and ZVONIMIR V. POPOVIĆ

Modern electronic industry is the greatest consumer of germanium, a metal which is used for the production of semiconductor elments. In the technology of the production of these elements, large amounts of wastes, very rich in germanium, accrue. The high price of germanium and the large amounts of wastes (about 80% of the germanium used remains as wastes) have imposed the necessity for the recovery of the metal from these wastes.

Starting from polycrystalline germanium, the losses of metal appear to be variously distributed, but mostly it is lost:

— as the residue in the crucible after monocrystal separation,
— as small plates formed in the course of monocrystal cutting,
— as waste powder left after monocrystal cutting,
— as wastes after grinding plates,
— as dissolved germanium salts in washings.

The technology of germanium recovery from wastes consists of the following:

a) Wastes (plates and pieces) of purity of above 1 Ohm cm, are washed, dried, and fused into rods for zone refining.

b) Chemical treatment of wastes of purity below 1 Ohm cm involves the purification of wastes, the preparation of technical germanium tetrachloride, and the production of metallic germanium according to standard technological processes. Plates and pieces are ground so that the size of grains is about 0.1—1 mm; wastes are washed with trichloroethylene in order to remove organic substances. Dried wastes and waste powder are then chlorinated with elementary chlorine to germanium tetrachloride; the residue after chlorination containing from 5 to 20% of germanium is treated with hydrochloric acid. In Poland, waste materials poor in germanium (about 15%) are leached with sodium hydroxide and hydrogen peroxide, and the obtained solution is treated with hydrochloric acid; germanium is converted to technical germanium tetrachloride by distillation.

c) The recovery of germanium from the solution is carried out by neutralization with ammonium hydroxide, whereby germanium is precipitated in the form of germanium dioxide.

According to the scheme proposed by Rösner⁽¹⁾, fine powder is chlorinated with gaseous chlorine in the presence of hydrochloric acid.

We have studied the possibility of germanium recovery from wastes obtained in the production of semiconductor elements at the E. I. enterprise, Niš. The main feature of the work was the recovery of germanium from wastes obtained by cutting and grinding. These wastes usually contain, in addition to germanium, the following impurities: siliconcarbide, silica, silicon, oil, dust from the air, etc. Moreover, in the course of cutting and grinding of the monocrystal, the temperature is raised so that the metal, being in contact with the air, is oxidized to germanium monoxide and dioxide. Germanium wastes are characterized by a nonuniform composition.

In order to find out an optimal technological process for the recovery of germanium from wastes obtained in the production of semiconductor elements, we have carried out a series of experiments with different working schemes, taking into account the yields of the metal recovered and material expenses. Separation of metal pieces of purity above 1 Ohm cm before zone refining involved no difficulties.

The method of leaching with sodium hydroxide and hydrogen peroxide was first examined. However, the recovery of germanium was low (below 40%) and the comsumption of reagents high, so that this method was established to be inconvenient for the available wastes.

We also examined the technological scheme for the recovery of germanium which involves treatment with hydrochloric acid. The scheme of the apparatus used is shown in Fig. 1. This apparatus gave optimal results with respect to the purity and the yield of germanium tetrachloride. The difficulties encountered in the development of this procedure were the following:

— a relatively large amount of germanium which remained in solution in the form of lower germanium chlorides and germanium oxychloride,

— slime, containing considerable amounts of germanium,

— difficult condensation of vapors on account of large amounts of hydrogen chloride.

These difficulties rendered such a low recovery yield of germanium that the solution and the slime had to be treated again. Since the total yield of the process with hydrochloric acid was low (below 70%), and the reagents used were expensive, we rejected this procedure despite a high purity of technical germanium tetrachloride.

The recovery of germanium from wastes by means of a process which involves the chlorination of germanium with elemenatry chlorine represented the most interesting procedure.

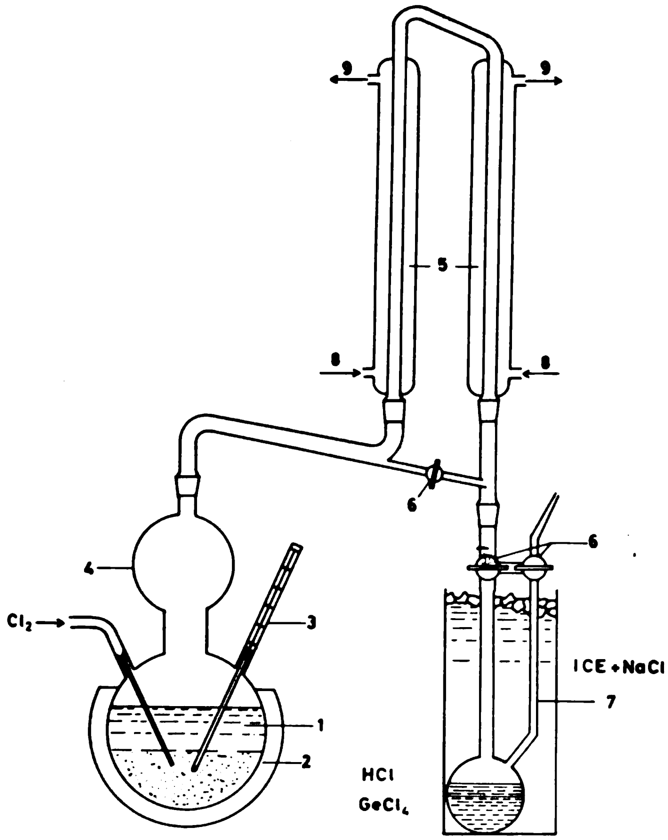


Figure 1

The scheme of the apparatus for chlorination of germanium with *HCl* and $HCl+Cl_2$

1. Hydrochloric acid+scrape
3. Heating mantle
3. Thermometer
4. Distillation flask
5. Condenser, Liebig
6. Stopcock
7. Flask for germaniumtetrachloride
8. Entrance for cooling water
9. Exit for hot water

The main reaction taking place in the reaction mixture was:

$$Ge+2Cl_2=GeCl_4+Q$$

In order to study the possibility of applying this procedure to the available germanium wastes, we constructed the apparatus described in the literature⁽²⁾. It was shown that the procedure involving chlorination with elementary chlorine has many advantages over the above described processes, that chlorination of the available wastes is possible, and that the consumption of hydrochloric acid could be reduced. Therefore, we developed all details of this procedure and constructed a new apparatus (Fig. 2). In the construction of the apparatus the following requirements were taken into account:

- the capacity,
- the regulation of the process rate,
- the regulation of the temperature,
- the condensation of germanium tetrachloride.

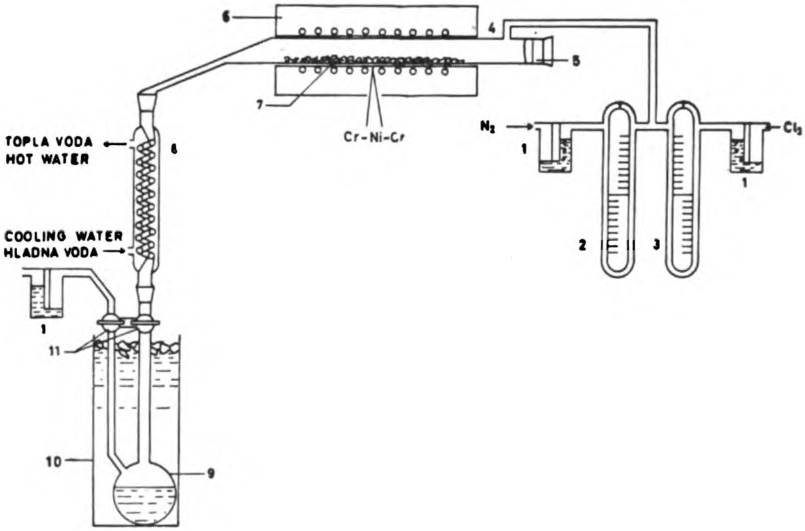


Figure 2

The scheme of the apparatus for chlorination of germanium with chlorine

1. Gas — washing bottle
2. Capillary "U" tube for measuring
3. Capillary "U" tube for measuring the flux of chlorine
4. Quartz tube
5. Hermetic stopper
6. Electric furnace
7. Charge
8. Condenser, spiral
9. Flask for germaniumtetra-chloride
10. Flask for icc
11. 3—way plug stopcock

The apparatus was constructed so that its capacity depended on the diameter of the quartz tube and the volume of the collecting flask. These characteristics of the apparatus can be calculated in the following way:

$$V = 1.68 \,.\, k$$

$$\frac{D}{2} = 2k$$

V=the volume of collecting flask (ml)
k=the capacity of the apparatus (g/operation)
D=the diameter of quartz tube (mm).

The rate of the process was regulated by the amount of gaseous chlorine and by the chlorination temperature. It was found that the optimal initial temperature was 400—500°. The amount of chlorine depended on condensation conditions, whereby the optimal condensation was achieved when there was no gas flow through the last wash-bottle, i.e., when chlorine was added in stoichiometric ratio. Since these conditions were difficult to be maintained, the chlorine flow was regulated so that a minimal flow, about 1—2 bubbles, passed into the last wash-bottle.

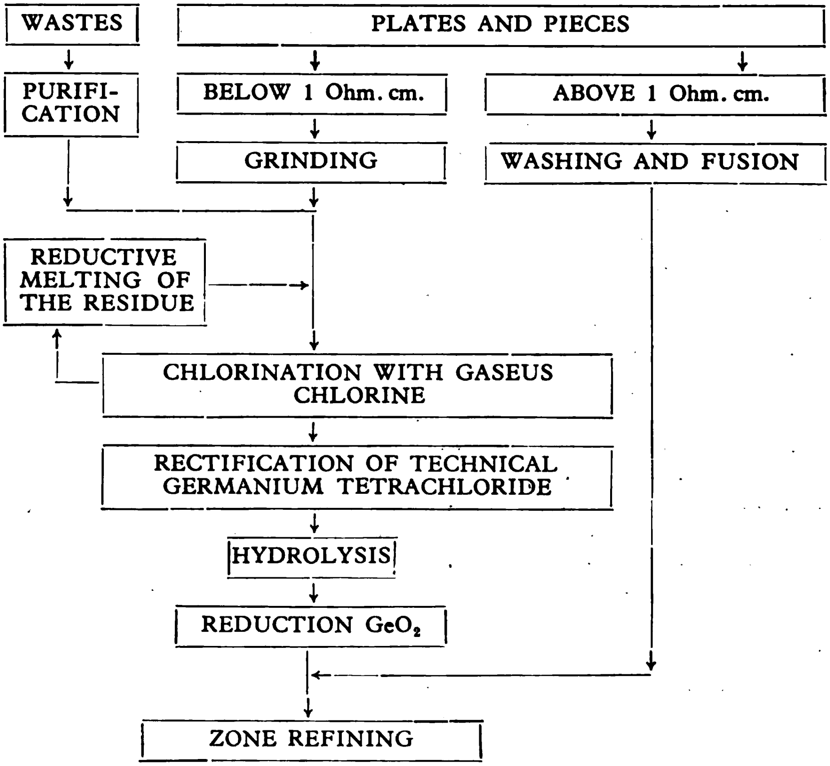
The condensation of germanium tetrachloride was carried out by a two-step cooling procedure, by means of water and of an ice-salt mixture.

The recovery of germanium involves, in addition to the problem of germanium tetrachloride preparation, the problem of purification of wastes prior to the chlorination. The purification of wastes consists of the removal of oils and the primary reduction of oxidized germanium. The removal of oil was carried out by combustion and by evaporating roasting in neutral atmosphere, or, by washing with trichloroethylene followed by drying. The primary reduction was performed by hydrogen in the same way as the reduction of pure germanium dioxide.

After chlorination with elementary chlorine the residue contained, in addition to some metallic germanium, considerable amounts of germanium oxides which either remained after the primary reduction of wastes or were formed in the course of chlorination. In order to recover germanium from the residue it was necessary to carry out the reduction. The reduction was carried out either by means of hydrogen or by reductive melting. Reductive melting of the residue was found to be an original method in the technology of recovery of germanium, which afforded a charge which could be chlorinated rather rapidly and completely with elementary chlorine.

Performance of the reductive melting represented a rather simple operation. A clay pot was charged with the residue obtained after chlorination and a mixture of proportional amounts of flux and charcoal, the latter acting as a reducing agent. Such a charged pot was placed into a furnace and the reduction was carried out at elevated temperatures. The temperature regime of this operation was similar to that applied in the several-step reduction of germanium dioxide with hydrogen. Analogy with this procedure is obvious since the residue contains germanium mainly in the form of oxides. In the first phase of the reductive melting the temperature was maintained at approximately 630°, whereby the reduction of oxides took place. When the reduction was over, the temperature was raised in order to produce a slag and to melt the metal The reduction of oxides should be completed first, otherwise germanium dioxide would be converted into the slag. Flux used in this process should be selected so that the formation of volatile germanium halogenides is excluded, that a good separation of germanium from the slag is possible, and that the slag is fusible at temperatures about 1000—1100°. The metal obtained under these conditons represents a very good material for chlorination with gaseous chlorine.

The optimal conditions for the reductive melting, especially the composition of the charge, depend upon the composition and the quality of the starting materials, i.e., wastes. Likewise, the regime of the reductive melting should be determined for each waste charge in dependence on its quality.



Scheme 1. The technological scheme for the recovery of germanium from wastes obtained in the production of semiconductor elements

On the basis of the above considerations and described processes, we have proposed a technological scheme for the recovery of germanium which involves rectification, reduction, and zone refining, i.e., standard processes for the production of highly pure germanium from technical germanium tetrachloride (Scheme 1).

The results obtained by means of the given technological scheme were satisfactory. Very good results were achieved in the chlorination of larger metal pieces whereby the recovery amounted to about 90% (including the yields obtained in standard technological processes which were not examined in this work.) It is known that the losses in the reduction of pure germanium dioxide range from 3 to 4%; therefore, the obtained recovery confirms the validity of the proposed technological scheme.

The basic problems in the technology of the recovery of germanium are the selection of a convenient procedure for the preparation of germanium tetrachloride and the treatment of the residue obtained by this procedure. Taking into consideration various procedures and their modifications, we came to the conclusion that the procedure involving chlorination with gaseous chlorine represents the most conveniant procedure with respect to the percentage of the recovery and to the economy. The problem of the recovery of germanium from the residue after chlorination was solved by the application of reductive melting.

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SEPARATION OF DIASTEREOISOMERIC 3, 5, 5-TRISUBSTITUTED 2-THIONO-THIAZOLIDINE-4-ONES

by

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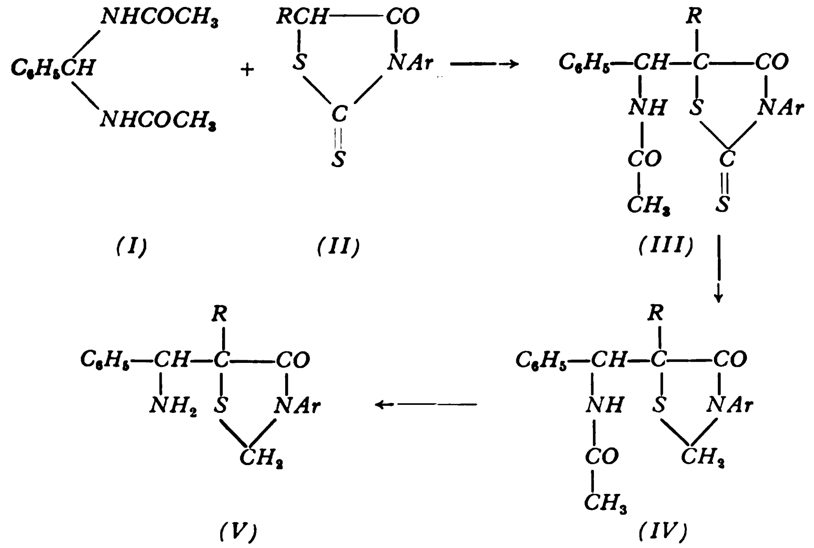
and ALEKSANDAR M. JOKIĆ

In our preceding papaer(1) a novel method for obtaining 3, 5,5-trisubstituted thiazolidine-4-ones derivatives (IV) was described, the reaction consisting of the condensation of aromatic bisamide (I) with rhodanine derivatives (II) in the presence of acetic anhydride(2) ("bisamide reaction"), followed by partial desulfuration with Raney nickel of the resulting condensation products (III). By acid hydrolysis of the N-acetyl compounds (IV), the free bases (V) were easily obtained.



$R=CH_3-$; C_2H_5-; $n-C_3H_7-$; C_6H_5-; $Ar=C_6H_5-$; $p-CH_3C_6H_4-$;

If the asymmetric carbon atom at C-5 of the thiazolidine ring is not involved in the keto-enol tautomerism of the cyclic rhodanine structure, introduction of a new asymmteirc C- atom in the side chain at C-5 would be expected to afford two racemic diastereoisometric condensation products of type (III), which can be resolved into four optically active forms(3).

By condensing 5-methyl-3-phenyl-rhodanine (II, R=CH_3; Ar=C_6H_5-) with benzylidenbisacetanide, a product of type (III, R=CH_3-; Ar=C_6H_5—), melting point 194°, was obtained, in which the keto-enol tautomerism of the rhodanine structure is excluded. The analysis of this product corresponded to the molecular formula $C_{19}H_{18}N_2O_2S_2$, i.e., to 5-methyl-5-α-acetylaminobenzyl-3-phenyl-2-thiono-thiazolidine-4-one (III, R=CH_3—; Ar=C_6H_5).

By checking the purity of this product by thin-layer chromatography, two different spots were observed, indicating the presence of two isomeric compounds. This mixture was separated on a column of silica gel, and two different substances were obtained, melting at 178° and 228°, respectively. Both of these products, according to analysis, corresponded to the same molecular formula, i.e., $C_{19}H_{18}N_2O_2S_2$.

Besides the diastereoisomeric 5-methyl-5-α-acetylamino-benzyl-3-phenyl-2-thiono-thiazolidine-4-ones, the diastereoisomeric 5-methyl-5-α-acetylaminobenzyl-3-p-tolyl-2-thionothiazolidine-4-ones (III, R=CH_3—; Ar=*p*—$CH_3C_6H_4$—) were also separated by column chromatography on silica gel, and two products of melting points 197° and 240° respectively, with molecular formula $C_{20}H_{20}N_2O_2S_2$, were obtained. It was also possible to separate these isomers by crystallization.

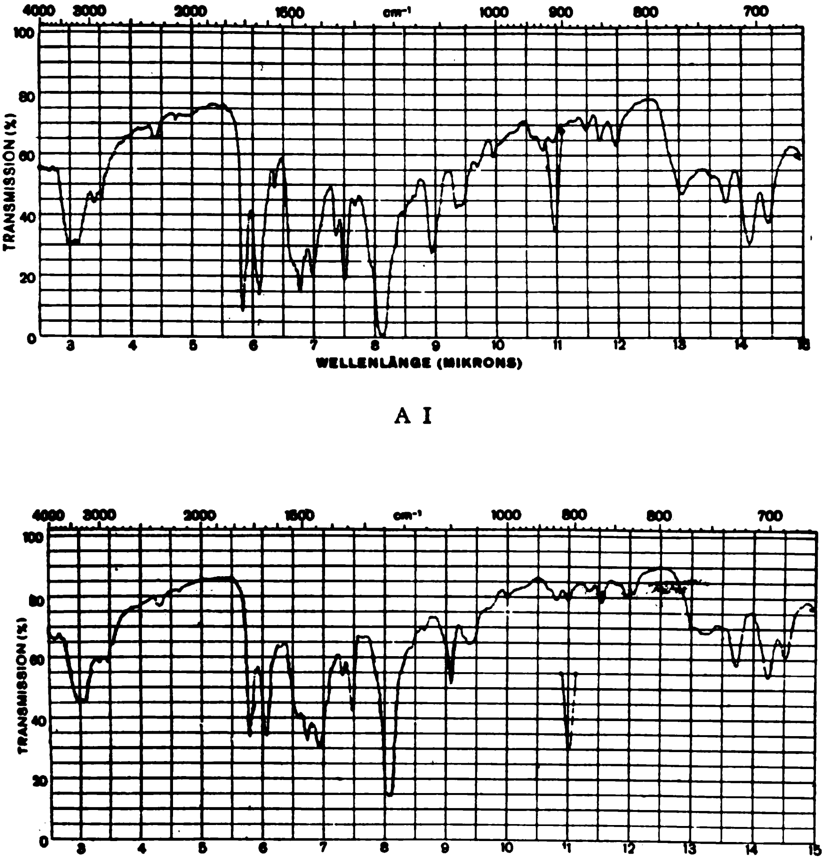
Other condensation products of type (III) containing different substituents in positions 3 (Ar=C_6H_5—; p—$CH_3C_6H_4$—;) and 5 (R=C_2H_5—; *n*-C_3H_7—; C_6H_5;) gave another two isomeric substances in differing amounts. The substances of type (IV) and their products of hydrolysis showed on thin layer chromatoplates two different spots each, but these were not separated.

The isomers of lower melting point were obtained in higher yield; in the case of (III, R=CH_3—; Ar=p—$CH_3C_6H_4$—), quantitative separation by fractional crystallization gave 65% of the lower melting point isomer, and about 25% of the higher melting point isomer. In other cases quantitative separations could not be performed, because elution from the column gave interfractions containing a mixture of both isomers. On thin layer chromatoplates the isomers of lower melting points have greater R_f values.

The infra-red spectra of diastereoisomeric substances contained the same characteristic maxima: for NH-vibrations at about 3350 cm^{-1}, C=0 of the thiazolidine ring at 1735 cm^{-1}, acetylamino at 1680 cm^{-1}, and C=S vibrations at 1250 cm^{-1}. In the "fingerprint" region of the infra-red spectra there were differences, showing undoubtedly that two products are in question. (Fig. 1.)

The UV-spectra were not examined.

The examination of Dreiding models of both diastereoisomeric forms of the substance of type (III or IV) suggests that one diastereoisomer — in its most stable conformation — should form an intra-



A I

B II

Fig. 1.

A, m. p. 178° *B*, m.p. 228°

IR-spectra of 5-methyl-5-α-acetylaminobenzyl-3-phenyl-2-thiono-thiazolidine-4--ones. (*A*), m. p. 178°; (*B*) m. p. 228°

molecular hydrogen bond between the -NH- of the acetylamino group in the side chain and the carbonyl group in C-4 of the thiazolidine ring. In the second isomer, the NH-group and the C=0 group are far apart from each other, so that no intramolecular hydrogen bonding is to be expected . On these grounds we suppose that the diastereoisomeric forms with lower melting points have the configuration (*A*), (Fig. 2.), which allows the formation of an intramolecular hydrogen bond, and that the diastereoisomeric form with higher melting points have the configuration (*B*), (Fig. 2.), which probably involves intermolecular hydrogen bonding.

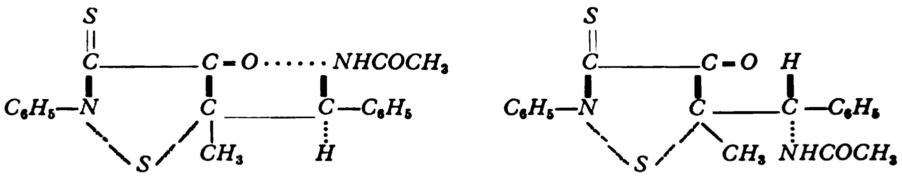
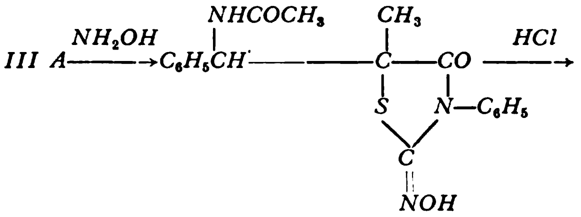


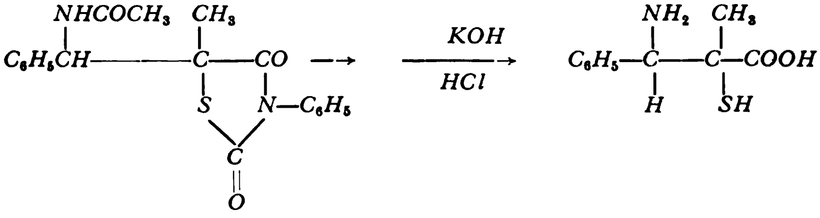
Fig. 2.

A B

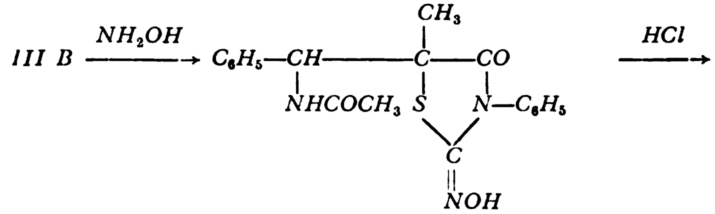
The assigment of *threo-* and *erythro-* configurations in our case is rather to be avoided, one asymmetric atom being a member of the thiazolidine ring. To establish the configuration of the diastereoisomeric forms of (III, R=CH_3–; Ar=C_6H_5–; *A* and *B*), the rhodanine ring should be opened using the reactions described in our paper(2), i.e., by passing through the oxime of 5-methyl-5-α-acetylamino-benzyl-3-phenyl-thiazolidine-2,4-dione (VIa and VIb), and the keto-derivatives (VIIa and VIIb), to the corresponding *threo* and *erythro* α-methyl-β-phenylisocysteine (VIIIa and VIIIb). For these isocysteine derivatives the appropriate configurations could be established by usual methods.



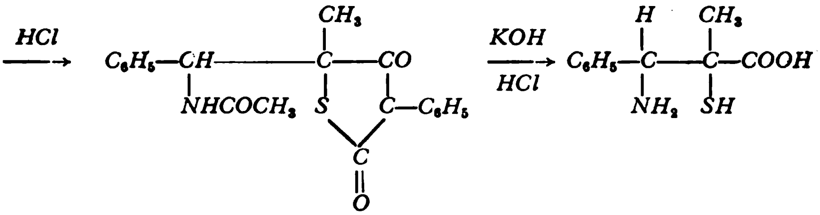
(VIa)



(VIIa) VIIIa *(threo)*



(VIb)



(VIIb)　　VIIIb *(erythro)*

EXPERIMENTAL

All m. p.s were determined in open capillary tubes, and are uncorrected. IR spectra were recorded in KBr pellets on a Perkin-Elmer Infracord. For chromatographic separations, Merck 0.08 mm silica gel was used. Thin layer chromatography (TLC) was performed on glass plates (0.3 x 13 x 15) usin silica gel-G according to Stahl; development was effected with the following mixture: toluene : glacial acetic acid : water (5 : 5 : 1)- upper phase, and the spots were exposed to iodine vapour.

3-*Aryl*-5-*alkyl*-2-*thiono*-*thiozolidine*-4-*ones* (II) were obtained from arylammoniumdithiocarbamate and the coresponding α-bromo-substituted aliphatic monocarboxylic acids according to the method reported by R.K. Raval and J.J. Trivedi in 1962(4).*

(II) ($R=CH_3-$; $Ar=C_6H_5-$), m.p. 177°, was obtained from phenylammoniumdithiocarbamate and α-brompropionic acid;

(II) ($R=CH_3-$; $Ar=p-CH_3C_6H_4-$), m.p. 100°, from p-tolylammonium-dithiocarbamate and α-brompropionic acid;

(II) ($R=C_2H_5-$; $Ar=C_6H_5-$), m.p. 85°, from phenylammoniumdithiocarbamate and α-brombyturic acid;

(II) ($R=C_3H_7-$; $Ar=C_6H_5-$), m.p. 118°, from phenylammoniumdithio-carbamate and α-brom-valeric acid;

(II) ($R=Ar=C_6H_5-$), m.p. 218° (lit.(4) m.p. 178°), from phenylammoniumdithiocarbamate and α-bromphenylacetic acid.

Analysis:

Calc. for $C_{15}H_{11}NOS_2$ (285,25):	C, 63.16; H, 3.89; N, 4.91%
Found:	C, 63.25; H, 4.08; N, 5.65%

5. *Alkyl*-5-α-*acetylaminobenzyl*-3-*aryl*-2-*thiono*-*thiazolidine*-4-*ones* (III) are obtained by condensation of bezylidenebisacetamide with 3,5-disubstituted rhodanine derivatives in the presence of acetic anhydride, according to the previously described procedure(1). The average yields are about 50%.

(III) ($R=CH_3-$; $Ar=C_6H_5-$), *m.p.* 194°

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* We find this method superior to the older procedure (5,1) in which rhodanine derivatives were obtained from trithiolactic acid and aniline derivatives.

Analysis:

Calc. for $C_{19}H_{18}N_2O_2S_2$ (370,35): C, 61.61; H, 4.90; N, 7,56%
Found: C, 61.18; H, 4.77; N, 7.44%

(*III*) (*R*=CH_3–; *Ar*=*p*–$CH_3C_6H_4$–), *m. p.* 200°

Analysis:

Calc. for $C_{20}H_{20}N_2O_2S_2$ (384,38): C, 62.49; H, 5.24; N, 7.29%
Found: C, 62.73; H, 5.38; N, 7.21%

(*III*) (*R*=C_2H_5–; *Ar*=C_6H_5–), *m.p.* 184°

Analysis:

Calc. for C_{20} $H_{20}N_2O_2S_2$ (384,38): C, 62.49; H, 5.24; N, 7.29%
Found: C, 61.03; H, 5.37; N, 7.44%

(*III*) (*R*=C_3H_7; *Ar*=C_6H_5–) *m.p.* 186°

Analysis:

Calc. for $C_{22}H_{24}O_2N_2S_2$ (412,43): N, 6.79%
Found: N, 6.83%

(*III*) (*R*=*Ar*=C_6H_5), *m.p.* 230°

Analysis:

Calc. for $C_{24}H_{20}N_2O_2S_2$ (432,42): N, 6.48%
Found: N, 6.56%

Separation of diastereoisomeric compounds by column chromatography

Chromatography was performed on a glass column filled with silica gel (Merck, 0.08) and the substances were eluted with chloroform. For 1 g of the mixture 30 g silica gel was used. The chromatographic procedure was controlled by means of thin layer chromatography. The isomer with lower melting point was first eluted, then a mixture of both isomers, and finally the diastereoisomer with higher melting point. The analysis of the separated diastereoisomeric 3,5,5-trisubstituted 2-thiono-thiazolidine-4-ones was in accordance with calculated data.

(*III*) (*R*=CH_3–; *Ar*=C_6H_5–), *m.p.* 178° (*A*. Fig. 2)

Analysis:

Calc. for $C_{19}H_{18}N_2O_2S_2$ (370,35): C, 61.61; H, 4.90; N, 7.56%
Found: C, 60.87; H, 5.17; N, 7.40%

(*III*) (*R*=CH_3–; *Ar*=C_6H_5–), *m.p.* 228° (*B*. Fig. 2)

Analysis:

Calc. for $C_{19}H_{18}N_2O_2S_2$ (370,35): C, 61.61; H, 4.90; N, 7.56%
Found: C, 61.15; H, 4.96; N, 7.72%

(*III*) *R*=CH_3–; *Ar*=*p*$CH_3C_6H_4$–), *m.p.* 197°

Analysis:

Calc. for $C_{20}H_{20}N_2O_2S_2$ (384,38): C, 62.49; H, 5.24; N, 7.29%
Found: C, 62.21; H, 4.98; N, 7.18%

(III) (R=CH_3–; Ar=p–$CH_3C_6H_4$), m.p. 240°

Analysis:

Calc. for $C_{20}H_{20}N_2O_2S_2$ (384,38): C, 62.49; H, 5.24; N, 7.29%
Found: C, 61.80; H, 5.60; N, 7.31%

Diastereoisomeric substances of *(III)* (R=CH_3–; Ar=p–$CH_3C_6H_4$–) separated by fractional crystallization gave the lower melting isomer (197°) in 65% yield, and the isomer melting at 240° in 25% yield.

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DETERMINATION OF TERTIARY AMINES AND SALTS OF ORGANIC ACIDS IN ACETIC ACID BY CATALY-THERMOMETRIC TITRATIONS

by

VILIM J. VAJGAND and FERENC F. GAÁL

Thermometric titrations belong to the group of the most universal methods for the detection of the titration end-point(1,2,3,4,5). They are independent of the medium in which they are performed.(6) T. Somiya(7) has for the first time applied theromometric titrations in nonaqueous media to the determination of water in concentrated solphuric acid and to the determination of acetic anhydride in acetic acid. It is known that the reaction heat of acetic anhydride with water is high (125.96.kcal) and that the reaction itself is slow. R. Szabo(8) was the first who noticed that strong acids accelerate the hydrolysis, and this reaction was successfully used for the thermometric determination of acetic anhydride and water in acetic acid.(9)

J. Keily and D. N. Hume(10) have determined different weak organic bases and salts of organic and inorganic acids by titrating them with perchloric acid in glacial acetic acid. The titrated system should not contain water and acetic anhydride simultaneously, since these twe components, which are knwon to react slowly until the equivalence point is reached, react very violently after the equivalence point in the presence of a small excess of perchloric acid as catalyst. Uncontrolled rise of the temperature appearing after the equivalence point renders impossible the thermometric titration of bases even when the differential method is used. The changes of the temperature at the titration end-point are small (below 0.1°C) and the titration curve has the usual shape, i.e., it ascends linearly up to the equivalence point, and then it descends linearly.

We have seen that the reaction of water with acetic anhydride interferes with the thermometric titrations in glacial acetic acid. However, on the basis of this reaction, we succeeded to develop a procedure which is based on the following principles: the base is titrated in glacial acetic acid which contains small amounts of water and acetic anhydride, with perchloric acid in glacial acetic acid solution. The reaction rate of water with acetic anhydride is slow till the equivalence point, but after it, due to the first amount of perchloric acid excess, it increases very rapidly. The main problem encountered in this work was the determination of the titration end-point. After numerous preliminary investigations of the system water-acetic anhydride and water-perchloric acid-acetic anhydride in glacial acetic acid, we developed three techniques for the determination of the titration end-point, the latter being determined either from the intersection point of two straight lines, or from the intersection point of a straight line and a curve, or from the calibration curve.

Many papers deal with the mechanism of acetic anhydride hydrolysis under the influence of strong acids. V. Gold and J. Hilton(11) have proposeed the following one:

$$Ac_2O + H^+ \rightleftarrows Ac_2OH \text{ (rapid)}$$

$$Ac_2OH^+ \rightarrow (Y^+) \rightarrow Ac^+ + AcOH \text{ (rate controlling)}$$

$$Ac^+ + 2\,H_2O \rightarrow AcOH + H_3O^+ \text{ (rapid)}$$

where Y^+ is the activated complex of the rate controlling step, J. Koskikallio *et al*(12) have found that this complex reaction is predominently of the first order.

In recent times many reactions based on catalysis have been investigated in order to develop new analytical methods.(13,14) Thus K. B. Iatsimirskii and T. I. Fedorova(15) developed a new type of chemical analysis, so-called catalymetric titrations, which involves the titration of a system with a catalyst solution, or vice versa. The reaction-rate or any other proportional magnitude is measured in the course of the reaction. By plotting the rate of the chemical reaction against the added volume of the titrating agent, two straight lines are obtained, the equivalence point being at their intersection. A modification of this method described by J. Bognar(13) was based on the same principle. Catalymetric titrations are carried out at constant temperature.

Our method is based on the titration of bases with perchloric acid which is a catalyst for the system water-acetic anhydride, and accordingly, it should represent a catalymetric titration method. However, the titration end-point is determined from the temperature rise, which is characteristic of thermometric titrations, and therefore we propose that our new method should be named the cataly-thermometric titration method.

EXPERIMENTAL

For titrations in acetic acid, solvent glacial acetic acid of sp. w. 1.051 (C. Erba) and of sp. w. 1.049—1.060 (Oswiecim zaklady chemiszni) mixed with acetic anhydride of sp. w. 1.08 (C. Erba) in a ratio of 12 : 1 was used. The titrating agent was the solution of perchloric acid of sp. w. 1.67 (p.a. Kemika) in glacial acetic acid. Standardization of 0.25 N perchloric acid solution was performed by means of potentiometric titration with solution of sodium acetate in glacial acetic acid. The changes of the potential were measured by means of the pH-meter "Radiometer type pH M 22m". The potentiometric standardization of perchloric acid and the potentiometric determinations of substances used were carried out with a glass electrode connected with a $Hg/Hg_2(CH_3COO)_2$ electrode filled with a saturated solution of sodium perchlorate in glacial acetic acid(16). In titrations of hydrohalogenides of organic bases, 3% mercuric acetate was added to the solution. On account of a high dilatation temperature coefficient of glacial acetic acid, corrections for the normality of the titrating agent were made(17). Thus, the normality of perchloric acid solution which ta 22°C is 0.2596, at 28°C falls to 0.2577. The solid substances were weighed separately for each experiment, except in the case of triethylamine where the solution was made and different amounts of liquied measured by burette.

The titrations were carried out by means of a 20 ml calibrated tap burette of type "E 274 Metrohm" graduated in 0.02 ml. This burette permits very rapid addition of 0.1 ml of the standard solution (for some seconds only). The temperature changes were measured on thermometer (1/10°C) and thermistor (5 k Ω). The length of the mercury reservoir was about 1.8 cm, whereas its diameter was about 0.6 cm. The reservoir was immersed 1 cm below the upper level of the solution. The temperature readings were made by means of a magnifying glass. All temperature measurements were performed with the thermometer, and the thermistor was used only for control.

Titrations were caried out in ordinary open 50 ml beakers. In thermometric investigations the beaker was wrapped in tin-foil and placed in a 100 ml beaker which was then placed in a larger 400 ml beaker, which had a cork on its bottom and whose inner walls were covered with filter paper. The larger beaker was fixed to a magnetic stirrer and the solution was magnetically stirred. It was observed that any radiation in the laboratory affected the temperature of the solution. Therefore, any temperature change or draught in the laboratory should be avoided during experiment performance. Experiments were also carried out in a Dewar vessel, but quite satisfactory results were obtained by the use of ordinary beakers.

PRELIMINARY INVESTIGATIONS

Since the catalytic effect of small amounts of perchloric acid on the reaction of water with acetic anhydride is very violent, our preliminary investigations were carried out with 0.25 N perchloric acid solution in order to develop a procedure for the determination of the titration end-point. First, it was necessary to determine the optimal ratio of the mixture acetic acid-acetic anhydride and the amount of water added before the titration. The solvent should contain the smallest possible amount of water which would cause a detectable temperature rise at the titration end-point.

Sodium acetate (about 1.25×10^{-3} of equivalent) was first titrated with perchloric acid in the presence of differing amounts of acetic anhydride and water in the solvent. The initial volume of the solution was 26 ml, so that the mercury reservoir could be sufficiently immersed into the solution. It was observed that in analyses performed in the presence of a too small amount of water (0.5%) the obtained results were lower when the amount of acetic anhydride was higher. This might be due to a greater reaction rate till the equivalence point caused by a larger amount of acetic anhydride. When the amount of acetic anhydride was small, the temperature rise at the titration end-point was detectable, but the results were not reliable. Therefore we added water and found that the temperature rise occured at the equivalence point. To avoid the negative effect of larger amounts of water in the determination of weak bases in glacial acetic acid (water being a weak base as well), the solvent used for the titration contained 8% of acetic anhydride and about 2% of water at the beginning of the titration. The amounts of water added and the acetic acid used were almost in stochiometric ratio.

However, the titration end-point had to be more precisely determined. Therefore we investigated the reaction of water with acetic anhydride in the absence of perchloric acid (the system existing before the equivalence point), and in the presence of perchloric acid, i.e., a proton, as the catalyst of this reaction. It has been already mentioned that the mechanism of this reaction is not precisely known. In the

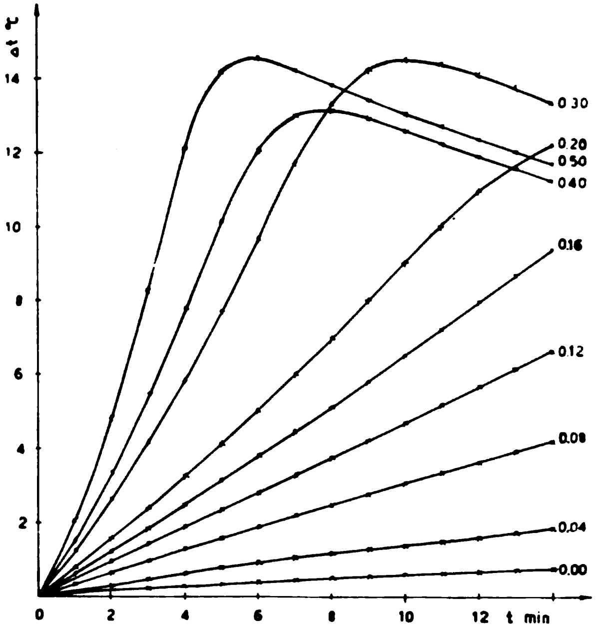

Figure 1

Changes in reaction rate $H_2O-(CH_3CO)_2O$ as seen from temperature changes of the reaction mixture, as a function of time, with different amounts of $HClO_4$, at the initial temperature of solution of 28°C.

absence of a catalyst the reaction is slow ($k = 1.10^{-4}$ sec^{-1} hydrolysis rate)(12); up to the equivalence point the temperature rises linearly and the curve has a small slope. For fifteen minutes, the temperature increase in the presence of a base is 0.30°C at the most, and in the presence of the solvent without base about 0.70°C. With the appearance of perchloric acid in the titrated system the temperature rise represents an exponential function which depends on the amount of the catalyst and the initial temperature. Therefore we measured the rate of water- acetic anhydride reaction in dependence on the amount of perchloric acid added as catalyst at initial temperatures of 22°C and 28°C by following the temperature changes of the reaction mixture. A mixture of 23.50 ml of acetic acid, 0.50 ml of water and 2.00 ml of acetic anhydride was placed in a beaker, stirred for 2—2.5 minutes, and the temperature of the mixture was determined. Then, an amount of 0.04 to 0.50 ml of 0.25 N perhcloric acid was added and temperature readings were made each minute for a period of ten to fifteen minutes. The results obtained at 28°C are shown in Fig. 1 where time-periods (abscissa) are plotted against temperature changes (ordinate). Diagram obtained at 22°C is of a similar shape.

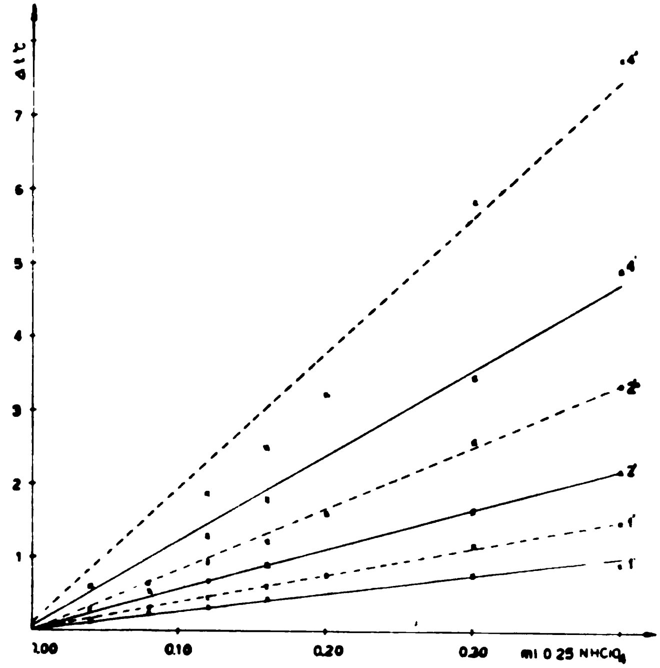

Figure 2

The rate of reaction $H_2O-(CH_3CO)_2O$ as a function of the amount of the catalyst added, at temperature reading interval of 1, 2 and 4 minutes.

—— Initial temperature of solution at 22° C. ----- Initial temperature of solution rt 28° C.

As it was expected the rate of this reaction increased with increasing temperature. It is worth mentioning that the titration results were obtained by means of these diagrams. In determinations carried out in a Dewar vessel greater temperature changes were observed since losses due to radiations were avoided; however, this had no important effect on the accuracy of the analyses. From Fig. 1 it follows that water and acetic acid react more rapidly in the presence of larger amounts of catalyst; the reaction temperature reaches a maximum and then begins to fall.

If the values of the temperature changes from the diagram in Fig. 1 are plotted against the amount of perchloric acid present, a linear dependence is obtained if the temperature readings are made every two minutes, regardless of the initial temperature of the solution (Fig. 2).

Accordingly, if the titration is carried out at equal time intervals, the temperature rise should have an exponential character, even when the catalytic effect of the temperature on the reaction rate, which is also augmenting exponentially, is neglected. This might be seen when the temperature changes in the course of the titration are drawn on ordinary and semi-log paper (Figs. 3a and 3b).

On ordinary paper the temperature augments uniformly until the equivalence point, and then it increases exponentially when temperature readings are made at one-minute intervals after each addition of the titrating agent. If the same changes are shown on a semi-log paper, a curve is obtained up to the equivalence, after which all points lay on a straight line. In the latter case the equivalence point is easily obtained since it lies at the intersection of the straight line and the logarithmic curve. In the former case the equivalence point is not easily obtained; in order to determine the equivalence point when the results are drawn on oridnary paper, we developed the following procedure: the titration was carried out by adding equal amounts of the titrating agent to the titrated system at equal time-intervals, and the temperature readings were also made at equal time-intervals, for example, each minute. The equivalence point was reached when an abrupt rise of temperature was observed. Then, an additional point was determined in the described manner, and the next temperature reading was made at half-time interval; thus a total of three points after the equivalence point was obtained. By connecting the points we got two straight lines, the equivalence point being at their intersection. Fig. 3a shows a titration carried out by this technique; at each point the time of the temperature readings is indicated. The points on the diagram represent the temperatures read one minute after each addition of the titrating agent, after which the next volume was added immediately. Numbers in circles represent values after which the addition of the titrating agent was interrupted. One can start to read the temperature changes when 74% of the base is titrated, since there is no need to make an earlier raeding.

A precise determination of the titration end-point from the oridnary mm paper diagram requires the knowledge of the value of the maximal temperature rise caused by the addition of 0.10 ml of

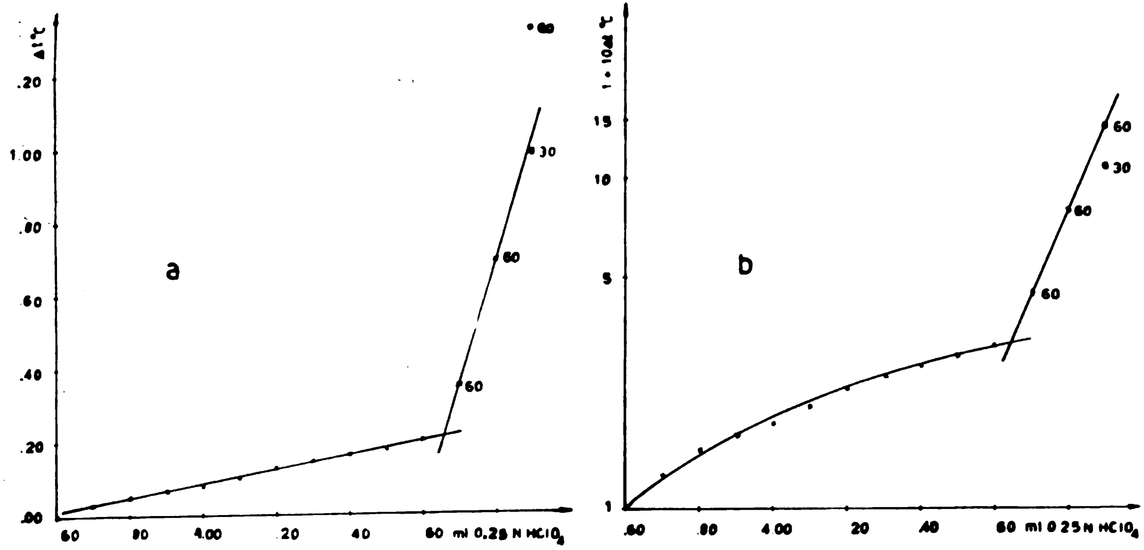

Figure 3

Cataly-thermometric titration curves for sodium acetate (1,2 · 10^{-3} equivalents)

a) Titration curve expressed on ordinary paper.

b) Titration curve expressed on semi-log paper.

0.25 N perchloric acid at the temperature just before the equivalence point. Maximal temperature changes produced by the addition of 0.10 ml of 0.25 N perchloric acid at different initial temperatures are shown in Fig. 4 (total volume: 26 ml).

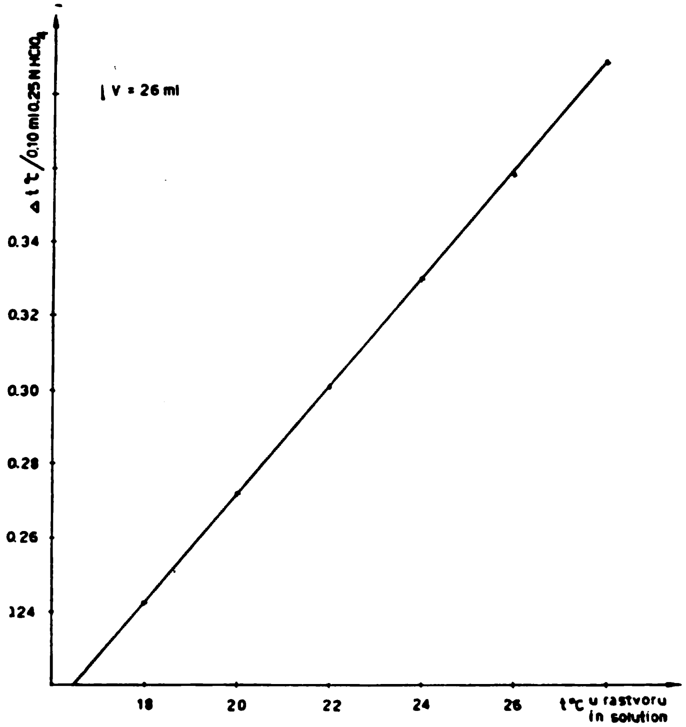

Figure 4

Temperature changes in 26 *ml* of solution after adding 0.10 *ml* of a 0.25 *N* $HClO_4$ solution, as a function of initial temperature of solution.

In addition to these two techniques, the titration end-point can be determined from a calibration curve. Titration is carried out as already described until the temperature rise after the equivalence point is reached. Then, further temperature readings are made each minute, but the solution is no longer titrated with perchloric acid. The effect of the unknown amount of the catalyst in the system water-perchloric acid-acetic anhydride is greater when the amount of perchloric acid excess is larger. This excess can be determined from the calibration curve, constructed from data given in Fig. 2. Products of the solution volumes and temperature changes are plotted on the ordinate against the volumes of the added catalyst, i.e., perchloric acid, on the abscissa. In this way two straight lines are obtained, their slopes being dependent on the initial temperature and temperature readings. By using the product of the solution volume and the temperature change, the unpredictable effect of the final solution volume was eliminated.

DETERMINATION OF INDIVIDUAL BASES AND DISCUSSION OF THE RESULTS OBTAINED

As already stated, we developed three techniques for the determination of the titration end-point. The results and the standard deviations obtained by means of the first two techniques were in good agreement with the results and standard deviations obtained by potentiometric methods; however, the results obtained by the third technique showed considerable deviations (Tables 1 and 2).

TABLE 1.

Ord. nbr.	(°C) Initial temp. of solution	Interval after which the temp. was read	Temp. change Δt (°C)	B. Δt (ml. °C)	Excess of perchloric acid (ml)
1	20	1	0.48	15.31	0.27
		2	1.02	32.54	0.26
2	20	1	0.53	16.91	0.31
		2	1.09	34.77	0.28
3	20	1	0.51	16.27	0.30
		2	1.02	32.54	0.26
4	22	1	0.65	20.65	0.31
		2	1.33	42.43	0.29
5	22	1	0.57	18.18	0.27
		2	1.22	38.92	0.27
6	22	1	0.63	20.10	0.31
		2	1.29	41.15	0.28

Mean value: 0.28

Standard deviation calculated from $\sigma = \sqrt{\frac{(x-m)^2}{n-1}}$ amounts to $\pm$ 0.02 ml

TABLE 2

Manner of determination	Nbr. of titration	Mean value for the 0.25 N $HClO_4$ used (ml)	Standard deviation %	Deviation from potent. titr. ml	Deviation from potent. titr. in %
By potentiometric titration	3	5.65	0.04	—	—
From the intersection of the logar. curve and straight line	6	5.65	0.17	—	—
From the intersection of two straight lines	6	5.66	0.07	+0.01	+0.17
From calibration curves	6	5.62	0.35	—0.03	—0.53

Table 1 shows the results obtained in the determination of triethylamine by means of the calibration curve. A volume of 20 ml of the standard solution of triethylamine in glacial acetic acid was diluted to 26 ml. The volume of the solution at the end of the titration was 31.90 ml (V), i.e., a total of 5.90 ml N perchloric acid was added. The titration end-point was determined by means of the methods described. The excess of perchloric acid, determined from the calibration curve, was substracted from the total volume of the standard perchloric acid solution. In the given example the result was obtained by substracting 0.28 ml from 5.90 ml leaving 5.62 ml with a stanadrd deviation of ±0.02 ml (±0.35%),

Stronger bases — tertiary amines and salts of organic acids were determined as well. For all bases studied, the half-neutralization potentials in a mixture of acetic acid with 8% of acetic anhydride were determined, although they are not always a good relative measure of the strength of the titrated base because of the nivelation effect (Table 3).

Weaker bases have smaller values of half-neutralization potentials. The determination of bases by means of the cataly-thermometric method is better when the potential jump in the vicinity of the titration end-point is higher. Accordingly, a success or a failure in the application of the cataly-thermometric method may be predicted from the potentiometric titration curve. In cases of bases which consume two equiva-

TABLE 3

Nbr.	Substance	Half-neutral. potent.	pK_b in aqueous solution
1.	Caffeine	127.5	13.39
2.	2-methyl-5-nitroimidazol	173.7	—
3.	Sodium salicylate	253.5	11.00
4.	Antipyrine	257.0	12.40
5.	Novalgin	275.0	—
6.	Flagyl	276.0	—
7.	Cinchonine	303.5	9.96
8.	Sodium benzoate	317.5	9.80
9.	Sodium formate	335.5	10.25
10.	Sodium acetate	336.0	9.24
11.	Iversal	340.0	—
12.	Pyridoxine-HCl	351.0	—
13.	Aminopyrine	355.5	9.16
14.	Potassium biphtalate	367.0	—
15.	Triethyl-amine	377.0	3.3

lents of perchloric acid (for example, aminopyrine), the titrating agent was added till the first potential jump. After that, the basicity of the substance was so weakened that the catalytic effect of perchloric acid was more pronounced. If the addition of the titrating agent is interrupted, the temperature can be observed to rise uniformly, indicating that perchloric acid combines slowly with the unreacted second equivalent of the base. Very weak bases, as for example caffeine or 2-methyl-5-nitro imidazol, cannot be determined under these conditions since their basicity is so weakened that the catalytic effects occurs preferentially to neutralization. Titration curves of such bases are shown in Fig. 5

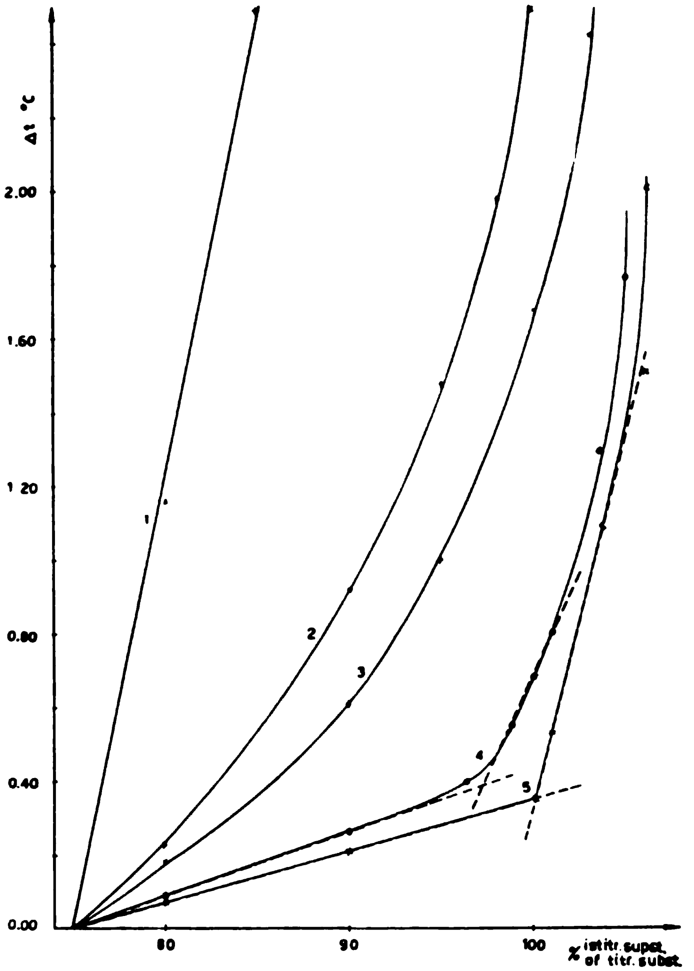

Figure 5

Cataly-thermometric titration curves for bases of different strength:

1. Caffeine.
2. 2-methyl 5-nitroimidazol
3. Novalgin.
4. Antipyrine.
5. Potassium biphtalate.

As seen from Fig. 5 antipyrine cannot be determined precisely (the error amounts to −2.8%) although the results are reproducible.

TABLE 4

Titrated substance	Taken g	Potentiometric titr.			Cataly-thermometric titr.		
		No. of titr.	Found g	Std. dev. %	No. of titr.	Found g	Std. dev.%
Aminopyrine	0.1500	4	0.1498	0.51	6	0.1495	0.40
Antipyrine	0.2000	4	0.2000	0.15	3	0.1942	0.14
Cinchonine	0.2000	3	0.1944	0.13	3	0.1940	0.31
Flagyl*	0.2000	4	0.1999	0.91	5	0.1985	0.06
Intra-iodine**	0.2000	4	0.1994	0.54	6	0.1999	0.07
Iversal***	0.2000	3	0.1850	0.17	4	0.1858	0.11
Potassium biphtalate	0.2000	3	0.2012	0.15	3	0.2016	0.28
Sodium acetate	0.1500	4	0.1500	0.20	6	0.1501	0.30
Sodium benzoate	0.1500	3	0.1498	0.08	6	0.1496	0.04
Sodium formiate	0.1000	3	0.0996	0.55	6	0.0990	0.25
Sodium salicylate with thermistor	0.2000	3	0.2008	0.40	6	0.2007	0.15
						0.2008	0.12
Triethylamine	0.1500	3	0.1500	0.04	6	0.1503	0.07
Pyridoxine-HCl****	0.2000	3	0.2021	0.36	3	0.2016	0.11

* β-oxyethyl-2-methyl-5-nitro-imidazol
** 1,3-triethylamonium-2-propanol-iodide
*** p-benzoquinone amidinohydrazone thiosemicarbazone
**** 5-hydroxy-6-methyl-3,4-pyridinedimethanol hydrochloride

On the other hand, in the case of potassium biphtalate, there is an easily detectable temperature rise which appears just after the disappearance of the base, i.e., at the titration end-point.

TABLE 5

No.	Added ml of 0.1 N $HClO_4$ by the potentiom. titr.	Added ml of 0.1 N $HClO_4$ by cataly-thermometric titration	
		I Way (1′)	II Way (2′)
1.	4.86	4.86	4.87
2.	4.87	4.86	4.87
3.	4.87	4.87	4.87
Mean	4.87	4.86	4.87

The results of cataly-thermometric determination of substances which react with perchloric acid giving insoluble precipitates (inversal, flagyl, potassium biphtalate, intraiodine) are more reproducible than those of potentiometric titrations. Table 4 shows the results and stan-

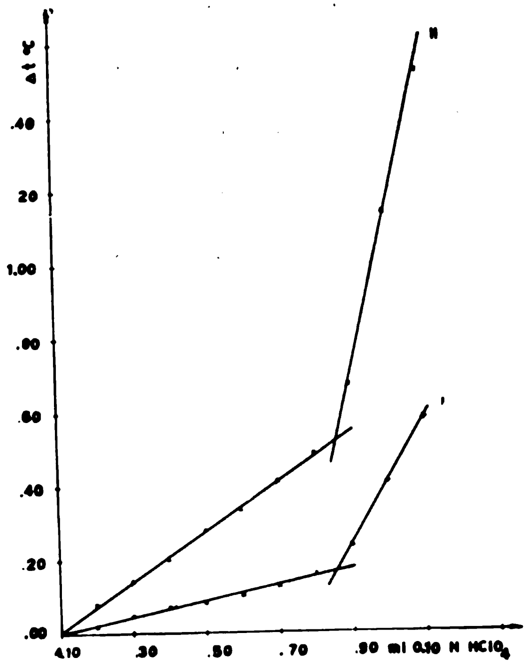

Figure 6

Titration curves for sodium acetate with 0.1 *N* perchloric acid solution ($4{,}9 \cdot 10^{-4}$ equivalents).

I. Titration in the first manner.

II. Titration in the second manner.

dard deviations obtained by both methods (in catalythermometric determinations the titration end-point was determined from the intersection of two straight lines).

In the case of flagyl, before reading the temperature, it is necessary to rub the walls of the beaker with a glass rod in order to induce the separation of the precipitate, since otherwise there is a temperature rise of about 0.1°C due to the crystallization heat, and there is a break at the first part of the titration curve. The concentration of titrated bases ranged from 2.5×10^{-2} to 5.7×10^{-2} N and the weighed quantities from 6.3×10^{-4} to 1.4×10^{-3} of equivalent. Even more diluted solutions can be titrated with this method. Thus 0.04 N sodium acetate solution was titrated with 0.1 N perchloric acid and the temperature readings were made at time-intervals of one or two minutes. Table 5 shows the results obtained in titrations of equal amounts of sodium acetate by potentiometric and by cataly-thermometric methods.

Titration curves obtained by both methods are shown in Fig. 6. They exhibit the same break but have different slope angles.

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CHANGES OF MAGNESIUM CONCENTRATION IN BLOOD PLASMA OF GUINEA-PIGS IN THE COURSE OF SENSITIZATION AND IN ANAPHYLACTIC SHOCK

by

MIHAILO D. MOJOVIĆ

Hyperpotassemia has been established in almost all forms of shock, and it has also been observed in anaphylactic shock by many authors(1,3,10,14,15,16,19). Changes of other cation concentrations in anaphylactic shock and in the course of sensitization have no been studeid to a great extent, so that this problem has not been fully explored. In a previous paper we established that in anaphylactic shock and in the course of sensitization not only potassium concentration, but also sodium concentration, was altered; in anaphylactic shock hyperpotassemia and hyponatremia were observed and in the course of sensitization of guinea-pigs hypopotassemia and hypernatremia. These changes of cation concentrations were explained by the alteration of the permeability of cell membranes, by the chemical modification of the cell, and by increased cell activity(16).

Some authors have investigated the concentration of magnesium in the sera of guinea-pigs in anaphylactic shock. Thus Corda(3) found a nonuniform decrease of this cation concentration. However, Shapira(19) observed an increase, whereas Bata, Condorelli and others(1) recorded only slight changes of this cation concentration, which in their opinion play no role in the appearance of anaphylactic shock symptoms.

It is known that changes of extracellular magnesium concentration can affect the irritability of peripheral nerves and muscles. An increase of magnesium concentration in the extracellular fluid brings about a decrease of the activity of the peripheral nervous system and a decrease of the irritability and contractibility of skeletal muscles, while a decrease causes an increase of the irritability of peripheral nerves and skeletal muscles, leading even to the appearance of tetany(8). Particular significance is ascribed to intracellular magnesium as a catalyst for many intracellular enzymatic reactions.

Assuming that the cell is chemically modified and functionally changed, and in view of the physiological importance of magnesium, it was of interest to investigate the changes of this cation concentration in the blood plasma of guinea-pigs in the course of sensitization and in anaphylactic shock.

METHODS

Investigations were carried out with quinea-pigs (of 500—600 g) of both sexes, which were divided into two groups: experimental and control. Guinea-pigs of the experimental group were sensitized with two injections of crystalline ovalbumin (5 mg per kg) given intraperitoneally at an interval of 48 hours. In all ten guinea-pigs anaphylactic shock was brought about by intracardial injection of 1 ml of physiologic solution containing the corresponding dose of crystalline ovalbumin, the allergen with which the sensitization was performed. In all ten cases anaphylactic shock and death were observed. Blood for magnesium analysis was taken from the heart just before intracardial injection of crystalline ovalbumin and again during anaphylactic shock before death. Accordingly, plasma magnesium was in each case determined before and at the end of the anaphylactic shock. The duration of anaphylactic shock ranged from 10 to 15 minutes.

From nonsensitized guinea-pigs of the control group, blood was taken from the heart and then the animals were given intracardial injections of 1 ml of physiologic solution containing the corresponding dose of crystalline ovalbumin. After 10—15 minutes blood was taken again. Hence plasma magnesium was determined before and after intracardial injection of allergen in each guinea-pig. All guinea-pigs survived and showed no anaphylactic reactions after injection of ovalbumin.

Determination of magnesium in blood plasma was carried out on a flame spectrophotometer (Unicam 900).

RESULTS

In eight (80%) guinea-pigs of the experimental group it was found that the concentration of magnesium in the blood plasma in anaphylactic shock was increased with respect to values found before the shock. In two (20%) cases it remained unchanged. The mean magnesium concentration in sensitized guinea-pigs was 0.57 mg%, and in anaphylactic shock 0.73 mg%, 0.16 mg% or 29% higher (Table 1).

TABLE 1

Mean plasma magnesium in guinea-pigs of control and experimental groups

			Normal	Sensitized	In shock
Mg^{++}	Plasma	mgr %	0.53	0.57	0.73
		mEq	0.43	0.46	0.60

The results were treated statistically by the method of H. Cramer(13) and it was established that the increase of plasma magnesium anaphylactic shock was significant ($p < 0.05$).

The mean value of plasma magnesium of normal (nonsensitized) guinea-pigs was 0.53 mg% (0.43 mEq) (Table 1), about the same as in the sensitized guinea-pigs (0.57 mg%, i.e., 0.46 mEq). After intracardial injection of crystalline ovalbumin, with which the sensitization of experimental guinea-pigs was performed, the plasma magnesium of the control group decreased 0.04 mg%, on account of blood dilution, and this was found to be not statistically significant.

DISCUSSION

In the course of antigen-antibody reaction the cell is irritated and this irritation is accompanied with a temporary increase of membrane permeability for certain cations(17). Histamine and other pharmaco-dynamically active substances which are liberated in the course of this reaction not only cause alteration of membrane permeability, but also step up cell metabolic processes. Thus many authors have observed(2,5,6,9) that in anaphylactic shock the concentration of potassium in the serum is increased, that potassium leaves the cell, and that sodium from the serum enters into the cell.(16) Valligini(22), Serafini(18), Frugoni(7), and Danilović and co-workers(9) have studied the variations of different electrolytes in the course of antigen-antibody reaction in asthmatics. It is assumed that these changes of electrolyte concentration in the course of antigen-antibody reaction result from the increased cell activity(8,16), altered membrane permeability, and higher rate of metabolic processes(12).

Normally, magnesium ions only penetrate through the cell membrane with great difficulty, because it is almost impermeable for them. Magnesium occurs in the extracellular fluid only in small concentrations; it belongs to the group of intracellular cations and is a normal constituent of mammalian tissue, playing an important role in intracellular enzymatic reactions. In this study we found that in anaphylactic shock its concentration is increased. This may be explained by its exit from the cells whose metabolic processes are disturbed, and whose membrane permeability is altered on account of the antigen-antibody reaction. It might be assumed that the exit of magnesium from the cells, in veiw of the role of magnesium as catalyst, causes disturbances of many enzymatic reactions which bring about a functional modification of the cell.

The significant increase of magnesium concentration in the blood plasma of guinea-pigs in anaphylactic shock cannot be explained by the hemoconcentration which occurs in shock, since other cations, studied under the same experimental conditions, did not show such alterations(16). For example, the concentration of sodium in anaphylactic shock was significantly decreased, whereas the concentration of calcium remained unchanged.

CONCLUSION

On the basis of the results, the following may be concluded:

1. The concentration of magnesium in the blood plasma of guinea-pigs in anaphylactic shock is increased with respect to the concentrations in sensitized and nonsensitized animals.

2. The increase is statistically significant.

3. The increase of magnezium concentration in the plasma of sensitized guinea-pigs with respect to that in nonsensitized animals is statistically nonsignificant.

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GLASNIK HEMIJSKOG DRUŠTVA, Vol. 31, No. 3, 1966, pp. 129—138

COMPLEX COMPOUNDS OF *l*-ASCORBIC ACID AND METAL IONS. III. DETERMINATION OF THE COMPOSITION AND STABILITY CONSTANTS OF LEAD AND ALUMINUM COMPLEXES IN ACID MEDIA BY MEANS OF pH-METRIC TITRATIONS

by

DRAGAN S. VESELINOVIĆ and MILENKO V. ŠUŠIĆ

The formation of complexes of *l*-ascorbic acid with ions of lead and aluminum, of the type $(MeA_n)^{x-n}$ (x = cation valency), is associated with the liberation of H^+ ions(1). The change of hydrogen ion concentration makes possible the application of the pH-metric method for determination of the composition and stability constants of the complex compounds formed. In this work we have applied the method given and developed by J. Bjerrum(2) and S. Ahrland(3, 4) which, with slight modifications, was used by I. J. Gal(5) in investigations of uranyl-ascorbic complexes. This method is based on the pH-metric titration of a solution of ascorbic acid and metal salts with sodium hydroxide solution.

At each titration point the average number of ascorbic acid anions linked to metal cations is determined by the value of $\bar{n}$ (formation function). This value is obtained from the following expression:

$$\bar{n} = \frac{C_{Na} + C_H - C_{NO_3} - k_c/C_H(C_{HA} + C_{NO_3} - C_{Na} - C_H)}{C^0{}_{Pb}} \qquad (1)$$

where k_c denotes the concentration dissociation constant of ascorbic acid at the given ionic strength of the solution, C°_{Pb} the total concentration of lead in the solution, C_{HA} the equilibrium concentration of undissociated ascorbic acid, and C the equilibrium concentration of the ion denoted in the index. This expression is valid when the solution contains free inorganic acid added to the solution (C_{NO_3}) in order to hinder the hydrolysis of the metal salts. In the absence of free inorganic acid, the above expression can also be used but $C_{NO_3} = 0$. The value of C_{Na} corresponds to the concentration of sodium from the added sodium hydroxide.

The concentration of ascorbic acid anions at each titration point is obtained from equation (2):

$$C_A = k_c/C_H \ (C_{HA} + C_{NO_3} - C_{Na} - C_H) \tag{2}$$

where C_{NO_3} has the same meaning as in equation (1).

The dependence of $\bar{n}$ on the concentration of ascorbic acid anion and the concentration of metal salt determines the number of complexly linked ascorbic acid anions and hence the type and number of complexes. If $\bar{n}$ is dependent only on the concentration of ascorbic acid, only mononuclear complexes are formed. On the other hand, the dependence of $\bar{n}$ on both the concentration of ascorbic acid and the concentration of metal, indicates the formation of polynuclear complexes.

The dissociation constants of ascorbic acid complexes are obtained from the following equation

$$\frac{C_A}{\bar{n}} = \frac{1 + \frac{1}{k_1} C_A + \frac{1}{k_2} C_A^2 + \cdots\cdots + \frac{1}{k_n} C_A^n}{\frac{1}{k_1} + \frac{2}{k_2} C_A + \frac{3}{k_3} C_A^2 + \cdots\cdots + \frac{n}{k_n} (C_A)^{n-1}} \tag{3}$$

by graphic extrapolation to $C_A = 0$, which gives the value of k_1. This can be done since equation (3) has the limit value

$$\lim \left(\frac{C_A}{\bar{n}}\right)_{C_A - 0} = k_1 \tag{4}$$

If the value of k_1 is known, the dissociation constants $k_2 \ldots\ldots k_n$ can be determined from equation (3).

EXPERIMENTAL

The data obtained in four titrations of a lead complex and in three titration of an aluminum complex, together with the experimental conditions, are given in Table 1 and Table 2. The titrations were carried out with different concentrations of ascorbic acid and metal salts, and also in the presence and in the absence of inorganic acid. In some titrations the hydrogen ion concentration was determined by means of a pH-meter calibrated to indicate the value of the negative logarithm of hydrogen ion concentration, pH_C, instead of the corresponding activity value. Calibration was performed with 0.0100 M HCl solutions maintaining the ionic strength of the solution at 0.10 with $NaNO_3$. In the other cases, the hydrogen ion concentrations were obtained from the measured activities and the factor of H^+ ion activity. The value of this factor was calculated from the Debye-Hückel equation(1) which, in this case, can give satisfactory data.

TABLE I

Potentiometric titrations of $HA + Pb(NO_3)_2$ mixture with NaOH solution; $t = 23 - 25°$, $\mu = 0.1$ *($NaNO_3$).*

Titration 1

$C^\circ_{Pb} = 0.0167\ M$; $C^\circ_{HA} = 0.100\ M$; $C_{NaOH} = 0.6857\ M$; $k^{25}_{HA} = 9.5\text{x}10^{-5}(7)$;
$V^\circ = 60\ ml$; $f_H = 0.6898$.

ml NaOH	1.00	1.35	1.70	2.00	2.35	2.70	3.00	4.02
pH	3.06	3.20	3.32	3.42	3.50	3.60	3.68	3.88

Titration 2

$C^\circ_{Pb} = 0.0125\ M$; $C^\circ_{HA} = 0.100\ M$; $C_{NaOH} = 0.6857\ M$; $k^{25}_{HA} = 9.5\text{x}10^{-5}(7)$
$V^\circ = 60\ ml$ $f_H = 0.6898$

ml NaOH	1.00	1.35	1.70	2.00	2.35	2.70	3.00	4.00
pH	3.14	3.28	3.40	3.50	3.60	3.69	3.76	3.96

Titration 3

$C^\circ_{Pb} = 0.0060\ M$; $C^\circ_{HA} = 0.050\ M$; $C^0_{HNO_3} = 0.01033\ M$; $k^{25}_{HA} = 9.5\text{x}10^{-5}(7)$;
$V^\circ = 200\ ml$; $C_{NaOH} = 0.6905\ M$.

ml NaOH	2.62	3.28	3.51	3.73_5	3.95	4.18	4.35_5	4.79_5	5.00	5.21
pH_c*	2.49	3.71	2.78	2.84_5	2.91	2.98	3.01_5	3.13	3.17_5	3.21_5
ml NaOH	5.43	5.88_7	6.12	6.34_5	6.56_5	6.78_5	7.00			
pH_c*	3.26_5	3.34	3.38	3.42	3.45_5	3.49	3.51_5			

Titration 4

$C^\circ_{Pb} = 0.0040\ M$; $C^\circ_{HA} = 0.050\ M$; $C^0_{HNO_3} = 0.01033\ M$; $k^{25}_{HA} = 9.5\text{x}10^{-5}(7)$;
$V^\circ = 200\ ml$; $C_{NaOH} = 0.6905\ M$.

ml NaOH	2.14_3	2.58	2.78_7	3.20_5	3.42	3.63	3.84_5	4.05_5	4.26	4.48
pH_c*	2.37	2.50	2.56	2.70	2.77_5	2.83_5	2.90_5	2.97	3.02	3.08
ml NaOH	4.69	4.90	5.00	5.18	5.43_5					
pH_c*	3.12_5	3.12	3.20	3.23_5	3.28					

* pH-meter was calibrated to indicate pH_C values (concentrations).

TABLE II

Potentiometric titrations of $HA + Al(NO_3)_3$ mixture with NaOH solution;
$t = 23-25°$, $\mu = 0.1$ ($NaNO_3$).

Titration 1

$C^{\circ}_{Al} = 0.00833\ M$; $C^{\circ}_{HA} = 0.100\ M$; $C_{NaOH} = 0.5096\ M$; $k^{25}_{HA} = 9.5\mathrm{x}10^{-5}$(7);
$f_H = 0.6898$; $V^{\circ} = 60\ ml$.

ml NaOH	0.00	0.30	0.60	1.00	1.50	2.00	2.50	3.00	3.50	4.00
pH	2.54	2.72	2.88	3.06	3.21	3.36	3.46	3.56	3.63	3.72

Titration 2

$C^{\circ}_{Al} = 0.0127\ M$; $C^{\circ}_{HA} = 0.100\ M$; $C_{NaOH} = 0.5096\ M$; $k^{25}_{HA} = 9.5\mathrm{x}10^{-5}$ (7);
$f_H = 0.6898$; $V^{\circ} = 60\ ml$.

ml NaOH	0.00	0.30	0.60	1.00	1.30	1.60	2.00	2.50	3.00	3.50	4.00	4.50	5.00	5.50
pH	2.52	2.68	2.83	2.98	3.08	3.17	3.29	3.38	3.47	3.55	3.63	3.68	3.73	3.79

Titration 3

$C^{\circ}_{Al} = 0.0820\ M$; $C^{\circ}_{HA} = 0.0500\ M$; $C^{0}_{HNO_3} = 0.01033\ M$; $C_{NaOH} = 0.6905\ M$;
$V^{\circ} = 200\ ml$; $k^{25}_{HA} = 9.5\mathrm{x}10^{-5}$(7).

ml NaOH	1.15_5	1.53_8	1.98	2.20	24.1_8	2.63	2.84_5	3.04_5	3.26_8	3.49	3.72	3.94_5	4.16	4.38	4.59_5	4.80_8	5.00	5.22	5.44	5.65_5	5.87_7	6.09_5	6.30_8	6.52_5	6.75	6.97	7.19_5	7.40_8	7.52	7.83
pH_c*	2.13_5	2.21	2.31	2.36_5	2.42	2.48	2.55	2.60	2.66	2.74	2.80	2.85	2.91	2.95	3.00	3.04	3.08	3.12	3.16	3.19	3.22	3.27	3.30	3.32	3.35	3.37	3.39	3.41	3.43	3.46

* p H-meter was calibrated to indicate pH_C values (concentrations).

In the course of the titration the initial volume of the solution, V_0, is altered by the addition of a certain volume of NaOH solution, v. On account of this change of solution volume in the course of the titration, all concentration values at the different titration points were reduced to the initial volume by means of a correction factor $(V^\circ + v)/V^\circ$.

Since $Pb(NO_3)_2$ and $Al(NO_3)_3$ hydrolyze in aqueous solution, giving different hydrolytic products in dependence on the concentration of the salt and the pH of the solution[6, 7], only those titration points which lie below pH = 3.5—4 were taken for calculations.

The dependence of $\bar{n}$ on C_A is given in Fig. 1 and Fig. 2. It can be seen that lead and aluminum form only mononuclear complexes with ascorbic acid, since $\bar{n}$ depends only on C_A and not on C_{Me}.

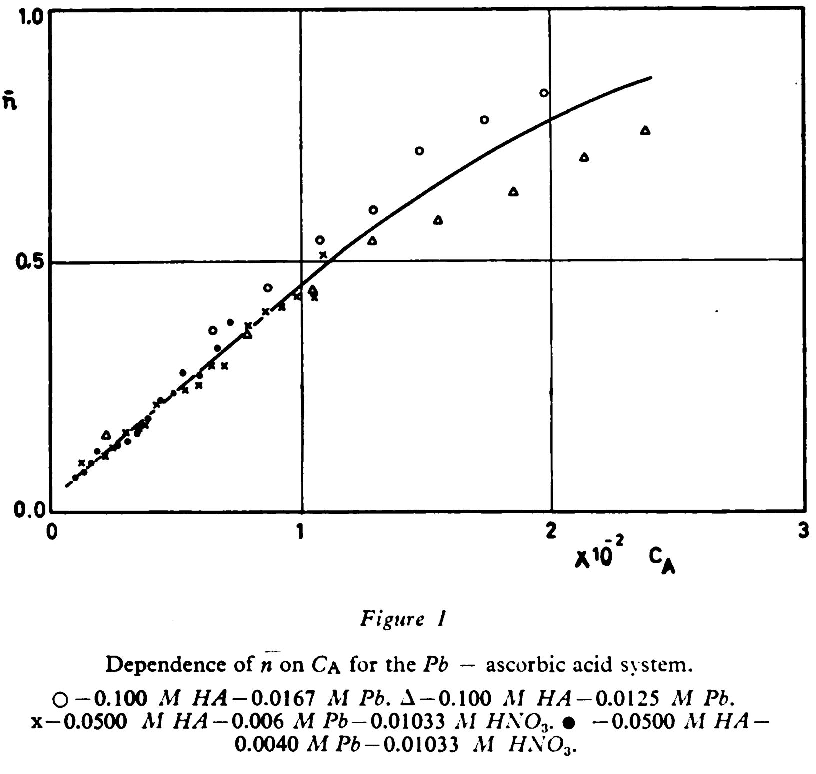

Figure 1

Dependence of $\bar{n}$ on C_A for the *Pb* — ascorbic acid system.

○ – 0.100 *M HA* – 0.0167 *M Pb*. Δ – 0.100 *M HA* – 0.0125 *M Pb*. x – 0.0500 *M HA* – 0.006 *M Pb* – 0.01033 *M* HNO_3. ● – 0.0500 *M HA* – 0.0040 *M Pb* – 0.01033 *M* HNO_3.

The values of $\bar{n}$ for lead do not exceed 1 and this means that there is only one complex, Pb^+. In the case of aluminum the values of $\bar{n}$ range from 0 to 2, indicating the existence of two complexes, AlA^{2+} and AlA_2^+.

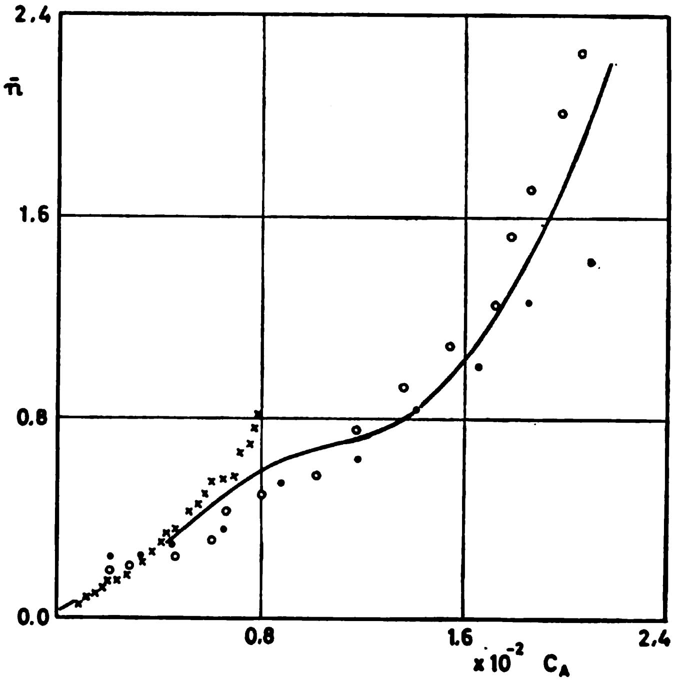

Figure 2

Dependence of $\bar{n}$ on C_A for the Al — ascorbic acid system.

○—0.100 M HA—0.0127 M Al. ●—0.100 M HA—0.00833 M Al.
x—0.0500 M HA—0.00833 M Al—0.01033 M HNO_3.

In Fig. 3 and Fig. 4 the dependence of $C_A/\bar{n}$ on C_A for each titration is shown. By extrapolating the obtained straight lines to $C_A = 0$, the values of the concentration dissociation constants for PbA^+ and AlA^{2+} were obtained; their numerical values are given in Table 3. The value of the dissociation constant of the AlA_2^+ complex was obtained from equation (3) using only that data which corresponds to points in Fig. 4, out of the straight-line part. These calculations gave 29 values for the constant k_2; hence, it was possible to treat the obtained data statistically. By the application of Chauvennet's criterium, it was established that all values obtained lie within the limits of the standard deviation. Accordingly, the mean value is given as the constant k_2 in Table 3.

DISCUSSION

The data obtained for the composition of ascorbic acid complexes with lead and aluminum are consistent with the results of our

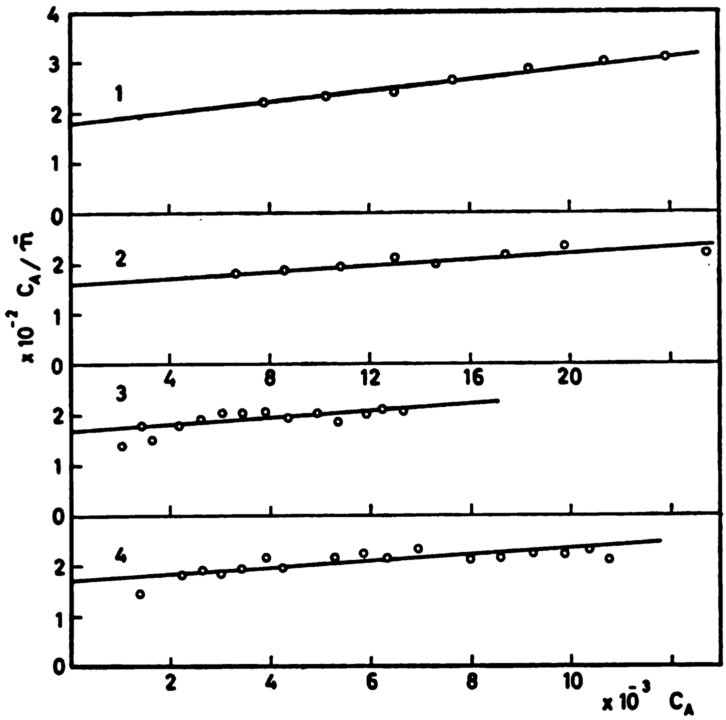

Figure 3

Dependence of $CA/\bar{n}$ on C_A for the Pb — ascorbic acid system.

1) 0.100 M HA–0.0125 M Pb. 2) 0.100 M HA–0.0167 M Pb. 3) 0.0500 M HA–0.0040 M Pb–0.01033 M HNO_3. 4) 0.0500 M HA–0.0060 M Pb –0.01033 M HNO_3.

previous investigations(1). The assumption that aluminum forms two cationic complexes by successive incorporation of ascorbic acid anions has also been confirmed.

The values of the dissociation constants can be compared with those previously obtained for PbA^+ and AlA_2^+(1). The pk$_1$ values are in good agreement with the corresponding values previously obtained(1). A slightly greater difference between these two values than expected with respect to the precision of the determination can be ascribed to the effect of nitrate ions. These ions are known to form complex compounds(9) with a relatively small stability constant ($pK = 0.68$ for Pb). For the aluminum complex AlA_2^+, this difference is probably caused by the formation of nitrate complexes as in the case of lead, although no data on nitrate complexes of aluminum have been reported in the literature. For these reasons the values obtained

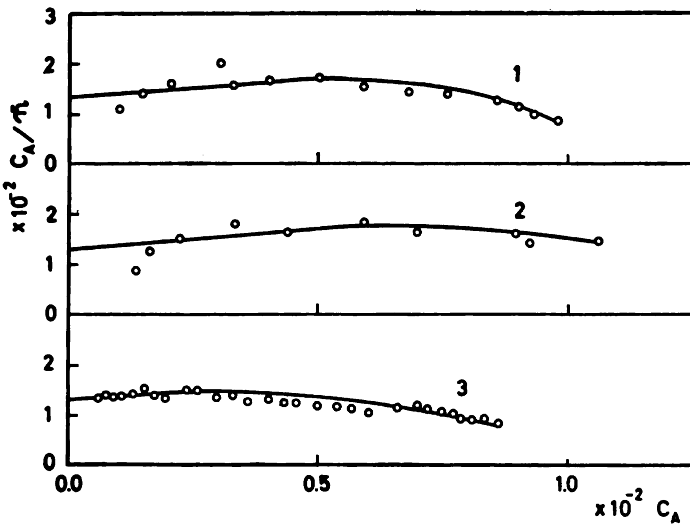

Figure 4

Dependence of $C_A/\bar{n}$ on C_A for the *Al* — ascorbic acid system.
1) 0.100 *M HA*—0.0127 *M Al*. 2) 0.100 *M HA*—0.00833 *M Al*. 3) 0.0500 *M HA*—0.00833 *M Al*—0.01033 *M* HNO_3.

TABLE III

Values of the concentration dissociation constant k_n* and $\log \beta_n$** for ascorbic acid complexes of *Pb* and *Al*; t=23—25°; $\mu=0.1$ ($NaNO_3$).

Titration No.	k_1		k_2
	PbA^+	AlA^{2+}	AlA_2^+
I	$1.7_0 \times 10^{-2}$	$1.3_0 \times 10^{-2}$	
II	$1.7_0 \times 10^{-2}$	$1.3_0 \times 10^{-2}$	
III	$1.6_5 \times 10^{-2}$	$1.4_0 \times 10^{-2}$	$2.8_0 \times 10^{-4}$
IV	$1.7_7 \times 10^{-2}$	—	
Average:	$1.7_7 \times 10^{-2}$	$1.3_0 \times 10^{-2}$	$2.8_0 \times 10^{-4}$
	$\log \beta_1 = 1.77 \pm 0.1$	$\log \beta_1 = 1.89 \pm 0.1$	$\log \beta_2 = 3.55 \pm 0.3$

* $-k_n = \dfrac{(C_{Me}) \times (C_A)^n}{(C_{MeA_n})}$ **$-\beta_n = 1/k_n$

for the dissociation constants of ascorbic acid complexes with lead and aluminum are valid only for the ionic strength of 0.1 in nitrate solutions.

APPARATUS AND REAGENTS

The pH-meters "Radiometer" M 22 and "Beckman" H-2 were used. Calibration of the pH-meters was carried out by means of potassium bitartarate ("Kemika", p.a.) and "Beckman" standard buffer solution. The lead nitrate, aluminum nitrate and all other reagents were of p.a. purity ("Kemika" and "Merck").

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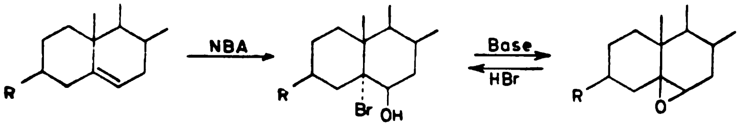
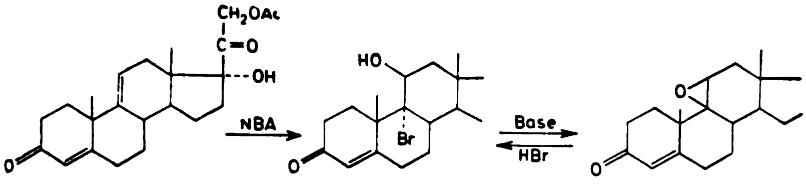
PREPARATION OF BROMOHYDRINS OF Δ^5-STEROIDS BY MEANS OF *N*-BROMOSUCCINIMIDE

by

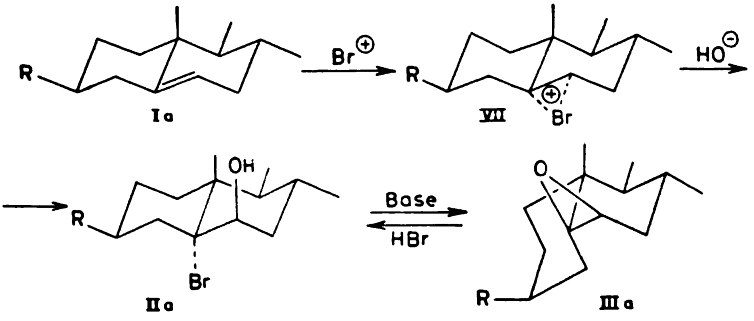
MILUTIN STEFANOVIĆ, ALEKSANDAR JOKIĆ
and MIHAILO LJ. MIHAILOVIĆ

In the chemistry of steroids, bromohydrins are used as valuable intermediates in various transformations and partial syntheses (1—7). They are usually prepared by the action of *N*-bromoacetamide (*NBA*) on unsaturated steroids dissolved in aqueous dioxane, in the presence of perchloric acid. When treated in this way, Δ^5-steroids (I) give *trans* diaxial 5α-bromo-6β-hydroxy derivatives (II) (2—6) and $\Delta^{9(11)}$-steroids (e. g. IV) afford *trans* diaxial 9α-bromo-11β-hydroxy compounds (V) (7) in yields up to 80%. The same *trans* bromohydrins are also formed by treating 5β,6β-epoxides (III) and 9β, 11β-epoxides (VI), with hydrogen bromide, both epoxides undergoing the usual diaxial cleavage (7, 8, 9). Under similar conditions 5α, 6α-epoxides are transformed, as expected, to 5α-hydroxy-6β-bromo derivatives (10).





The key intermediate in these reactions with *N*-bromoacetamide, which represent in fact additions of hypobromous acid to double bonds*, is presumably a cyclic bromonium ion (VII)⁽¹¹⁾, formed by the electrophilic attack of a $Br^{\oplus}$ ion on the less hindered α-face of the double bond (rear side attack), as illustrated on the case of Δ^5-steroids (Ia). Subsequent attack of this ion (VII) by $OH^{\ominus}$ on the side opposite the three-membered ring with inversion at C_6 would account for the formation of the 5α,6β-bromohydrin (IIa) ⁽⁸, ¹²⁾. This type of addition does not follow the Markownikoff rule (according to which the positive fragment of the reagent, i.e. $Br^{\ominus}$, should add to the less substituted carbon atom C_6), thus suggesting that a "true" bromonium ion (VII) is formed as an intermediate (rather than more or less developed carbonium ions**), followed by an S_N2-like attack of $OH^{\ominus}$ on the less hindered C_6 carbon atom. Similar reasoning applies also to the formation of 9α,11β-bromohydrins (V) from $\Delta^{9(11)}$-steroids (IV) and *N*-bromoacetamide (i.e. hypobromous acid). In general, in rigid ring systems, steric effects are much more important than electronic factors in controlling the orientation of attack on a halonium ion ⁽¹³⁾.



Ia VII IIa IIIa

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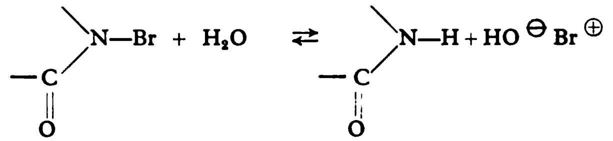
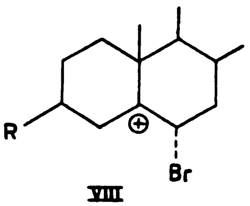
* *N*-Bromoacetamide, *N*-bromosuccinimide and other reagents of similar structure undergo partial hydrolysis in the presence of water and are therefore in equilibrium with hypobromous acid:



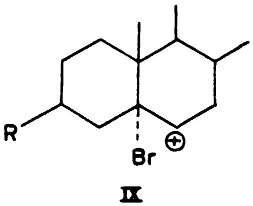
$$\begin{matrix}\diagdown \\ \;\;\; N{-}Br \\ \diagup \\ -C \\ \| \\ O\end{matrix} + H_2O \rightleftarrows \begin{matrix}\diagdown \\ \;\;\; N{-}H \\ \diagup \\ -C \\ \| \\ O\end{matrix} + HO^{\ominus}Br^{\oplus}$$

For that reason the bromine atom of bromoamides is described as a "positive" halogen.

** If the rear attack of $Br^{\oplus}$ on Ia were to furnish as intermediate a standard carbonium ion, the tertiary ion VIII would have preference over the secondary carbonium ion IX, and the predominant *trans* reaction product should then be the 6α-bromo-5β-hydroxy compound (in accordance with the Markownikoff rule), which, however, is not formed in this reaction.



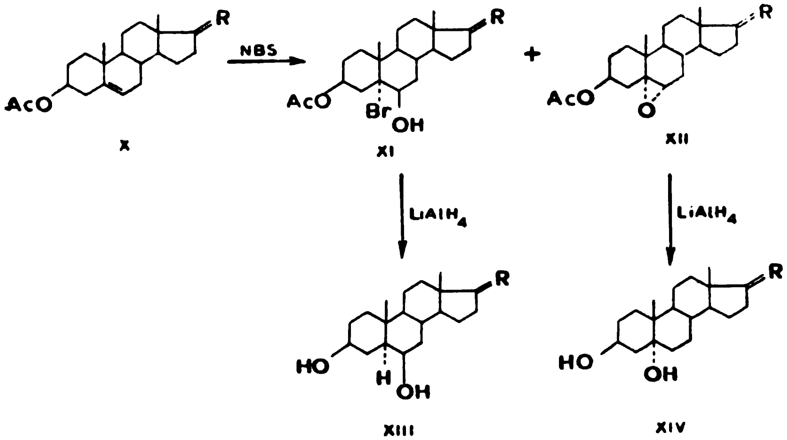
VIII



IX

In the course of our studies on the synthesis of 19-norsteroids involving cyclization and fragmentation reactions with lead tetraacetate (3,4,5,) one of the problems consisted in the rapid preparation of larger amounts of the starting bromohydrins of Δ^5-steroids, by means of a "positive" bromine-containing reagent (acting as the source of hypobromous acid), which would be more stable and more easily available than the usual *N*-bromoacetamide. It appeared that such a reagent might be *N*-bromosuccinimide (*NBS*), since it was reported in the literature that in a few cases bromohydrins had been obtained by the action of *N*-bromosuccinimide on some olefinic compounds, using aqueous acetone (14), water (15), water-glyme (16), or aqueous diglyme (17), as the solvent, the yields ranging from 35 to 80%.

As expected, the reaction between *N*-bromosuccinimide and acetates of cholesterol (Xa), dehydroisoandrosterone (androstenolone) (Xb) and pregnenolone (Xc), respectively, in acetone solution containing 10% water and perchloric acid, afforded, 60—70% of the corresponding pure (recrystallized) bromohydrin (XI). The reaction was carried out by dissolving the steroid in acetone, adding water, heating if necessary until a clear solution was obtained, cooling to room temperature, adding 60% perchloric acid and finally treating the solution (in one portion) with an equivalent amount (+ 10% excess) of *N*-bromosuccinimide. After 30 minutes the reaction was completed, as indicated by thin-layer chromatography. The bromohydrin was precipitated by the addition of ice-cold water, separated after a few hours by filtration, and recrystallized from a suitable solvent.



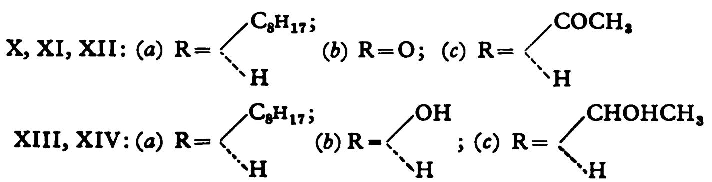
X

XI

XII

XIII

XIV



$$\text{X, XI, XII: }(a)\ R=\left\langle\begin{matrix}C_8H_{17};\\ H\end{matrix}\right.\quad (b)\ R{=}O;\quad (c)\ R=\left\langle\begin{matrix}COCH_3\\ H\end{matrix}\right.$$

$$\text{XIII, XIV: }(a)\ R=\left\langle\begin{matrix}C_8H_{17};\\ H\end{matrix}\right.\quad (b)\ R=\left\langle\begin{matrix}OH\\ H\end{matrix}\right.;\quad (c)\ R=\left\langle\begin{matrix}CHOHCH_3\\ H\end{matrix}\right.$$

Melting points, specific rotations and infrared spectra of the bromohydrins (XI) obtained by means of *N*-bromosuccinimide were identical with those of the bromohydrins prepared by the *N*-bromoacetamide method (in aqueous dioxane in the presence of perchloric acid). In the case of cholesterol acetate (Xa), the structure of the corresponding bromohydrin, 5α-bromocholestane-3β,6β-diol 3-acetate (XIa), was also confirmed by hydrogenolysis with lithium aluminium hydride, the known cholestane-3β,6β-diol (XIIIa) being isolated in 56% yield.* It should be noted that the facile replacement of bromine by hydrogen in this case contrasts with the usual lithium aluminium hydride reduction of halides and that it proceeds without inversion at C_5 (18).

In addition to the bromohydrins (XI), treatment of Δ^5-steroids (X) with either *N*-bromosuccinimide or *N*-bromoacetamide yielded the corresponding 5α,6α-epoxides (XII) as by-products. The structure of 5α,6α-epoxycholestan-3β-ol acetate (XIIa), obtained as a by-product from cholesterol acetate (Xa), was confirmed by conversion, upon lithium aluminium hydride reduction, to the known cholestane-3β, 5α-diol (XIVa) (19).

In contrast to *trans* diaxial 5α,6β-dibromo steroids, which are readily isomerized to the corresponding, more stable, *trans* diequatorial dibromides (8,10,20), ** *trans* diaxial 5α-bromo-6β-hydroxy steroids (XI) were not converted to the diequatorial 6α-bromo-5β-hydroxy derivatives upon heating in chloroform solution.

EXPERIMENTAL

Melting points (uncorrected) were taken on a Kofler hot-stage apparatus. Infrared spectra were recorded (in *KBr* pellets) on a Perkin-Elmer spectrophotometer, Infracord Model 137. Optical rotations were measured in chloroform. Thin-layer chromatography was performed on silica-gel *G* (Stahl) with cyclohexane-ethyl acetate (7 : 3); detection was effected by 50% sulphuric acid and subsequent heating at 100°. The light petroleum used had b.p. 40—60°.

(*A*) 5α-*Bromocholestane*-3β,6β-*diol* 3-*acetate* (XIa).

(*a*) Perchloric acid (7.35 *ml*, 60%) and 5 *ml* of water were added slowly to a solution of 10 *g* of cholesterol acetate (Xa) in 100 *ml* of acetone, the temperature being maintained at 18—20°. The stirred solution was then treated, in one portion, with 5 *g* of *N*-bromosuc-

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* In addition, two other products were obtained in lower yields. These products were not investigated for the time being, but it was established that none of them was the other possible stereoisomer, *i.e.* coprostane-3β, 6β-diol, which would result from the attack of lithium aluminium hydride at C_5 *with inversion* of the configuration.

** This rearrangement is of general occurrence in the steroid field (21), and a whole series of such diaxial-diequatorial isomerizations is now known (17,22).

cinimide, and stirring was continued for another 30 minutes at room temperature. The mixture was poured into ice-cold water, and the precipitate was filtered off and dried *in vacuo*. After crystallization from methylene chloride - ether - light petroleum, 7 *g* (57%) of pure bromohydrin (XIa), was obtained, m.p. 168—169°, $[\alpha]_D = -41°$.(3, 6, 9)

(*b*) A solution containing 5 *g* of cholesterol acetate (Xa) in 100 *ml* of acetone was first treated, with stirring, with 3.7 *ml* of perchloric acid (60%) and 2.5 *ml* of water at 18—20°, and then, in one portion, with 2.5 *g* *N*-bromosuccinimide. After stirring for another 30 minutes at room temperature the mixture was cooled to 5°, treated with 30 *ml* of a 1% aqueous solution of sodium thiosulphate, diluted with water and the resulting emulsion extracted with ether. The ethereal layer was dried over anh. sodium sulphate, the solvent evaporated *in vacuo* and the residue recrystallized from methylene chloride - ether - light petroleum to give 3.3 *g* (54%) of 5α-bromocholestane-3β,6β-diol 3-acetate (XIa), m.p. 169—170° (purity checked by thin-layer chromatography). According to thin-layer chromatography, the residue obtained by evaporation of the mother-liquor contained three components. The product with the highest R_f value corresponded to unreacted cholesterol acetate (Xa), and the product with the lowest R_f value was bromohydrin (XIa). The third product, isolated upon column chromatography of the residue on silica-gel, proved to be 5α,6α-epoxycholestan-3β-ol acetate (XIIa), m.p. 96—97°, $[\alpha]_D = -46°$ (23). Its structure was confirmed by reaction (C).

(*c*) Water (10 *ml*) was added to 5 *g* of cholesterolacetate (Xa) dissolved in 100 *ml* of acetone, and the mixture was stirred (and heated if necessary to 50°) until a clear solution was obtained. The stirred solution was then treated, in one portion, with 2.5 *g* of *N*-bromosuccinimide. After stirring for 12—15 hours at room temperature, the mixture was poured into ice-cold water, and the solid precipitate was filtered off and dried *in vacuo*. Crystallization from acetone-light petroleum yielded 49% of pure bromohydrin (XIa), m.p. 168—170°.

The bromohydrin (XIa) prepared in (*a*), (*b*) and (*c*) was identical with the product obtained from cholesterol acetate and *N*-bromoacetamide according to the procedure described by Kalvoda *et al.* (3).

(*B*) *Cholestane*-3β,6β-*diol* (XIIIa)

5α-Bromocholestane-3β,6β-diol 3-acetate (XIa) (2 *g*), obtained from cholesterol acetate (Xa) and *N*-bromosuccinimide (see *A*), was dissolved in dry ether and the resulting solution was slowly added (30 minutes) to a suspension of 0.5 *g* of lithium aluminium hydride in ether. After refluxing for two hours, the mixture was cautiously hydrolyzed with 20% sulphuric acid and the aqueous layer was extracted with ether. The combined ethereal layers were washed with aqueous sodium carbonate and water, and dried over anh. sodium sulphate. Evaporation of the solvent and crystallization of the residue from methanol yielded 0.9 *g* (56%) of cholestane-3β, 6β-diol (XIIIa), m.p. 186—187°, $[\alpha]_D = +12°$ (19,24). (Found: *C*, 80.28; *H*, 12.09. Calc. for $C_{27}H_{48}O_2$: *C*, 80.14; *H*, 11.96%). The infrared spectrum of this diol was identical with that of an authentic product prepared according to Plattner *et al.* (19)*.

(*C*) *Cholestane*-3β,5α-*diol* (XIVa)

5α,6α-Epoxycholestan-3β-ol acetate (XIIa) (0.4 *g*), obtained as a by-product in the reaction of cholesterol acetate (Xa) with *N*-bromosuccinimide (see *A*, *b*), was reduced with lithium aluminium hydride (0.2 *g*) as described above (*B*) to give as the only product (0.2 *g*) cholestane-3β,5α-diol (XIVa), m.p. 223—224.5° (from ethyl acetate), $[\alpha]_D = +18°$ (19,23). It was identical with the diol prepared by lithium aluminium hydride reduction of authentic 5α, 6α-epoxycholestan-3β-ol acetate (19).

(*D*) 5α-*Bromoandrostane*-3β,6β-*diol*-17-*one* 3-*acetate* (XIb)

(*a*) Perchloric acid (4 *ml*, 60%) and 2 *ml* of water were added slowly and with stirring to a solution of 3 *g* of Δ^5-androsten-3β-ol-17-one acetate (dehydroisoandrosterone acetate, androstenolone acetate)(Xb) in 50 *ml* of acetone, the temperature being maintained at 18—20°. The stirred solution was then treated, in one portion, with 1.5 *g* of *N*-bromosuccinimide, and stirring was continued for another 30 minutes at room temperature. The mixture was poured into ice-cold water, and the precipitate was filtered off and dried *in vacuo*. The crude product (4.2 *g*) was recrystallized from acetone—light petroleum to give 2.7 *g* (53%) of pure bromohydrin (XIb), m.p. 174—175°, $[\alpha]_D = +2°$ (2,6).

(*b*) A solution containing 9 *g* of dehydroisoandrosterone acetate (Xb) in 100 *ml* of acetone was first treated, with stirring, with 7 *ml* of perchloric acid (60%) and 10 *ml* of water, at 18—20°, and then, in one portion, with 4.5 *g* of *N*-bromosuccinimide. After stirring for another 30 minutes at room temperature, the mixture was cooled to 5°, treated with 60 *ml* of 1% aqueous solution of sodium thiosulphate, diluted with water and extracted with ether. After drying over anh. sodium sulphate, the solvent was evaporated *in vacuo* and the product recrystallized from methylene chloride—ether—light petroleum. The bromohydrin (XIb), m.p. 173—175°, was obtained in a 61% yield (7.1 *g*).

(*E*) 5α-*Bromopregnane*-3β,6β-*diol*-20-*one* 3-*acetate* (XIc)

(*a*) Perchloric acid (3.7 *ml*, 60%) and 2.5 *ml* of water was added slowly and with stirring to a solution of 5 *g* of Δ^5-pregnen-3β-ol-20-one acetate (pregnenolone acetate) (Xc) in 100 *ml* of acetone, the temperature

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* The other possible reduction product, *i.e.* coprostane-3β,6β-diol (25), was not detected in this reaction, but two other products, which were not identified, were formed in low yield.

being maintained at 18—20°. The stirred solution was then treated, in one portion, with 2.5 *g* of *N*-bromosuccinimide, and stirring was continued for another 30 minutes at room temperature. The mixture was poured into ice-cold water, and the precipitate was filtered off and dried *in vacuo*. Crystallization of the crude product from methylene chloride – ether – light petroleum yielded 3.5 *g* (70%) of pure bromohydrin (XIc), m.p. 166—169°, $[\alpha]_D = +7°$ (4,6).

(*b*) A solution containing 5 *g* of pregnenolone acetate (Xc) in 100 *ml* of acetone was first treated, with stirring, with 3.7 *ml* of perchloric acid (60%) and 2.5 *ml* of water, at 18—20°, and then, in one portion, with 2.5 *g* of *N*-bromosuccinimide. After stirring for another 30 minutes at room temperature, the mixture was cooled to 5°, treated with 30 *ml* of a 1% aqueous solution of sodium thiosulphate, diluted with water and extracted with ether. The crude product, isolated upon drying and evaporation of the solvent, was recrystallized from methylene chloride – ether – light petroleum and gave 4 *g* (63%) of pure bromohydrin (XIc), m.p. 166—169°.

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SYNTHESIS OF 4'-HYDROXY-5-BROMO-2-THIOFURANILIDE

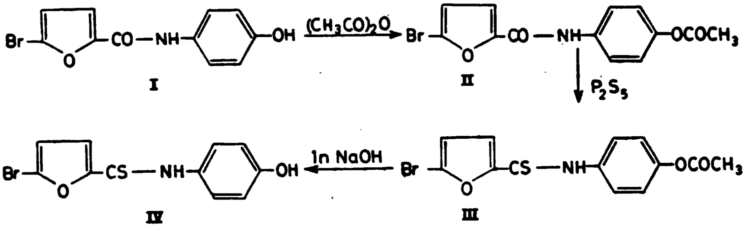
by

MIROSLAVA M. JANČEVSKA

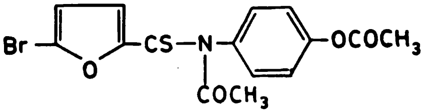
All attempts to convert 4'-hydroxy-5-bromo-2-furanilide (I)⁽¹⁾ into the corresponding hydroxythioamide by treatment with phosphorus pentasulfide in anhydrous organic solvents (pyridine, dioxane, benzene, xylene, etc.) were unsuccessful. By changing the reaction conditions (temperature, time of heating, solvent, etc.) an undefined resinous product was always obtained.

However, the method of protecting the hydroxyl group with an acetyl group was shown to be very effective⁽²⁾. When the obtained acetoxyanilide (II)⁽¹⁾ was treated with phosphorus pentasulfide in anhydrous hylene, 4'-acetoxy-5-bromo-2-thiofuranilide (III) was obtained; by alkaline hydrolysis (1 N NaOH) the acetyl group was eliminated and the desired compound (IV) was obtained.

The synthesis of 4'-hydroxy-5-bromo-2-thiofuranilide (IV) is shown in the following scheme:



The presence of the free hydroxyl group in compound (IV) was proved by acetylation with acetic acid anhydride, whereby the thioamide group was acetylated as well. The structure of the 0, N-diacetyl thioderivative (V) ia as follows:



V

The results reported in this paper confirm our previous conclusions that the preparation of hydroxythioamides (of aromatic and heterocyclic series) from the corresponding amides by means of phosphorus pentasulfide is successful only provided the hydroxyl group is protected with a suitable acyl group (acetyl, benzoyl, furoyl, carbomethoxy, carbethoxy, carbobenzoxy etc). The acetyl group was proved to be the most suitable, since it does not react with phosphorus pentasulfide and it is easily eliminated without affecting the introduced thioamide group(3).

EXPERIMENTAL

The melting points are not corrected.

4'-Acetoxy-5-bromo-2-thiofuranilide (III)

A mixture of 3.25 g (0.01 mole) of 4'-acetoxy-5-bromo-2-furanilide (II)(1) (colorless bright plates, m.p. 145—146°), 2.22 g (0.01 mole) of phosphorus pentasulfide and 15 ml of anhydrous xylene was heated for 10 minutes in an oil bath at 130—140°. The color of the reaction mixture changed from orange to red and finally do dark red (a proof that the reaction was over). The hot colored solution was filtered rapidly and the filtrate was left to crystalize slowly. The separated yellow crystalline precipitate was filtered off, washed with petroleum-ether and dried at room temperature.

The yield of the crude product was 3.2 g (94%); m.p. 131—132°. Recrystallization from 96% ethanol gave yellow needles, m.p. 134—135°.

Analysis

$C_{13}H_{10}NO_3Br$ (382.256) Found: C 45.81%; H 2.91%; N 4.37%.

Calculated for: C 45.92%; H 2.96%; N 4.12%.

4'-Hydroxy-5-bromo-2-thiofuranilide (IV)

By heating (50—60°) 3.4 g (0.01 mole) of 4'-acetoxy-5-bromo-2-thiofuranilide with 20 ml of 1 N sodium hydroxide solution on a water bath for 10 minutes a yellow solution was obtained. The cooled alkaline solution was filtered and acidified with 1 N hydrochloric acid to pH 5—6, whereby a voluminous precipitate was separated. The latter crystallized on cooling and the crystals were filtered off, washed with water and dried in a thermostat at 80—90°. The yield of the crude product was 2.7 g (93%), m.p. 143—144°. Recrystallization from 50% ethanol gave greenish-yellow prisms of m.p. 149—150°.

Analysis

$C_{11}H_8NO_2BrS$ (289.174) Found: C 44.49%; H 3.08%; N 4.89%.

Calculated for: C 44.33%; H 2.73%; N 4.70%.

O,N-Diacetyl-4'-hydroxy-5-bromo-2-thiofuranilide (V)

To a solution of 2.98 g (0.01 mole) of 4'-hydroxy-5-bromo-2-thiofuranilide (IV) in 10 ml of anhydrous pyridine, 6.2 g (0.006 moles) of acetic acid anhydride was added in drops with constant stirring. After standing for two hours at room temperature, the red reaction mixture was poured into 300 ml of ice water. The separated red crystalline product was filtered off, and washed first with water containing hydrochloric acid and then with distilled water. After drying, the yield of crude product was 3.5 g (91%), m.p. 127—128°. Recrystallization from 50% ethanol gave red prisms, m.p. 129—130°.

Analysis

$C_{15}H_{12}NO_4SBr$ (382.256) Found: C 47.22%; H 3.22%; N 3.78%.

Calculated for: C 47.16%; H 3.17%; N 3.67%.

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INTERFEROMETRIC TITRATIONS OF ACIDS AND BASES IN WATER AND GLACIAL ACETIC ACID

by

VILIM J. VAJGAND and TODOR J. TODOROVSKI

It is known that by means of the refractometric method four decimals of the refractive index value can be determined; more precise determinations are carried out with an interferometer by means of which one can follow very small changes of the refractive index value. The interferometric method has so far been applied to analyses of gas mixtures and analyses of solutions. It is used for the determination of small differences between the refractive indexes of organic compounds and has became a method for the check of their purity(1). It is also used for the determination of very small concentrations of a substance in a solution(2), and D_2O in water(3). In addition, in some cases the rate of a chemical reaction can be determined interferometrically. However, the application of the interferometric method for the determination of the titration end point in volumetric processes is very rare. E. Berl *et al.*(5) have performed titrations of some acids and bases, and B. F. Marti *et al.*(6) have carried out argentometric titrations in very dilute solutions. In both cases the determinations were carried out in aqueous solutions. There is no data on the use of the interferometric method for determination of the titration end point in nonaqueous solutions.

From the aforesaid it follows that the interferometric method offers the possibility of determining the titration end point, especially in cases where convenient visual indicators and instrumental methods are lacking; however, no systematic investigations have been carried out so far.

In this paper we describe a study of the conditions for the performance of interferometric titrations in aqueous and monaqueous solutions, and of possible techniques for the determination of the equivalence point. The possible applications of this method are discussed as well.

Procedures and results of interferometric titrations of bases with acids in aqueous solutions are presented, together with results in nonaqueous solutions obtained by titrating salts of organic acids and some tertiary amines in glacial acetic acid. The latter determinations show that this new method can be used in the pharmaceutical industry, since it makes possible any determination based on the neutralization process in any solvent.

EXPERIMENTAL

All measurements were done with a Zeiss interferometer which was adapted for titration. By means of this instrument seven decimals of the refractive index value were obtained.

The solutions used for the titrations in aqueous solutions (solutions of HCl, H_2SO_4, NaOH and CH_3COOH) were prepared and standardized in the usual way.

In nonaqueous titrations we used a solution of perchloric acid and sodium acetate in acetic acid. Anhydrous acetic acid was prepared from glacial acetic acid (p.a. "Kemika" or "C. Erba") in which the water content was determined by the K. Fischer method(7). To a measured amount of the acid, an amount of acetic anhydride equivalent to the water content was added, and the reaction mixture, after being refluxed at 100°C for 5—6 hrs, was left to stand for some days. Anhydrous acetic acid was also prepared by means of chromium trioxide: the reaction mixture was reflexed for 5—6 hrs and the acetic acid was redistilled at 117°C. Special care should be paid to the preparation of anhydrous acetic acid, since the presence of water or excess acetic acid anhydride can affect the shape of the titration curve. If the perchloric acid solution is not carefully cooled, it can become yellow upon the addition of acetic anhydride, but this does not affect the course of the titration.

The solutions were standardized by means of potentiometric titrations.

TITRATIONS IN AQUEOUS MEDIA

The titrations were usually carried out directly in cuvettes of a length of 10 or 20 mm depending on the concentration of the titrated solution. Longer cuvettes were rarely used since they are designed for work with more dilute solutions. The concentration of the titrated solutions was 0.1 M, and the concentrations of the titrating agents ranged from 0.1 M to 2 M. The titrations were performed at room temperature and the solution temperature was checked with a precision thermometer. The cuvettes were thermostated to ±0.1°C with water. The titration solutions were stirred with a mechanical stirrer.

The titrations were carried out in burettes of 1, 2 and 5 ml, depending on the concentration of the titrating agent. The time required for one titration amounted to ten minutes.

Measurements were made 45 seconds after each addition of the titrating agent. The reference solution was either distilled water or an already titrated solution of the substance studied.

The diagrams showing the shapes of the interferometric titration curves and their dependence on the acid or base strength are similar to those obtained in conductometric titrations.

In the beginning of the titration, larger volumes of titrating agent may be added, but in the vicinity of the equivalence point it is best to add from 0.1 to 0.2 ml. The equivalence point lies at the intersection of two straight lines.

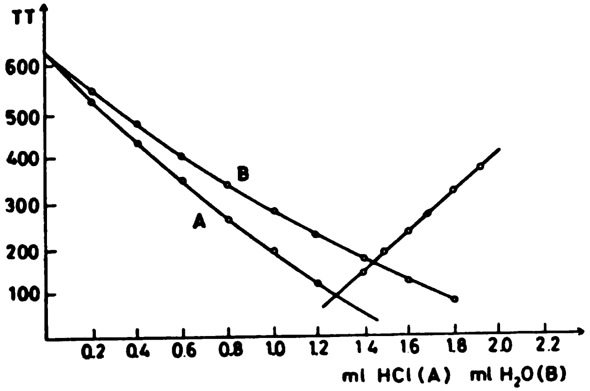

Figure 1

Curve *A*: 1.82 *ml* of 0.1186 *N NaOH* titrated interferometrically with 0.1193 *N HCl*

Curve *B*: 1.82 *ml* of 0.1186 *N NaOH* diluted successively with water TT (on ordinate): Scale units of micrometer screw, proportional to the refractive index change

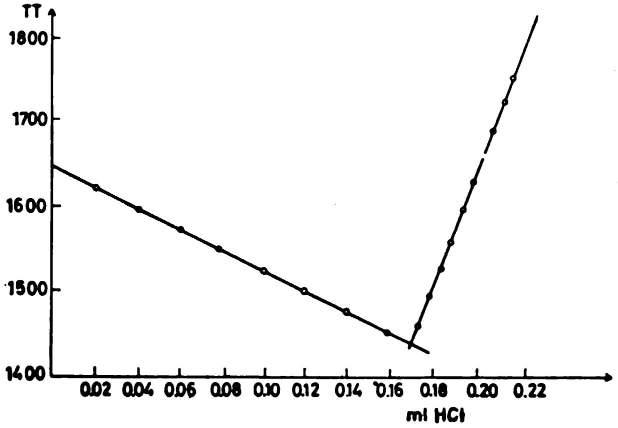

Figure 2

3.20 *ml* of 0.1186 *N* solution of *NaOH* titrated interferometrically with a 2.294 *N* solution of *HCl*

The accuracy and precision of the method are satisfactory. The best accuracy was achieved in titrations of dilute solutions in a 40 mm cuvette, since the instrument is more sensitive for smaller concentrations. When the titrations were carried out with a decinormal acid solution which approximately corresponded to the concentrations of the titrated substances, the accuracy of the results was affected by the dilution of the solution during the titration. In this case the obtained points did not lie on a straight line. This effect is shown in Fig. 2 in which curve A represents the neutralization curve of an approximately 0.12 N sodium hydroxide solution with 0.1 N hydrochloric acid solution. Curve B shows the changes of the refractive index of the same sodium hydroxide solution upon dilution.

The dilution effect is avoided when the concentration of the titrating agent is several times greater than the concentration of the titrated substance: then the error is smaller and the reproducibility is better. In titrations of solutions of greater concentration, the amounts of titrating agent which are added after the equivalenced point should be very small in order to avoid changes of the refractive index value.

Fig. 2 shows the typical shape of the titration curve which is obtained in the titration of a strong base with a strong acid. The titration is rapid and precise; the deviations of some points are due to changes of the temperature in the course of the titration. Moderate amounts of salts do not affect the results.

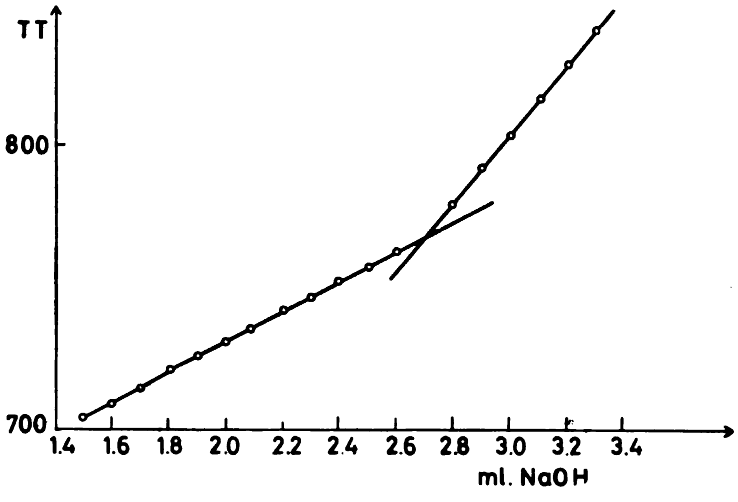

Figure 3

3.00 *ml* of 0.1077 *N* CH_3COOH titrated interferometrically with a 0.1186 *N* solution of *NaOH*

The diagram in Fig. 3 shows the neutralization curve of acetic acid and sodium hydroxide; it differs from the above curve in that the refractive index increases constantly, the increase being abrupt after the equivalence point. The neutralization curve of acetic acid in greater dilutions is almost the same as the so-called salt line of sodium acetate.

The results of interferometric titrations of bases with acids in water are given in Table 1.

TABLE I

Length of the cuvette used (*mm*)	Normality of the *HCL* or CH_3COOH*	Number of determinations	*NaOH* taken	*NaOH* found mg	Error in %
10.05	0.1193	6	26.00	25.83±0.40	−0.65
20.01	0.1193	3	17.00	16.99±0.01	−0.05
10.05	0.3055	4	16.00	16.24±0.16	1.5
10.05	0.8256	6	16.00	15.94±0.17	−0.37
10.05	2.2940	6	14.00	13.86±0.06	−1.00
10.05	0.2484*	3	19.00	19.00±0.08	0.00

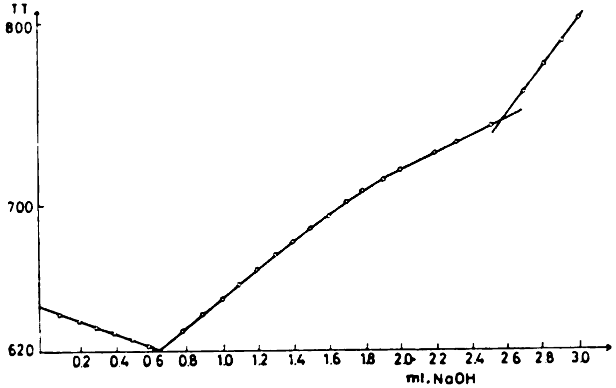

Figure 4

Mixture of 0.82 *ml* of 0.9948 *N* H_2SO_4 and 2.10 *ml* of 0.1077 *N* CH_3COOH titrated interferometrically with a 0.1270 *N* solution of *NaOH*

A mixture of a strong and a weak acid can also be determined by interferometric titration, but the error is rather great. Fig 4 shows the neutralization curve of a mixture of sulphuric and acetic acid with sodium hydroxide and the results of some titrations are given in Table 2.

TABLE 2.

Length of the cuvette (mm)	Normality of *NaOH*	Nr. of determinations	Taken a) H_2SO_4 + b) CH_3COOH (mg)	Found a) H_2SO_4 + b) CH_3COOH (mg)	Error %
20.01	0.1210	6	a) 7.00 b) 13.00	a) 6.82±0.06 б)13.31±0.12	2.9 2.4

The above described titrations were carried out directly in the cuvette. In order to avoid difficulties in selecting the concentration and cuvette length, we also carried out titrations in an erlenmeyer flask which was kept at the same temperature as the interferometer cuvette. In the course of the titration small amounts of solution were transferred by means of a pipette from the flask to the cuvette. In this way the concentration and volume of the titrated solution do not represent any problem. The mean deviation from six determinations amounted to ±0.37% with respect to 74 mg of sodium hydroxide.

TITRATIONS IN GLACIAL ACETIC ACID

Titrations in nonaqueous solutions are almost exclusively carried out in closed systems in order to avoid the effect of moisture. Titrations in glacial acetic acid represent an exception since they can be performed in open systems as well. Therefore we carried out the interferometric titrations in glacial acetic acid.

Preliminary investigations showed that the presence of water in the solvent affects the results of interferometric titrations much more than in other electrochemical methods, where the percentage of water in the solvent can amount to 1%(8). Therefore the acetic acid used for interferometric titrations should contain the minimal amount of water or excess acetic anhydride. The system should be protected from atmospheric moisture, but the performance of titrations in hermetically closed systems requires special adaptation of the instrument.

The titrations were carried out in closed erlenmeyer flasks from which portions of 1.00—1.50 ml were pipetted and transferred into the cuvette which was then closed; measurements were made five minutes later. This time period is required for the equilibration of the temperature of the solution in the cuvette. Thermostating of the cuvette by means of water leads to the deformation of the interferometric curve on account of the interaction of acetic acid vapors and water, thermostating by means of glacial acetic acid requires the use of special plastic flasks. The "ascending" of the acetic acid solution along the walls of the cuvette represented another difficulty met in the course of the work, the latter was avoided by spreading a thin layer of a silicon grease on the upper border of the cuvette and by closing the cuvette with a plastic cover.

Glacial acetic acid was used as the reference solution.

The equivalence point of the titrated solutions was determined by means of the following procedures:

1) By direct titration of the solution with perchloric acid solution of known normality;

2) By indirect titration, i.e. by adding an excess of perchloric acid to the solution, and by retitrating its excess with standard sodium acetate solution;

3) By back-titration, i.e. by titrating the perchloric acid solution of known normality with the solution of the substance studied.

In the direct titration, in the vicinity of the equivalence point there appears an abrupt decrease of the refractive index value which sometimes renders impossible the determination of the titration end point. This effect is shown in the following diagram, in the case of the direct titration of cinchonine:

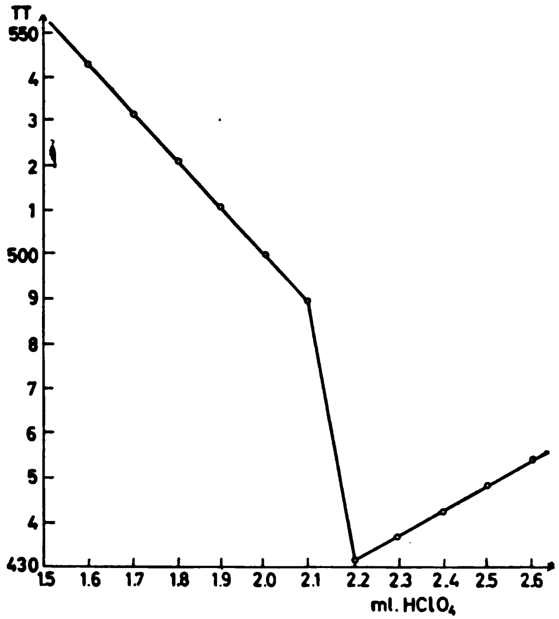

Figure 5

Interferometric titration of 38 *mg* cinchonine in 10 *ml* glacial acetic acid with a 0.1189 *N* solution of $HClO_4$

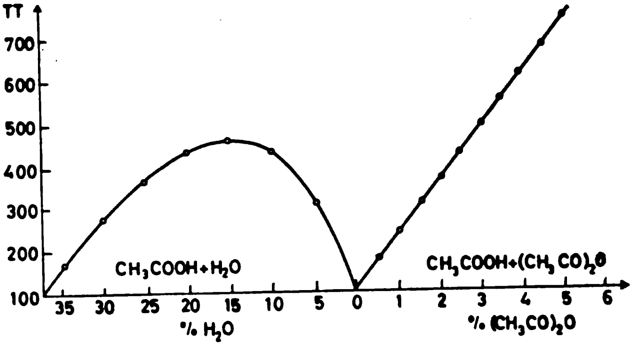

Figure 6

Changes in refractive indexes of a mixture of acetic acid and water (left), and acetic acid — acetic anhydride (right).

This behavior of the system in the vicinity of the equivalence point arises from the reaction of water with acetic acid anhydride, catalyzed by perchloric acid. Different amounts of water and acetic acid anhydride are present in the solvent and in the titrating agent; until the equivalence point there is no free perchloric acid in the system and the reaction of water with acetic acid anhydride is very slow. The appearance of a small excess of perchloric acid at the equivalence point catalyzes the reaction of water and acetic acid anhydride, which leads to an abrupt decrease of the refractive index value. This effect may be expected also on the basis of the diagram in Fig. 7. The right line shows the increase of the refractive index value of acetic

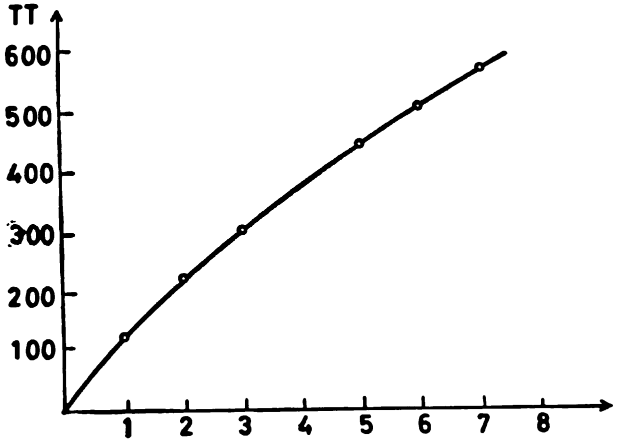

Figure 7

Changes of refractive indexes of a mixture of $CH_3COOH—HClO_4$

acid solution with an increasing amount of acetic acid anhydride, and the left line shows the changes obtained by adding water to the acetic acid solution.

From the diagram it follows that the reaction between small amounts of water and acetic acid anhydride always causes a decrease of the refractive index value, since the reaction product is acetic acid, whose refractive index is the lowest. When perchloric acid solution is added after the equivalence point, the values obtained on the micrometer increase, indicating that the refractive index of the system is also increasing, and this is consistent with the diagram of the acetic acid-perchloric acid system (Fig. 8).

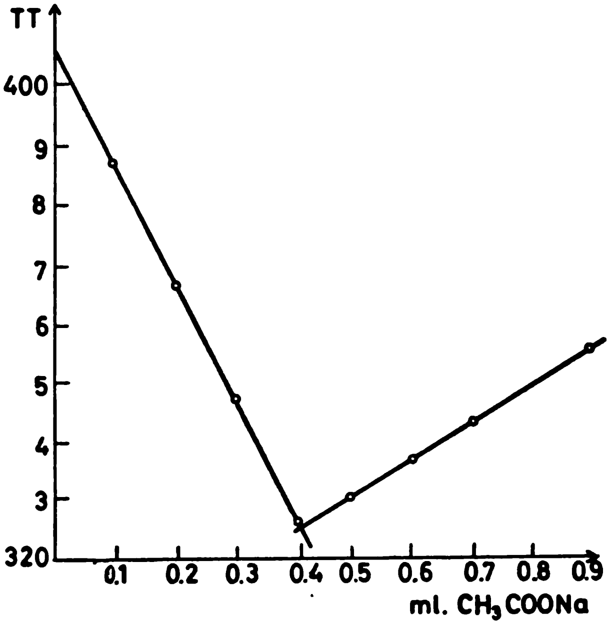

Figure 8

Neutralization curve obtained by indirect interferometric titration: 24.68 *mg* of triethylamine were mixed with 2.40 *ml* of 0.1189 *N* solution of perchloric acid and the mixture was titrated back with a 0.1000 *N* solution of sodium acetate in acetic acid.

Direct titration with perchloric acid gives satisfactory results, but its disadvantage is that the titrating agent, in the vicinity of the equivalence point, must be added drop by drop. Therefore the titration is time-consuming. In the determination of the titration end point we assume that an excess of perchloric acid appears after the equivalence point, and this is true only when strong or medium strong bases are titrated; in the case of weak bases this procedure is not adequate on account of solvolysis$^{(9)}$. In this way we have determined novalgin with satisfactory accuracy (Table 3); novalgin

TABLE 3.

Normality of $HClO_4$	Novalgin taken in *g*	Found by interferometric titr. in %	Error in %
1.0000	0.1000	98.4	−0.6
0.7843	0.1300	98.45	−0.55
0.4785	0.1300	98.5	−0.5
0.2415	0.1000	98.9	−0.1
0.2415	0.0900	98.0	−1.1
0.2415	0.0875	98.9	−0.1
0.2415	0.0850	99.1	0.1
0.2473	0.0820	98.5	−0.5
0.2473	0.0800	98.9	−0.1
0.2415	0.0800	98.9	−0.1

TABLE 4.

		Indirect titration			Back titration		
Titrated substance	Nr. of det.	Taken *mg*	Found *mg*	Error in %	Taken *mg*	Found *mg*	Error in %
Sodium acetate	6	21.00	20.98±0.03	−0.14	55.00	52.09±0.30	−1.72
Novalgin	6	29.00	29.23±0.10	0.79	30.00	30.26±0.11	0.87
Sodium formate	6	34.00	34.00±0.18	0.00	14.00	14.24±0.27	1.90
Sodium salicylate	6	34.00	33.88±0.17	−0.35	16.00	15.84±0.28	−1.0
Sodium benzoate	6	31.00	31.02±0.15	0.06	14.00	14.21±0.14	1.5
Diethylamine	6	—	—	—	12.00	11.91±0.13	−0.75
Triethylamine	6	28.00	27.92±0.07	−0.29	16.00	15.95±0.09	−0.31
Cinchonine	6	40.00	39.90±0.22	−0.25	25.00	25.06±0.24	0.24
Antipyrine	6	30.00	29.92±0.14	−0.27	33.00	33.14±0.31	0.42

determination by means of retitration and back-titration gave less accurate results.

Interferometric titrations are more rapid when the indirect procedure or back-titration are applied. Difficulties arising from the reaction of water with acetic acid anhydride are avoided, only in some cases the first values after the equivalence point do not lie on a straight line. However, the titration end point is obtained from the intersection point of two straight lines in these cases also. The dilution effect is not apparent. The curve obtained in the determination of triethylamine by indirect titration is shown in Fig. 8.

All titrations were carried out in an erlenmeyer flask from which portions of the solution were transferred into a cuvette of 5 mm or into a cuvette with a glass wedge in which the thickness of the layer was 1.05 mm.

The titrated substances and the results are shown in Table 4.

From table 4 it is seen that the results obtained by indirect titration are more accurate than by back-titration.

The examples given show that interferometric titrations can be successfully carried out in glacial acetic acid although with greater difficulties than in aqueous solutions. If the titrations are performed in special closed cuvettes, the accuracy is augmented, the required titration time is shortened and the experimental technique is simplified. Further research is in progress.

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INDIRECT COULOMETRIC TITRATIONS. PART I. THE DETERMINATION OF ZINC

by

OLIVERA Ž. PAVLOVIĆ and SRETEN N. MLADENOVIĆ

Continuing our earlier investigations on indirect coulometric methods(1, 2, 3, 4), we studied the possibility of direct determination of zinc ions in aqueous solutions as with aluminum ions. The method is based on the use of the hydrolysis phenomenon.

Zinc salts, being salts of a weak base, hydrolyze in aqueous solutions, giving slightly soluble hydroxide and liberating an equivalent amount of acid:

$$Zn^{2+} + 2H_2O \rightleftarrows Zn(OH)_2 + 2H^+ \qquad (1)$$

By removing the hydrogen ions from the system — either by the addition of alkalis, with which the hydrogen ions are converted into undissociated water molecules, or by means of electrolysis, whereby they are reduced at the cathode — the equilibrium is shifted from the left to the right side, and the hydrolysis can be carried out quantitatively. The quantitative precipitation of zinc hydroxide is reported to take place at pH = 8; at pH = 10.5 the dissolution begins to occur and at pH = 12—13 the dissolution of the precipitate is complete(5). On the basis of these properties, we carried out a determination of zinc salts by coulometrically titrating the liberated acid in the presence of an acid-basic indicator whose interval of color change lies within the region of pH 8—10. The amount of electricity consumed for the reduction of $2H^+$ ions, as seen from equation (1), is equivalent to the total amount of zinc salt which had hydrolized.

The aim of our investigation was to find out the experimental conditions necessary for the electrolysis of zinc salt solutions with the catholyte being separated from the anolyte, which would allow only the reduction of hydrogen ions to take place at the cathode. Moreover, we desired to study the effect of current density, zinc ion concentration and temperature on the accuracy of the results.

EXPERIMENTAL

The starting substances were of p.a. purity.

The titer of 0.05 N zinc sulphate solution, obtained by dissolving the weighed amount of salt in redistilled water, was determined by complexometric titration with 0.05 N EDTA solution in the presence of Eriochrom black T(6). The factor of the solution for titration was determined by means of a standard 0.05 N zinc sulphate solution prepared by dissolving metallic zinc (p.a. Merck) in dilute sulphuric acid.

The investigations were carried out by means of the apparatus which is used in all coulometric determinations at constant current.

The source of the constant current was a Yugoslav current and voltage stabilizer "Nikola Tesla", which gives a current of 4—140 mA, stabilized 1‰ for currents above 10 mA.

The current strength in the circuit was measured by means of an "Iskra" precision milliamperometer, type BL 2, class 0.5, which was gauged (adjusted) by compensation method against a precise resistor Trüb-Träuber, class 0.02.

The time of current flow was measured by means of a chronometer with an accuracy of ±0.2 second.

The cell for the electrolysis consisted of two glasses connected with an electrolytic bridge containing agar-agar saturated with potassium chloride. The cathode was a Winkler electrode of Pt-gauze, whose surface was about 85 cm^2 (the height of the cylinder was 50 mm and its diameter 50 mm); the anode was a platinum spiral electrode of 2.8 cm^2 surface (Ø of the wire = 0.5 mm, l = 18 cm). Intense mixing of the catholyte during the titration was effected by means of an electric stirrer.

Before the beginning of the determination, the catholyte was titrated in the presence of phenolphtalein until the appearance of a pink color. Then, a weighed amount of the substance to be tested was added to the catholyte. The acid liberated upon hydrolysis was then titrated until the appearance of the same pink color. The catholyte was a zinc sulphate solution which contained no additional conducting salt, and the anolyte was a 0.05 N sodium sulphate solution. The amount of electricity consumed in the titration of the acid liberated upon hydrolysis is equivalent to the amount of Zn^{2+} ions.

RESULTS AND DISCUSSION

The effect of the current density, the concentration of zinc ion in the solution, and the temperature on the determination of zinc by the indirect coulometric method is shown in Table 1. From Table 1, it is seen that the deviations between individual measurements depend on the amount of substance used, or the concentration of zinc ions in the solution, on the current density and on the temperature of the solution. It was found that a decrease in current density and a decrease in the concentration, as well as an increase in the temperature, diminish the deviations between individual measurements.

TABLE 1.

Effect of current density, concentration and temperature on the indirect coulometric titration of zinc

anolyte: 0.5 *N* Na_2SO_4

indicator: phenolphtalein

No. of exper.	*D* (*mA/cm*^{2})	Temp. (°*C*)	Conc. of Zn^{2+} (*M*.10^3)	Amount of *Zn*		Relative error (%)
				Taken (*mg*)	Found (*mg*)	
1	2	3	4	5	6	7
1	2.88	room	1	5.09	4.40	−13
2	1.44	„	1	5.09	4.50	−12
3	0.15	„	1	5.09	4.78	− 7
4	0.11	„	1	4.75	4.62	− 3
5	0.11	„	1.5	6.73	6.24	− 7
6	0.11	„	2	8.41	7.54	−10
7	0.11	70	2	8.41	8.07	− 4
8	0.11	85	2	8.41	8.89	+ 6

TABLE 2.

Indirect coulometric titration of zinc

anolyte: 0.5 *N* Na_2SO_4

current density: 0.11 *mA/cm*^{2}

temp.: room

concen. of Zn^{2+}: $2.10^{-4}-10^{-3}$ *M*

No. of exper.	No. of determn.	Titration of acid		Amount of *Zn*		Mean error (%)	Max. error (%)
		Current (*mA*)	Time (*sec*)	Taken (*mg*)	Found (*mg*)		
1	2	3	4	5	6	7	8
1	3	10.01	302.0	1.018	1.024	+0.6	+1.0
2	3	10.01	399.7	1.357	1.355	−0.1	+0.5
3	3	10.01	501.6	1.967	1.700	+0.2	+1.0
4	3	10.01	587.0	2.035	2.039	+0.2	+0.4
5	3	10.01	748.2	2.535	2.537	+0.1	−0.5
6	4	10.01	848.5	2.882	2.877	−0.2	−0.7
7	3	10.01	1000.7	3.390	3.393	+0.1	+0.3
8	3	10.01	1092.7	3.730	3.705	−0.7	−0.9
9	3	10.01	1247.8	4.239	4.231	−0.2	−0.4

Accordingly, to reduce the error of the determination, one should work with small current densities (obtained either by decreasing the current strength or by augmenting the surface of the electrode), with small concentrations of zinc in the solution and at elevated temperatures. This error is probably due to the formation of basic salts and the slow rate of hydrolysis.

A survey of the experimental conditions and the results obtained in the determination of zinc in concentrations ranging up to 10^{-3} M, with a current density of 0.11 mA/cm^2, is given in Table 2. The accuracy and reproducibility of the results are satisfactory. Maximal deviations between individual measurements in the region of these concentrations lie within the limits of ±1%. Hence, the indirect determination of zinc-with a current density of 0.11 mA/cm^2 at room temperature, and with an error less than +1%, can be carried out only with concentrations of up to 10^{-3} M. On account of a too vague change of indicator color, the method is not convenient for the determination of zinc concentrations smaller than 10^{-4} M. Inspite of the favorable effect of elevated temperatures on the results obtained, the measurements were carried out at room temperature on account of the troublesome work at elevated temperatures.

The accuracy and precision of the method for amounts of zinc up to 4.2 mg (1×10^{-3} M) were determined by statistical analysis of the results, i.e. by application of the method of minimal squares(7, 8). Statistical analysis showed that the accuracy and precision of the method for the given range of concentrations are satisfactory; this means that no systematic error is involved. The accuracy of the method was found to be —0.15% and the precision ±0.19%. The precision of the results lies within the limits of the standard error of the method ±0.3%) determined for the smallest amount of zinc investigated.

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COULOMETRIC DETERMINATION OF SOME SULFONAMIDES

by

ZORA T. BLAGOJEVIĆ, KOSTA I. NIKOLIĆ
and RADOMIR B. POPOVIĆ

In a previous paper(1) we described a precise and simple method for the coulometric determination of some sulfonamides. Continuing our study of the coulometric titration of these compounds, we developed a procedure which made possible the coulometric titration of those sulfonamides which, on account of their slight solubility in acid and neutral media, we could not determine before.

Slightly soluble sulfonamides were converted into soluble salts by the addition of sodium hydroxide in excess. The amount of sulfonamide was calculated from the difference between the number of coulombs consumed for the titration of sodium hydroxide solution in the absence and in the presence of sulfonamide. By means of this procedure, sulfadiazine, sulfamethoxypyridazine and sulfacetamide were determined.

The coulometric method described in the previous paper(1) was applied to the determination of the following sulfonamides: sulfadimethoxine, irgamide and sulfafurazole. The results obtained showed that in these cases a satisfactory accuracy was obtained as well.

EXPERIMENTAL

Reagents:

— 1 M sodium sulfate solution (322.21 g of sodium sulfate + + $10H_2O$ was dissolved in water and made up to 1000 ml)

— 0.01 N sodium hydroxide solution

— Thymolphtalein: 1 g was dissolved in 100 ml of 96% ethanol

— Phenolphtalein: 1 g was dissolved in 70 ml of 96% ethanol and the solution was diluted to 100 ml

— 96% Ethanol

Apparatus:

Direct current was obtained by means of the apparatus described in the previous paper. Platinum electrodes were used. The cathodic and anodic spaces were separated and connected by means of a small flask with a porous bottom which was covered with agar-agar containing dissolved potassium nitrate.

Procedure:

The concentrations of the investigated sulfonamides, solvents and indicators used are given in Table 1.

TABLE 1.

Substance	Solvent	Concentration % g/V	Indicator
Sulfadiazine (2-sulfonamido-pyrimidine)	70 *ml* 0.01 *N NaOH* + 30 *ml* H_2O	0.1	Thymolphtalein
Sulfamethoxypyridiazine (3-sulfanilamido-6-methoxy-pyridazine)	70 *ml* of 0.01 *N NaOH* + 30 *ml* H_2O	0.1	Thymolphtalein
Sulfacetamide (sulfanilacetamide)	70 *ml* 0.01 *N NaOH* + 30 *ml* H_2O	0.1	Phenolphtalein
Sulfadimethoxine (4-sulfonamido-2,6-dimethoxypyrimidine)	96% Ethanol	0.5	Thymolphtalein
Irgamide (sulfanildimethylacyrlic amide)	96% Ethanol	0.5	Thymolphtalein
Sulfafurazole (5-sulfanilamido-3,4-dimethylisoxazole)	96% Ethanol		Phenolphtalein

The determinations were carried out with pure substance- which are used as raw materials in the production of galenic sulfos namide drugs.

Determination of sulfadiazine, sulfamethoxypyridazine and sulfacetamide

Solutions of the corresponding sulfonamides were prepared according to the data given in Table 1. A volume of the sulfonamide solution containing 10 mg of the substance was pipetted into the anodic space of the flask and 100 ml of sodium sulfate solution and 2 drops of the indicator were added. The solution was then stirred and a current of constant strength was passed through until a change in the indicator color was apparent; the time period of the current flow was measured. Simultaneously a blank run was titrated coulometrically. The solution for the blank run contained all substances except sulfonamides.

The difference between the number of coulombs consumed in the titration of the blank run and the sulfonamide solution is the number of coulombs used for the titration of the sulfonamide. The amount of sulfonamide is calculated from Faraday's law.

Determination of sulfadimethoxine, irgamide and sulfafurazole

A volume of the sulfonamide solution containing 10 mg of the substance was pipetted into the cathodic space and 10 ml of sodium sulfate solution (in the case of sulfafurazole, 20 ml) and 2 drops of indicator were added. The solution was stirred and a constant current was passed through until the color change of the indicator; the current flow time was measured.

At the same time a blank run was titrated (ethanol, sodium sulfate solution, indicator).

The difference between the number of coulombs consumed in the titration of the sulfonamide solution and the blank run is the number of coulombs consumed for the titration of the sulfonamide, and the corresponding amount of sulfonamide can be calculated from Faraday's law.

DISCUSSION

The results obtained by the coulometric procedure are shown in Table 2.

TABLE 2.

Substance	Taken *mg*	Number of determinations	Found *mg*
Sulfadiazine (2-sulfanilamido-pyrimidine)	10	5	10.024 ± 0.003
Sulfamethoxypyridazine (3-sulfanilamido-6-methoxy-pyridizine)	10	5	9.988 ± 0.002
Sulfacetamide (sulfanilacetamide)	10	5	10.052 ± 0.003
Sulfadimethoxine (4-sulfanilamido-2-6-dimethoxy-pyrimidine)	10	5	9.974 ± 0.004
Irgamide (sulfanildimethylacrylic amide)	10	5	10.044 ± 0.001
Sulfafurazole (5-sulfanilamido-3,4-dimethyl-isoxazole)	10	5	9.976 ± 0.003

From Table 2 we see that the results showed quite satisfactory accuracy although in some cases positive or negative deviations were obtained. These deviations can be ascribed to the noncoincidence of the equivalence point with the titration end point, and not to any concurrent reaction which would affect the electrochemical process. Since the errors are within the limits permitted by Yugoslav Pharmacopeia, we used phenolphatalein and thymolphatalein as the indicators even in the case of those sulfonamides which showed deviations. The titration end point was easily detected on account of the use of one-colored indicators. The results show that this method can be recommended for the determination of small amounts of sulfonamides.

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SPECTROCHEMICAL ANALYSIS OF IMPURITIES IN GRAPHITE

by

SRBOBRAN R. RAJIĆ

1. INTRODUCTION

Determinations of impurities in graphite have been reported in many papers. Since the sensitivity required for the detection of impurities was not achieved by means of the direct spectrochemical method, this problem was approached in different ways. One way of increasing the sensitivity consisted in concentrating the impurities by partial or complete combustion of the graphite and by analyzing the ash obtained(1, 2), or the graphite was mixed with a suitable carrier and the mixture was burnt up. The carrier was then analyzed by means of a convenient spectrochemical method. By these procedures only a small number of elements were usually determined; moreover, some of these methods are insufficiently reproducible.

Another kind of investigation aimed to increase the sensitivity of direct spectrochemical methods. Thus, the double arc method for the combustion of samples was used(6). A number of different carriers were also investigated, as for example in the determination of boron in graphite(7). In boron determination, fluorides of some metals were used as carriers in order to increase the volatilization of boron from the electrode crater into the plasma of the direct arc. The Webb's effect(8), which consists in the increased intensity of the spectral lines of some elements in the arc if sodium chloride is previously added to the graphite, was used by Goleb *et al.*(9) for the determination of a great number of elements by the direct spectrochemical method. This procedure rendered the method very sensitive, but its disadvantage lies in the semiquantitative results obtained, the estimations being carried out visually in comparison to standard samples. The same authors also report a procedure for the determination of poorly volatile elements in graphite ash.

In our investigations we wanted to estimate which sodium salt can be used as the best carrier and to explain the effect of these salts in the intensity of the spectral lines of the impurities; moreover, we wanted to increase the reproducibility of the method.

2. ANALYTIC PROCEDURE

a) *Procedure with a carrier added*

The procedure used for the determination of 24 elements in graphite was based on the use of spectrographically pure sodium fluoride as the carrier and bismuth as the internal standard. Sodium fluoride increases the intensity of the spectral lines of a great number of elements and decreases the background blackening of the spectrum. In addition, it depresses the cyanogen bands. Samples were prepared by mixing 84 parts of graphite with 16 parts of sodium fluoride which contained 60 ppm of bismuth; 25 mg of the mixture was placed in a graphite electrode and was burnt up in a direct arc of 10 amperes. The spectra were taken with a Jarrell Ash spectrograph with a flat grating in the first spectral order in which the dispersion was 5 Å/mm. Ilford Ordinary photoplastes were used and they were developed in a Kodak-19 developer for 40 minutes at 20°C. The electrodes were made from graphite rods produced by the National Carbon Co. The diameter of the electrode crater was 4 mm and its depth was 4 mm as well. The thickness of the wall was 0.5 mm. The upper electrodes were raw sticks of a diameter of 3.1 mm produced by the same company. Standards for the analysis of graphite with sodium fluoride as the carrier were prepared by mixing spectrographically pure graphite with oxides of the investigated elements in a mortar. Other standards containing a smaller content of impurities were obtained by successive dilution of the mixture with graphite. By this procedure, the presence of Al, Ag, Au, Ba, Cd, Cu, Cr, Ga, Ca, In, Fe, Pb, Mg, Mn, Mo, Ni, Si, Sb, Sn, V, Ti, Zr and Zn in graphite was determined.

For the determination of boron in graphite, zinc fluoride was used as the carrier and simultaneously as the internal standard. Graphite samples were mixed with zinc fluoride in a weight ratio of 9 : 1; 150 mg of the mixture was weighed and placed in graphite electrodes whose crater had a diameter of 5 mm and was 12 mm deep. These electrodes were made of boron-free graphite produced by the National Carbon Co. The upper electrode was a graphite rod of a diameter of 3.1 mm. The samples were burnt in a direct arc of 15 amperes. Exposure time was 50 seconds. Photographs were taken on Eastman Kodak SA-1 photoplates. By this procedure, amounts of boron ranging from 0.05 to 5 ppm were determined.

b) *Procedure without a carrier*

Another procedure, without a carrier, was applied in the determination of As, Be, P, Te, Bi, Hg and Cd. Samples were directly spectrographed in a direct arc of 10 amperes. Kodak B-10 emulsion was used. Standards for the estimation of these elements were made by mixing graphite with oxides of the various elements, except in the case of phosphorus, where sodium phosphate was used. Standards with a smaller content of impurities were made by diluting the mixture with graphite. Fifty miligrams of the sample or the standard were weighed and placed in electrodes having a crater of a diameter of 4 mm and a depth of 6 mm.

The spectrograms obtained by means of all three techniques were measured with a Jarrell Ash microphotometer. Calibration of the photoplates was carried out by means of the iron spectrum obtained with a rotating step sector. Working curves were drawn in a log-log system. The precision of the method was calculated from standard deviation and was found to range from ±5 to 15%.

3. DISCUSSION OF RESULTS

In order to establish the effect of sodium salts on the volatilization of impurities in graphite we used the moving plate technique. Differences in the volatilization of elements were obvious (Figs. 1 and 2).

The extent of intensification was different for different elements. It might be stated that sodium and lithium halides exhibit a greater intensifying effect than other salts of sodium and lithium. The mechanism of the action of carriers on impurities is different. The results in Table 1 show that the intensities of the spectral lines of elements

TABLE 1

Effect of some sodium and lithium salts on the intensification of the spectral lines of elements present in graphite

Wavelength, λ	Intensities						
	Be 2348	*Hg* 2536	*B* 2498	*Mn* 2575	*Ni* 3050	*V* 3184	*V* 2952
Without carrier	4.25	6.0	3.0	2.8	1.1	N.D.	1,2
With teflon	2.7	5.6	3.1	2.8	3.1	4.2	1.3
With *NaCl*	3.3	3.7	2.5	2.1	2.9	9.5	1.0
With *NaF*	3.2	4.8	2.3	3.7	5.6	9.7	1.1
With Na_2SO_4	2.1	3.8	2.1	2.6	2.8	8.8	1.1
With *LiCl*	2.8	2.9	1.8	2.6	3.7	8.7	1.2
With *LiF*	3.5	4.0	2.7	4.5	6.0	9.8	1.2

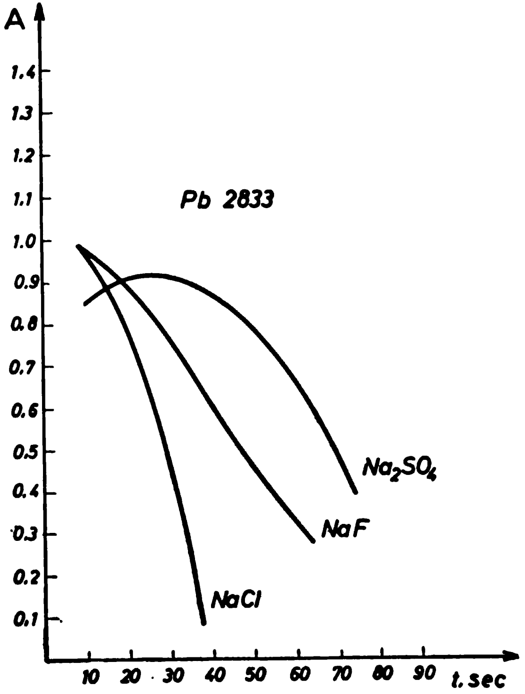

Fig. 1. Volatilization curves of lead in the presence of NaF, NaCl and Na_2SO_4

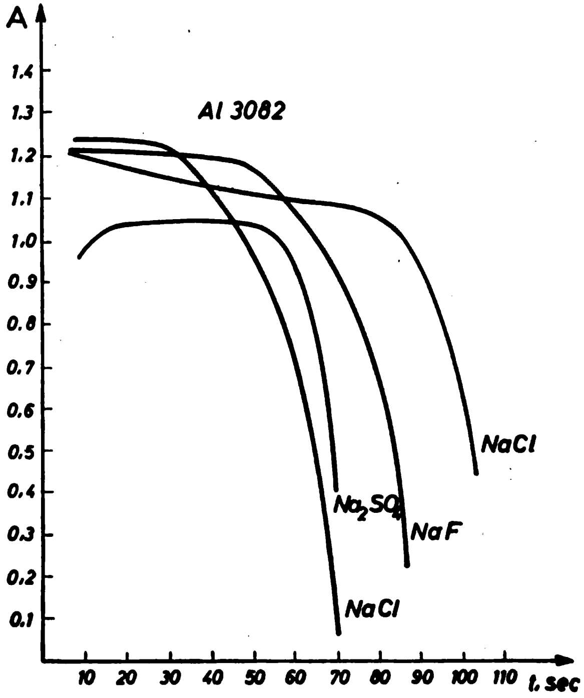

Fig. 2. Volatilization curves of aluminum in the presence of NaF, NaCl, and Na_2SO_4

with a high ionization potential are decreased when sodium and lithium salts are used as carriers, since the latter metals possess low ionization potentials. This depressive effect of the carriers on the spectral lines of elements with a high ionization potential is brought about by a decrease of the plasma temperature. This effect is very pronounced in the case of Be, Hg and B.

With elements not possessing a high ionization potential, such as Al, V and Mo, the carrier exhibits an intensifying effect. If the intensities of an arc and a spark line of the same element are measured, the extents of intensification are different. As an example, we can take the results for the vanadium lines, 3184.0 Å and 2952.1 Å, given in Table 1.

The chemical processes taking place at high temperatures in the electrodes between the elements present in the graphite and the substances added involve the formation of very volatile chlorides and fluorides. We were especially interested in the effect of the fluoride ion on the volatilization of impurities. Therefore we used teflon, which easily dissociates and liberates fluorine, as a carrier. Fluorination of impurities was observed with a great number of elements (V, Mo), but not with all of them.

As can be seen, the temperature of the plasma has a great effect on the intensities of the boron spectral lines. Thus, the use of a carrier having a high ionization potential should augment the detectable limit of boron, and this is in accordance with the results given in Table 2. In this way we can also explain the difference between the detectable limits of boron in the presence of LiF and CaF_2 (Table 2).

TABLE 2.

Detectable limits of boron with different carriers, in ppm

With ZnF_2	With NaF	With LiF	With CaF_2
0.1	0.8	1.0	2.0

The volatilization curves of boron in the presence of different carriers confirm this assumption as well. It is likely that thermochemical reactions involving the formation of boron compounds with the fluorides are involved.

We came to the conclusion that the detection and volatilization of an element from the electrode crater into the plasma of the direct arc depend on the change of the plasma parameter and on thermochemical reactions taking place in the crater of the electrode.

On the basis of these investigations, we decided to use sodium fluoride as the carrier; it intensifies also the spectral lines of silicon, but has no great advantages for other elements. In the selection

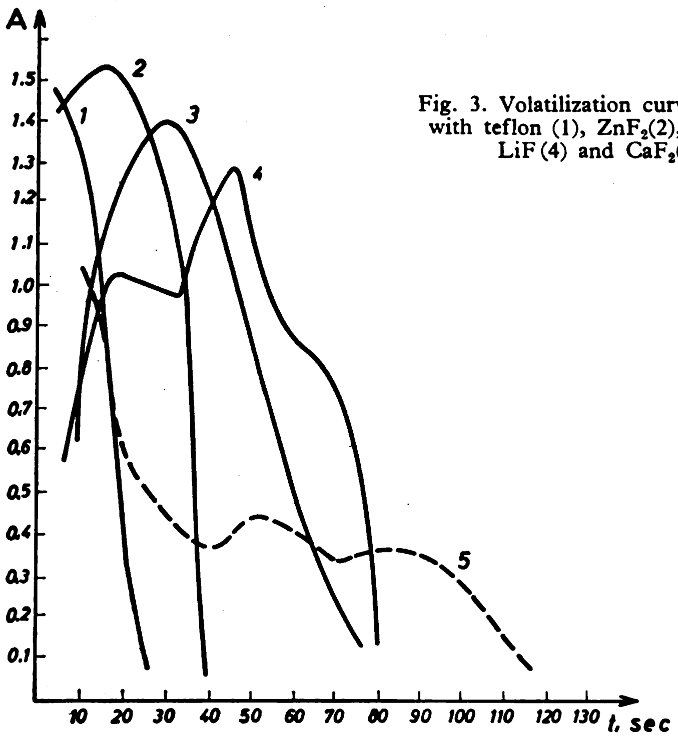

Fig. 3. Volatilization curves of boron with teflon (1), ZnF_2(2), NaF (3), LiF (4) and CaF_2(5)

of the electrode shape we took into account the fact that the elements volatilize more easily from shallow electrodes and that the basis does not essentially affect the background blackining. Sodium and lithium salts were found to depress molecular cyanogen bands.

Contrary to the success of many authors, our determinations of boron in graphite by means of sodium fluoride under the given

TABLE III

Spectrographic (a) *and spectorophotometric* (b) *analysis of a graphite sample*

Element	Content in *ppm*	
	a	b
Al	10.3	12.0
B	0.8	0.6
Fe	38.0	42.0
V	26.0	22.0
Mn	2.0	1.4
Cu	<1	<1
Mo	<5	<1

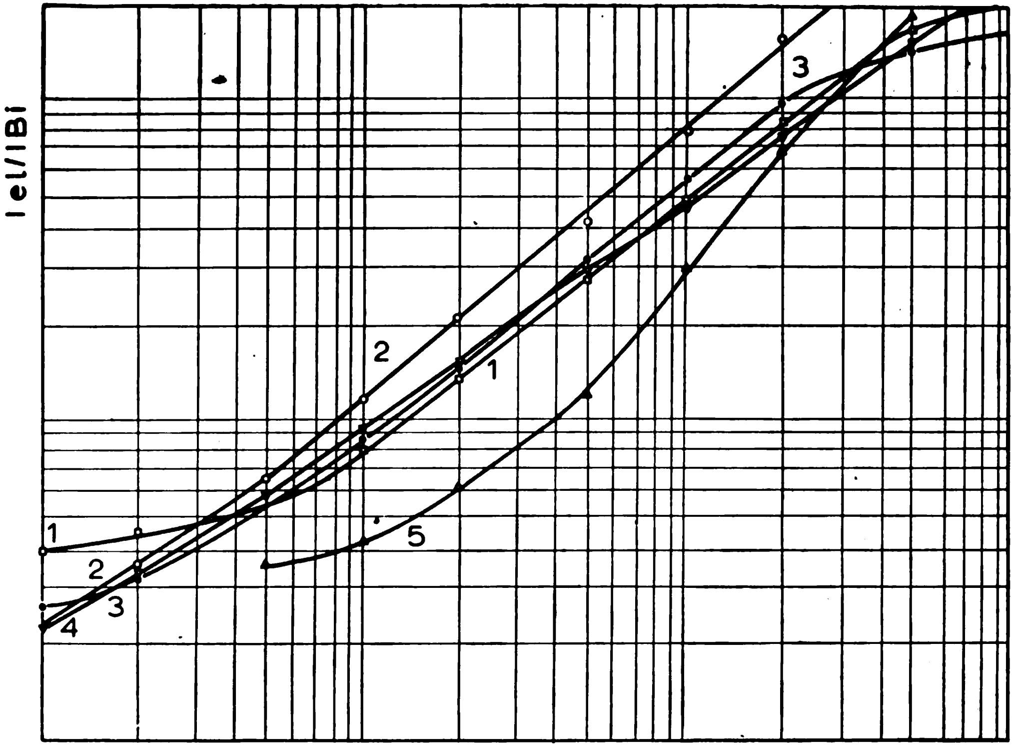

Fig. 4. Working curves for Mg (1), V (2), Ni (3), Mn (4) and Mo (5)

experimental conditions (combustion of samples in a direct arc of 15 ampers) were not satisfactory. The above described investigations may inpart explain our failure.

The method described is a modification of the semiquantitative method developed by Goleb *et al.* By taking an internal standard and by employing slightly different experimental conditions we obtained quantitative results.

Graphite samples were analyzed by the developed procedure and the results were compared with those obtained spectrophotometrically. The agreement between results was within the limits of the method error.

The sensitivity of the method for all elements ranges from 1 to 10 ppm, but it is limited by the content of the element used as the standard.

I wish to express my thanks to prof. Dr. Slobodan Ristić for suggestion given in the course of these investigations.

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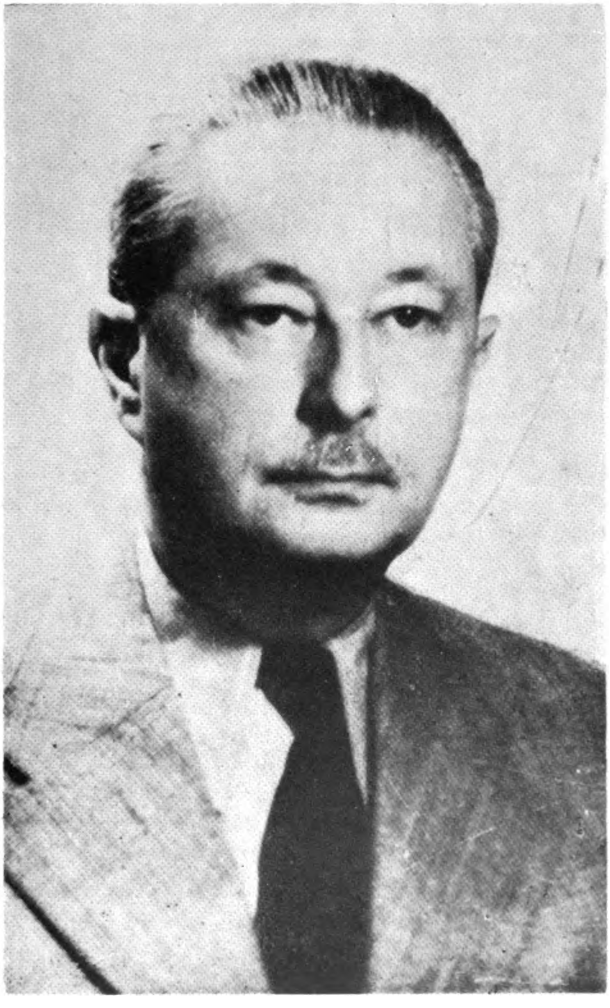

Panta S. Tutundžić
1900—1964

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PANTA S. TUTUNDŽIĆ
1900—1964

The life and work of Professor Tutundžić, Fellow of the Serbian Academy of Arts and Sciences, was bound up not only with teaching and research at the School of Technology, but also with the activity of the Serbian Chemical Society and the Union of Chemical Societies in popularizing science, and with local government work.

Panta Tutundžić was born in Belgrade on 15 November, 1900 in a civil servant's family. He attended elementary school and realgymnasium in Belgrade. After two terms at the Department of Mechanical Engineering of the Technical School of Belgrade University he enrolled, in October 1920, at the Technical High School in Berlin—Charlottenburg of the School of Industrial Chemistry. He graduated at this school at the beginning of 1925 and the same year, after having defended his doctoral thesis, he obtained the status of Doctor of Chemistry.

He began his University career on 1 July 1926, when he was appointed "docent" (assistant professor) for physical chemistry and electrochemistry at the Department of Technology of the Technical School of Belgrade University. As docent, in 1926 he founded, within the Department of Technology, the Laboratory for Physical Chemistry and Electrochemistry, as part of the Chemical—Technical Institute. He also organized experimental work in physical chemistry, in theoretical and industrial electrochemistry, in technical analyses of gases and microscopy.

In 1933 he was elected Associate Professor, and in 1948 Professor for physical chemistry and electrochemistry at the School of Technology.

From July 1926 to 1929 Prof. Tutundžić lectured in physical chemistry with theoretical and industrial electrochemistry, and when N. Pušin was elected professor for physical chemistry, Prof. Tutundžić lectured in theoretical and industrial electrochemistry as a separate

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In memory of one of the founders and longtime professors of the former Department of Technology and the School of Technology, the faculty of the School of Technology have decided on 8 November, 1964 to set up the Panta S. Tutundžić Prize for students of the present School of Technology and Metallurgy.

subject, from 1929—1941. After the liberation, when the Department of Technology was restored in the first post-war academic year 1945/46, Prof. Tutundžić re-commenced lecturing in theoretical and industrial electrochemistry, electrometallurgy, and colloid chemistry. In 1947 after the death of Prof. Pušin he resumed lecturing in physical chemistry and lectured on both subjects till his death in 1964. From 1952—1962 he taught electrochemical measurements.

In addition to lecturing at the School of Technology, he also taught at other schools of Belgrade University. From September 1950 to July 1952, as part time professor at the High School of Transport Engineering he lectured in Technology of Metals and Technology of Materials, from September 1952 to July 1957 at the School of Natural Sciences and Mathematics in electrochemistry, and from 1957 to 1958 at the Electrotechnical School in physical chemistry. He also lectured at refresher courses for secondary-school teachers.

He was the first dean of the School of Technology at which post he remained for several years (1948—1952). He also took part in the administration of the University as a whole, and for two years was Pro-Rector (1954—1956).

In 1930 when the Laboratory of Physical Chemistry and Electrochemistry was separated from the Chemical-Technological Institute and became an institute in its own right in the new building of the Technical School, with Prof. Pušin as Head, Prof. Tutundžić took advantage of these new opportunities to expand his teaching and research work.

After the liberation of Belgrade in 1944 he continued to work at the Department of Technology and applied himself vigorously to the restoration and improvement of the Department of Technology which had been greatly damaged during the war.

When the Technical School was separated from the University and became the Technical High School in 1948, the Department of Technology became the School of Technology whose first dean was Prof. Tutundžić. After that the School of Technology developed and expanded its activities rapidly, becoming an important teaching and scientific institution in which Prof. Tutundžić's influence was seen when new subjects and practices were introduced or planned and when new staff were elected.

Throughout his work at the University and the School of Technology he sought recognition of the School not only as the highest teaching institution but also as a recognized research institution.

He was the first lecturer in electrochemistry at the School of Technology of Belgrade University. He lectured for 38 years with the same enthusiasm and the same feeling of responsibility as the first day. He endeavored to acquaint his students with the latest achievements in the subjects on which he was lecturing. Lecturing and other teaching duties were for him commitments which had priority before any others. He could make contact with his audience immediately, thanks to his eloquence and very rich vocabulary. In a way all his own he knew how to approach the students, doing practical work or writing diploma theses, to encourage them and urge them on, using his knowledge as a teacher and his broad general education. He behaved in the same way with his graduate students.

The development of the School of Technology on modern lines in chemistry, technology, chemical engineering and metallurgy was made possible by the erection of a new building in 1959—1960, largely thanks to the persistence of the Dean, Professor Tutundžić. At this time he was extremely active in planning the curriculums, programs of particular subjects, etc., with his department and the School as a whole.

The foundation of the Chair and the Institute of Physical Chemistry and Electrochemistry, in all its scientific and other aspects of teaching, was the work of Professor Tutundžić. He was Professor and Director from 1948 to 1964.

Prof. Tutundžić was the initiator of the celebration of the 25th anniversary of the foundation of the Department of Technology at the Technical School. On his initiative and with his help the booklet "From the Department to the School of Technology 1925—1950" was published.

From 1926—1956 he encouraged and helped the publishing of scientific, teaching and other works by the members, of his department and of the Institute of Physical Chemistry and Electrochemistry.

In the same spirit he conceived the celebration of the 35th anniversary of the foundation of the Institute of Physical Chemistry and Electrochemistry and left in writing the titles of theses which would show the development of the Institute from 1930 to 1965.

He encouraged the collaboration of his department with similar institutions and enabled young people from other schools and institutions to get acquainted, individually or through courses, with the fields taught at his department.

He helped make it possible for a number of his collaborators to spend some time abroad in order to become acquainted with achievements in the fields taught, or to be taught at his department.

Modern aspects of electrochemistry and prospects for development of the electrochemical industry in Yugoslavia led Prof. Tutundžić to found, together with his co-workers, an electrochemical section. Within the Institute for Chemical, Technological and Metallurgical Research Prof. Tutundžić and his collaborators founded the Department of Electrochemistry in which projects that he had conceived in his first scientific works 30 years ago, were started or further developed.

Prof. Tutundžić personally and together with his collaborators worked in several fields of physical chemistry and electrochemistry. One of the fields of his scientific interest was electrochemical analytical methods. In this field, alone and with his collaborators he produced a number of outstanding works.

Galvanoelectric determination of metals only became widely applied after his work in this field. The rotating mercury electrode which he was the first to use showed that work with a mercury cathode could be simple and useful, and now mercury is widely used in analytical chemistry for separating cations.

His most important work in the field of electrochemical methods was on coulometric titrations. He began working in this field at the end of 1949, eleven years after the appearance of the first and almost the only works in it, which concerned only acidimetry. Prof. Tutundžić, who realized that coulometric titration may be extended to all fields of volumetric analysis, can be considered the originator or a pioneer of the following coulometric methods: iodometry, argentometry, metallometry, permanganometry, bichromatometry, indirect coulometric titration and coulometric titration of a multi-component system. His determination of thiosulphate by electrolytically produced iodine opened up the field of coulometric iodometry. This work demonstrated that constant current coulometric titrations can be done with very simple apparatus, and hence the importance of this titration for which it is not necessary to have a solution of iodine with a defined titer, which anyhow is not constant. Quantities of thiosulphate of 30—160 mg were determined to an accuracy of 0.75 to 0.30%.

Instead of titration of chlorides, bromides and iodides with a solution of silver nitrate, Prof. Tutundžić proposed their determination with silver cations obtained by anodic oxidation of silver using adsorption indicators to determine the end point. As it is possible to get very pure silver and as at the silver anode only the reaction $Ag \rightarrow Ag+ e$ occurs, it is possible to determine anions of halogens from the quantity of electricity passed with great accuracy. It was shown that it is possible to determine a halogen concentration from 1.10^{-2} to 8.10^{-4} mol/l to an accuracy of 0.17—1.30%. Ferro and ferricyanide ion were also titrated against silver cation but with amperometric determination of the end point.

In addition to argentometry, Prof. Tutundžić developed some new methods of metallometry such as: plumbometry, mercurometry, cuprimetry, bismuthometry. Using cations produced by anodic oxidation of these metals it is possible to determine a whole range of substances which with the cations form hardly soluble compounds. It was shown how to determine chromate, bichromate, oxalate, molybdate, tungstate, and iodate ion, and anthranylic acid, the latter being determined with cupric ion.

Prof. Tutundžić's most important contribution to the development of coulometric titration was his work on coulometric permanganometry, as he and his collaborators were the creators of this method. From considerations of the current density potential for a platinum anode in a solution of sulfuric acid and manganese sulfate conditions were determined under which the reaction $Mn^{2-} + 4H_2O \rightarrow MnO_4^- + 5e$ proceeds quantitatively. Permanganate ion so produced is immediately used for determining ferrous ion, arsenite, hydrogen peroxide, ferrocyanide and iodide. The end point of titration is determined by the redox indicators ferroin and nitroferroin, Microquantities of the substances mentioned were determined with an accuracy of ±1.0%. By working out the exact conditions for producing permanganate ion electrolytically Prof. Tutundžić developed a method for the coulometric determination of all substances whose oxidation potential is more negative than the reduction potential of permanganate ion.

Prof. Tutundžić also initiated coulometric bichromatometry, analogous to permanganometry.

With his work on indirect coulometric titration, for which the determination of aluminum and copper may be taken as examples, Prof. Tutundžić achieved further development of coulometry. Aluminum ion can be determined indirectly by coulometrical determination of hydrogen ion obtained by hydrolysis of an aluminum salt. It is possible to determine copper in acid solutions by electrolysing at constant current and evolution of hydrogen to the point of neutralization of the acid. If the quantity of electricity necessary for the neutralization of the acid and the total quantity of electricity for the deposition of copper plus the neutralization of acid is known, it is possible to determine copper in the sample without measuring its precipitate.

Prof. Tutundžić's last work in the field of coulometry was the application of coulometry to complex systems. As early as 1960 he and his co-workers announced their results on the coulometric determination of permanganate, bichromate and ferrous ion in the same sample. In the first stage permanganate and bichromate are titrated by electrolytically produced ferric ion. In the second stage, permanganate is reduced by adding a determined quantity of hydrochloric acid and only bichromate is determined by electrolytically produced ferrous ion. In the third stage, after reducing permanganate, bichromate and ferric ion with zinc, ferrous ion is titrated with electrolytically produced permanganate. In this titration both the anodic and cathodic spaces are used for the electrolysis. This indicates the possibility of applying coulometric titration to complex systems and its advantage over simple titration as it is not necessary to have standard volumetric solutions, and it is even possible to use as the titrant electrolytically produced substances whose solutions are not chemically stable. Considering that micro- and semi-micro quantities may be determined by the coulometric method, that it is possible to determine titers of standard solutions and perform oxidations with unstable oxidizing agents, that the coulometric method can be applied in physical chemistry for following the process and mechanism of formation of complexes, for the determination of valency states, for following the reaction rates, and that it enables the determination of 10^{-12} g/eq quantities of the titrant, the importance of Prof. Tutundžić's work for the development and application of coulometric analysis method is clear.

On the basis of results obtained in the field of coulometry, Prof. Tutundžić proposed before the International Union of Pure and Applied Chemistry, in Lisbon, in 1956, that the coulomb — the unit of quantity of electricity — should be taken as the universal standard in analytical chemistry, instead of the different substances used so far, i. e. that the titers of standard solutions should be determined coulometrically. By introducing the coulomb as a standard, all difficulties which analysts encounter in making standard solutions would be overcome, especially all subjective errors would be avoided, as the Lavoisier's masses in use so far, as Prof. Tutundžić used to say, would be substituted by the coulomb on the basis of Faraday's laws. Special interest was shown in this proposal as can be seen from the fact that it has been accepted by a number of scientists.

In 1933 Prof. Tutundžić started work in the field of physical chemistry and electrochemistry of non-aqueous systems, and continued it later with his collaborators. His works in this field may be divided in two groups: the first presenting results of studying these systems by viscosimetry, refractometry, conductometry, graphically by diagrams of state and density measurements, and the second group presenting results obtained by the potentiometric method.

As opposed to the previous methods used by others, Prof. Tutundžić introduced potentiometry for the study of non-aqueous systems. According to his conception this method should provide additional information about the behaviour of non-aqueous systems as it is based on measurement of individual relative electrode potentials, and not on the properties of the system as a whole. In order to be able to apply the potentiometric method, it was necessary to investigate the behaviour of a hydrogen and glass electrode in such systems and the influence of diffuse potentials on e. m. f. measurements in them.

It was proved that the potentiometric method for non-aqueous systems is not inferior to other methods in sensitivity, and that the differences observed with various methods for non-aqueous systems result from the specific properties of the methods, so that general results cannot be obtained using only one of them, but a comparative investigation by all these methods is necessary, as was carried out.

However, if instead of the usual compounds of simple stoichiometric composition the problem of dynamic equilibrium of various association and dissociation products in the liquid state of these systems is considered, all the results obtained including those of the potentiometric method acquire a new importance in the field of binary non-aqueous liquid systems.

Another field of research Prof. Tutundžić worked in was polarized electrode phenomena. His work on this covered both anode and cathode polarization, measurement of local potential and the potential distribution in the electrolyte, the inter-electrode potential and the potential and dissociation potential of non-aqueous liquid systems.

The work of Prof. Tutundžić in physico-chemical analysis of drinking and natural mineral waters showed the importance which these measurements may have for following changes in the composition of natural waters. All the well-known natural mineral waters of the Socialist Republic of Serbia were examined by these investigations.

In two fields of investigating Yugoslav raw materials Prof. Tutundžić was a pioneer; either alone or with his collaborators he produced a number of works. The first were connected with the possibility of electrical processing of oxide copper ores to obtain metallic copper. Laboratory scale tests were made of sulfuric acid leaching of copper-bearing limonite, quartzite, white and red sandstone and propylitic andesites of Eastern Serbia. The second relate to investigation of germanium and trace elements in ashes of Yugoslav coals; 31 kinds of coal ash of various age were investigated by spectography. It was found that they contained 27 kinds of trace element but no regularity in relation to coal content could be proved. Although Yugoslav coal ashes do not come into consideration for the extraction of rare metals, the results given in these works will be of great importance for geochemists and geologists.

During the short time he worked in the Department of Technical Sciences of the Serbian Academy of Sciences he read and published papers on investigations of Yugoslav coal ashes with regard to germanium and rare metals.

At the World Fair in Brussels in 1958 his exhibit "The coulomb as the universal original substance in analytical chemistry" was displayed in the international pavilion of sciences. The exhibit is now in the permanent exhibition of the Palace of Sciences in Brussels.

In 1960 Prof. Tutundžić received the 7th July Prize of Serbia for his research in the field of coulometry.

In recognition of his work and contributions to science, the Serbian Academy of Sciences elected him associate fellow in January 1958, and fellow on 5 December, 1961 in the Department of Technical Sciences, thus publically acknowledging his life's work and his work in chemistry.

As its Fellow, Tutundžić was entrusted by the Academy of Sciences to organize a symposium on waste waters. This symposium was of importance for all the countries having common waters with Yugoslavia, and so it was to have an international character. Unfortunately Prof. Tutundžić did not live to bring this idea to fruition.

Prof. Tutundžić showed great interest in the history of teaching chemistry and in the historical development of physical chemistry, and contributed to this field, too. On his initiative his collaborators collected and classified material about the work of the first Serbian chemists Mihajlo Rašković and Živojin Jocić, and also about the teaching of chemistry from the Lyceum to the University.

As public official Prof. Tutundžić devoted himself to many other activities.

His activity was particularly outstanding in the Serbian Chemical Society, of which he was successively elected Member of the Board, Secretary, Vice-President, and President, and in January 1962 in recognition of his unselfish work of 35 years, during which he devoted himself unstintingly to the organization of social activities, he was elected Honorary President. His love for this task and the work he carried out before and after he was elected Honorary President can only be felt by those who took part in it. It called for constant conscientiousness, and high standards and at the same time an understanding of people and the conditions under which they work.

Prof. Tutundžić devoted a great deal of his time to ensuring the regular appearance of the Bulletin of the Chemical Society (Beograd). First as a member of the Editorial Board, then as the Editor-in-Chief, he managed to attract a great number of scientists not only from Serbia but also from other republics to publish their papers in this journal.

Prof. Tutundžić took an active part in the foundation and work of new sections and branches of the Serbian Chemical Society, the aim of which is to bring together all chemists doing similar work.

Thanks to Prof. Tutundžić's efforts a list of all the chemical literature to be found in the area of the People's Republic of Serbia was published by the Serbian Chemical Society in 1958.

With regard to popularizing chemistry he was one of the originators and founders of the periodical "Hemijski Pregled" (Chemical Review).

The foundation of the Union of Chemical Societies in 1955 and its success are connected with Prof. Tutundžić, who was its first Secretary, Vice-President and President.

While he was working in the Union several committees were formed, the First Yugoslav Congress of Pure and Applied Chemistry was organized in Zagreb in 1960, and the very successful International Symposium on the Hydrogen Bond in Ljubljana in 1957. One of the manifestations in which Prof. Tutundžić's part was outstanding was the 9th International Colloquium on Spectroscopy in Belgrade in 1963.

As delegate of the Yugoslav Union of Chemical Societies he was active at all conferences of the International Union of Pure and Applied Chemistry, at which he called for the equality of all members of the Union.

As President of the Scientific and the Supervizory Committee his part in the organization of the 34th International Congress of Industrial Chemistry in Belgrade in 1963 was especially outstanding. On that occasion the Société de chimie industrielle de Paris showed its recognition by electing him Honorary Member for contributions in the field of science and industry.

Although he had numerous research commitments and many duties as a teacher, he devoted a lot of his time to the work of managing and organizing the Yugoslav Nikola Tesla Society of which he was President. In 1936, with a group of professors of Belgrade University, he was among the founders of the society. At the same time he was an active member of the editorial board of the periodical "Nauka i Tehnika" (Science and Technology), which the society published from the beginning of its existence. He was one of the initiators of the revival of the society after the liberation. He was present at all the working section meetings of the society, both those which prepared plans and programmes, and those which carried them out.

Under the leadership of Prof. Tutundžić, Nikola Tesla Society achieved significant results both at home and abroad. Liaison was established between the society and the society for the propagation of scientific knowledge "Znanie" (Knowledge) in the USSR. In recognition for its work the Yugoslav society was awarded the Lomonosov medal. This was given in Belgrade by Soviet Academician Artobolovski to the President of the society, Academician Tutundžić.

For special merit in popularizing science and technology, on 12 June, 1961 Prof. Tutundžić was awarded a Nikola Tesla Gold Plaque.

Prof. Tutundžić was prominent in his work on the Presidental Board of the Council of People's Technology of Yugoslavia and endeavored, with his rich experience and ideas, to provide a wider and fuller technical education for young people and adults in the movement for the technical education of the Yugoslav people.

From the beginning of his teaching career Prof. Tutundžić worked on the popularization of science, giving many popular scientific lectures at the Kolarac People's University, and after the liberation he undertook a number of duties connected with the adult education. He was the Chairman of the Culture and Education Board of District VII of Belgrade in 1946 and 1947. From 1947 to 1949 he was President of the Cultural Center at Senjak, from 1949 to 1952 he was member and President of the Culture and Education Societies of District VII of Belgrade, from 1952 to 1962 President of the Administrative Board of the Topčidersko Brdo People's University, and from 1962 to his death a member of the Council of the Cultural Center at Senjak and its President.

Prof. Tutundžić imbued his popular lectures and his contact with his audience in general an earnestness particular to himself. He had a special gift for popular scientific lectures and was able to explain very complex problems in a very short time and in a language understood by everyone. This quality of his contributed to his being one of our rare lecturers who always lectured to a full audience.

In addition to his teaching, scientific work and other activities already mentioned, Prof. Tutundžić was also a member of various university and faculty commissions, member of the Council of the School of Technology, Expert Advizor to the Directorate for the Protection of Industrial Property, was on various expert commissions, and was a member of the State Examination Board for Engineers and Technologists, and the State Administration for Public Property, Head of the Section for the Chemical and Pharmaceutical Industry, a member of the Administrative Board of State Enterprises for the Production of Medicaments, member of the Scientific Council of the Chemical Institute of the Serbian Academy of Sciences, and of the Nikola Tesla Institute, member of the Committee for Scientific Research of the Executive Council of the P. R. of Serbia, member of the Council for Scientific Research of Serbia and President of the Committee for Technical Science, President of the Expert Council of the University Laboratory for Electron Microscopy, member of the Administrative Board of the Fund for Publishing of Serbia, and of the Administrative Board of the Institute for the Promotion of the Textile Industry. He was the Head of the Scientific Research Institute for the Chemical and Pharmaceutical Industry, of the Chemical Institute of the Serbian Academy of Sciences and the Chemical Institute of Serbia.

He was the editor and co-editor of Yugoslav scientific and technical periodicals and encyclopedias, the editor of Bulletin Scientifique--Sectio A published by the Council of the Yugoslav Academy of Arts and Sciences, and member of the editorial board of the international periodical for analytical chemistry "Talanta". He was member of the Committee for Electrochemistry of the Section for Physical Chemistry of the International Union of Pure and Applied Chemistry, member, secretary or president of scientific societies, national committees, scientific and organizational boards and delegations for international collaboration in the field of development and propagation of science and technology, President of the Topčidersko Brdo People's University, member of the City Committee of the Culture and Education Community of Beograd, Vice-President and later President of the Executive Committee of the People's Front of District VII, Representative of the People's Committee of District VII and of the Topčidersko Brdo Community.

He was a member of the Council and President of the Scientific and Technical Board of the Institute for Chemical, Technological and Metallurgical Research, member of the Scientific and Technical Council for Chemical Technology and Metallurgy of the Federal Council for the Coordination of Scientific Research, member of the board of the Svetozar Marković University Library, member of the Council of the Boris Kidrič Institute of Nuclear Sciences, and a member of other boards, committees, juries, etc.

This many-sided and self-sacrificing work consumed Prof. Tutundžić's physical strength prematurely. With the end of his so fruitful life not only the School of Technology but also our country has lost a respected professor and famous scientist, and a personality full of vitality whose absence will be felt for a long time.

In our chemical science this loss will be felt, but the life and work of Prof. Tutundžić will remain as a shining example of how one can serve school, science and society without thought for self.

S. Đ. ĐORĐEVIĆ
D. J. STOJKOVIĆ

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Belgrade, 11 September 1964.

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STUDY OF THE STRUCTURE OF SOME AROMATIC DISULPHIDES AND DISELENIDES BY PHYSICO-CHEMICAL METHODS*

by

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In this work we studied organic compounds possessing a two-membered "bridge" of sulphur or selenium atoms. Properties of compounds of this type are of particular importance for biochemistry, since the "sulphide bridge", either two- or poly-membered, appears very often in natural products.

In the compounds studied sulphur and selenium are bivalent. The angle between the two sulphur bonds is 90—110°(1). In case of a two-membered bridge of the type

$$R_1—\Sigma—\Sigma—R_2$$

where Σ denotes an atom of either sulphur of selenium, it was observed that the rotation of the $\Sigma—R$ bonds about the direction of the $\Sigma—\Sigma$ bond is restricted(1). Therefore, in spite of the presence of single bonds in the molecule, there is no free rotation of atomic groups, and this makes possible the existence of two different orientations of atomic groups which can be described as "*cis*" and "*trans*" positions. The compounds studied were of the aromatic series.

The physico-chemical properties and the behavior of these compounds are undoubtedly connected with the orientation of their phenyl nuclei and represent very interesting problems in view of the planar structure of the benzene ring.

In the present investigation three physico-chemical methods were used: X-ray (Debye-Scherrer's method), thermal analysis

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* Some of the experimental data given in this paper was communicated at XI Colloquium Spectroscopicum Internationale, Belgrade, 1963, under the title: "Application des spectres infrarouge sur l'étude de disulfures et disélénures aromatiques".

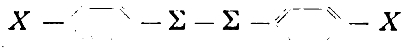
(Kofler's method) and infrared spectrophotometry. These three methods gave data which allowed conclusions about:

(a) isotypical cases among the compounds studied;

(b) the presence of molecular and intermolecular symmetry elements, and inductive effects observed in the infrared spectra;

(c) the spatial molecular configuration, common to the series of compounds studied.

Of the aromatic compounds possessing a disulphide or a diselenide bridge the following were chosen: diphenyl-disulphide, diphenyl-diselenide and their halogenated derivatives containing chlorine or bromine atoms in the *para*- and *para*-positions. These compounds can be represented by the formula



where *Σ* denotes either sulphur or selenium atom, and *X* the atoms of hydrogen, chlorine or bromine.

At room temperature all the compounds studied are crystalline, either colorless or of a yellow to orange color; all are easily soluble in organic solvents. The crystal structure of some of them is described in the literature (2,3), but for most of them no data on their properties are reported. The first synthesis of these compounds was in 1905(4); today numerous methods for their preparation are available(7).

The results obtained from the Debey-Scherrer diagrams are shown in Table 1.

TABLE 1

Maximum lattice dimension

No.	Substance	d_{max} Å
1	$(C_6H_5S)_2$	11.9
2	(C_6H_5Se)	11.9
3	$(BrC_6H_4S)_2$	14.6
4	$(BrC_6H_4Se)_2$	7.4
5	$(ClC_6H_4S)_2$	5.6
6	(ClC_6H_4Se)	13.0

Since the maximum lattice dimension is related to one of the dimensions (the maximum) of the elementary crystal cell, the comparison of values in Table 1 allows the following conclusions.

In the case of the first pair of substances (No. 1 and No. 2) the replacement of the central sulphur atoms by selenium is not accompanied by a change of the maximum lattice dimension; this shows that the dimensions of the elementary cell remain unchanged.

In the case of the second pair of substances (Nos. 3 and 4) (bromine derivatives) the lattice dimensions are approximately in the 1:2 ratio. The same is observed with the third pair (Nos. 5 and 6).

Accepting the criterion that in a series of homologous compounds the dimensions of the elementary call are related to the molecular dimensions, it may be assumed that the dimensions of compounds Nos. 4 and 5 are smaller by a half. In view of the possibility of the *cis* and the *trans* configurations for molecules of this type it may be concluded that compounds 4 and 5 have the *cis*, and all the others the *trans* configurations.

In order to define more precisely the similarities and differences among the substances examined we studied the thermal behavior of binary mixtures by Koffer's method. The compounds $(C_6H_5S)_2$ and $(C_6H_5Se)_2$ behaved as an isomorphic pair. These two substances gave eutectic mixtures with all the other four, and this proves that they possess a different crystal structure.

$(BrC_6H_4S)_2$ and $(ClC_6H_5S)_2$ were also found to be isomorphic and different from the other two. However, $(BrC_6H_4Se)_2$ and (ClC_6H_4Se) were also isomorphic.

This grouping in pairs deduced from the thermal analysis data is not fully consistent with the conclusions drawn from the Debey-Scherrer diagrams. The discrepancy may be due to nonuniform distribution of electron densities in the molecules which may cause different conditions for the difraction and interference of X-rays, in spite of the analogous substituent positions.

Infrared spectra were taken in different spectral regions on a UR—10 Karl Zeiss and a Perkins—Elmer M—21 apparatus. Samples were studied as solids by means of two different preparation techniques: in the form of a suspension in paraffin oil, and as potassium bromide disks. Paraffin suspensions were studied in the spectral region 2 to 15 microns (Perkins—Elmer M—21), and potassium bromide disks in the region 5 to 25 microns (UR—10). The most intense bands in all spectra were identified. All bands identified were, with small frequency differences, common to the halogenated derivatives with *para*-substituted benzene rings. Compounds which did not contain halogen atoms behaved as monosubstituted benzene derivatives. The frequencies observed, regardless of the vibration type, were more or less affected by the substituents, thus expanding the spectral range in which they were identified. The results are shown in Table 2. The infrared spectra are schematicallly shown in Fig. 1 and 2. The height of the lines corresponds to the intensity of the absorption band, and the line position to the wavelength of the absorption maximum. Spectra are grouped in similar pairs. This grouping corresponds to the division into isomorphic pairs on the basis of thermal analysis data.

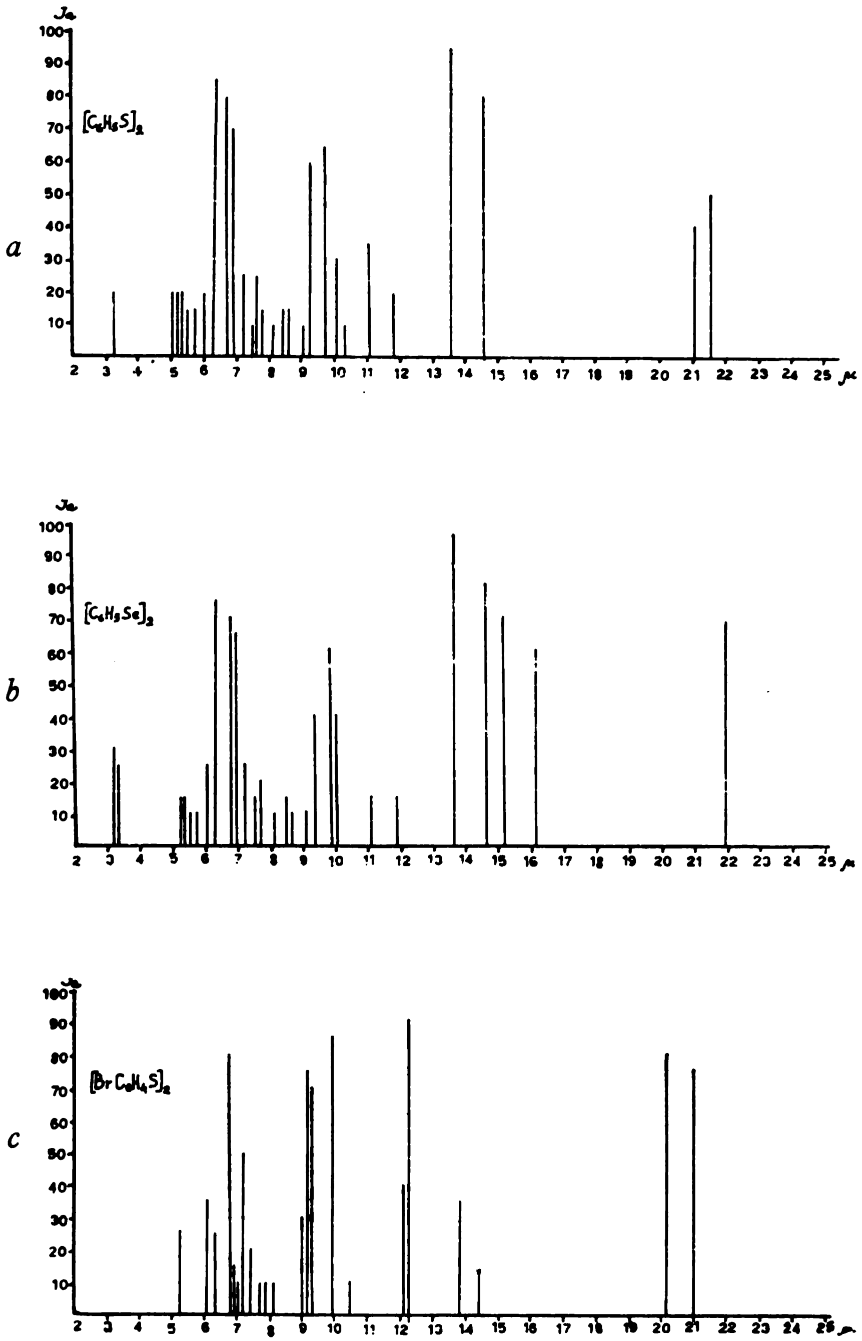


Fig. 1

Schematic representation of infrared spectra

a. spectrum of $(C_6H_5S)_2$ b. spectrum of $(C_6H_5Se)_2$ c. spectrum of $(BrC_6H_4S)_2$

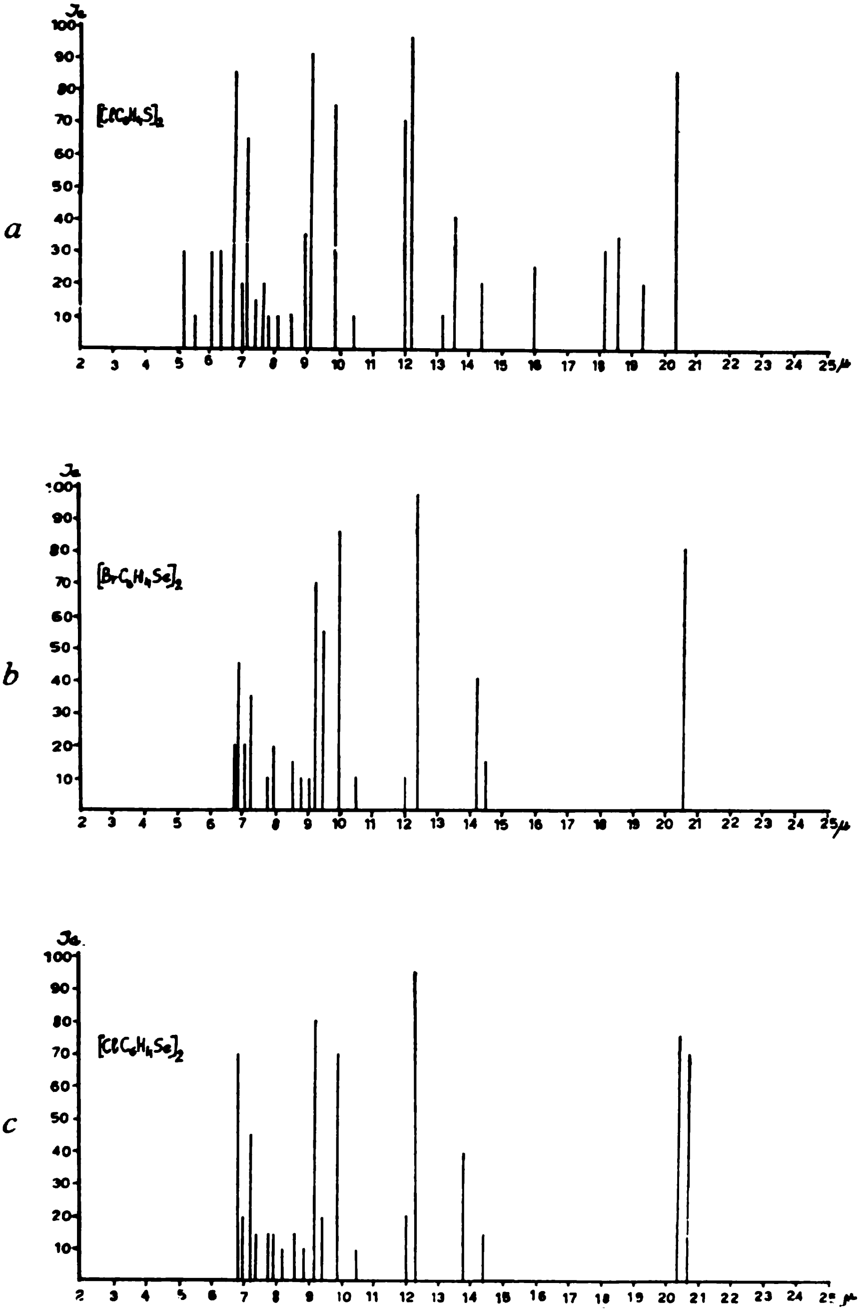


Fig. 2

Schematic representation of infrared spectra

a. spectrum of $(ClC_6H_4S)_2$ b. spectrum of $(BrC_6H_4Se)_2$ c. spectrum of $(ClC_6H_4Se)_2$

TABLE 2

Frequencies of infrared absorption bands and the assignment of vibration modes

Spectral region	Vibration mode corresponding to benzene nucleus
450— 500 cm $^{-1}$	Σ—Σ (Σ—Σ stretching vibration)
685— 740 cm $^{-1}$	ν_4 (or Σ—C stretching vibration)
812— 835 cm $^{-1}$	ν_{11} (for para-substituted der.)
1005—1026 cm $^{-1}$	ν_{14}
1060—1180 cm $^{-1}$	ν_{10} and ν_{17}
1200—1400 cm $^{-1}$	nonidentified
1468—1580 cm $^{-1}$	ν_{13}
1550—1580 cm $^{-1}$	ν_{16} (absent in spectra of diselenide crystals
1620—1650 cm $^{-1}$	nonidentified (absent in spectra of diselenide crystals)
1880—1915 cm $^{-1}$	ν_9 (absent in spectra of diselenide crystals)

From the assignment given in Table 2 it is seen that the frequencies corresponding to symmetrical molecular vibrations (ν_4, ν_{14}) are infrared active although they should be inactive in case there is a centre of symmetry, or partly inactive in the presence of a symmetry plane. Since these two bands are pronounced in all spectra, the molecules of the studied substances possess neither the *cis* nor the *trans* configuration. The position of the Σ—C bond with respect to the central Σ—Σ bond might be assumed as "*cis*-folded" as in some compounds (for example: hydrogen peroxide) of oxygen, which is in the same group of the periodic table as sulphur and selenium. This assumption is confirmed by data reported for one of the compounds studied(6).

The absence of some absorption bands from the spectra of the halogenated diphenyl-diselenides, present in the spectra of the analogous sulphur compounds, can be explained as follows. The bands which have dissapeared correspond to vibrations active even in the presence of a symmetry centre in the molecule. The spectra of these substances in solution contain the corresponding bands, but of a medium intensity; this proves that their inactivity in the crystalline state is due to some intermolecular symmetry elements in the crystal. On the basis of the vibration type of the frequencies which became inactive we can assume the presence of an intermolecular symmetry centre. This symmetry element can be explained by means of the following model.

The *para*-substituted aromatic nucleus is more or less polarized, depending on the nature of the substituent. This polarization is considerable in case one substituent is a halogen atom and the other a selenium atom. Thus one half of the molecule may be taken as a dipole: $\overset{(-)}{X}—C_6H_4—\overset{(+)}{Se}—$. In the crystal, the inductive bond between two such dipoles in two molecules orients and determines the crystal structure. The presence of the inductive bond is supported by the relatively high melting points of these compounds (85°C and 109°C).

These pairs, linked by an inductive bond, possess a local centre of symmetry. The existence of such a symmetry centre causes the disappearance of some bands in the spectra of the crystals.

The inductive bond between the oriented dipoles also affects the formation of the crystals, which are different from the crystals of the related sulphur compounds and unsubstituted diphenyl diselenide.

From the above it may be concluded that in spite of the differences in the crystal structure determined by thermal and X-ray methods, a "*cis* folded" molecular configuration can be ascribed to the whole series of compounds examined, in addition to already established fact that there is no free rotation about the $\Sigma—\Sigma$ bond. In view of the properties of this type of bridge established for oxygen, sulphur and selenium, analogous properties might be hypothesized for tellurium in analogous compounds.

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CONDUCTOMETRIC AND pH-METRIC INVESTIGATIONS OF THE REACTION OF SODIUM MOLYBDATE WITH MONOBASIC ORGANIC ACIDS

by

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Data obtained in the study of the reaction of molybdate with inorganic and organic acids indicate that the nature of the ionic forms of *Mo* (VI) in the presence of these acids is very different. The possibility of the formation of different types of isopoly- and heteropoly-acids and complex ions in inorganic acid solutions (in dependence on the nature and concentration of the acid), and also the possibility of the formation of complex ions containing some organic acids as ligands, led to the discovery of a great number of *Mo* (VI) compounds in solutions of these acids. The composition of these compounds has been studied by a number of physico-chemical methods, but on account of the complexity of the systems, the conclusions reached were often either contradictory or of a hypothetical character.

In inorganic acid solutions the presence of numerous isopolyions has been either established or hypothesized: MoO_2^{2+}^(1, 2, 3, 4), $(MoO_2^{2+})_2$^(2), $MoO_2(MoO_3)_n^{2+}$^(5), $Mo_4O_{13}^{2-}$^(6 7, 8, 9), $Mo_6O_{20}H^{3-}$^(6, 8, 10), $Mo_6O_{20}^{4-}$^(6, 9, 10), $Mo_6O_{21}^{6-}$^(11), $Mo_6O_{21}H_2^{4-}$^(11), $Mo_7O_{24}^{6-}$^(6, 9, 10, 12, 13), and $Mo_8O_{26}^{4-}$^(12, 13). Complex ions of the type $(MoO_3SO_4H_2)^+$ in H_2SO_4^(8), and $H(MoO_2Cl_3)$ in HCl^(14) appear at high concentrations of the acids.

The reactions of molybdate with organic acids were studied in most cases from the standpoint of complex ion formation. A great many data on the oxalato complex ion of *Mo*(VI) are reported in the literature (3, 15, 16, 17). Data on complex compounds of molybdate of 1:1 composition with citric and tartaric acids are also available(17, 18), although some authors state that in solutions of these acids no reaction of *Mo*(VI) complex formation was observed, but that a displacement reaction takes place giving H_2MoO_4 and the corresponding alkaline salt of the organic acid.(19) Complex compounds of molybdate with malic and succinic acids are also reported(18). Some authors found that several types of molybdate-acetate ion are formed, depending on the acetic acid concentration: $[MoO_2(AcO)]^+$ and $[MoO_2(AcO)_2]^\circ$ at lower, and $[MoO_2(AcO)_4]^{2-}$ at higher concentrations(20).

Data reported in the literature indicate that the reaction of molybdate with organic acids, has not been studied from the standpoint of polyion formation. Since these polyions are formed by the polymerization of MoO_4^{2-}, with the participation H^+ acid ion, it might be expected that in organic acid solutions polyions are present as well as complex ions.

This paper deals with the reaction of sodium molybdate with the following acids: $HCOOH$, CH_3COOH, and CH_3CH_2COOH, from the point of view both of complex ion and polyion formation. Since the reactions of *Mo*(VI) with these acids from the standpoint of complex formation have not be fully investigated, we studied the composition of the complex ion of *Mo*(VI) with ligands of these acids. A simultaneous investigation of the known and already studied molybdate-inorganic acid systems (HCl, HNO_3) was carried out for comparison.

Reactions of sodium molybdate with acids in the presence of H^+ ion and the complexing ligand of a monobasic organic acid can be represented by the following equations:

$$(1)\qquad 2Na^+ + MoO_4^{2-} + 2H^+ + 2A^- \rightleftarrows 2Na^+ + 2A^- + H_2MoO_4$$

$$(2)\qquad x\,MoO_4^{2-} + y\,HA \rightleftarrows H_{(y-2z)}Mo_xO_{(4x-z)} + y\,A^- + z\,H_2O$$

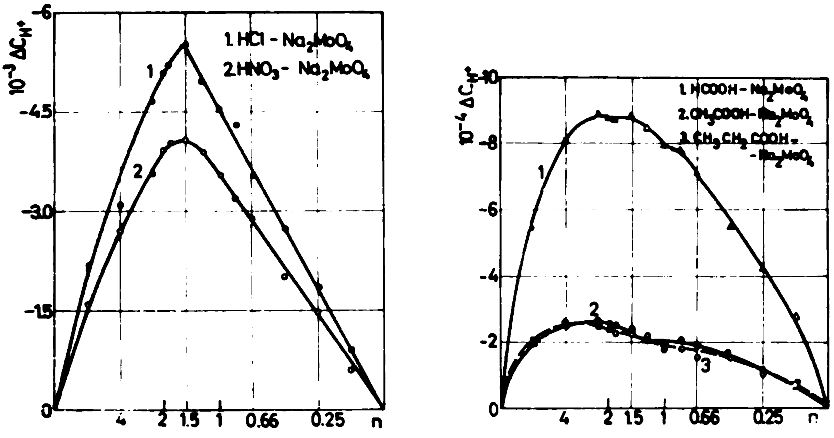
$$(3)\qquad MoO_4^{2-} + y\,H^+ + yA^6 \rightleftarrows (MoO_{(4-x)}\,A_y/^{(2+y-2x)-} + x\,H_2O$$

Since in all the three cases, the total number of ions as well as the H^+ ion concentration, is changed, the reaction of sodium molybdate with the given acids can be investigated by means of the method of continual variation (by measuring pH and the conductivity), and by conductometric and *pH*-metric titration. The first method cannot be expected to give a complete solution of the problem on account of the complexity of the system, which involves several ion equilibria. In a previous paper dealing with sodium tungstate(21) we described the experimental conditions for the application of these methods.

EXPERIMENTAL

Solutions of sodium molybdate and monobasic organic and inorganic acids used in the method of continual variation were of 0.010 M concentration. The desired molar ratio (n) of molybdate and acid was obtained by mixing the corresponding volumes of these solutions. The prepared solutions were kept in a thermostat for ten hours at a temperature of 25±0.02°C before measurement.

Conductometric and *pH*-metric titrations were carried out in the following way: to 50 ml of 0.02 M molybdate solution 0.2 M solution of the titrant was added and the volume of the solution made up to 100.0 ml with distilled water. These solutions were also kept in a thermostat at the temperature of 25.±0.02°C for ten hours before conductometry or *pH*-metry.

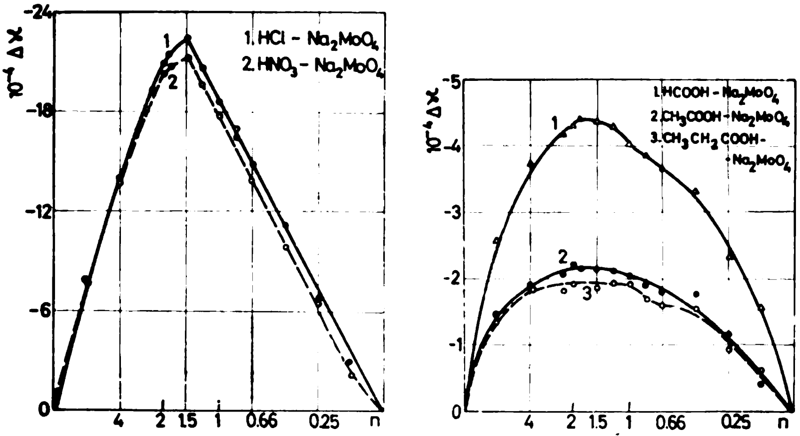


(a) (b)

Fig. 1 *The dependence of* $\Delta c_{H}{}^{+}$ *on n for the systems:*

(a) 0.01 M inorganic acid — 0.01 M sodium molybdate
(b) 0.01 M organic acid — 0.01 M sodium molybdate

The results obtained by the method of continual variation are given in Fig. 1 and Fig. 2, and the *pH*-metric and conductometric titration curves in Fig. 3, Fig. 4 and Fig. 5.



(a) (b)

Fig. 2 *The dependence of* $\Delta\varkappa$ *on n for the systems:*

(a) 0.01 M inorganic acid — 0.01 M sodium molybdate
(b) 0.01 M organic acid — 0.01 M sodium molybdate

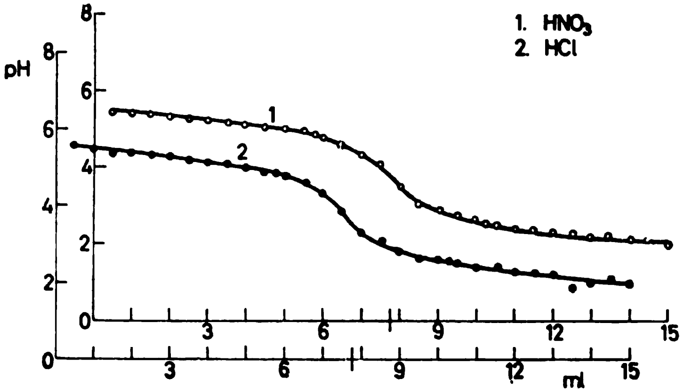


Fig. 3 *pH-metric titration curves of 100 ml of 0.01 M sodium molybdate with 0.2 M inorganic acid.*

The shapes of the continual variation curves indicate a decrease of the absolute value of ΔC_{H^+}, i. e. Δx, with decreasing acid strength. In the case the organic acids the sharpness of the titration end-point was lost with decreasing acid strength. Therefore the end-points in *pH*-metric titrations of molybdate with organic acids could not be determined.

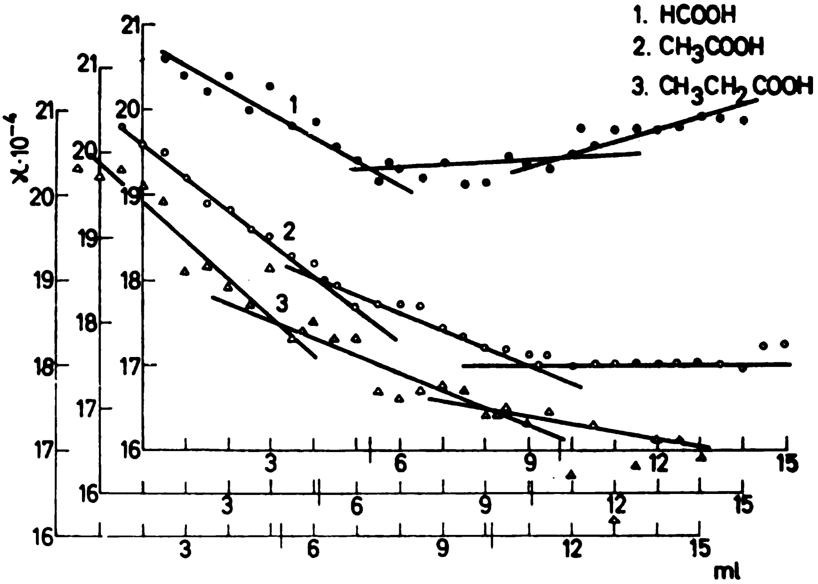


Fig. 4 *Conductometric titration curves of 100 ml of 0.01 M sodium molybdate with 0.2 M organic acid.*

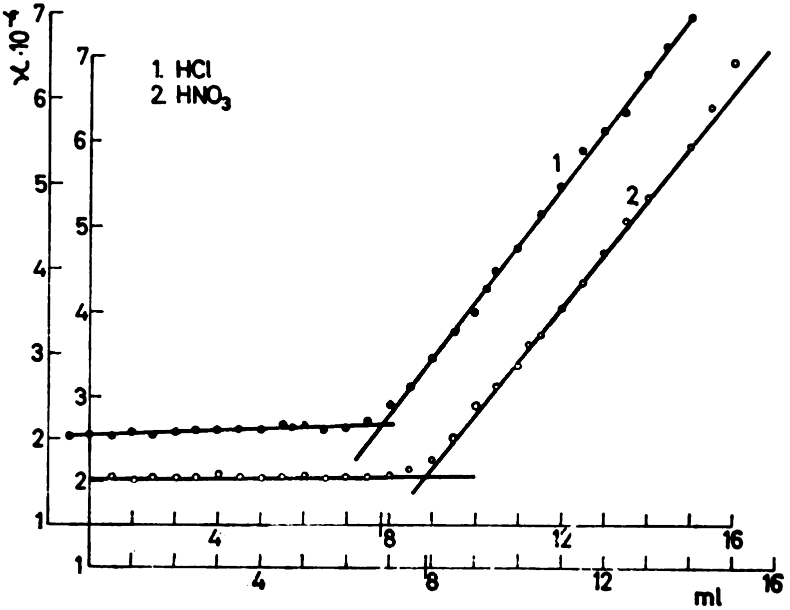


Fig. 5 *Conductometric titration curves of 100 ml of 0.01 M sodium molybdate with 0.2 M inorganic acid.*

The values of the molar ratio *n* which correspond to products of the reaction of molybdate with the corresponding acids are given in Table 1.

TABLE 1

Molar ratio n, obtained by different methods

	Method of continual variation				Titrations		
	pH measurement		κ-measurement		pH-metric	conductometric	
Acid	n_1	n_2	n_1	n_2	n	n_1	n_2
$HCOOH$	2	1	2	1	—	1.06	1.94
CH_3COOH	2	1	2	1	—	1.02	2.00
CH_3CH_2COOH	2	1	2	1	—	1.04	2.02
HCl	1.5	—	1.5	—	1.55	1.57	—
HNO_3	1.5	—	1.5	—	1.55	1.57	—

DISCUSSION

As seen from Table 1, in the case of the reaction of sodium molybdate with the organic acids, two values for the molar ratio $Mo{:}HA$

were obtained, $n\sim2$ and $n\sim1$, by the method of continual variation and by conductometric titration. This shows that the monobasic organic acids form two types of compound; $n\sim2$ indicates the exsistence of the complex ion $[MoO_3(A)_2]^{2-}$ (where A^- is the monobasic acid anion), and $n\sim1$, which is similar to the ratio 1.14 for the polyion of the type $Mo_7O_{24}^{6-}$ and to the ratio 1.17 for the polyion formed by the polymerization of six MoO_4^{2-} ions(19), indicates the presence of polyions formed by the action of H^+ acid ion. However, since the differences in the values of n are within the limits of experimental error, it is not possible to establish whether one or both of these types of polyanion is formed.

For the inorganic acids the method of continual variation gave a value of $n=1.5$, and the *pH*-metric and conductometric titrations $n=1.55$ and $n=1.57$. All these values correspond to the formation of polyanions $Mo_4O_{13}^{2-}$, $Mo_6O_{20}H^{3-}$, and $Mo_8O_{26}^{4-}$, which are formed at the molar ratio $n=1.5$ according to data reported in the literature.

APPARATUS AND REAGENTS

A Beckman Model H—2 *pH*-meter, laboratory equipment for the measurement of conductivity with a precision of 0.5%, and VEB Prüfgeräte Werk Model NB thermostat were used. All reagents were of p. a. purity, produced by "Kemika", "Carlo Erba" and "Merck".

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COMPLEX COMPOUNDS OF *l*-ASCORBIC ACID AND METAL IONS. IV.

INVESTIGATION OF THE COMPOSITION OF COBALT, NICKEL, MANGANESE, ZINC AND CADMIUM COMPLEXES IN WEAK ACID AND ALKALINE MEDIA BY MEANS OF *pH*-METRIC TITRATION

by

DRAGAN S. VESELINOVIĆ and MILENKO V. ŠUŠIĆ

Different data on the composition of metal-ascorbic acid complexes are reported in the literature. According to some authors complexes containing OH^- ions (hydroxocomplexes) are formed; however, according to others, the number of ascorbic acid anions in the complex is increased with increasing pH of the solution$^{(1)}$. This question could be cleared up by pH-metric titration of mixtures of ascorbic acid and metal salts with alkaline hydroxide solution. The appearance of a new jump in the titration curve and an increased consumption of the base proportional to the amount of metal present in the solution, would undoubtedly confirm the formation of metal-ascorbic hydroxocomplexes. On the other hand, the formation of complexes with a different number of ascorbic acid anions can neither cause a new jump on the pH-metric titration curve, nor lead to an increased consumption of hydroxide solution. This may be best illustrated by comparing the equation of hydroxocomplex formation

$$Me^{x+}+nHA+(N+m)NaOH \rightleftarrows (MeA_n(OH)_m)^{x-m-n}+nH_2O+$$

$$+(n+m)Na^+ \qquad (1)$$

with the equation representing the formation of a complex containing a greater number of ascorbic acid anions:

$$Me^{x+}+nHA+nNaOH \rightleftarrows (MeA_n/^{x-n}+nH_2O \qquad (2)$$

From equation (1) it follows that the excess of hydroxide consumed, calculated with respect to the amount of the metal present in the solution, gives the number of OH^- ions incorporated in the complex.

EXPERIMENTAL

All titrations were carried out in an inert atmosphere (nitrogen). This is indispensable on account of the oxidation of ascorbic acid with atmospheric oxygen; the oxidation of ascorbic acid is very easy in an alkaline medium⁽²⁾, especially in the presence of cations, which act catalytically⁽³⁾, or in the presence of light⁽⁴⁾. The oxidation also depends on the type of base used⁽⁵⁾. In titrations in an inert atmosphere the decomposition of ascorbic acid is less than 0.5% and this may be neglected.

All the solutions were prepared with water from which oxygen was expelled by passing a current of hydrogen or nitrogen. The solutions prepared were kept in a hydrogen atmosphere, and after mixing for titration a current of nitrogen was again passed through for 10 to 15 minutes, in order to remove oxygen dissolved in the course of measuring out.

A Beckman H—2 *pH*-Meter with additional equipment for potentiometric titration was used. The *pH*-meter was calibrated by means of standard buffer solutions produced by Beckman. The metal salts [$Co(No_3)_2$, $Ni(No_3)_2$, $Zn(No_3)_2$, $CdCl_2$ and $MnCl_2$] and all reagents used were of p. a. purity, produced by "Kemika", "Reanal" and "Merck". Nitrogen and hydrogen (obtained by electrolysis) were purified by being bubbled through an alkaline pyrogallol solution.

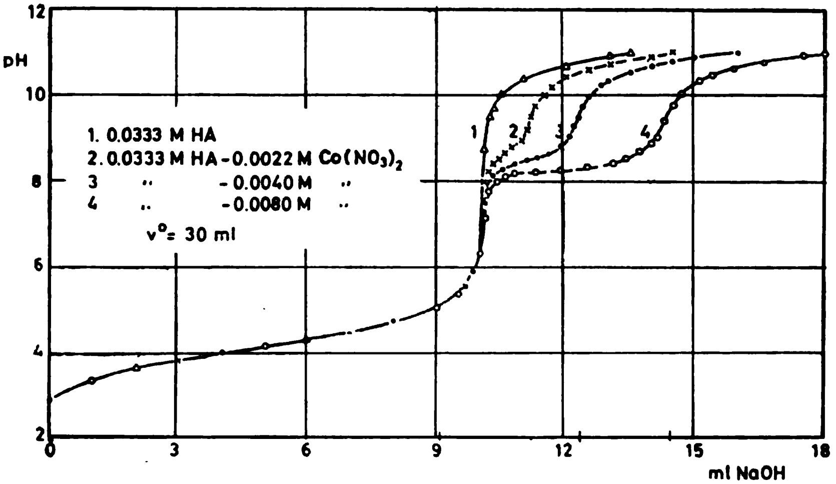

Figure 1

pH-Metric titration curves of ascorbic acid and ascorbic acid-$Co(NO_3)_2$ *mixtures with 0.0994 M NaOH*

Titration curves are given in Figs. 1, 2, 3, 4 and 5. Number 1 denotes the titration curves of ascorbic acid solutions, the concentration of which was the same as that in the solutions containing the

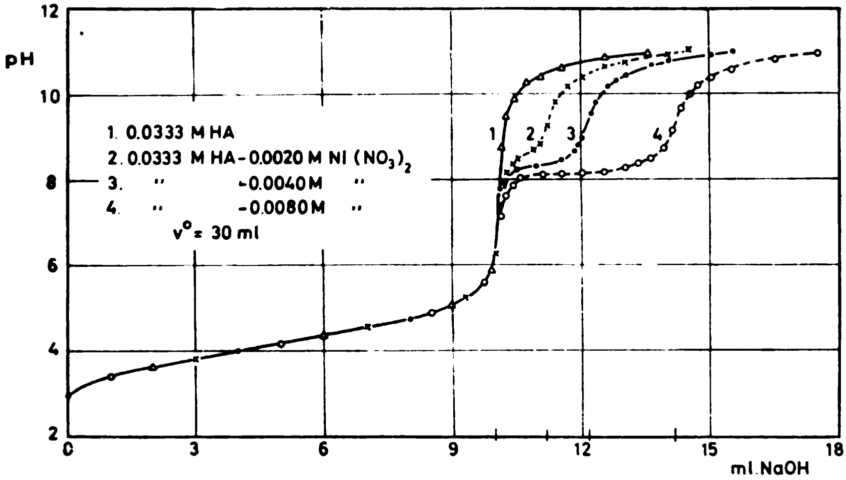

Figure 2
pH-Metric titration curves of ascorbic acid and ascorbic acid-$Ni(NO_3)_2$ *mixtures with 0.0994 M NaOH*

metal salts. Curves 2, 3 and 4 represent the titration curves of mixtures of ascorbic acid and metal salts: curves 2 correspond to solutions with the lowest and 4 to those with the highest concentration of the corresponding metal salt. The titration curves of metal salts in the absence of ascorbic acid are denoted by 5. In this case the concentration of the metal salt was the same as that in the solution which gave curve 4 in the case of zinc, and the curve 5 in the case of manganese salt.

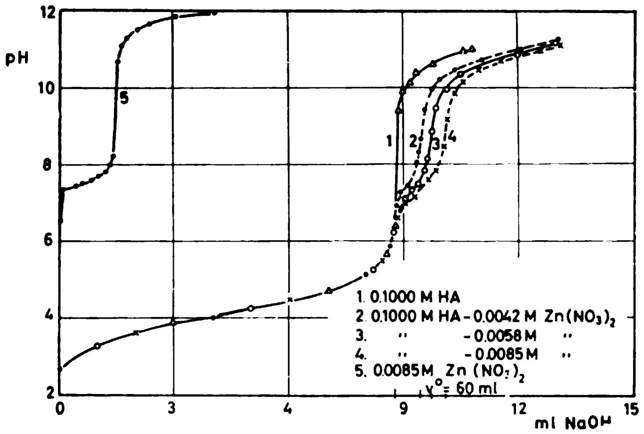

Figure 3
pH-Metric titration curves of ascorbic acid, ascorbic acid-$Zn(O_3)_2$ *mixtures and* $Zn(NO_3)_2$ *solution with 0.6857 M NaOH.*

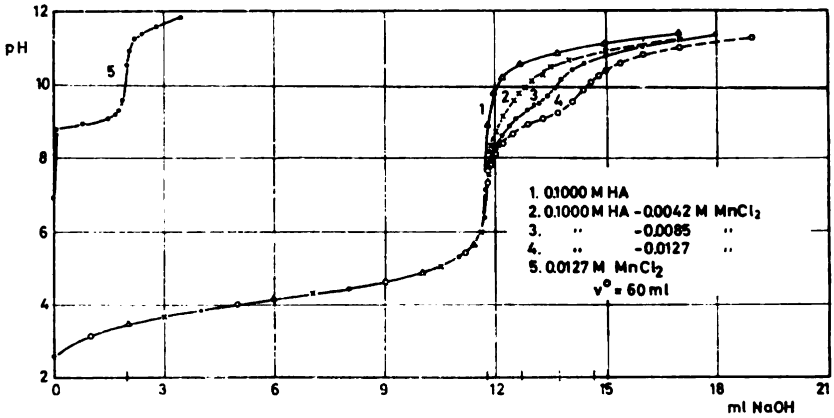

Figure 4

pH-Metric titration curves of ascorbic acid, ascorbic acid-$MnCl_2$ mixtures and $MnCl_2$ solution with 0.5096 M NaOH.

All the titration curves obtained with mixtures of ascorbic acid and metal salts show two jumps. The first jump denotes the end of the neutralization of the acid, since the amount of hydroxide consumed does not depend on the amount of the metal salt present. It is equivalent to the amount of hydroxide consumed for the titration of the acid alone. However, the height of this jump is slightly lower since other reactions can take place in the presence of hydroxide. The second jump on is less abrupt, and the amount of hydroxide consumed depends

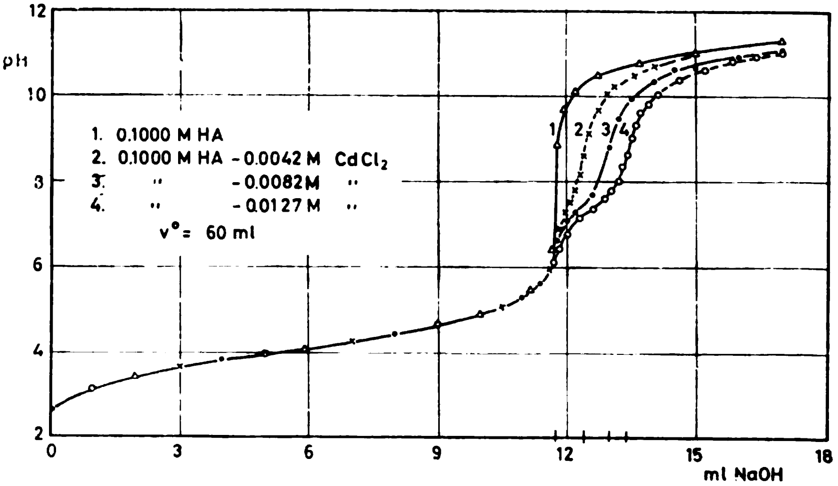

Figure 5

pH-Metric titration curves of ascorbic acid and ascorbic acid-$CdCl_2$ mixtures with 0.5096 M NaOH.

on the amount of the metal salt present in the solution. Since in the absence of ascorbic acid metal hydroxides are deposited in the *pH* region 7 to 11, and in its presence no hydroxide is separated, it may be concluded that the excess of hydroxide is used for the formation of complex compounds. The appearance of a color, which is dark red in the case of cobalt complex and slightly yellow in the case of other metals of this group, may be taken as a proof of complex formation.

The difference in amount of hydroxide consumed for the first and the second equivalence point, calculated in relation to the amount of metal salt, gives the ratio of metal and OH^- ions in the complex formed. Results obtained from titration data are given in Table 1.

TABLE 1

Potentiometric titrations of HA + Me mixtures with NaOH solution

Me mmole	Equivalence point (ml *NaOH*)		*NaOH* mole/l	*ml NaOH* for acid neutralization	Difference	Ratio *Me:NaOH* (mmole)	Molar ratio *Me:OH*−
	I	II					
Co 0.060	10.06	11.20	0.0994	10.06	1.14	1 : 1.88	1 : 2
Co 0.120	"	12.35	"	"	2.29	1 : 1.90	1 : 2
Co 0.240	"	14.45	"	"	4.39	1 : 1.82	1 : 2
Ni 0.060	"	11.23	"	"	1.17	1 : 1.94	1 : 2
Ni 0.120	"	12.23	"	"	2.17	1 : 1.80	1 : 2
Ni 0.240	"	14.20	"	"	4.14	1 : 1.72	1 : 2
Zn 0.250	8.75	9.45	0.6857	8.75	0.70	1 : 1.86	1 : 2
Zn 0.350	"	9.70	"	"	0.95	1 : 1.92	1 : 2
Zn 0.500	"	10.05	"	"	1.30	1 : 1.78	1 : 2
*Zn** 0.500	1.45	—	"	—	1.45	1 : 1.98	—
Mn 0.250	11.75	12.65	0.5096	11.75	0.90	1 : 1.83	1 : 2
Mn 0.500	"	13.70	"	"	1.95	1 : 1.98	1 : 2
Mn 0.750	"	14.65	"	"	2.90	1 : 1.98	1 : 2
*Mn** 0.500	1.95	—	"	—	1.95	1 : 1.95	—
Cd 0.250	11.75	12.40	"	11.75	0.65	1 : 1.32	1 : 1
Cd 0.500	"	13.00	"	"	1.25	1 : 1.26	1 : 1
Cd 0.750	"	13.40	"	"	1.65	1 : 1.11	1 : 1

*—Solution of metal salt without ascorbic acid.

They show that the $Me:OH^-$ ratio in alkaline media is 1:2 in the case of *Co*, *Ni*, *Mn* and *Zn*, and 1:1 in the case of *Cd*. This indicates the possibility of the formation of monohydroxo - and dihydroxo-ascorbic metal complexes. Complexes of *Co*, *Ni*, *Mn* and *Zn* containing one OH^- ion, and cadmium complex with two OH^- ions might also be expected to exist, although the corresponding jumps on the titration curves were not detected. It might be assumed that in the case of very close values of the stability constants for the monohydroxo and dihydroxo ascorbic complexes, no distinct separation of jumps would be observed. The incorporation of the second OH^- ion in the cadmium complex would take place at pH-values at which the second acid H^+ ion dissociates, thus masking the corresponding jump on the titration curve.

DISCUSSION

The results show that the ascorbic complexes of Co, Ni, Mn, Zn and Cd in alkaline media can be represented by a general formula $[MeA_n(OH)_n]^{n-}$, or $[MeA_nOH]^{n-1}$, depending on the number of OH^- ions which take part in the complex formation. Dihydroxo-complexes are formed at pH 8—10 in the case of Co, Ni, Mn and Zn, whereas in the case of Cd the pH must be higher than 10. Monohydroxo-complexes are formed at lower pH-values. The formation Cd monohydroxo-complex and the dihydrocomplexes of other cations studied takes place in the same pH region.

The number of ascorbic acid anions in hydroxo-complexes has not been determined so far. However, according to our results which will be published in the next paper, n—1. Therefore, we assume that the dihydroxo-ascorbic complexes of the metals studied are represented by the formula $[MeA(OH)_2]$, and the monohydroxo-complex by $[MeA(OH)]$. These types of complex correspond to the composition of the isolated uranyl-dihydroxo-ascorbic complex(1) $[UO_2A(OH)_2]^-$ and to the monohydroxo-ascorbic complex of divalent iron $[FeA(OH)]$(6).

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GLASNIK HEMIJSKOG DRUŠTVA, Vol. 31, No. 4—5—6, 1966, pp. 237—242

SOME FLUORESCENT PROPERTIES OF CADMIUM IODIDE AND CADMIUM BROMIDE ACTIVATED WITH SILVER

by

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and ILIJA Đ. BURIĆ

In one of his papers S. Šljivić(1) reported that cadmium iodide with a very small amount of silver nitrate activator gives an orange fluorescence. The fluorescence of cadmium halides phosphors has been investigated in detail by one of the authors of this paper(2).

In the present investigation it was found that cadmium bromide activated with silver nitrate gives a fluorescence in the yellow-green part of the spectrum. The aim of this work was to find the optimal activator concentration for both fluorescent materials giving the most intense fluorescence. Cadmium halides (iodide and bromide) were chosen for study since they possess a layer-structured crystals which allow easy incorporation of an activator with which the corresponding luminiscent centers are formed.

PREPARATION AND PROPERTIES OF FLUORESCENT MATERIALS

Cadmium iodide is activated with silver nitrate or silver halides, always giving a red-orange fluorescence. Hence it may be concluded that the activator anion has no effect on the color of the fluorescence. The luminophore can be prepared in different ways depending on the silver compound used: fusing by a mixture of components, or by crystallization from solution at room or elevated temperature. In this work the luminophores were prepared by crystallization from aqueous solutions.

The size and the shape of the cadmium iodide crystals were found to depend on the activator concentration when the crystallization was carried out at room temperature over seven days. At low activator concentration the crystals had an almost regular hexagonal cross-section, while crystals containing a higher concentration were of irregular shape. The size of the microcrystals ranged from 0.5 mm to 1.2 mm depending on the activator concentration. Figure 1 shows that the size of crystals is different for different cases.

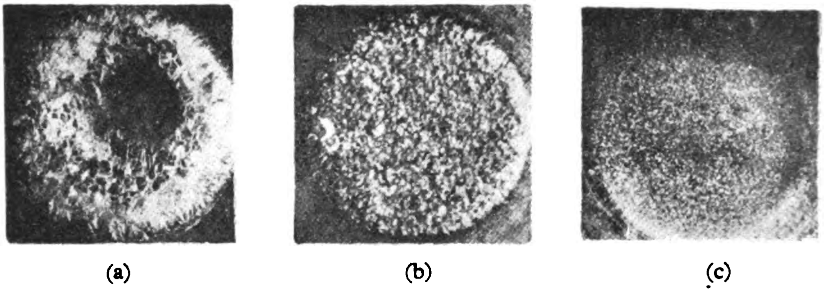
(a) (b) (c)

Figure 1

1. *Size of microcrystals of* $CdJ_2 \times Ag$ *in dependence on the activator concentration.*

(a) $c_{act} = 1$ mole%; $b_{act} = 5$ mole % $c_{act} = 10$ mole %

With samples obtained by crystallization in a drying oven at a temperature of 100° no difference was observed, since the crystals were not well-defined as in the case of slow crystallization at room temperature.

The color of the microcrystals was also different in depended on the activator concentration. Samples containing a lower concentration were white, and increase of the activator concentration produced first light yellow, and then yellow.

The second luminiphore used was cadmium bromide activated with silver nitrate. It gave a yellow-green luminescence when obtained by crystallization. It should be noted that the same fluorescent material can be obtained with silver halides as well, even by simple grinding of a mixture of cadmium bromide and silver halide. When such a mixture was heated at 400° and irradiated with ultraviolet light of wavelength 3650 Å, a light green fluorescence was observed on subsequent radiation.

Another preparation technique involves the fusion of components; the products thus obtained showed a light green fluorescence. Hence it may be concluded that the preparation technique does not affect the color of the fluorescence.

EFFECT OF THE PREHEATING TEMPERATURE

A factor which affects the appearance of the fluorescence in case of $CdBr_2 \times Ag$ is the temperature of preheating. This effect was studied in the following way: samples were first heated at various temperatures, and then cooled and irradiated with ultraviolet. Figure 2 shows the curve of the relative change of fluorescence intensity of $CdBr_2 \times Ag$ against temperature, for the temperature range 200° to 470°. A gradual increase of the preheating temperature results in an abrupt increase of the fluorescence intensity.

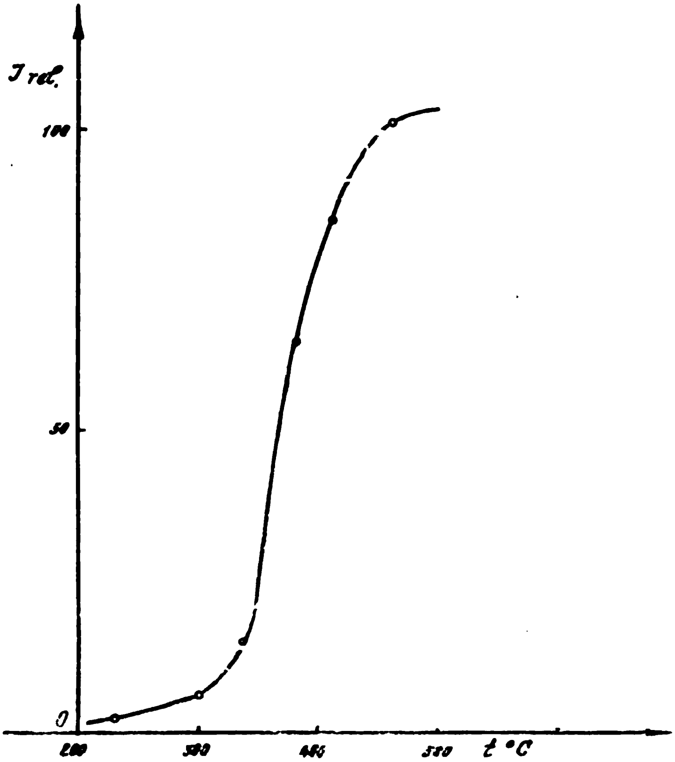

Figure 2

Relative change of the fluorescence intensity of $CdBr_2 \times Ag$ *against temperature* I_{rel} *is given in arbitrary units.*

EFFECT OF THE ACTIVATOR CONCENTRATION

The dependence of the fluorescence intensity on the activator concentration was studied by means of a fluorimeter (reflection photometer), samples being irradiated with ultraviolet light of wavelength 3650 Å. Fluorescent light emitted by the material falls on a photomultiplier, which feeds a galvanometer. This technique of measurement was satisfactory since only relative changes were observed.

Figure 3 shows the change of the fluorescence intensity of $CdBr_2 \times \times Ag$ in dependence on the activator concentration and Figure 4 the same for cadmium iodide activated with silver nitrate obtained by crystallization at different temperatures. Curve I in Fig. 4 shows the change of the photocurrent for samples obtained by crystallization at room temperature, curve II for samples obtained at 100°C, and curve III for samples II which were subsequently heated at 100°C.

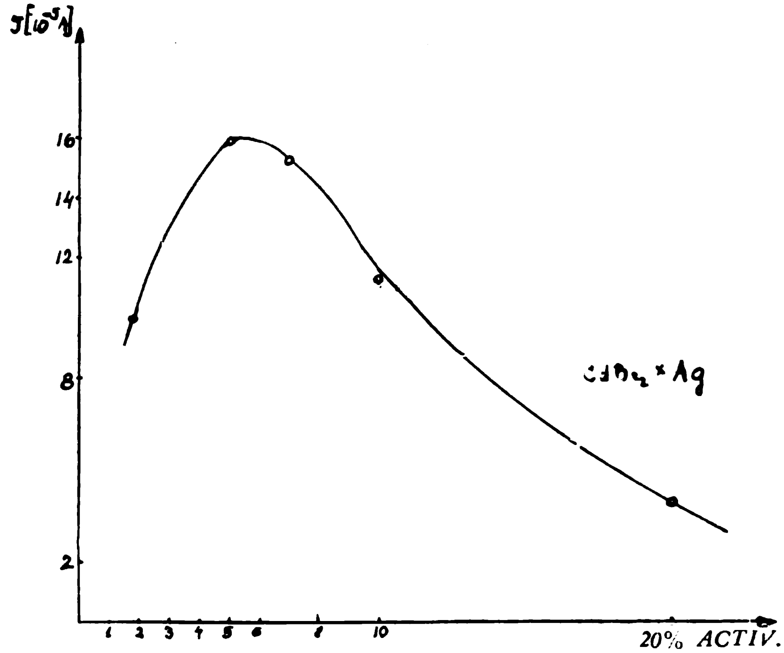

Figure 3

Changes of the fluorescence intensity of $CdBr_2 \times Ag$ *in dependence on the activator concentration.*

It may be seen that the intensity maxima are shifted in dependence on the crystallization temperature. It is also observed that the photocurrent maximum of the same sample is shifted to a higher activator concentration, if the sample is heated.

In case of $CdI_2 \times Ag$ a fluorescence of an orange-red color is obtained. The color changes only slightly with irradiation time. With increasing activator concentration the maximum in the fluorescence spectrum is shifted towards the red end.

It should be noted that on irradiation of $CdI_2 \times Ag$ with ultraviolet light the intensity of the photocurrent is not initially stable: in 2—3 minutes it falls usually to half its initial value. Samples obtained at room temperature are even less stable. It might be assumed that a photochemical reaction occurs which results in the formation of a thin black layer on the surface of the sample examined.

The activator concentration which gives the maximum photocurrent can be seen in Figure 3 and in Figure 4. The existence of an optimal activator concentration is connected with the phenomenon of concentration quenching.

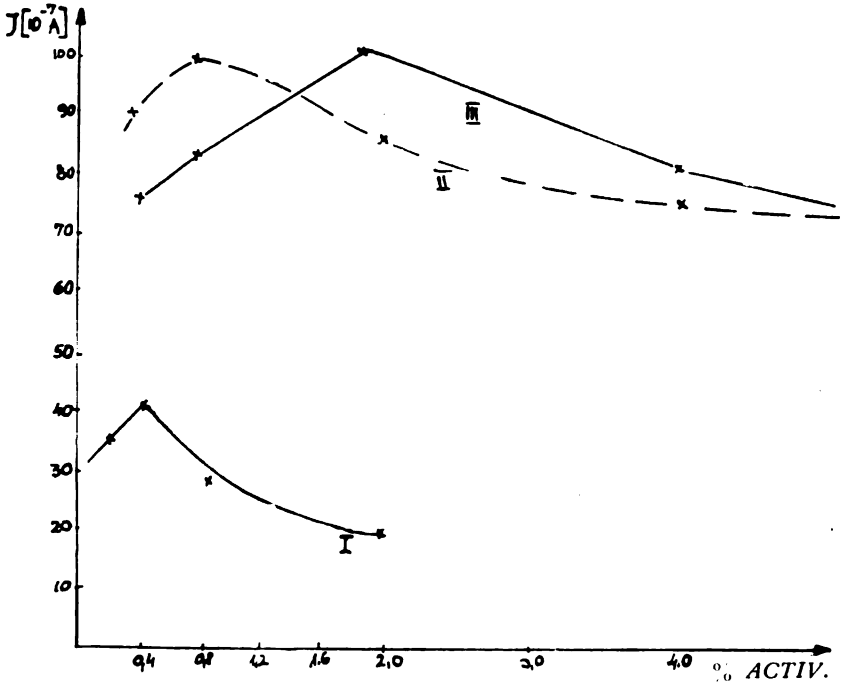

Figure 4

Changes of the fluorescence intensity of $CdBr_2 \times Ag$ in dependence on the activator concentration

The effect of the activator concentration on other crystals with a layer-structure is under investigation.

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OXIMES, DERIVATIVES OF 1-BENZOYL- AND 1-PHENACYL-PYRIDINIUM CHLORIDES, AND OF 1-PHENYL-, 1-BENZYL-, 1-BENZOYL, AND 1-PHENACYL-4-ALDEHYDE-PYRIDINIUM CHLORIDE

(SYNTHESES AND BIOCHEMICAL PROPERTIES)

by

ZLATKO J. BINENFELD, MILOJE M. MILOJEVIĆ, MILENKO P. MILOŠEVIĆ and DRAGINJA I. ANĐELKOVIĆ

In recent years a whole series of aliphatic, aromatic, and heterocyclic oximes have been synthesized and used as antidotes in poisonings with organophosphorus compounds. Among them the best action is exhibited by various pyridinium compounds possessing an oxime group in positions 2 and 4. These compounds are able to reactivate the cholinesterase (*ChE*) whose action is inhibited by organophosphorus compounds *in vivo* and *in vitro*. In the opinion of a great many authors this is their chief mode of action, but some authors consider that some other factors, play an important role in the protecting action of oximes(1,2,3).

Today it is assumed that the reactivating action of these compounds is due to the quaternary nitrogen of the pyridine ring and to the oxime group which facilitate the rupture of α phosphorylated enzyme and its reactivation (4).

1-Phenacyl-oxime-pyridinium chloride (*PhAOP*) was synthesized at the beginning of this century(5), but its pharmocological properties were investigated only much later, by Rumanian authors(6, 7, 8, 9) who showed that it exhibits a very complex action on the cholinergic and adrenergic nervous system. In view of these facts it seemed of interest to synthesize and examine *PhOAP* and related compounds which possess a quaternary pyridine nitrogen and oxime group in the aliphatic part of the molecule, and their analogs which possess an oxime group in position 4 of the pyridine ring.

EXPERIMENTAL

Oximes of 1-substituted-pyridinium chloride and of 1-substituted-4-aldehydo-pyridinium chloride can be prepared in the following ways:

A. By the condensation of aromatic chloro-ketones with pyridine or pyridine-4-aldoxime, and subsequent oximation:

$$\text{a) PhCORCl} + \left[\begin{array}{ll} C_5H_5N & \rightarrow \text{PhCOR}\overset{+}{N}C_5H_5 \quad Cl^- \\ C_5H_4N(CHNOH) & \rightarrow \text{PhCOR}\overset{+}{N}C_5H_4(CHNOH) \quad Cl^- \end{array}\right.$$

$R = —;\ CH_2$

$$\text{b) PhCOR}\overset{+}{N}C_5H_5 \quad Cl^- + NH_2OH \rightarrow \text{PhC(NOH)R}\overset{+}{N}C_5H_5Cl^-$$

$$\text{PhCOR}\overset{+}{N}C_5H_5(CHNOH) \quad Cl^- + NH_2OH \rightarrow$$

$$\text{PhC(NOH)R}\overset{+}{N}C_5H_5(CHNOH) \quad Cl^-$$

$R = —;\ CH_2$

B. By the oximation of aromatic chloro-ketones and subsequent condensation with pyridine or pyridine-4-aldoxime:

$$\text{a) PhCORCl} + \quad NH_2OH \rightarrow \text{PhC(NOH)RCl}$$

$$\text{b) PhC(NOH)RCl} + \left[\begin{array}{ll} C_5H_5N \rightarrow & \text{PhC(NOH)R}\overset{+}{N}C_5H_5 \quad Cl^- \\ C_5H_4N(CHNOH) & \text{PhC(NOH)R}\overset{+}{N}C_5H_4(CHNOH) \quad Cl^- \end{array}\right.$$

$R = —;\ CH_2$

C. By the condensation of aromatic chlorides with pyridine -4-aldoxime:

$$\text{PhRCl} + C_5H_4N(CHNOH) \rightarrow \text{PhR}\overset{+}{N}C_5H_4(CHNOH) \quad Cl^-$$

$R = —;\ CH_2$

In our work procedures *A* and *C* were used. The oximation was carried out with a neutralized aqueous or alcoholic solution of hydroxylamine hydrochoride, prepared by the method of Ginsburg and Wilson(10). Qualitative identification of oximes was performed according to Feigl and Demant(11).

1- phenyl-4-aldoximino-pyridinium chloride (Ph-11)

To a solution of pyridine-4-aldoxime (6.1 g) in ethanol (100 m) chlorobenzene (6.75 g) was added, and the reaction mixture was refluxed (upright condenser) for several hours on a water bath. The solution was then evaporated to a small volume, and ether was added until the separation of a precipitate finished .The precipitate was purified by redissolution in ethanol and subsequent precipitation with ether. The white crystals (7.1 g) melted at 186—188° (decomposition) and were easily soluble in water.

1-benzyl-4-aldoximino-pyridinium chloride (Ph-7)

A solution of pyridine-4-aldoxime (6.1 g) in a mixture of ethanol and ether (1:1, 100 ml) was left to stand for several hours at room temperature. The addition of ether caused the precipitation of pale pinkish-white crystals. The crystals were purified by dissolution in ethanol and subsequent precipitation with ether. The yield was 10 g; m. p. 205—206° (decomposition); the crystals were slightly soluble in water.

*1-Benzoyl-4-aldoximino-pyridinium chloride (Ph-9)**

To a solution of pyridine-4-aldoxime (12.21 g) in a mixture of absolute ethanol and absolute ether (1:1, 100 ml), benzoyl chloride (14.06 g) was slowly added, the reaction mixture being kept cool in a mixture of ice and sodium chloride. A white precipitate was obtained immediately. After standing for several hours, the precipitate was filtered off, washed with ether and recrystallized from absolute ethanol. White crystals (24 g) of m. p. 215—217°, easily soluble in water were obtained.

Oxime of 1-benzoyl-4-aldoximino-pyridinium chloride Ph-10

To a solution of 1-benzoyl-4-aldoximino-pyridinium chloride (6.57 g) in absolute ethanol (50 ml) a neutralized solution of hydroxylamine hydrochloride (2.65 g) was added. The reaction mixture was refluxed for two hours on a water-bath, then it was acidified with hydrochloric acid and evaporated in vacuo almost to dryness. Upon addition of ether yellow-green crystals, easily soluble in water, were obtained (485 g), m. p. 237—240°.

1-Phenacyl-4-aldoximino-pyridinium chloride (Ph-1)

Pyridine-4-aldoxime (12.21 g) was dissolved in a mixture of absolute ethanol and absolute ether (1 : 1) and chloroacetophenone (15.46 g) was added, the mixture being shaken until the complete dissolution of chloroacetophenone. The reaction mixture was then left to stand at orom temperature for several days whereby a precipitate was obtained. The precipitate was filtered off, disolved in absolute ethanol and upon addition of absolute ether white crystals (23.5 g) were again precipitated, m. p. 209.5—210.5°, easily soluble in water.

Oxime of 1-phenacyl-4-aldoximino-pyridinium chloride (Ph-3)

To a solution of 1-phenacyl-4-aldoximino-pyridinium chloride (6.92 g) in ethanol (100 ml) a neutralized aqueous solution of hydroxylamine hydrochloride (2.65 g) was added. The reaction mixture was refluxed for two hours on a water-bath; then it was acidified with

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* This compound was used by Hinterbuchner and Nachmansohn(10) but it was not fully described.

hydrochloric acid and evaporated to dryness. The dry residue was extracted several times with hot absolute ethanol. The extracts were combined and left to stand for two hours at room temperature, whereby a small amount of sodium chloride crystals was precipitated. They were filtered off and the filtrate was evaporated till the first appearance of crystals. Upon addition of ether crystals of a yellow-green color were precipitated. They were redissolved in ethanol and precipitated with ether. Yellow-green crystals were obtained (5.1 g) m. p. 181.—183°, easily soluble in water.

*Oxime of 1-Benzoyl-pyridinium chloride (Ph-12)**

1-Benzoyl-pyridinium chloride(14): pyridine (5.13 g) was dissolved in a mixture of absolute ethanol and absolute ether (1 : 1, 100 ml) and freshly distilled benzoyl chloride was added, the reaction mixture being kept cool in a mixture of ice and sodium chloride. Immediately after the addition of benzoyl chloride a white hydroscopic precipitate was obtained. Small amounts of absolute alcohol were poured several times over the precipitate and decanted in order to remove any traces of unreacted components. The yield was 12 g; m. p. could not be determined since in air the product decomposed on slight heating.

To a solution of 1-benzoyl pyridinium chloride (12 g) in absolute alcohol (100 ml) a neutralized alcoholic solution of hydroxylamine hydrochloride (5.6 g) was added. The reaction mixture was refluxed (upright condenser) for two hours on a water-bath, then slightly acidified with hydrochloric acid and evaporated in vacuo till the appearance of crystals. The addition of ether resulted in the formation of a precipitate, which was dissolved in ethanol and precipitated again with ether. White crystals (7.6 g) easily soluble in water were obtained; m. p. 147—151°.

Oxime of 1-phenacyl-pyridinium chloride (PhAOP)

Oxime of 1-phenacyl-pyridinium chloride was prepared according to the procedure given by Chiosa *et al*(6) in the following way: chloroacetophenone (15.4 g) and pyridine (8.7. g) were dissolved in a mixture of ethanol and ether (1 : 1, 100 ml), and the solution was left to stand at room temperature for several days. The crystals obtained were filtered off, dissolved in ethanol and precipitated with ether. 1-Phenacyl-pyridinium chloride (20.5 g) was obtained in the form of white crystals easily soluble in water; m. p. 196—198° (lit. 196—198°).

1-phenacyl-pyridinium chloride (23.37 g) was dissolved in ethanol (100 ml) and a neutralized aqueous solution of hydroxylamine hydrochloride (9.1 g) was added. The mixture was refluxed for two hours (upright condenser) on a water-bath, then it was slightly aci-

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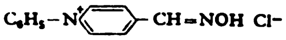
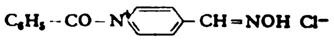
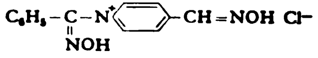
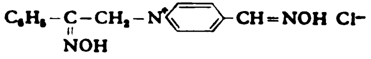
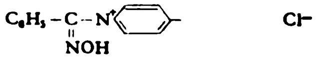
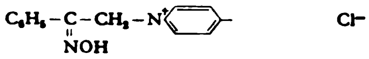
* This compound was reported by Navech *et al.*(13), but only infrared spectra were given.

TABLE 1

Analytical data

Code	Formula	Mol. formula	Mol. weight	% N		% Cl	
				Calc.	Found	Calc.	Found
Ph—11		$C_{12}H_{11}N_2OCl$	234.5	11.94	11.6	15.14	15.2
Ph—7		$C_{13}H_{13}N_2OCl$	248.5	11.27	10.9	14.29	14.6
Ph—9		$C_{13}H_{11}N_2O_2Cl$	262.4	10.67	10.4	13.52	13.3
Ph—10		$C_{13}H_{12}N_3O_2Cl$	277.5	15.13	14.9	12.43	12.2
Ph—1		$C_{14}H_{13}N_2O_2Cl$	276.5	10.13	10.4	12.48	12.7
Ph—3		$C_{14}H_{11}N_3O_2Cl$	291.5	14.41	13.8	12.19	11.8
Ph—12		$C_{12}H_{11}N_2OCl$	234.5	11.94	11.7	15.14	15.1
PhAOP		$C_{13}H_{13}N_2OCl$	248.5	11.27	11.4	14.29	14.4

dified and evaporated in vacuo till dryness. The residue was extracted several times with hot absolute ethanol. The extracts were combined and left to stand for two hours at room temperature, whereby a small amount of sodium chloride crystals was deposited. The crystals were filtered off and the filtrate was evaporated to dryness yielding white crystals (18.7 g) easily soluble in water; m. p. 208—210° (lit. 208—210°).

The determination of cholinesterase activity. This was carried out with a Warburg apparatus by the manometric method. The enzyme source was human erythrocytes which were washed twice with 0.9% sodium chloride solution and suspended in water (1 : 4 vol.). The following technique was used: 1.0 ml of a buffet solution (0.164 M $NaCl$+0.15 M $NaHCO_3$) and 0.5 ml of erythrocyte suspension was put in the middle of a Warburg vessel; 0.4 ml of 2% acetylcholine solution in a buffer solution was placed in the side-arm. A stream of 95% N+5% CO_2 gaseous mixture was passed through the system for five minutes. After pouring acetylcholine solution from the side-arm into the middle of the vessel, equilibration of the temperature (30 min. at 37°) was performed, and the pH of the substrate-enzyme mixture was raised to 7.4. Readings of CO_2 evolution were taken each 5 minutes in the course of 30 minutes. The cholinesterase activity was expressed in μl CO_2 (30 min.) 0.1 ml of pure erythrocytes. The results were corrected for nonenzymatic hydrolysis.

Measurement of cholinesterase inhibition

The cholinesterase inhibition was measured in the way described above by placing 0.9 ml of buffer solution, 0.5 ml of erythrocyte suspension and 0.1 ml of oxime solution in the middle of the Warburg vessel. The concentration of the oxime in the substrate-enzyme mixture was 1×10^{-3}M.

Reactivation of inhibited cholinesterase

Paraoxone (diethylphosphoryl-*p*-nitrophenolate) was used as an irreversible inhibitor of cholinesterase and the solutions were prepared just before use.

A solution of paraoxone in 0.9% sodium chloride solution was added to washed erythrocytes to a paraoxone concentration of $1.2 \times \times 10^{-5}$M. After an incubation of 30 minutes, the unreacted paraoxone was removed by washing the erythrocytes twice with 0.9% sodium chloride solution, and the washed erythrocytes were suspended in water (1 : 4 vol).

0.5 ml of the suspension of inhibited erythrocytes, 0.9 ml of buffer solution and 0.1 ml of oxime solution were placed in the middle of the Warburg vessel. The concentration of the oxime in the substrate-enzyme mixture was 1×10^{-4}M. The experimental technique and the readings of the results were carried out in the same way as in the determination of normal chlolinesterase activity. 2-Aldoximino-pyridinium methyl-methanesulphonate (P—2—S) was used as the standard.

RESULTS AND DISCUSSION

Most of the synthesized oximes were easily or very easily soluble in water and were very convenient for use.

TABLE 2

Inhibition of human erythrocytes ChE by oximes

Oxime	% of the inhibition
Ph—11	10
Ph— 7	65
Ph— 9	15
Ph—10	6
Ph— 1	17
Ph— 3	80
Ph—12	7
PhAOP	78
P—2—S	10

In the concentration of 1×10^{-3} M *PhAOP*, *Ph*-3 and *Ph*-7 exhibited a strong inhibitory action on human erythrocyte *ChE* activity. Other oximes examined did not show such a pronounced effect, but their anticholinesterase action corresponded to that of P—2—S. *PhAOP* and *F*—3, even in the concentration of 1×10^{-5}M, caused the inhibition of erythrocyte *ChE* activity (20%)(15), whereas the other oximes examined, including P—2—S, exhibited no action in such a low concentration.

TABLE 3

Reactivation of human erythrocytes ChE inhibited by paraoxone

Oxime	% of reactivation
Ph—11	0
Ph— 7	5
Ph— 9	0
Ph—10	3
Ph— 1	10
Ph— 3	7
Ph—12	0
Ph AOP	0
P—2—S	90

At a concentration of 1×10^{-4}M for 30 minutes most of the compounds examined showed no ability to reactivate inhibited human erythrocyte *ChE* activity, while some of them showed a slight action. The same concentration of *P—2—S* almost completely reactivated the inhibited cholinesterase.

If the structure of the compounds examined is considered, it will be noted that compounds which do not possess an oxime group in position 4 of the pyridine ring show no reactivation ability in this concentration (*PhAOP*; *F*-12). On the other hand, the slight reactivation ability of pyridine-4-aldoxime derivatives depends on the distance of the benzene nucleus from the pyridine ring, so that the order is the following: $Ph-1 > Ph\text{-}3 > Ph-7 > Ph-11$, the greater the distance the stronger the reactivation action.

The reactivation of phosphorylated enzyme by means of oximes might be assumed to take place through their anionic forms(16). It could be expected that *Ph*-1 and *Ph*-7 are better nucleophiles on account of a higher pK_a than $P-2-7$(17), and hence better reactivators. One reason why their strong nucleophilicity is not expressed in their reactivation ability may be the fact that their pK_a values are too high, so that the reactivation maximum cannot be achieved at the *pH*-value of the experiment, and that the concentrations used are too high. Further experiments with more concentrated solutions of oximes ($>1 \times 10^{-4}$M) and phosphate buffer ($pH=8$) will show whether this is the case.

The lower reactivation ability of the oximes examined than $P-2-S$ can most probably be assigned to the inhibition of the orientation effect of positively charged nitrogen atom by aromatic groups.

Protecting action. — None of the compounds examined, except *PhAOP*, showed a protective action in mice poisoned by paraoxone. In combination with atropine they exhibited a very pronounced protective action(18).

Although our experience with oximes of this series is limited, it indicates that the cholinesterase reactivating action of oximes should not be taken as the only factor which contributes to their ability to exhibit a protective action in poisonings with organophosphorus compounds.

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GLASNIK HEMIJSKOG DRUŠTVA, Vol. 31, No. 4—5—6, 1966, pp. 251—254

SYNTHESIS OF SOME 7,8-DIALKYLGLYCOLURILS

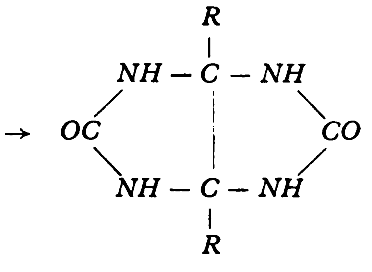
by

ZLATKO J. BINENFELD

Chlorinated 7,8-dialkyl- and diaryl-glycolurils have shown excellent properties as active substances in ointments for the decontamination of vesicants (blister gases)(1,2). In order to examine the effect of the alkyl group on the efficiency of chlorinated glycolurils we synthesized some new, so far undescribed, 7,8-dialkylglycolurils.

The starting substances were fatty acid ethyl esters (I), which were converted through acyloins (II) into diketones (III); the reaction of the diketones (III) with urea yielded the corresponding 7,8-dialkylglycolurils (IV).

$$\underset{\text{I}}{RCOOC_2H_5} \rightarrow \underset{\text{II}}{RCICHOHR} \rightarrow \underset{\text{III}}{RCOCOR} \rightarrow$$



IV

$R = CH_3-,\ C_2H_5-,\ C_3H_7-,$

$iso-C_4H_9-,\ C_5H_{11}-,$

EXPERIMENTAL

Acetoin, propionoin, butyroin, isovaleroin and caproin were synthesized from the ethyl esters of acetic, propionic, butyric, isovaleric and caproic acid, respectively, according to Organic Syntheses(3). Oxidation of these acyloins was carried out by the method of P. Ruggli and P. Zeller(4)*, whereby butanedione- 2, 3, hexandione-3, 4, octanedione-4, 5; 2, 7-dimethyloctanedione-4, 5 and dodecanedione-6, 7 were obtained.

Syntheses of 7,8-dialkylglycolurils were carried out according to the Franchimont-Klobbie(6) method in the following way:

7,8-*Dimethylglycoluril* ($C_6H_{10}O_2N_4$) — In an erlenmeyer flask butandione-2,3 (2 g) and urea (3.5 g) were dissolved with stirring in water (5 ml). The clear solution was left to stand at room temperature for 4—5 days, and white flakes separated out; they were filtered off and dissolved in boiling water (1000 ml). On cooling white needle-form crystals were obtained; m. p. > 300° (lit. (6) m. p. > 300°). The yield was 60% (2.49 g).

Analysis for $C_6H_{10}O_2N_4$:

Calcd.: N 32.9%
Found: N 33.1%

7,8-*Diethylglycoluril* ($C_8H_{14}O_2N_4$) — In an erlenmeyer flask hexandione-3,4 (0.8 g) and area (1.54 g) were dissolved in water (1.9 ml). After standing for 6—8 days a white flaky precipitate separated; it was filtered off and dissolved in boiling water (300 ml). On cooling white prismatic crystals were obtained, m. p. > 300°. The remaining liquid was evaporated to half of its original volume, and on cooling a further amount of the same crystals was deposited. The total yield was 43% (0.6 g).

Analysis for $C_8H_{14}O_2N_4$:

Calcd. C 48.8, H 7.1, N 28.3%
Found: C 48.6, H 7.0, N 28.4%

7,8-*Dipropylglycoluril* ($C_{10}H_{18}O_2N_4$) — In an erlenmeyer flask octanedione-4,5 (2.8 g) and urea (4.9 g) were dissolved in water (7 ml). After standing for 3—4 days a white powder began to precipitate, but the reaction was not over until 14 days of standing. The white powder precipitate was filtered off, and dissolved in boiling water (1300 ml). On cooling small white crystals were obtained, m. p. > 300°. The remaining liquid was evaporated to half its original volume and on cooling a further amount of the same crystals was obtained. The total yield was 58% (2.6 g).

Analysis for $C_{10}H_{14}O_2N_4$:

Calcd. : N 24.8%
Found : N 24.5%

7,8-Diisobutylglycoluril ($C_{12}H_{22}O_2N_4$) — In an erlenmeyer flask a mixture of 2, 7-dimethyloctanedione-4,5 (3.2 g) and urea (5.6 g) was dissolved in water (8 ml). After standing for a month, the white powder precipitate was filtered off, and dissolved in boiling water (1.5 l). On cooling white prismatic crystals were obtained, m. p. > 300°.

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* This method was used by H. Bloch *et al.*(5). It consists in the oxidation of acyloins, suspended in acetic acid, by means of cupric acetate.

Evaporation of the filtrate and cooling yielded no further crystalline precipitate. The yield was 58% (2.8 g).

Analysis for $C_{12}H_{22}O_2N_4$:

Calcd.: C 56.7, H 8.9, N 22.1%
Found: C 57.1, H 8.9, N 21.9%

7, 8-Dipentylglycoluril ($C_{14}H_{26}O_2N_4$) — In an erlenmeyer flask a mixture of dodecanedione-6, 7 (2.8 g) and urea (2.13 g) was dissolved in water (4 ml). After standing for three months the white powder precipitate was filtered off and dissolved in boiling water (1 l). On cooling white crystalline needles were obtained, m. p. > 300°. Evaporation of the filtrate gave no further crystals. The yield was 50% (2.09 g).

Analysis for $C_{14}H_{26}O_2N_4$:

Calcd.: N 19.9%
Found: N 20.2%

The described glycolurils do not change color and do not decompose on heating above 300°. They are sparingly soluble in boiling ethanol and insoluble in ether, chloroform and benzene.

The analyses were performed at the Laboratory of the Institute for Organic Chemistry, School of Technology, University of Belgrade, for which the author is grateful to Prof. Đ. Dimitrijević.

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SYNTHESIS OF 4-HYDROXY-4'-BROMOTHIOBENZANILIDE

by

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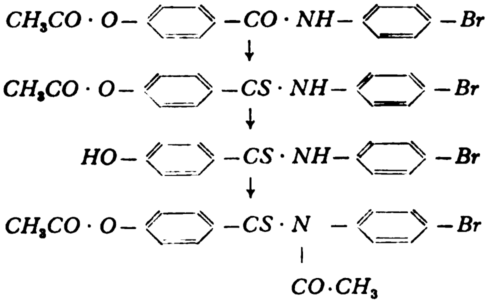
As a continuation of our investigations in the field of hydroxythioamides and in connection with conclusions$^{(1, 2)}$ already reported, we have synthesized 4-hydroxy-4'-bromothiobenzanilide. The starting substance was the corresponding hydroxybenzanilide in which the hydroxyl group was protected by an acetyl group, namely the 4-acetoxy-4'-bromobenzanilide (I) which was obtained from 4-acetoxybenzoyl chloride and 4-bromoaniline. By refluxing this compound with phosphorpentasulphide in anhydrous organic solvents (dioxane, pyridine, xylene) the corresponding acetoxythioamide (II) was obtained in a yield of about 80%. Alkaline hydrolysis of the product II yielded the desired 4-hydroxy-4'-bromothiobenzanilide (III).

The presence of the free hydroxyl group in compound III was proved by acetylation with acetic anhydride. However, upon treatment with acetic anhydride the thioamide group was acetylated as well, so that the corresponding *O*, *N*-diacetyl thioamide derivative IV was obtained. The same compound (IV) was also obtained by the acetylation of compound II.



I

II

III

IV

EXPERIMENTAL

Melting points are not corrected.

4-Acetoxy-4'-bromobenzanilide (I)

Freshly prepared 4-acetoxybenzoyl chloride(3) (3.98 g; 0.02 mole) was added dropwise to the cooled, stirred solution of 4'-bromoaniline(4) (3.44 g; 0.02 mole) dissolved in pyridine (12 ml). After standing for half an hour the reaction mixture was poured into icy water (300 ml) and the separated crystalline product was filtered off, washed and dried. The yield of the crude product was 6.2 g (92.4%) Recrystallization from ethanol gave colorless needles melting at 212—215°.

Anal. $C_{15}H_{12}NO_3Br$ (334.17)
Calc.: C 53.94, H 3.62, N 4.19%
Found: C 53.86, H 3.78, N 3.90%

4-Acetoxy-4'-bromothiobenzanilide (II)

Phosphorus pentasulphide (2.22 g; 0.01 mole) was added to the hot solution of compound I (3.4 g; 0.01 mole) in dioxane (10 ml). The reaction mixture was heated under reflux in an oil-bath at 90—100° for 45 minutes. In the course of heating the color of the reaction mixture changed from yellow to red and then dark red, showing that the reaction was going in the desired direction. The warm reaction mixture was then poured into water (250 ml) and the separated dark-yellow oil which separated soon crystallized. After standing overnight at room temperature the yellow crystalline product was filtered off washed with water and dried. The yield was 3.3 g (81.4%), m. p. 147—149°. Recrystallization from ethanol gave crystals melting at 152—153°.

Anal. $C_{15}H_{12}NO_2SBr$ (350.24)
Calc.: C 51.18, H 3.44, N 3.98%
Found: C 50.93, H 3.22, N 3.70%

Some experiments were carried out in dry pyridine as solvent (5, 6) but the yield of the crude product was practically unchanged (79.2%). The same yield was also obtained (81.7%) when dry xylene was used as solvent(2, 7, 8).

The attempts to brominate 4-acetoxy-thiobenzanilide(9) by the usual procedure with bromine in glacial acetic acid were unsuccesful. Under various reaction conditions non-sulphur compounds were obtained.

4-Hydroxy-4-bromothiobenzanilide (III)

A mixture of compound II (3.5 g; 0.01 mole) and 1 *N* sodium hydroxide solution (15 ml) was heated on a water-bath for 10—15 minutes at 70—80°. The yellow alkaline solution was filtered, cooled and acidified with dilute hydrochloric acid (1 *N HCl*) to *pH* 7, whereby a yellow precipitate was obtained. The precipitate was filtered off, washed with water and dried, yielding 2-9 g (94%) of the crude product of m. p. 200—202°. Recrystallization from water-ethanol (2 : 1) gave yellow prisms melting at 203—204°.

Anal. $C_{13}H_{10}NOSBr$ (308.20)
Calc.: C 50.61, H 3.30, N 4.55%
Found: C 50.62, H 3.45, N 4.56%

N-Acetyl-O-acetyl-4-hydroxy-4'-bromothiobenzanilide (*IV*)

Acetic anhydride (6 g; 0.006 mole) was added dropwise to a stirred solution of compound III (3 g; 0.01 mole) in anhydrous pyridine (10 ml). After standing overnight at room temperature the red reaction mixture was poured into icy water (500 ml). The separated crystalline product was filtered off, washed with water and dried. The yield of the product of m. p. 114—115° was 3.4 g (97.3%). Recrystallization from water-ethanol (1 : 1) yielded red prisms melting at 117—118°.

Anal. $C_{17}H_{14}NO_3SBr$ (392,28)
Calc: C 52.08, H 3.70, N 3.59%
Found: C 51.98, H 3.89, N 3.62%

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DETERMINATION OF AMINO ACIDS BY GAS CHROMATOGRAPHY

by

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and VELIMIR D. CANIĆ

By gas chromatography the amino-acid analysis of a protein hydrolyzate requires at most one hour and the apparatus is several times cheaper than any amino-acid analyzer.

The greatest difficulty in gas chromatographic analysis of amino acids is the nonvolatility of the acids. Therefore before chromatographing in the gaseous phase the amino acids have to be converted into volatile derivatives. This can be achieved in different ways: by oxidation, acylation, decarboxylation, esterification, etc.

One way of preparing volatile compounds involves the oxidation of amino acids by means of ninhydrin into the corresponding aldehydes with one *C*-atom less(1). The aldehydes are then oxidized with potassium permanganate into the corresponding acids, which are esterified and chromatographed in the form of esters(2). However, this method is limited to amino acids which give volatile aldehydes. There are other methods for the conversion of amino acids into volatile derivatives: for example, it has been shown that amino acids can be converted into α-chlorocarboxylic acids by the action of nitric and hydrochloric acid; the chloro acids are then esterified and chromatographed as methyl esters(3). Amino acids can be converted into the corresponding amino alcohols by the reduction of ethyl esters of *N*-acetyl derivatives with lithium aluminum hydride(4). Very good results were recently obtained by chromatographing *N*-trifluoroacetylated esters(5) and *N*-trimethyl-silyl derivatives(6).

The simplest way of increasing the vapor pressure of amino acids is the esterification with some lower alcohol. It has been shown that some amino-acid methyl esters can be separated on a column with silicone oil(7), but some amino acids could not be separated since at a high temperature their methyl esters underwent condensation giving off methanol. Better results were obtained by converting the amino acids into the corresponding *N*-acetylated esters, i. e. by blocking both the functional groups(8).

Johnson *et al.* investigated *N*-acetylated ethyl, butyl, *n*-amyl, isobutyl, and isoamyl esters of amino acids; the best results were achieved with *n*-amyl esters(9). In their procedure 17 amino acids were chromatographed on two columns with Carbowax 1540 (polyethylene glycol, molecular weight 1540), at different temperatures. To prevent the condensation of amino acids a low ratio of liquid phase to solid support was used, viz. the column was 240 cm long and contained 1% of Carbowax 1540 on Chromosorb W. Good separation of 14 amino acids was effected. The remaining three amino acids were separated on a shorter column (60 cm), packed with 1/2% Carbowax 1540 on Chromosorb W, at a temperature of 148°C. A Barber-Colman gas chromatograph with argon as the carrier gas and β-argon as the ionization detector was used.

In the work reported here we attempted to apply the gas chromatographic procedure for the separation of amino acids in the form of the corresponding *N*-acetyl *n*-amyl esters under experimental conditions different from those cited above(9). A Beckman GC—2A chromatographic unit with a thermal conductivity detector (T/C detector) was used, the stationary phase consisted of Carbowax 1000 and 4000 and the mobile phase, i. e. the carrier gas, was hydrogen, helium or nitrogen.

EXPERIMENTAL

n-Amyl esters of individual *N*-acetyl amino acids and amino--acid mixtures were prepared according to the procedure given by Johnson *et al*(9), in the presence of hydrogen bromide as catalyst; however, the yields were not quantitative. Slightly better results were obtained by carrying out the esterification with absolute *n*-amyl alcohol in benzene, in a Dean-Stark aparatus, in the presence of hydrogen bromide as catalyst. The best yields were obtained by a modification of Johnson's method, described by Darbe and Blau(10), in the presence of hydrogen chloride as catalyst.

n-Amyl esters of 13 *N*-acetyl amino acids were prepared from 10 mg of each acid, and the mixture of these amino acid's derivatives was obtained from a mixture of the acids containing 10 mg of each. Derivatives of individual amino acids and the mixture of derivatives gave no positive color reaction with ninhydrin, indicating that the amino groups were blocked. Since the investigations were carried out with small quantities of amino acid, the areas under the peaks of individual amino acid esters were taken as the criterion for the *n*-amyl ester yield.

Carbowax 1000 and 4000 on solid supporter Chromosorb W were used as stationary phases. Since the T/C detector is less sensitive than the β-argon ionization detector, we were obliged to use larger amounts of substances, viz. 50 mg of *n*-amyl ester of each *N*-acetyl amino acid, both in the mixture and individually. This led to overloading of the column, so that separations with a small percentage of the liquid phase were not satisfactory. On the other hand, increasing the amount of the liquid phase caused an increase of the retention time, i. e. the analysis was prolonged.

The time required for the analysis could be shortened either by increasing the temperature, or by increasing the flow rate of the gas carrier. Since Carbowax 1000 decomposes at temperatures above 150°C, it was found to be inconvenient as a liquid phase, and the flow rate of the gas carrier could not go beyond a certain value. Much better separations were obtained with Carbowax 4000 as the stationary phase, in a ratio of 5% with respect to the solid supporter.

The effect of the gas carrier on the chromatographic separation of *n*-amyl esters of N-acetyl amino acids was investigated by using three different carriers: hydrogen, helium and nitrogen. Nitrogen was found to be inconvenient on account of traces of oxygen, which caused the decomposition of the stationary phase and considerable "bleeding" of the column. Hydrogen was much better than nitrogen, but the separation of individual amino acids was not complete. The best was found to be helium. With it 11 out of the 13 amino acids were separated. The esters of alanine and valine appeared as a single peak, and those of phenylalanine and aspartic acid could not be eluted from the column.

The separation of the *n*-amyl esters of the *N*-acetyl amino acids is shown on the chromatogram in Fig. 1. Retention times, retention volumes, characteristics of the column, peak areas and their relative percentages are given in Table 1. The experimental conditions were as follows:

Gas chromatograph: Beckman GC-2A
Column: 180×0.6 cm stainless steel
Stationary phase: Carbowax 4000, 5%
Solid support: Chromosorb W 45/60 mesh (ASTM), acid washed
Temperature of the column and detector: 177°C
Gas carrier: Helium at 120 ml/min at the outlet. Inlet pressure: 40 psi (2188 mm Hg). Outlet pressure: atmospheric (759.2 mm Hg)
Detector: T/C. Detector current: 200 mA
Recorder: Bristol 1 mV/sec, chart speed 0.5 inch/min
Sample size: 5 mm
Analysis time: 115 min for *n*-amyl ester of *N*-acetylmethionine

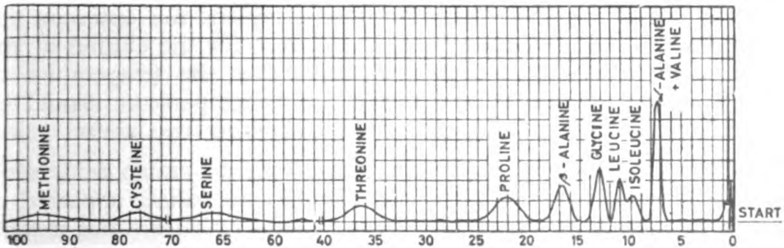

Figure 1

Gas chromatogram of a mixture of n-amyl esters of 11 N-acetyl amino acids

Individual peaks were identified by means of the retention times of the *n*-amyl esters of the *N*-acetyl amino acids chromatographed separately.

TABLE 1

Amino acid	Retention time (t_{dr})		Retention volume, corrected $V_{dr}^{p,T}$ *(ml)*	*HETP (mm)*	*n*	*R*	Peak area *(cm²)*	Relative percentage
	(min)	*(cm)*						
1. α-alanine+valine	7,3	9,3	645	3,04	591	1,34	13,59	22
2. isoleucine	9,8	12,4	865	5,41	333	0,80	5,26	8,4
3. leucine	11,1	14,2	980	2,32	776	1,19	6,18	9,9
4. glycine	13,1	16,7	1157	1,41	1277	1,62	7,60	12
5. β-alanine	16,9	21,5	1492	2,03	886	1,40	7,68	12,3
6. proline	22,2	28,3	1960	4,42	407	3,09	8,53	13
7. threonine	36,5	47,6	3223	1,47	1226	4,24	3,82	6
8. serine	68,5	85,9	6049	—	—	1,23	4,10	6,6
9. cysteine	79,0	99,2	6976	—	—	2,55	3,54	5,7
10. methionine	99,5	127	8787	—	—	—	1,74	2,7

DISCUSSION

The above experimental conditions represent the optimum for the separation. The retention time of 115 min for the elution of the *n*-amyl ester of *N*-acetylmethionine shows that the temperature of 177°C is hardly sufficient, and that a higher temperature should be applied for the elution of esters of the remaining two amino acids.

The chromatogram shows that the first four amino acids were poorly separated, i. e. the first two, alanine and valine, appeared as a single peak and the separation of leucine and isoleucine was incomplete. The first two amino acids were not separated at a temperature of 130°C either. Between peaks for proline and threonine there was a difference of about 10 minutes, between threonine and serine 26 minutes, and between cysteine and methionine about 10 minutes. This indicates that programming of the temperature would afford better separations. From the chromatogram a certain regularity in the order of elution could be observed. Esters of the six aliphatic monoamino-monocarboxylic acids were eluted first, the ester of proline was eluted next, and then the esters of the aliphatic hydroxy--monoaminocarboxylic acids, threonine and serine. The sulphur--containing amino acids cysteine and methionine were eluted the last.

Esters of dicarboxylic amino acids, aromatic amino acids and other heterocyclic and diamino acids were not eluted at the temperature of 177°C. Since Carbowax is a strongly polar stationary phase, the order of elution is not dependent on the physical properties of the amino acid esters (boiling point or vapor pressure), as in the case of a nonpolar column, but on their chemical structure. Percentages calculated from areas under peaks for individual amino acid esters in the mixture were not consistent with their actual percentages. Hence, a quantitative determination indispensably requires the use of standards.

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COULOMETRIC DETERMINATION OF SODIUM TETRABORATE AND POTASSIUM BIPHTHALATE

by

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The principles of coulometric acidimetry and coulometric alkalimetry prompted P. Tutundžić and S. Mladenović to develop a new field of coulometric determination — indirect coulometric titration, which has two variants: the first variant involves indirect coulometric titrations based on hydrolysis and solvolysis(1, 2), which are performed by one-step coulometric determination of the acid or base formed by hydrolysis; the second variant comprises two-step coulometric titrations which are performed by carrying out electrolysis of the aqueous solution of the substance examined, whereby an acid or base is formed, and then determining the acid or base coulometrically.(3, 4, 5)

Regradless whether the determination involves the one-step or the two step-procedure, the acid or base formed is related to the starting substance, so that from the number of coulombs consumed in its titration one can draw quantitative conclusions about the substance examined. The results can be expressed either with respect to the salt, i. e. the compound examined, or with respect to its cation or the anion.

From the hydrolysis equations

$B^+ + H_2O \rightleftharpoons BOH + H^+$ (1) salt of a strong acid and a weak base

and $A^- + H_2O \rightleftharpoons HA + OH^-$ (2) salt of a weak acid and a strong base

and the hydrolysis constants

$$K_h = \frac{[BOH]\,[H^+]}{B^+} = \frac{K_W}{K_b} \tag{3}$$

$$K_h = \frac{[HA]\,[OH^-]}{A^-} = \frac{K_W}{K_a} \tag{4}$$

it is easy to conclude that the coulometric determination is based on the fact that change of the concentration of one hydrolysis component causes a concentration change of other components, such that the constant K remains unchanged.

The removal of H^+ ions from equation (1) by the addition of OH^- ions, or the removal of OH^- ions from equation (2) by the addition of H^+ ions, can make the reaction go from left to right, and bring it to completion. From the amounts of alkalis or acids added, which are equivalent to the amounts of salts hydrolyzed, one can calculate the amount of the salt, metal, or anion examined. The removal of one of the hydrolytic products from the system makes possible complete hydrolysis.

To make the change of the concentration of one hydrolytic product convenient for the coulometric determination, the aqueous solution of the salt which hydrolyzes is submitted to electrolysis; in this way one hydrolytic product can be removed electrolytically and it can be determined coulometrically from Faraday's laws, on the basis of which we can draw conclusions about the amount of the substance being determined.

In view of P. Tutundžić's proposal (7,8) to use the electron, i. e. the coulomb as the fundamental unit in volumetry and analytical chemistry instead of other variously convenient substances, it was of interest to carry out the coulometric determination of solutions of sodium tetraborate and potassium biphthalate(2) which are sometimes used as primary substances in volumetry.

These investigations had a double aim: on the one hand we wanted so widen the range of application of coulometric titration using hydrolysis, and on the other, we wished to give an electronic basis for the further application of these substances in the laboratory and reduce their determination to the electron i. e. the coulomb, as a universal unit in coulometric determinations, both in analysis and preparation(6,7,8,9).

Coulometric determinations at constant current were carried out in a simple electrolysis apparatus with separate anode and cathode spaces. The current curcuit was switched on and switched off against a chronometer. The quantity of the salt hydrolyzed was calculated from the number of coulombs consumed for the neutralization of the acid or base formed during hydrolysis.

COULOMETRIC DETERMINATION OF SODIUM TETRABORATE

Coulometric determination of sodium tetraborate, as a special case of acidimetric-coulometric determination of the base formed during hydrolysis, was carried out in the anolyte, which was connected with the catholyte by means of an electrolytic bridge of agar-agar in saturated potassium nitrate solution. The supporting electrolytes in the anolyte and the catholyte were 0.3 M and 0.4 M potassium nitrate solutions. Konwn amounts of N/40 sodium tetraborate solution were placed in the anolyte. The anolyte was stirred with a magnetic stirrer. The current source was an electronic current stabilizer connected in series with a precision milliammeter. The cathode and the anode were cylindrical electrodes of platinum gauze. The titration end-point was determined by means of methyl-red, added to the anolyte. In order to minimize the visual error, the indicator color at the end-point was compared with the color in a dummy run. Boiled distilled water and p. a. reagents were used for the preparation of solutions.

The results of the sodium tetraborate determinations are given in Table 1.

TABLE 1

Coulometric determination of sodium tetraborate

The supporting electrolyte for the 10^{-4}M sodium tetraborate solution was 0.4 M potassium nitrate solution, and for the 10^{-3} M solution, 0.3 M potassium nitrate solution.

The volumes of the catholyte and the anolyte were 50 ml each; 1% methyl-red solution was used as indicator.

Generator current I = 30.0 mA.

Approximate concentration of $Na_2B_4O_7 \cdot 10H_2O$	Taken	Found	Error		Current	Time
Mole/l	mg	mg	mg	%	mA	sec.
$2.48 \cdot 10^{-4}$	4.768	4.80	0.03	0.64	30.0	80.4
$4.96 \cdot 10^{-4}$	9.536	9.62	0.08	0.80	30.0	160.8
$7.40 \cdot 10^{-4}$	14.304	14.39	0.09	0.62	30.0	241.2
$0.99 \cdot 10^{-4}$	19.072	19.17	0.10	0.53	30.0	321.0
$1.20 \cdot 10^{-3}$	23.840	23.92	0.08	0.32	30.0	402.0
$1.40 \cdot 10^{-3}$	28.608	28.73	0.13	0.45	30.0	482.4

Table 1 shows that the determinations were carried out with micro and semi-micro quantities ranging from 4.768 mg to 28.608 mg. The results are within the limits of error permissible in analytic determinations.

COULOMETRIC DETERMINATION OF POTASSIUM BIPHTHALATE

Coulometric determination of potassium biphthalate, as a special case of alkalimetric-coulometric determination of the acid formed during hydrolysis, was carried out in the catholyte, which was connected with the anolyte by means of an electrolytic bridge of agar-agar in saturated potassium nitrate solution. The supporting electrolyte in the catholyte and the anolyte was 0.25 N and 0.5 M KNO_3, respectively. Sodium sulphate(10) can also be used as the supporting electrolyte. Known amounts of M/80 potassium biphthalate were put into the catholyte. The catholyte was stirred with a magnetic stirrer. The current source was an electronic current stabilizer which was connected in series with a precize milliammeter. The cathode and the anode were cylindrical platinum electrodes. The titration end-point was determined visually using phenolphthalein as indicator. Amounts from 0.67 mg to 25.5 mg were determined with a current ranging from 10.0 to 50.0 mA.

In order to avoid the effect of carbon dioxide from the water it is necessary to use boiled distilled water for the preparation of solutions.

TABLE 2

Coulometric determination of potassium biphthalate

The supporting electrolyte for the 10^{-4} M potassium biphthalate solution was 0.5 $M\,KNO_3$ and for the 10^{-3} M solution 0.25 $M\,KNO_3$.

The volumes of the catholyte and anolyte were 50 ml each; 0.5% alcoholic phenolphthalein solution was used as indicator.

Generator current I = 10.0, 20.0, 30.0, 40.0, and 50.0.

Approximate concentration of $KHC_8H_4O_4$	Taken	Found	Error		Current	Time
Mole/l	mg	mg	mg	%	mA	sec.
$0.6 \cdot 10^{-4}$	0.637	0.649	+0.025	1.99	10.0	30.1
$9.0 \cdot 10^{-4}$	10.20	10.24	+0.04	0.45	20.0	241.3
$1.2 \cdot 10^{-4}$	1.274	1.268	—0.006	—0.49	30.0	20.1
$2.4 \cdot 10^{-4}$	2.55	2.565	+0.015	+0.40	30.0	40.2
$4.8 \cdot 10^{-4}$	5.10	5.15	+0.06	1.28	30.0	80.3
$7.4 \cdot 10^{-4}$	7.65	7.70	+0.05	0.74	30.0	120.6
$9.9 \cdot 10^{-4}$	10.20	10.27	+0.07	0.76	30.0	160.8
$1.2 \cdot 10^{-3}$	12.75	12.87	+0.12	0.96	30.0	201.0
$7.4 \cdot 10^{-4}$	7.65	7.71	+0.06	0.75	40.0	90.4
$1.2 \cdot 10^{-3}$	12.75	12.80	+0.05	0.42	40.0	150.8
$2.4 \cdot 10^{-3}$	25.50	25.69	+0.019	0.75	50.0	241.2

The results given in Table 1 and Table 2 represent mean values from 4 to 6 determinations.

In the determination of sodium tetraborate OH^- ions are accumulated in the catholyte, and in the determination of potassium biphtalate H^+ ions in the anolyte; by diffusion and migration these ions can cause positive errors in the determination. This explains the positive errors in Table 2. Therefore it is necessary to monitor the supporting electrolyte by means of an indicator, or in each determination use fresh supporting electrolyte. The undesirable accumulation of OH^- and H^+ ions can be avoided by the addition of sulphuric acid to the catholyte or potassium hydroxide to the anolyte, respectively.

When several experiments are carried out with the same electrolytic bridge it is necessary that always the same ends are placed in the anolyte and catholyte, respectively.

The simplicity of the apparatus and the technique for the coulometric determination of micro and semi-micro amounts of sodium tetraborate and potassium bipthaplate indicate the possibility of wide application of this method in modestly equipped laboratories.

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INDIRECT COULOMETRIC TITRATIONS. PART II. THE DETERMINATION OF FERROUS AND FERRIC IONS

by

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INTRODUCTION

The possibility of indirect coulometric determination of ferrous and ferric ions using the hydrolysis phenomenon was investigated, in view of the fact that ferrous and ferric salts, being salts of weak bases, hydrolyze in aqueous solutions giving sparingly soluble hydroxides and liberating an equivalent amout of the acid:

$$Fe^{2+}+2H_2O \rightleftharpoons Fe(OH)_2+2H^+ \qquad (1)$$

$$Fe^{3+}+3H_2O \rightleftharpoons Fe(OH)_3+3H^+ \qquad (2)$$

Quantitative hydrolytic decomposition of the salt may be achieved either by neutralizing the acid with an added base, or by forming the base in the system itself; the latter is effected by the decomposition of water molecules at the cathode. The amount of the salt can be calculated from the quantity of electricity, or from the amount of the base used in neutralizing the acid in the presence of a convenient acid-base indicator. However, since visual determination of the titration end-point is not possible on account of the properties of ferrous and ferric hydroxides, we applied a modified method which consists in an indirect determination of cations by means of the acid liberated in the separation of cations from the system in the form of precipitated hydroxides. Accordingly, this method can only be applied if the experimental conditions are chosen so that after the separation of cations the system contains just the amount of the acid which is equivalent to the amount of the hydrolyzed salt. This can be achieved by electrolytic precipitation of hydroxide with the catholyte separated from the anolyte, and by using electrolysis conditions such that the reduction takes place at the cathode, and the oxidation of water molecules at the anode:

$$2H_2O+2e \rightarrow H_2+2OH^- \qquad (3)$$

$$H_2O—2e \rightarrow 1/2O_2+2H^+ \qquad (4)$$

At first the base formed in the catholyte is used for the precipitation of iron hydroxide, i. e. for the neutralization of H^+ ions. In the literature it is reported that ferrous hydroxide is quantitatively precipitated at $pH=9.7$, but that at $pH=13.5$ it begins to dissolve, whereas ferric hydroxide is quantitatively precipitated at $pH=4.1$ and begins to dissolve at $pH=14$(2). After the quantitative precipitation of hydroxide in the presence of an excess of OH^- ions, the catholyte is filtrated, and the filtrate is added to the anolyte. The excess of OH^- ions is thus neutralized with the acid which had been formed in the anolyte by an equivalent quantity of electricity, and the solution contains only an amount of the acid equivalent to the amount of the salt taken. Therefore no strict monitoring of the electrolysis (current and time) is necessary in the course of the precipitation of iron hydroxides.

The oxidation of ferrous into ferric ions by atmospheric oxygen in the course of the electrolysis, or upon standing of the solution before analysis, does not affects the results, since the reaction gives rise to OH^- ions which compensate the excess acid formed by the hydrolysis of ferric ions:

$$4Fe^{2+}+O_2+2H_2O \rightarrow 4Fe^{3+}+4OH^- \qquad (5)$$

In the present work we examined the effect of the current strength, the duration of hydrolysis, and the temperature of the solution during the electrolytic precipitation of ferrous and ferric hydroxides on the results obtained, in order to find out the optimum experimental conditions for the application of this method. In addition, we also examined the possibility of determining ferrous and ferric ions in mixtures by the application of two coulometric methods: indirect coulometric titration and coulometric permanganometry. By indirect coulometric titration the total amount of ferrous and ferric ions in the solution is determined, and by coulometric permanganometry the amount of ferrous ions in the mixture is determined in a separate run.

EXPERIMENTAL

In these experiments reagents of p. a. purity were used.

All solutions were prepared with redistilled water.

The titer of a slighty acid 0.05 N ferric chloride solution, prepared by dissolving a known amount of the salt in 0.002 N sulphuric acid, was determined gravimetrically(3).

The titer of a slightly acid 0.05 N ferrous sulphate solution was determined by coulometric permanganometry(4).

These experiments were carried out with the apparatus described in a previous paper(5). The electrodes, both anode and cathode, were made of platinum wire 0.5 mm in diameter (surface area 2.8 cm^2) which was fused into a glass tube and twisted into a spiral.

The solution for the titration was prepared by adding a known volume of a standard ferrous or ferric salt solution to the supporting electrolyte (a sodium sulphate solution of a given concentration and volume). The solution prepared was then connected with the anolyte, a sodium sulphate solution of the same concentration, by means of an electrolytic bridge, and ferrous and ferric hydroxides were precipitated by electrolysis at constant current; during the latter operation the catholyte was vigorously stirred with a magnetic stirrer. The precipitation of hydroxides (ferrous and ferric) has to be made quantitative. It was found that the optimum pH for this lies in the range from 11.05 to 11.20. The separated hydroxides were filtered off, the precipitate was washed and the filtrate obtained was united with the anolyte and the content of the electrolytic bridge, filled up with the same sodium sulphate solution. In the second phase of the determination, the free acid in the solution obtained by joining the filtrate, anolyte and the bridge content was determined by coulometric titration at constant current, in the presence of methyl red. The titration current was chosen so that the titration error for the amount of substance taken was reduced to a minimum.

The coulometric-permanganometric determination of ferrous ions in a mixture with ferric ions was carried out in a separate run. A solution of the following composition was used as the anolyte: 0.11 $M\ MnSO_4+5.4\ NH_2SO_4$; the catholyte was 1.8*N* sulphuric acid solution. The electrolytic bridge was filled with the anolyte. The current density at the anode was 1.4 mA/cm^2 for the given acidity of the anolyte (5.4 N) and a temperature of 30°C. A mixture of ferrous and ferric ions of a known composition was added to the anolyte which had been previously titrated till change of the indicator color (ferroin: 4 ml of 0.1 *N* Moore's salt+4 ml of 0.025 *M* phenatroline-ferrous sulphate +30 ml of water) from red into blue. Ferrous ions were titrated with electrolytically produced permanganate till the reappearance of the blue color. Chloride ions interfere with the determination since they can be oxidized with permanganate.

RESULTS AND DISCUSSION

The results of the determination of ferric ion in amounts from 1 to 7 mg (from 5.10^{-4} to 5.10^{-3}M) are shown in Table 1.

The effect of the current strength on the precipitaion of ferric hydroxide was studied with currents ranging from 5 to 50 mA. It was found that the current strength has no influence on the final results, but that the precipitate formed at higher current strengths is not so easily filtered, and that the evolution of hydrogen can be so vigorous as to cause losses by sprinkling of the electrolyte.

The maximum time required for the electrolysis was found to be achieved at $pH=11.5$; for a given amount of the substance and a given current strength it was determined from the *pH*, time curve recorded in the course of hydroxide precipitation. The recording were made on a Radioneter-22 *pH*-meter by successively switching out the generator circuit and taking reading after 30 to 60 seconds. It was found that a considerably extended duration of the electrolysis ($pH > > 11.20$) gave rise to slightly higher results (by 1 to 2%). This effect could be due to an increased concentration of OH^- ions in the solution, which results in an increased adsorption of OH^- ions on the surface of the precipitate.

The effect of the temperature of the solution in the ferric hydroxide precipitation on the final results of the determination was examined by precipitating the hydroxide at room temperature and at a temperature very near to the boiling point of the solution. It was found that the temperature and the way of working up the precipitate (washing with either redistilled water or warm 0.05 N sodium sulphate solution) do not affect the final results.

TABLE 1

Indirect coulometric titration of ferric chloride

Precipitation of ferric hydroxide
Catholyte: 0.5 N Na_2SO_4
Anolyte: 0.5 N Na_2SO_4
Conc. of Fe^{3+}: $5.10^{-4} - 5.10^{-3}M$

Titration of the acid
Anolyte: 0.5 N Na_2SO_4
Indicator: methyl red

Expt. no.	Precipitation of $Fe(OH)_3$		Titration of the acid		Amount of iron		Relative error
	Current (mA)	Time (min)	Current (mA)	Time (sec)	Taken (mg)	Found (mg)	%
1	5	45	9.99	1019.4	1.873	1.908	+1.9
2	5	40	9.99	971.8	1.873	1.873	0.0
3	5	45	9.99	978.8	1.873	1.888	+0.8
4	10	45	9.99	1945.6	3.746	3.748	+0.1
5	10	45	9.99	1946.2	3.746	3.750	+0.1
6	10	60	9.99	1970.2	3.746	3.787	+1.1
7	50	12	20.09	1190.8	4.611	4.615	+0.1
8	50	12	20.09	1196.4	4.611	4.637	+0.6
9	10	75	20.09	1464.4	5.615	5.676	+1.1
10	10	80	20.09	1471.8	5.615	5.702	+1.6
11	10	80	20.09	1488.7	5.707	5.770	+1.1
12	10	90	20.09	1933.2	7.477	7.493	+0.2
13	20	50	20.09	1960.8	7.477	7.619	+1.6
14	30	33	20.09	1922.2	7.477	7.450	—0.4
15	50	20	20.09	1934.6	7.477	7.497	+0.3
16	50	20	20.09	1944.2	7.477	7.535	+0.8

The repreducibility of the results given in Table 1 is satisfactory. The accuracy and the precision of the method for the range of quantities examined was determined by statistical treatment of the results(6,7). By means of the t and F test, applied to the slope and intercept of the straight line of the amount of iron taken (X) against the amount found (Y), it was shown that the results do not include a constant error but include a systematical proportional error of +0.95%. The precision of the results is $+0.19\%$ and lies within the limits of the method accuracy calculated for the smallest amount of ferric ions taken ($+0.3\%$). The systematic proportional error may be ascribed to an excess of acid introduced into the system by the substance itself.

The results of the determination of ferrous ions under the experimental conditions which were found to be the optimum for the titration of ferric ions, are shown in Table 2. It may be seen that they are satisfactory. The minimum time required for the quantitative precipitation of ferrous hydroxide was determined by following the change of the pH with time during hydroxide precipitation. It was found to be independent of the amount of the substance taken and to correspond to a pH of 11.10. As in the determination of ferric ions the optimum time corresponds to a pH range from 11.10 to 11.20, since on prolonged electrolysis the results are higher by 1 to 2%.

TABLE 2

Indirect coulometric determination of ferrous sulphate

Precipitation of $Fe(OH)_2$	*Titration of the acid*
Catholyte: 0.5 N Na_2SO_4	Anolyte: 0.5 N Na_2SO_4
Anolyte: 0.5 N Na_2SO_4	Indicator: methyl red

Expt. no.	Precipitation of $Fe(OH)_2$		Titration of the acid		Amount of iron		Relative error
	Current (mA)	Time (min)	Current (mA)	Time (sec)	Taken (mg)	Found (mg)	%
1	50	10	20.09	788.3	4.603	4.583	—0.4
2	50	12	20.09	802.1	4.603	4.663	+1.3
3	50	15	20.9	1211.4	7.067	7.042	—0.4
4	50	13	20.9	1194.6	7.067	6.944	—1.7

The results of the determination of ferrous and ferric ions in a mixture are shown in Table 3. Since the errors lie within the limits permitted in coulometric titrations, we consider that the results are satisfatory. Hence these two coulometric methods can be successfully applied for the determination of ferrous and ferric ions in mixtures.

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TABLE 3

Determination of ferrous and ferric ions in a mixture by indirect coulometric titration and coulometric permanganometry

Expt. no.	Indirect coulometric titration of Fe^{2+} and Fe^{3+}				Permanganometric determination of Fe^{3+}		Taken		Found		Relative error	
	Precipitation of iron hydroxide		Titration of the acid									
	Current (mA)	Time (min)	Current (mA)	Time (sec)	Current (mA)	Time (sec)	Fe^{3+} (mg)	Fe^{2+} (mg)	Fe^{3+} (mg)	Fe^{2+} (mg)	Fe^{3+} %	Fe^{2+} (%)
1	50	14	20.09	1324.0	5.02	1587.0	1.858	4.603	1.856	4.606	—0.1	+0.1
2	50	13	20.09	1320.0	5.02	1583.0	1.858	4.603	1.849	4.595	—0.5	—0.2
3	50	13	20.09	1356.4	5.02	1067.0	2.975	3.069	2.981	3.097	+0.2	+0.9
4	50	13	20.09	1353.6	5.02	1062.0	2.975	3.069	2.980	3.082	+0.2	+0.4

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INDIRECT COULOMETRIC DETERMINATION OF COPPER USING A MERCURY CATHODE

by

OLIVERA Ž. PAVLOVIĆ and SRETEN N. MLADENOVIĆ

INTRODUCTION

Electrolyses with a mercury cathode are of great practical importance and are ever increasingly applied in modern analytical methods. The prospects for the use of mercury for the coulometric determination of metals are great because of the requirements of modern technology for combined and individual determination of microgram quantities of metals, in cases where other methods for metal separation, on account of simultaneous metal precipitation, do not give satisfactory results.(1)

As far as is known, two methods for indirect coulometric determination of copper have been introduced and developed so far: (i) in the presence of an indirect electrolyte — sulphuric acid(2), (ii) by means of acid liberated at a platinum cathode in the course of metal separation(3). Quantitative separation of the less noble metals (*Cd*, *Zn*, etc) at the platinum cathode from an acid electrolyte, as used in the indirect coulometric determination of copper, is not possible on account of their corrosion and evolution of hydrogen.

However, from 0.1 N sulphuric acid solution the following metals can be quantitatively deposited on a mercury cathode: *Fe*, *Cu*, *Ni*, *Co*, *Zn*, *Ge*, *Ag*, *Cd*, *In*, *Sn*, *Cr*, *Mo*, *Pb*, *Bi*, *Se*; *Te*, *Hg*, *Au*, *Pt*, *Ir*, *Rh* and *Pd*(4). Deposition of less noble metals (*Fe*, *Cd*, *Zn*, etc) on a mercury cathode occurs because of the greater overvoltage of hydrogen evolution.

Indirect coulometric determination of copper from acid electrolyte using a mercury cathode indicates the possibility of indirect coulometric determination of all metals which are deposited on a mercury cathode, even those which are less noble than hydrogen.

This method for the coulometric determination of copper is based on the same principles as the coulometric method for copper using platinum electrodes. However, the possibilities for indirect coulometric determination with a mercury cathode are much greater.

The application of this method for the coulometric determination of copper is based on reactions which take place at the mercury-cathode and platinumanode during the electrolysis of an acid copper sulphate solution:

$$\left.\begin{aligned} Cu^{2+}+2e &\rightarrow Cu(Hg) \quad &(1)\\ 2H_2O+2e &\rightarrow H_2+2OH \quad &(2)\end{aligned}\right\} \text{at the cathode}$$

$$H_2O-2e \rightarrow 1/2\,O_2+2H^+ \quad \text{at the anode} \qquad (3)$$

From equations (1), (2) and (3) it may be seen that the liberated acid will be equivalent to the amount of the copper reduced, independently of the duration of electrolysis, since the base which is formed at the cathode is neutralized by the acid formed at the anode during the passage of an equivalent amount of electricity. Therefore no measurement of the electrolysis (current density and time) is necessary, since after the quantitative deposition of copper, the electrolytic decomposition of water is the sole process which occurs.

The deposition of copper on mercury was carried out from slightly acid copper sulphate solution without addition of any conducting salt, so that only the reactions given by the above equations could take place at the electrodes, the *Hg*-cathode and *Pt*-anode. The amount of acid added was chosen so that the time required for its titration and the time required for the titration of the acid equivalent of the amount of the substance taken were not of the same order of magnitude.

To determine the optimum experimental conditions we studied both the effect of the amount of the substance taken and of the current, and also the effect of the duration of the electrolysis, on the results.

EXPERIMENTAL

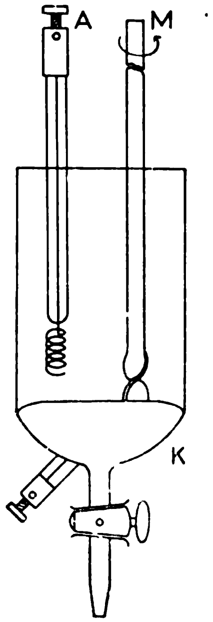
In these experiments reagents of p. a. purity were used.

All solutions were prepared with redistilled water.

The titer of a slightly acid 0.05 N copper sulphate solution was determined by electrogravimerty.

These experiments were carried out with the apparatus described in a previous paper(5). Deposition of copper on mercury was performed in the cell shown in Fig. 1. The area of the mercury cathode was about 15 cm^2 and its volume about 20 ml. The anode was a platinum spiral of 3.5 cm^2 surface area, and it served as the cathode in the second phase of the determination, i. e. in the titration of the acid. The solution and mercury were vigorously stirred with an electric stirrer. The determinations were performed at room temperature.

The determination of copper involved first the deposition of copper on the mercury cathode by electrolysis at constant current from a solution consisting of about 70 ml of 3.10^{-4} N sulphuric acid. After complete copper deposition, the mercury was let out of the cell. The solution was then connected with the anolyte, 0.5 N sodium sulphate



A: *Pt*-anode
K: *Hg*-cathode
M: stirrer

Figure 1
Electrolysis cell with mercury cathode

solution, by means of an electrolytic bridge (agar-agar) saturated with potassium chloride), the curcuit was made and the acid was titrated coulometrically in the presence of methyl red indicator. The quantity of electricity equivalent to the amount of acid added was also determined coulometrically in a separate run.

RESULTS AND DISCUSSION

Determinations of copper were carried out with amounts ranging from 1 to 10 mg (10^{-4} —10^{-3} M). This weight range was found to be the most convenient for the method on account of the low sensitivity and precision of the indicator method for amounts smaller than 1 mg, i. e. concentrations smaller than 10^{-4} M, and too long a duration of copper deposition on mercury in case of quantities larger than 10 mg.

The eletrolytic deposition of copper was carried out at currents of 20, 30 and 50 mA. The results obtained with 20 mA are shown in Table 1. It may be seen that the results are satisfactory; deviations of individual measurements are within the limits permitted in coulometry ($\pm 1\%$). However, with currents of 30 and 50 mA, the results were higher by 1 to 4%. These deviations might be due to the presence of small amounts of impurities which, at these current strengths, are probably deposited together with copper.

TABLE 1

Indirect coulometric determination of copper by deposition on a mercury cathode

Titration of the acid: Indicator: methyl red

Anolyte: 0.5 N Na_2SO_4 Concentration of Cu^{2+}: $10^{-4} - 10^{-3}$ M

Expt. no.	Deposition of *Cu*		Titration of the acid		Amount of *Cu*		Relative error (in %)
	Current (mA)	Time (min)	Current (mA)	Time (sec)	Taken (mg)	Found (mg)	
1	20	60	10.01	467.4	1.547	1.541	−0.4
2	20	45	10.01	470.2	1.547	1.550	+0.2
3	20	45	10.01	480.8	1.580	1.586	+0.4
4	20	60	10.01	725.6	2.370	2.392	+0.9
5	20	60	10.01	811.6	2.687	2.676	−0.4
6	20	60	10.01	960.2	3.160	3.166	+0.2
7	20	60	10.01	1203.0	3.950	3.966	+0.4
8	20	60	10.01	1445.6	4.744	4.766	+0.5
9	20	75	20.09	848.2	5.530	5.613	+1.5
10	20	75	20.09	959.8	6.322	6.351	+0.5
11	20	90	20.09	1089.4	7.111	7.143	+0.4
12	20	90	20.09	1202.8	7.900	7.959	+0.7
13	20	90	20.09	1540.6	10.11	10.20	+0.8

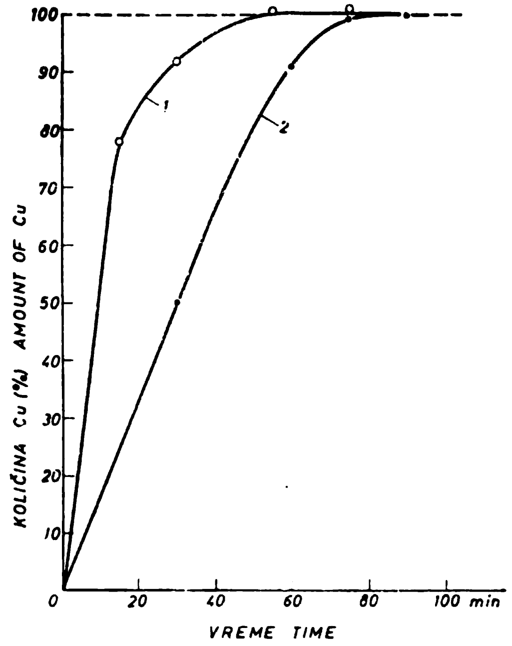


Figure 2

Deposition of copper on a mercury cathode from a slightly acid copper sulphate solution

Current strength: 20 mA

Curve 1: 1580 mg of copper

Curve 2: 10.110 mg of copper

The deposition of copper (current 20 mA) was carried out in times ranging from 45 to 90 minutes, depending on the amount of the substance taken. The minimum time required for quantitative deposition of quantities ranging from 1 to 10 mg from a solution of the given acidity at a current strength of 20 mA was determined from curves of the yield of deposited copper as a function of the duration of the electrolysis. The curves are given in Fig. 2. According to these curves the minimum time required ranges from 45 to 90 minutes. A longer duration of the electrolysis does not affect the results since after the complete deposition of copper the electrolysis of water is the only process which occurs, and this does not change the amount of the acid but only increases its concentration.

The accuracy and precision of the method for the range examined was determined by statistical treatment of the results given in Table 1(6,7). By means of the *t* and *F* tests applied to the straight line [amount of copper taken (X)] against [amount of copper found (Y)], it was found that the results do not have a constant error but that they include a systematic error of +0.81%. The precision of the method is quite satisfactory, ±0.27%, and this lies within the limits of the standard error (±0.3%) calculated for the minimum amount of copper taken. In our opinion the systematic error is most likely due to extra of acid introduced by the examined substance itself.

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DETERMINATION OF ORIENTATION OF GERMANIUM AND SILICIUM MONOCRYSTALS BY REFLECTOMETRY

by

ANDREJA V. VALČIĆ and MILAN G. BREKIĆ

INTRODUCTION

To prepare a surface for the determination of monocrystal orientation by reflectometry, it has first to be polished with emery paper and then with a polishing paste. The fine mechanical treatment is followed by chemical etching.

Microscopic examination of an etched monocrystal surface reveals a large number of tiny hollows commonly called etching pits. Etching pits are unrelated to the dislocations in the crystal surface, but are closely related to the anisotropic nature of the crystals, i.e. the fact that crystals dissolve at different speeds in different directions. The occurrence of etching pits and their shape are not random; they comply with the symmetry of the given crystal plane. Every pit forms a geometric figure which is always determined by the degree of symmetry of the crystal planes involved. Hence the degree of crystal symmetry may be determined from the shape of etching pits. For a monocrystal surface all etching pits are oriented in the same direction.

The principle of the reflectometric method is the reflection of light from the surfaces surrounding an etching pit. A beam of light thrown on an etched monocrystal surface splits into as many components as an etching pit has surrounding surfaces. Projected on a screen this reflection shows a pattern called a reflectogram. Reflectograms can be used to determine the orientation of monocrystals.

ETCHING

For studying the etching of monocrystals of germanium and silicium attention was paid to the choice of etchant and etching conditions for the sharpest reflectogram.

Table 1 gives etching conditions and the corresponding reflectograms. The change in thickness of the test slides as a function of etching time was examined. It was found that the best formed etching pits, and hence the sharpest reflectograms, are obtained after a layer of 10μ has been removed from the crystal surface.

All etching was done on 10 × 10 × 0.5 mm germanium and silicium plates. The germanium was of the p-type, 2—3 ohm cm, the number of dislocations ranging around 3000 per cm^2. The silicium was of the p-type, 10 ohm cm, number of dislocations 40,000 per cm^2. Etching a (111) surface of germanium or silicium monocrystal produces pits with the form of a rounded triangular pyramid. Figure 1 shows the microscopic appearance of a (111) germanium monocrystal surface etched with mixture 4 (Table 1), magnified 450 ×. Etching pits on a (100) surface have the form of a rounded quadrilateral pyramid. Figure 2 shows the microscopic appearance of a (100) germanium monocrystal surface etched with mixture 15 (Table 1), magnified 450 ×.

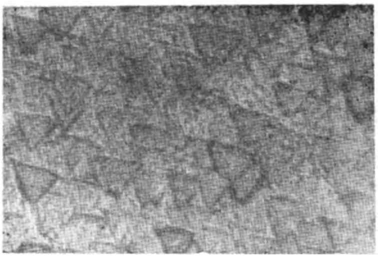


Figure 1

Etching pits on a (111) surface of a germanium single crystal. (450 ×)

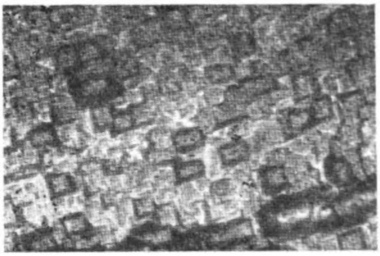


Figure 2

Etching pits on a (100) surface of germanium single crystal. (450 ×)

Etching with mixtures 1 through 6 (Table 1) was done in a 250 ml polyethylene vessel with constant mixing. Observation of the etched surfaces and their reflectograms reveals with increasing HF to H_2O_2 concentration ratio the face surfaces of the etching pit get deformed. As a result the form of the reflectogram changes. Using mixtures 1 to 4 (Table 1) reflectograms in the form of three spots are obtained (Fig. 3). With the higher concentration of HF in mixture 5 (Table 1) the reflectogram shows an elongated pattern (Fig. 4). Further raising of the HF concentration, mixture 6 (Table 1), produces a reflectogram of three lines (Fig. 5). Each reflectogram has a bright spot in the center (Figs. 3, 4 and 5), resulting from the light reflected from the surfaces between the etching pits and the surfaces at the bottom of the pits.

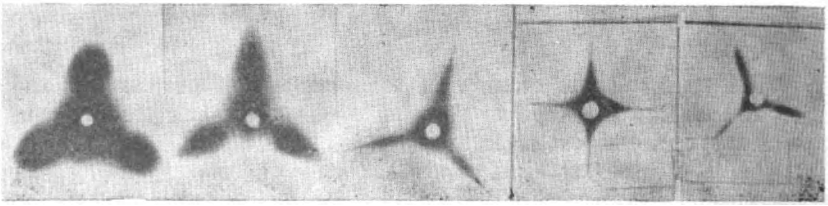
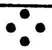
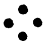


Fig. (3) *Fig.* (4) *Fig.* (5) *Fig.* (6) *Fig.* (7)

Reflectograms of germanium single crystal: Fig 3, 4, 5, and 7 from (111) plane, Fig. 6 from (100) plane.

TABLE 1

Element	Plane	No.	Etchant	Time (min)	Temp. (C°)	Reflecto-gram
GERMANIUM	(111)	1	$HF:H_2O_2=1:1$	2	22	
		2	$HF:H_2O_2:H_2O=1:1:1$	2	22	
		3	$HF:H_2O_2:H_2O=1:1:2$	2	22	
		4	$HF:H_2O_2:H_2O=1:2:4$	12	22	
		5	$HF:H_2O_2:H_2O=3:4:5$	5	22	
		6	$HF:H_2O_2:H_2O=2:1:4$	5	22	
		7	1 g KOH, 4 g $K_3Fe(CN)_6$ in 50 ml of water	5	tb **	
		8	3 g KOH, 4 g $K_3Fe(CN)_6$ in 50 ml of water	5	,,	
		9	6 g KOH, 4 g $K_3Fe(CN)_6$ in 50 ml of water	5	,,	
		10	$HNO_3:HF=5:3$	3	22	
		11	$HNO_3:HF=1:1$	5	22	
		12	$HNO_3:HF=1:1$ (1% $AgNO_3$*)	10	22	
		13	$HNO_3:HF=1:1$ (2% $AgNO_3$*)	12	22	
	(100)	14	$HF:H_2O_2:H_2O=3:4:8$	12	22	
		15	15% KOH in water	5	tb**	
Silicon	(111)	16	50 % KOH in water	3	tb**	
		17	15 % KOH in water	5	tb**	
	(100)	18	50 % KOH in water	12	tb**	

* $AgNO_3$ percentages refer to the whole mixture. Etchants are given in volume ratios. Concentrations: hydrofluoric acid 49%, hydrogen peroxide 30%, nitric acid 60%. Mixtures 7, 8, 9 are given in weight ratios.

** tb — boiling temperature.

Etching with mixtures 7 to 9 (Table 1) was done in a glass vessel at the boiling temperature of the mixture and with intensive mixing. With increasing KOH concentrations in the etchant the face surfaces of the pit got deformed and the reflectograms changed. The reflectograms from these surfaces are identical with those in Figs. 3, 4 and 5.

With mixtures 10 to 13 (Table 1) it was noticed that the higher the HNO_3 concentration in the etchants the faster the rate of dissolution. It was noted that silver nitrate in this mixture acted as an inhibitor and slowed down the process of dissolution. Figure 6 shows the reflectogram of a (100) surface of a germanium monocrystal etched with mixture 15 (Table 1).

A (111) surface of a silicon monocrystal was etched in an aqueous solution of KOH. It was noted that with decreasing KOH concentrations in the etchant the face surface of the pits became deformed and the reflectograms changes: from three bright spots to three bright lines. Figure 7 shows the reflectogram of a (111) surface of a silicon monocrystal etched with mixture 17 (Table 1).

From comparing the results obtained by measuring the changes in thickness in direction (111) and in direction (100) it was concluded that etching in the latter direction proceeds at a faster rate.

APPARATUS

The apparatus rests on a rail (*A*) which functions as the optical bench. The rail is grooved all along its length on both sides. The grooves insure stability of the three sliding supports, each of which has an adjustment screw to toghten it to the rail. One support carries the light source (*B*): a 30 W electric bulb and a lens at whose focus the bulb filament lies. This source emits a parallel beam of light which can be adjusted by a diaphragm situated at the end of the source setup. The second support carries a panel (*C*) which has a 3 mm slit through which the beam of light passes. The panel carries a movable screen

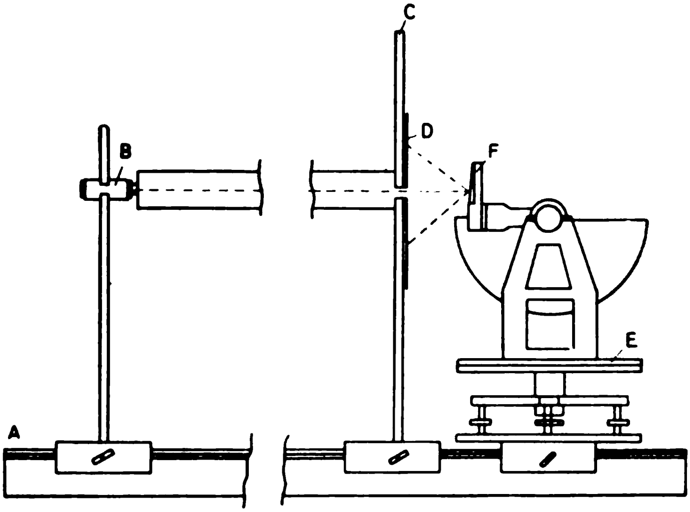


Figure 8
Instrument for optical orientation

(*D*). The figure expected from the etched crystal surface when the crystal is well oriented is drawn on the screen. The third support carries a goniometer (*E*). A carrier for the monocrystal plate (*F*) or the crystal itself is attached to the goniometer. The goniometer is used to determine the angle of deviation from the desired orientation. The apparatus is shown in Fig. 8.

The beam of light passes through the panel with the screen, falls on the surface of the crystal and is reflected back on the screen.

DETERMINATION OF ORIENTATION

Before the determination of the orientation of a monocrystal the zero position of the apparatus is adjusted by placing a plane mirror at point (*F*). Light falls on the mirror surface and the goniometer is adjusted to the position in which the reflected light falls back in the center of the beam. Then an etched monocrystal plate is mounted for the determination of orientation. Unless the plate is precisely oriented its reflectogram will be irregular (e. g. the angle between the lines of a (111) reflectogram will be different from 120°).

By adjusting the goniometer with the monocrystal plate and moving the screen on its supporting panel coincidence between the reflectogram and a drawing on the screen is sought. When coincidence is obtained, the angle of deviation from the desired orientation is read.

TABLE 2

No.	Direction of measurement	Misorientation	
		X-ray	Reflect. method
1	Horizontal	6′	2′
	Vertical	8′	7′
2	Horizontal	— 40′	— 39′
	Vertical	130′	121′
3	Horizontal	34′	34′
	Vertical	—13′	—20′
4	Horizontal	—63′	—53′
	Vertical	—68′	—76′

In determining the orientation of a monocrystal it is found that the procedure is far simpler and more precise when using reflectograms with bright lines rather than those with bright spots. It is easily concluded that by this method the orientation of the surface resting on the support is determined rather than that of the surface on which the beam of light falls.

To verify the accuracy of the reflectometric method, its results were compared with those obtained by the X-ray method. Comparable measurements are presented in Table 2.

It is seen that the discrepancy does not exceed ± 10′.

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DETERMINATION OF NOVALGIN. I.

GRAVIMETRIC METHODS

by

VILIM J. VAJGAND, VERA LJ. NIKOLIĆ and DRAGAN J. KRSTIĆ

Novalgin is the sodium salt of 1-phenyl-2,3-dimethyl-5-pyrazolon-4-methylaminomethane sulfonic acid ($C_{13}H_{16}O_4N_3S\,NaH_2O$) which crystallizes with one molecule of water (this molecule is driven off on drying at 105°C). Nearly every pharmacopoeia prescribes a purity range for this salt of 99—101%. The methods published so far in practice give results far below these accuracy limits which means that the analytical methods for the determination of novalgin are not satisfactory in most cases. This is most frequently so with the iodometric method about which much has been written and which is still in use today. We have undertaken a systematic study of these methods always using the same sample of novalgin, with the intention of discovering the reason for their failure and to find a rapid and reliable method of determination.

This paper reports the results of our examination of gravimetric methods based on the presence of sulphur and sodium.

Data on the gravimetric determination of novalgin are scant and frequently contradictory.

The USSR *Pharmacopoeia VIII*(1) suggests a gravimetric determination of novalgin in the form of barium sulphate after oxidation with an excess of 0.1 N solution of iodine.

Rapaport and Shvartsburd(2) report that "knowledge of novalgin analysis is very limited". They tried to develop a fast, accurate method for qualitative and quantitative analysis of novalgin. In their study they only enumerate the quantitative methods they investigated, including three gravimetric ones: via barium sulphate, sodium sulphate, and sodium chloride, remarking that the first method is long and complex. They held that the volumetric method of oxidation with iodine or iodochlorine was the most suitable and stated their results only for this method.

Shub and Kobzareva(3) slightly modified the idometric procedure. Of the eight different samples of novalgin examined they give comparable results only for four samples in which barium sulphate was used after oxidation with iodine, and only for three samples to which the gravimetric determination of sulphur after Carius was applied. It may be noted here that they obtained 98.47% and 99.79% for the same sample of novalgin using the same method(1), and that the three consistent results of this method were in disagreement with the Carius method. These authors also favor the iodometric method because of the long duration of gravimetric determination.

Kaleïs and Volkova (4) find that the gravimetric determination of novalgin as barium sulphate after oxidation with iodine depends on "luck", which made them resort to an indirect volumetric determination, i.e. of sulphate by means of a complexon, oxidation being carried out with a mixture of hydrogen peroxide with nitric acid.

Fecko(5) oxidized novalgin with hydrogen peroxide in a neutral solution, and determined the sulphate by titration with 0.1 N solution of barium chloride.

Burić(6) applied the gravimetric determination of novalgin in the form of sodium sulphate, because the barium sulphate variant after oxidation with iodine produced variable results. He only gives eight results of his method, including five for pure novalgin and three for a mixture with aminopyrine and phenobarbital, with a mean value 99.70% ±0.40.

The Hoechst factory prescribes the same gravimetric method for novalgin analysis.

Although determination of novalgin as barium sulphate after oxidation with iodine has given unsatisfactory results, nobody has explained why, although this gravimetric method is the most accurate for the determination of sulphates. Aside from this the literature gives no data on the gravimetric determination of sodium ion in aqueous solution of novalgin.

No data is available about the determination of novalgin as sodium chloride. Since sodium occurs here in the presence of sulphide or sulphate ion, which must be separated, thus making the already long analysis still longer and more difficult, such determination is ruled out for practical purposes.

EXPERIMENTAL

For all tests Hoechst novalgin, known for its purity, was used. Check investigations of this preparation showed the following:

1. Chromatographic analysis on a thin silica gel layer proved the absence of other pyrazolon bases(7).
2. Complete solubility in methyl alcohol evidenced the absence of sodium salts of sulfurous or sulfuric acid.
3. Crystalline water content was 5.13% (theoretical value 5.12%) allowing the use of this preparation for analysis which is advantageous over the anhydrous one for not being hygroscopic.
4. Nitrogen content by Dumas' micromethod in the anhydrous sample was 12.46% (theoretical value 12.60%).
5. Sulphur content was determined by two standard methods of organic analysis: electrooxidation according to Gasparini(8), which

gave 9.14%, and fusing with sodium peroxide in Parr's cylinder, which gave 9.15% sulfur (theoretical value 9.12%).

6. Potentiometric titration of the novalgin in acetic anhydride⁽⁹⁾, which we modified by substituting 0.1 N perchloric acid for HCl, gave a 99.96% novalgin content (mean value from six samples).

All other chemicals were of *pro analysi* purity.

DETERMINATION OF NOVALGIN AS SULPHUR IN $BaSO_4$

The determination of novalgin as sulfur in the form of barium sulphate requires the previous oxidation of the bisulfide ion, which, according to Wagner⁽¹⁰⁾, appears as a direct product of novalgin hydrolysis.

In the present study, novalgin was oxidized in solution in two ways: with an excess of 0.1 N solution of iodine, and with 30% hydrogen peroxide. Sulphate was precipitated according to Kolthoff and Sandell⁽¹¹⁾.

Oxidation with Iodine Solution — Results obtained by the USSR *Pharmacopoeia VIII* method⁽¹⁾ showed that this way of oxidation was not reliable. In ten samples the novalgin percentage varied between 91% and 99%. It was noticed that the addition of iodine colored the solutions differently, yellow or violet, that the precipitate disappeared at an uneven rate or, in some samples, some remained in the form of a resin. It was not possible to observe any correlation of these occurrences with the results obtained. It is well known⁽¹²⁾ that the addition of iodine to a neutral novalgin solution produces pH values between 1.5 and 2, which means that oxidation proceeds in an acidic solution.

Our observations (to be reported in another paper) led us to conclude that the hydrolysis of novalgin is not complete. We hold that the direct products of novalgin's decomposition in an acidic medium are bisulfide ion and formaldehyde, some of which can combine into a formaldehyde-bisulfide compound (oximethane sulfonic acid). This is borne out by the fact that novalgin does not fully oxidize on the addition of an oxidizing agent, while the rate of bisulfide ion oxidation is instantaneous.

The following test proved what part the rate of HSO_3' ion liberation playes in this method. Four 0.2000 g novalgin samples were disolved in 10 ml water each. An equivalent amount of iodine was added to the first sample, $3/4$ of the amount to the second sample, $1/2$ to the third, and $1/4$ to the fourth. The samples were immediately diluted, heated and barium sulfate precipitated. It was reckoned in advance that the samples with less iodione would produce higher results because of oxidation with oxygen from the air. The values obtained were 92.67% novalgin for the first sample, 78.75% for the second, 56.46% for the third, and 28.42% for the fourth, which indicated that the reaction in which bisulfide ion is liberated is very much slowed down at the end. This led us to prolong oxidation with iodine and after the samples were left for 1 h, with excess iodine, good results were obtained with all samples (Table 1).

TABLE 1

	Novalgin taken in g	% of novalgin
1	0.2030	100.39
2	0.2041	100.14
3	0.2016	100.49
4	0.2017	100.37
5	0.2001	100.19
6	0.2019	100.34
7	0.2005	100.34
Mean value: 100.33 ± 0.10*		

TABLE 2

	Novalgin taken in g	% of novalgin
1	0.2012	100.09
2	0.2013	100.19
3	0.2018	100.18
4	0.2030	100.17
5	0.2000	100.31
6	0.2022	99.90
7	0.2006	100.16
8	0.1998	100.11
Mean value: 100.13 ± 0.06*		

* Average deviation $\frac{\Sigma |d|}{n}$.

Oxidation with Hydrogen Peroxide — To obviate the possible loss of SO_2 in acidic solution a neutral solution was used. To a novalgin sample dissolved in 35 ml water a 30% solution of hydrogen peroxide (not conserved with sulfuric acid) was added and the sample was left for 15 min for the precipitation of barium sulfate. Results after 15 min gave 94.5%, and after 1 h about 98.3% on an average. This proved that oxidation in a neutral medium, as applied by Fecko⁽⁵⁾, is not satisfactory.

When after hydrogen peroxide several drops of 10% solution of sodium hydroxide (pH around 12) were added to the solution, complete oxidation took 15 m and the results were very good (Table 2).

DETERMINATION OF NOVALGIN AS SODIUM IN Na_2SO_4

Since novalgin is a sodium salt of a sulfonic acid it would seem that a standard gravimetric method of evaporation with sulfuric acid and conversion to sodium sulfate would be most suitable for its determination. In this procedure the organic substance becomes carbonized and burns when heated to red heat. This is the method suggested bu Treadwell⁽¹³⁾ precisely for the analysis of alkaline metals from organic salts. Burić⁽⁶⁾ also mentions that novalgin in a mixture with any organic aubstance can be determined like this. In verifying Burić's method low and inconsistent results were obtained as a rule, and on repeated treatment of the dry residue with sulfuric acid the liberation of hydrogen sulfide was noticed. This agrees with the known fact that sulfates easily reduce to sulfides in the presence of carbon. We therefore added 1 ml 20% solution of sulfuric acid and 2—3 drops of nitric acid to a novalgin sample in a porcelain vessel. Evaporation was done with the utmost care in an air bath until complete dryness.

The sample was again moistened with sulfuric acid and the further procedure was standard. The results obtained in this way are good and reproducible (Table 3).

TABLE 3

	Novalgin taken in *g*	% of novalgin
1	0.3004	99.46
2	0.3001	99.90
3	0.3033	100.29
4	0.3015	100.26
5	0.3008	100.16
6	0.3022	100.16
7	0.3001	99.56
Mean value:		99.97±0.26

The sulfuric acid should be of around 4—6 *N*, because higher concentrations of the acid solution reduce the sulfates more easily. Attention should be called to the fact that heating of novalgin must be conducted with great care at the beginning, because it readily transforms to a resin-like liquid mass which boils and can easily spit.

Apart from its long duration, the disadvantages of this method are: a very high gravimetric factor for conversion to novalgin equivalent (4.9479 for sample with water), and a difference of 0.2 *mg* of sodium sulfate for the stated quantities, which changes the apparent composition of the novalgin by 0.35%.

DETERMINATION OF NOVALGIN AS Na^+ ION IN THE FORM OF $NaZn(UO_2)_3(CH_3COO)_9 \cdot 6\,H_2O$

The presence of sodium ion in the aqueous solution of novalgin and high solubility of this salt led us to try to determine it by precipitation of sodium in the form of sodium zinc uranyl acetate(14). It is generally known that this method calls for a small amount of sodium in a very small volume of solution (about 8 *mg/ml*) because of the high solubility of the salt. With novalgin, this can be attained by the direct dissolution of corresponding amount of substance in 1 *ml* of water, and immediately proceeding to precipitation so that the whole gravimetric analysis takes no more than two hours. Another advantage of this method is a very low gravimetric factor for conversion to novalgin equivalent — 0.2285 for crystalline and 0.2176 for anhydrous samples.

Method — Samples of 0.10 to 0.13 g precisely weighed novalgin are dissolved in 1 ml water in a 50 ml beaker, to which 10 ml of a precipitant is added during mixing. The sample is left for 1 h and mixed occasionally to prevent the formation of a saturated solution of the salt. The precipitate is filtered through the densest glass Gooch crucible first reduced to constant weight. It is first washed four times with 2 *ml* of precipitant each time, and then ten times with 2 ml ethyl alcohol saturated with sodium zinc uranyl acetate. It is highly important that the next portion of washing liquid should not be added before the previous one has been entirely removed and the precipitate dried. Finally the precipitate is washed with ether, air blown through for 5—10 m, the outer surface of the funnel is wiped dry and the funnel with precipitate is left in an exsiccator for 10 m, through this is not essential. The funnel can be weighed immediately.

Errors are likely only if the precipitant is excessively saturated or dilute. We made the precipitant thus$^{(15)}$:

20 *g* uranyl acetate $UO_2(CH_3COO)_2 \cdot 2\,H_2O$ is dissolved in 4 ml glacial acetic acid and 100 ml water, with heating if necessary.

60 *g* zinc acetate $Zn(CH_3COO)_2 \cdot 3\,H_2O$ is dissolved in 3 ml glacial acetic acid and 100 ml water in the same way.

TABLE 4

	Novalgin taken in *g*	Weight of precipitate	Novalgin found in *g*	% of novalgin	% *Na*	Note
1	0.1382	0.6344	0.1375	99.49	6.86	Anhydrous sample (6.89 % *Na*)
2	0.1357	0.6257	0.1355	99.85	6.88	
3	0.1290	0.5956	0.1291	100.07	6.89	
4	0.1271	0.5855	0·1269	99.84	6.88	
5	0.1246	0.5762	0.1249	100.24	6.90	
6	0.1218	0.5635	0.1221	100.24	6.90	
7	0.1176	0.5150	0.1176	100.00	6.54	Sample with crystalline water (6.54 % *Na*)
8	0.1116	0.4884	0.1115	99.91	6.53	
9	0.1103	0.4840	0.1105	100.18	6.55	
10	0.1081	0.4753	0.1085	100.37	6.56	
11	0.1053	0.4620	0.1055	100.18	6.55	
12	0.1018	0.4453	0.1017	99.93	6.53	
13	0.1017	0.4449	0.1016	99.94	6.54	
14	0.1004	0.4382	0.1001	99.70	6.52	Novalgin solution
15	„	0.4400	0.1005	100.09	6.54	
16	„	0.4378	0.0999	99.50	6.51	
17	„	0.4380	0.1001	99.70	6.52	
18	„	0.4388	0.1002	99.80	6.52	
19	„	0.4392	0.1003	99.90	6.53	

Mean value: 99.94±0.19

Standard deviation:* 0.24

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* Standard deviation, $\sqrt{\frac{\Sigma|d^2|}{n-1}}$.

The two solutions are mixed and left 24 h for the salt to crystallize with sodium from the precipitant. The precipitate is filtered and the solution is kept in a plastic flask.

Our results are shown in Table 4. Analyses 14—19 refer to the same solution of novalgin, from which determinations were done daily for six days.

The results for novalgin content by methods applied in this study are summarized in Table 5

TABLE 5

Method	Number of determination	% of novalgin
As sulphur in the form of $BaSO_4$:		
Oxidation with I_2	7	100.33
Oxidation with H_2O_2	8	100.13
Electrooxidation in HNO_3 according to Gasparini	2	100.19
Decomposition in the Parr cylinder with Na_2O_2	1	100.24
As sodium:		
In the form of Na_2SO_4	7	99.97
In the form of $NaZn(UO_2)_3(CH_3COO)_9 \cdot 6H_2O$	19	99.94
As base:		
Potentiometric titration in acetic anhydride	6	99.96
As nitrogen:		
Microanalysis according to Dumas	1	98.88

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SPECTROPHOTOMETRIC DETERMINATION OF MICRO-AMOUNTS OF VANADIUM WITH *N*-BENZOYL-*N*-PHENYLHYDROXYLAMINE IN ALUMINUM AND OTHER MATERIALS*

by

VERICA G. ANTONIJEVIĆ

Of the spectrophotometric methods for the micro-determination of vanadium the one using *N*-benzoyl-*N*-phenylhydroxylamine has recently come to the fore because of being highly selective and sensitive. It is superior to the well-known and recognized methods such as those using hydrogen peroxide, 8-oxyquinoline, or phosphotungsten vanadate(3).

Working independently from one another, Ryan(1) and Priyaradshini(2) suggested *N*-benzoyl-*N*-phenylhydroxylamine as a reagent to determine vanadium. Ryan(1) proposed a method for the determination of vanadium in steel, chromite and chromomagnesite.

We were interested in examining the possibilities of determining vanadium with this reagent in aluminum and uranium. Since *N*-benzoyl-*N*-phenylhydroxylamine reacts with numerous elements in weakly acidic or neutral media, conditions for a specific and selective determination of vanadium were obtained by extracting vanadium from a solution of hydrochloric acid with 1.5—5 N chloroform solution of the reagent. Under these conditions the reaction and extraction of many other metals does not take place. By measuring the absorption of the chloroform layer vanadium can be determined in amounts of 10—200 μg.

EXPERIMENTAL

Reagents, Solutions and Apparatus — *N*-benzoyl-*N*-phenylhydroxylamine (hereinafter NBPH) was of laboratory grade, produced by BDH.

All acids used were of *p.a.* purity, produced by Kemika.

Uranium was either metallic or $UO_2(NO_3)_2 \cdot 6\,H_2O$ of *p.a.* purity, produced by Merck.

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* Communicated in part at the 2nd Yugoslav Congress for Pure and Applied Chemistry, Belgrade, June 1966.

Metallic aluminum was of *p.a.* purity, produced by Merck.

The standard solution of vanadium was made up from ammonium vanadate (*p.a.*, Merck) by heating to 625°C and conversion to vanadium pentoxide. A known quantity was dissolved in sodium hydroxide to obtain the final concentration of 1 *mg V/ml* in 0.1 *N* sodium hydroxide.

Chloroform was of *p.a.* purity, produced by Merck. Before use it was further purified by mixing up with a dilute solution of sulfuric acid, with sodium hydroxide and finally with water. The NBPH solution in chloroform was 0.1%; before use it was mixed with 4 *N* hydrochloric acid.

Absorption was measured on a Beckman DU spectrophotometer.

Effect of Reagent Concentration and Hydrochloric Acid — The spectrum of the reagent in the presence of vanadium was first analyzed, establishing the absorption maximum of the vanadium complex at 530 mμ and the molar absorptivity at 4490.

The influence of acidity on vanadium extraction was investigated. Best results were attained by extraction from 1.5—5 *N* solution of hydrochloric acid with a 0.1% concentration of the reagent in chloroform.

Color Stability of Vanadium Complex and Effects of Other Ions — The color stability of the vanadium complex was satisfactory;

TABLE 1

Ion	Quantity of other ions in *mg*/50 *μg* of *V*	Absorption at 530 *mμ*
		0.243 ± 0,009
Cu^{2+}	1.0	0.234
Fe^{2+}	1.0	0
Fe^{3+}	1.0	0.249
Ni^{2+}	1.0	0.246
Co^{2+}	1.0	0.248
Mn^{2+}	1.0	0.249
Mo^{VI}	1.0	0.252
Zr^{4+}	1.0	0.259
W^{VI}	1.0	0.246
Ti^{4+}	1.0	0.242
CrO_4^{-}	0.5	0.280
”	1.0	0.305
Sn^{2+}	0.5	0.123
Sn^{4+}	1.0	0.247
$KMnO_4$	0.5	0.257
Na^+	460	0.247
NO_3^-	0.25 *N*	0.286
”	0.80 *N*	0.759
SO_4^{2-}	0.5 *N*	0.247
PO_4^{3-}	6.1 *N*	0.234
ClO_4^-	1.0 *N*	0.246
F^-	1.0 *g*	0.170

the absorptions of the chloroform layer did not change after 24 h. The color stability was adversely affected only by traces of ethanol in the chloroform, which is, however, avoidable by previous washing of the chloroform.

The effects of other ions were investigated (Table 1). The results show that Fe^{2+} and Sn^{2+} interfere, but this can be avoided by oxidation of these elements to a higher state of oxidation. The presence of nitrates in amounts above 0.25 *N* increases the result, as does the presence of chromates and permanganates in concentrations higher than 500 μg because of the oxidation of reagents coloring the chloroform layer yellow.

Zr^{4+} and Sn^{4+} in amounts exceeding 1 *mg* produce precipitates with the reagent. Ti^{4+} gives a yellow color with this reagent, but with a far lower absorptivity values so that its presence in a ratio of 25 : 1 does not matter.

Aside from this, other possible sources of interference due to the formation of precipitates are cations which form hardly soluble chlorides, if they are present in large amounts. Table 1 does not review them individually.

For aluminum and uranium of nuclear purity interferences of this sort are out of the question because their impurities are below the said limits.

Calibration Curve for Vanadium and Influence of Aluminum and Uranium on the Determination of Vanadium — Solutions containing 25—200 *μg* of vanadium were poured into separation funnels, and hydrochloric acid was added to obtain 4.0 *N* aqueous phase in relation to chloride ion, and a total volume of this phase of 20 *ml*. Vanadium was extracted twice with 10 *ml* 0.1 NBPH solution in chloroform each time. The total volume of the organic extract was 20 *ml*. After separation of the extracts the absorption of the chloroform layer at 530 mμ (absorption maximum) was measured.

Table 2 shows calibration curve data for pure vanadium and in the presence of aluminum and uranium.

TABLE 2

Calibration curve data for vanadium

μg V/20 ml of organic extract	ABSORPTION		
	pure vanadium	in the presence of 0.05 *g U/ml*	in the presence of 0.0125 *g Al/ml*
25	0.125	0.085	0.111
50	0.243±0.009	0.212±0.008	0.250
75	0.382	0.329	
100	0.499±0.008	0.469±0.015	0.502±0.009
150	0.758	0.704	0.
200	1.020	0.960	1.014

Determination in the presence of 1 *g* uranium added in the form of chloride produces absorption values somewhat lower than those for pure vanadium. The cause of this phenomenon is the influence of other salts on the extraction of vanadium. The higher the charge of an ion, the less the distribution ratio. This was particularly marked in the extraction of vanadium in the presence of aluminum chloride. The calibration curve was then shifted by some 20% for a 0.025 *g/ml* concentration of aluminum. We reduced the concentration of aluminum to 0.0125 *g/ml* by increasing the volume of the aqueous phase. In this way it was possible to determine smaller amounts of vanadium in the presence of aluminum as well. The aluminum concentration in the aqueous phase should not exceed the said limit.

The calibration curves for vanadium in the presence of aluminum and uranium do not pass exactly through the origin, but they are straight lines.

Procedure for the Determination of Vanadium in Aluminum and Uranium — A sample of metallic uranium or an alloy is dissolved with 15 *ml* 1 : 1 nitric acid and 5 *ml* 70% perchloric acid with heating. The solution is evaporated nearly to dryness, during which a white vapor is constantly given off. The residue is dissolved in water with heating, and 3—4 drops of potassium permanganate are added. The sample is boiled 10 *m* and cooled off. Next, hydrochloric acid is added to the solution to a final concentration of 4.0 *N* in the aqueous phase. An aliquot containing up to 200 μg vanadium is extracted with 0.1% NBPH solution in chloroform and the absorption is measured at 530 *m*μ. For calculation, the method of standard addition or a calibration curve for the same uranium concentration should be used. The accuracy for the determination of 50 *μg* vanadium is ± 3.7%. The determination range for vanadium is 10 to 200 *μg*.

To determine vanadium in aluminum, an up to 0.5 *g* sample is dissolved in 40 *ml* 1 : 1 nitric acid, 6 *ml* of conc. perchloric acid and a few drops of hydrofluoric acid with heating. The same procedure is used for aluminum-vanadium alloys containing up to 5% vanadium. The solution is evaporated giving off a dense white vapor, until a small amount of liquid is obtained above the precipitate. The residue is dissolved in water and a few drops of 0.1 *N* solution of potassium permanganate added, the mixture heated 10 *m* and then hydrochloric acid added to a final concentration of the solution of 4.0 *N*. Aliquots containing not more than 0.0125 *g* Al/ml of aqueous phase are used. Vanadium is extracted with 0.1% NBPH solution in chloroform, twice with 10 *ml* each time. Absorption is measured at 530 *m*μ. Vanadium is calculated by the standard addition method or read from the calibration curve for the given aluminum concentration in the aqueous phase. To get higher sensitivity the volume of the aqueous phase must be increased. Extracts with 40 and 80 *ml* of aqueous phase were investigated, the volume of the organic extract remaining 20 *ml*.

If iron is present in the aluminum in a concentration above 0.1%, phosphoric acid is added to the samples in order to complex Fe^{III}.

Comparative Review of Methods for Vanadium Determination — The method described here is sufficiently sensitive and specific as to permit the spectrophotometric determination of vanadium in aluminum and uranium, for only vanadium gives a violet color with NBPH in chloroform at extraction from 1.5—5 *N HCl.* When vanadium is determined either as phosphotungsten vanadate, or as a complex with 8-oxyquinoline, or as a peroxide complex, the interference of other ions is much greater, while the molar absorptivities of these compounds are lower as a rule. Vanadium oxinate gives a more sensitive reaction but selectivity is low so that the method has to be combined with the separation of vanadium from the intefering elements by means of extraction of vanadium cuproferronate(4).

The determination of vanadium with NBPH and with benzohydroxaminic acid described in the literature(5) does not produce satisfactory results in the presence of other ions because interference is much greater, as other ions, especially aluminum and iron, react in the 1.9—2.8 *pH* range used in the procedure. Certainly entirely different types of colored compound are involved here, whose investigation is under way.

The spectrophotometric method with *N*-benzoyl-*N*-phenylhydroxylamine can be recommended for the determination of vanadium in uranium, uranium-vanadium alloys, aluminum and aluminum--vanadium alloys with vanadium contents of up to 5%.

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SPECTROPHOTOMETRIC STUDY OF IRON-MECONIC ACID COMPLEX*

by

JOLANDA M. HOJMAN and ANĐELIJA B. ĐUKANOVIĆ-STEFANOVIĆ

The formation of a red complex between meconic acid and ferric ion in a strongly acidic solution has been used both for the photometric determination of meconic acid in opium⁽¹⁾ and for the photometric determination of ferric ion. According to Mannelli and Biffoli⁽²⁾, ferric ion can be determined by means of meconic acid at *pH* 1 in the 0.5—28 $\mu g/ml$ concentration range. The same authors found a 1 : 1 molecular ratio between ferric ion and meconic acid in this complex, but they did not take into consideration the dissociation of meconic acid. We established the formation constant of this complex and then studied the possibility of the formation of other complexes as a function of *pH*, and reaction mechanisms. We were able to determine the optimum conditions under which a complex of a given composition and good stability is formed.

EXPERIMENTAL

Reagents: 1. meconic acid (3-hydroxy-4-keto-1, 4-pyrane-2, 6-dicarbonic acid, $C_7H_4O_7 \cdot 3H_2O$), a BDH preparation; 2. ferric ion solution, standardized gravimetrically and volumetrically; 3. 2M solution $NaClO_4$, used for adjustment of ionic strength ($\mu = 0.20$).

Apparatus: 1. Beckman spectrophotometer, DU model, with 1 *cm* echelon cell used; 2. Radiometer 22 *pH*-meter.

RESULTS AND DISCUSSION

Meconic acid with ferric ion produces solution complexes of different colors depending on solution *pH*. The color is red in strongly acidic media, orange-red in weakly acidic ones, and orange-yellow in neutral or weak alkaline solutions.

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Effect of pH on Absorption Curve of Ferric Ion Solution with Meconic Acid — Absorption curves in Fig. 1 show that the absorbance

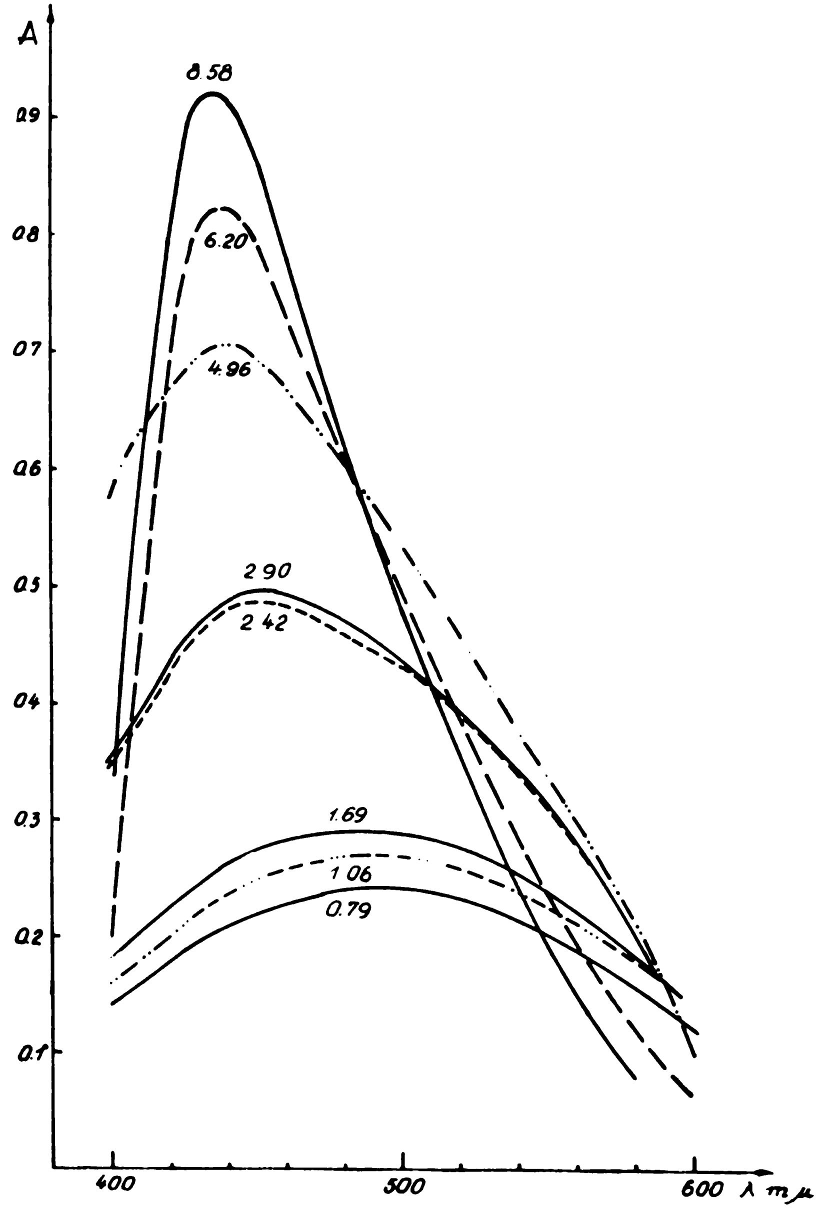


Figure 1

The effect of *pH* on the absorption curve of Fe^{III} -ion solution with meconic acid. The *pH* value is shown above the curve

$c_{Fe^{3+}} = 2 \cdot 10^{-4} M$; $c_R = 1.5 \cdot 10^{-3} M$; $\mu = 0.20$ ($NaClO_4$)

of the complex increases with *pH*, with a simultaneous shift of the absorbance maximum to shorter wavelengths.

Two isosbestic points at the intersection of absorption curves for different solution *pH* indicate the existence of three types of colored complex. The first isosbestic point at λ_{iI} 590 mμ (isosbestic point of red complex 1 and orange-red complex 2) is the intersection of $pH < 4.96$ curves. Curves of $pH > 4.96$ intersect at the second isosbestic point λ_{iII} at 480—482 mμ (isosbestic point of orange-red complex 2 and orange-yellow complex 3).

Analysis of Absorbance Curves Depending on pH — Curves of absorbance as a function of *pH* are of different form at the wavelengths of the maximums of complexes 1, 2 and 3, and at the wavelengths of the isosbestic points (Fig. 2), which is consistent with the formation of different colored complexes.

In the *pH* range 0.79—2.90 the rising branches of the curves for all wavelengths are more or less steep, except for 590 *m*μ. As the *pH* increases further, the curve for 490 mμ (λ_{max} of complex 1) and the curves for 510, 560 and 590 *m*μ change more slowly to reach their maximums at 4.2—5.0 *pH* and then fall gradually. In the $pH > 7.0$ range all the curves except for 440 mμ (λ_{max} of complex 3) are level. A comparison of the curve leads to the following conclusions:

a) The first, red complex forms already in a strongly acidic solution.

b) The second, orange-red complex has its maximum concentration between 4.2 and 5.2 pH; at lower pH (2.9—4.2) it is in equilibrium with the first, at higher pH (5.2—6.2) with the third complex.

c) The third, orange-yellow complex is fully formed at $pH > 7$.

Job's Curves — The composition of the red complex was determined by Mannelli and Biffoli⁽²⁾ using Job's method of equimolecular solutions at 1 *pH*. We used the same method⁽³⁾ for the determination of golden-red complex's composition (Fig. 3), in a urotropine buffer system ($pH = 5.20 \pm 0.03$), because this buffer does not react with ferric ion.

Job's curves of equimolecular solutions at *pH* values of 5.20 ± 0.03 were measured at wavelengths of 440, 450, 480, 490, and 590 *m*μ. All the curves have the same maximum, at 0.33 on the abscissa which agrees with the theoretical value of the abscissa for complex FeR_2.

$$\frac{[Fe^{3+}]}{[Fe^{3+}] + [R]} = 0.33$$

The composition of the orange-yellow complex could not be determined because at lower concentrations of meconic acid ferric ion hydrolysis takes place in the neutral or weakly alkaline solution.

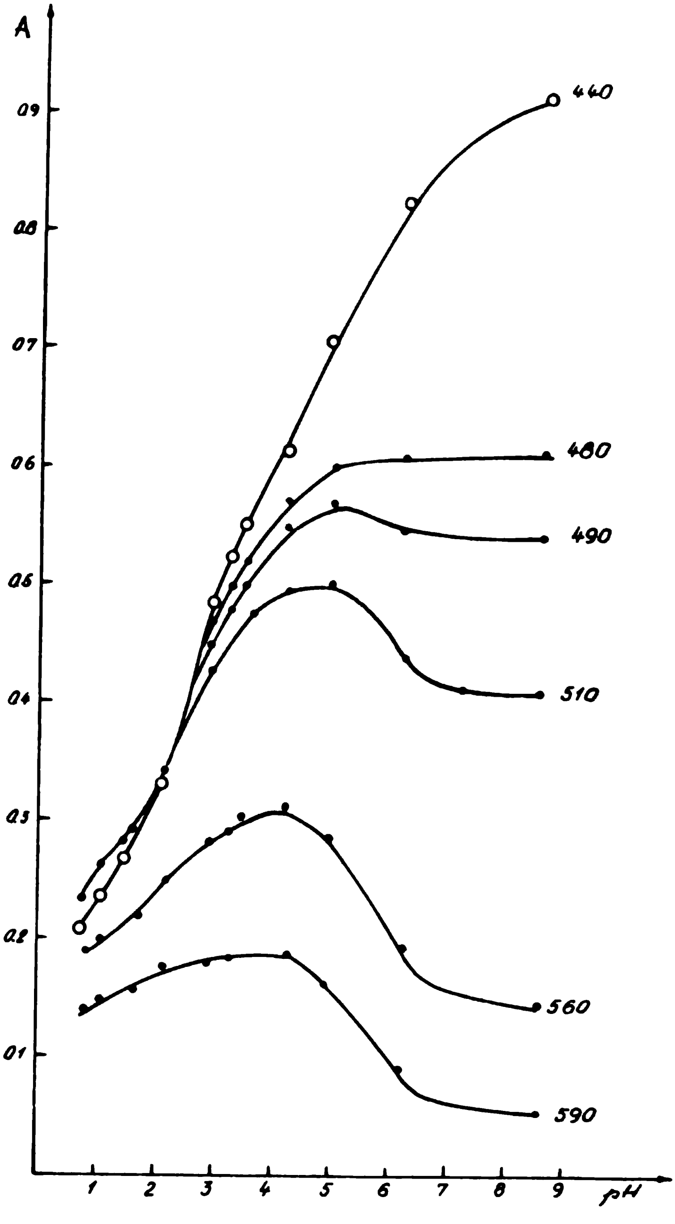


Figure 2

The dependence of absorbance on *pH*.

$c_{Fe^{3+}} = 2 \cdot 10^{-4} M$; $c_R = 1.5 \cdot 10^{-3} M$; $\mu = 0.20$ ($NaClO_4$)

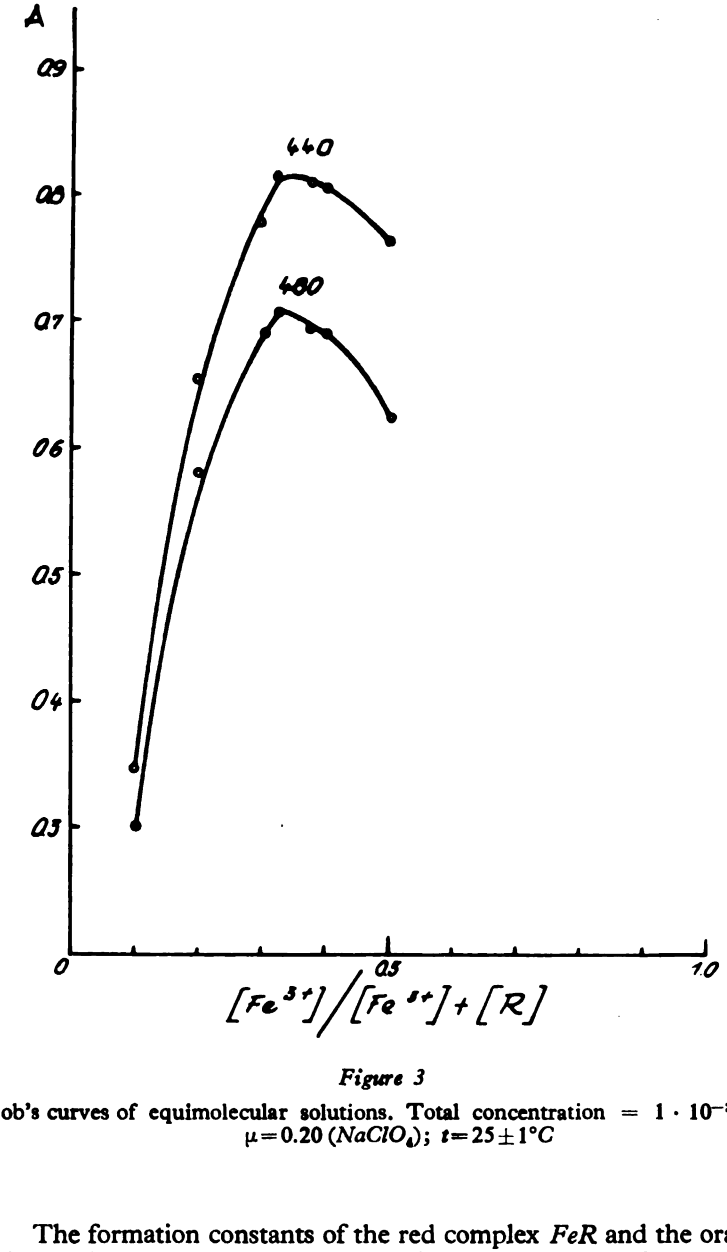


Figure 3

Job's curves of equimolecular solutions. Total concentration = $1 \cdot 10^{-3}M$; $\mu = 0.20$ ($NaClO_4$); $t = 25 \pm 1°C$

The formation constants of the red complex *FeR* and the orange-red complex FeR_2 were determined from Job's curves for nonequimolecular solutions at *pH* 1.50 (±0.02), or *pH* 5.20 (±0.03) with an ion strength 0.20(3). At all wavelengths of measurement (440, 480, 490, 560, and 590 *m*μ) the maximums of Job's curves have the same value. Figure 4 shows Job's curves of nonequimolecular solutions of meconic acid with ferric ion at 1.50 *pH*.

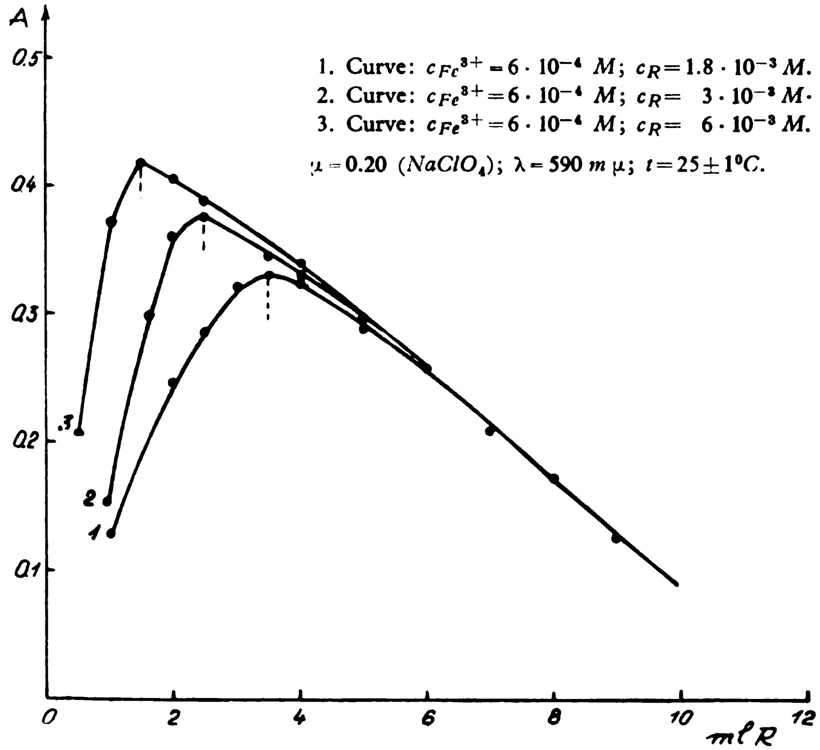


Figure 4

Job's curves of nonequimolecular solutions at *pH* 1.50. Total volume in each case 12 *ml*.

At triple concentration of meconic acid ($p = 3$), x_{max} was 0.292, while fivefold ($p = 5$) and tenfold ($p = 10$) concentrations gave x_{max} 0.208 and 0.125 respectively.* The formation constant of the red complex *FeR* was obtained from the following Job's expression (3):

$$K' = \frac{(p-1)(1-2x_{max})}{c_{Fe^{3+}}\left[(1+p)\,x_{max}-1\right]^2}$$

The results are shown in Table 1.

TABLE 1

$c_{Fe^{3+}}$	*pH*	*p*	x_{max}	log *K'*
$6 \cdot 10^{-4}$ *M*	1.50 ± 0.02	3	0.292	4.69
$6 \cdot 10^{-4}$ *M*	„	5	0.208	4.70
$6 \cdot 10^{-4}$ *M*	„	10	0.125	4.90
		Mean value	*log K'* $= 4.76 \pm 0.09$	

---

* Values for x_{max} are obtained by dividing the abscissa values of the curve maximum in Fig. 4 by 12.

In Fig. 5 Job's curves of nonequimolecular solutions of meconic acid and ferric ion at *pH* 5.20 are shown.

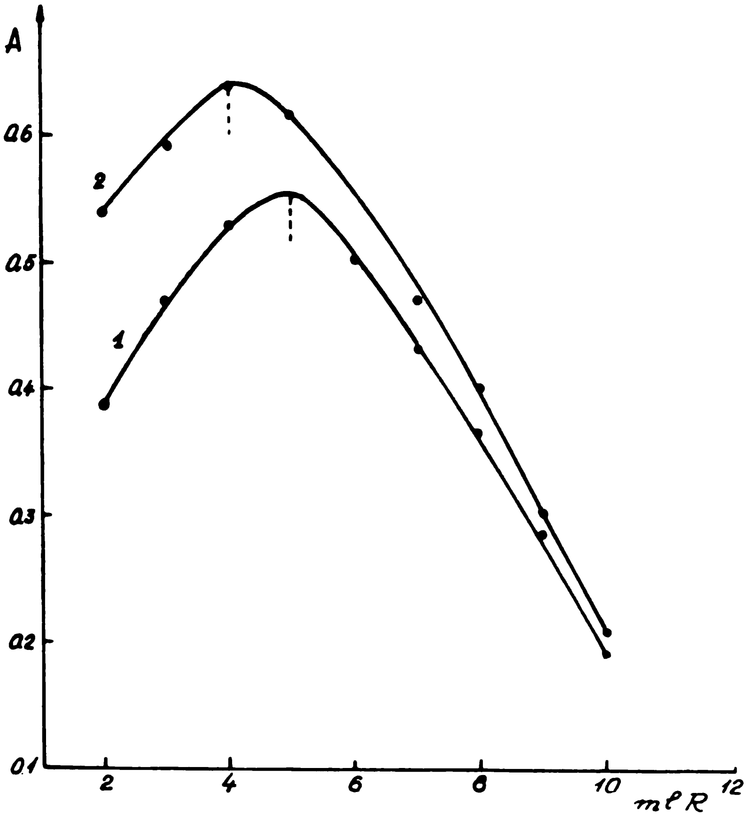


Figure 5

Job's curves of nonequimolecular solutions at *pH* 5.20. Total volume in each case 12 *ml*.

Curve 1: $c_{Fe^{3+}} = 3 \cdot 10^{-4} M$; $c_R - 1.5 \cdot 10^{-3} M$.
Curve 2: $c_{Fe^{3+}} = 3 \cdot 10^{-4} M$; $c_R - 3 \cdot 10^{-3} M$.
$\mu = 0.20$ ($NaClO_4$); $\lambda - 440$ $m\mu$; $t = 25 \pm 1^0 C$

The x_{max} values of the Job's curves are: 0.412 at $p=5$ and 0.333 at $p=10$. The formation constant of the orange-red complex FeR_2 was computed from the following Job's term:

$$K' = \frac{(p-1)^2 \cdot [2-(2+1)\,x_{max}]}{c^2_{Fe^{3+}} \cdot p \cdot [(2+p)\,x_{max} - 2]^3}$$

The results are presented in Table. 2.

TABLE 2

$c_{Fe^{3+}}$	pH	p	x_{max}	log K'
$3 \cdot 10^{-4}M$	5.20 ± 0.03	5	0.417	7.54
$3 \cdot 10^{-4}M$	5.20 ± 0.03	10	0.333	7.05
				Mean value *log* $K' = 7.29 \pm 0.25$

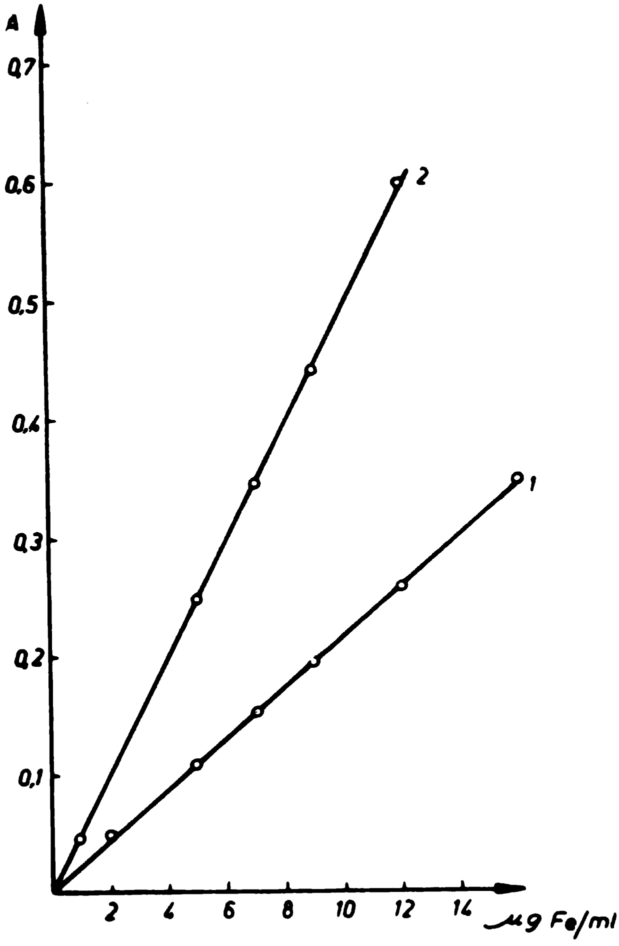


Figure 6

Calibration curves.

Curve 1: $pH=0.85$; $\lambda=480$ $m\mu$
Curve 2: $pH=5.20$; $\lambda=440$ $m\mu$

Spectrophotometric Determination of Iron (III) — In view of the fact that the FeR_2 complex, formed at pH 5.20, is stabler, we explored the possibility of employing spectrophotometry to determine iron with meconic acid at this pH. Beer's law was verified in the 0.5—12 μg Fe/ml concentration range (Fig. 6).

Calibration curves obtained at pH 0.85 and 5.20 show that the reaction to ferric ion is more sensitive at pH 5.20. The molecular absorptivity of the color at pH 0.85 is 1212 ± 9 ($\lambda = 480\ m\mu$), at pH 5.20 2766 ± 20 ($\lambda = 440\ m\mu$).

Procedure for the Determination of Iron by Spectrophotometry — 3 *ml* 0.12 % solution of meconic acid and 2 *ml* buffer consisting of a 0.5 *M* solution of urotropine and 0.2 N *HCl* are placed in a measuring vessel. To this, 0.1 to 1.5 *ml* of test solution (10 to 150 γFe) is added and double-distilled water added to 10 *ml*. Measurement is made 10 *m* later.

As in the procedure after Mannelli and Biffoli(2), the ions Cu^{2+}, Ti^{4+}, VO_3^-, Ca^{3+}, Pb^{2+}, Ag^+, and UO_2^{2+} interfere with the determination of iron (III).

Study of the Reaction Mechanisms — Formation of different complexes in dependence on pH indicates the participation of protons:

$$Fe^{3+} + n\,Rh \rightleftarrows FeR_n + n\,H^+$$

Hence

$$\log \frac{C_{FeR_n}}{C_{Fe^{3+}}} = n\,pH + \log K$$

Substituting the corresponding components for the concentration of absorbance we get

$$\log \frac{A}{A_0 - A} = n\,pH + \log K$$

This allows the number of protons to be determined from the logarithm of the rising branches of the absorbance curves in a function pH(4). "A" is the absorbance at a point of the rising branch of the curve in Fig. 2, while "A_0" is the maximum absorbance, i.e. at the closest point of the horizontal branch. Logarithmic analysis of the rising branches of the absorbance curves obtained at 480 and 490 $m\mu$ is shown in Fig. 7.

The number of protons (n) released during the reaction was investigated in the pH range 1.06—3.50 by means of the slope of the tangent to the curve. This slope changes as the pH rises. The number of protons released during formation of the red complex in the range $pH < 1.69$ is very small ($n = 0.11$), while it is 0.66 in the pH range 2.12—2.90.

In the $pH < 2.90$ range, where the red complex is stable, the first degree of the dissociation of meconic acid (H_3R) as a strong acid,

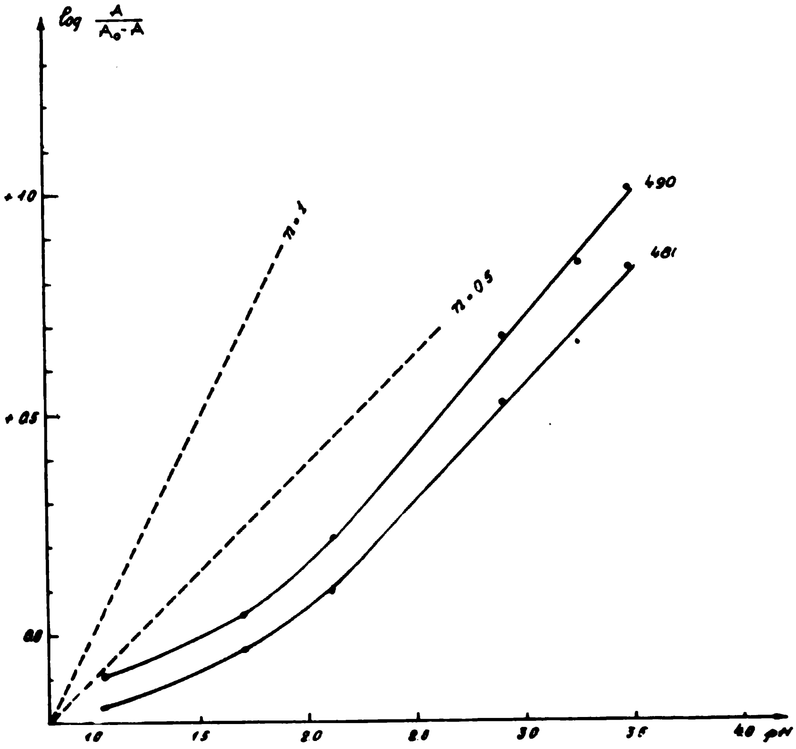


Figure 7

The dependence of log $\frac{A}{A_0-A}$ on pH.

$c_{Fe^{3+}}=2\cdot10^{-4}\,M$; $c_R=1.5\cdot10^{-3}M$; $\mu=0.20$ ($NaClO_4$)

is complete and the acid occurs as a monovalent ion H_2R^- in equilibrum with ion HR^{2-}. The constants of the second and third degree dissociation of meconic acid are known$^{(5)}$: $pK_2=2.13$, $pK_3=10.01$. Hence the ions H_2R^- and HR^{2-} can take part in the reaction which forms the first, red complex, according to the following equations:

$$Fe^{3+}+H_2R^- \rightleftarrows [FeHR]^+ + H^+ \tag{1}$$

$$Fe^{3+}+HR^{2-} \rightleftarrows [FeR]+H^+ \tag{2}$$

The number of protons released (n) should be 1. Our test, however, showed that n was only 0.11 in the $pH<1.69$ range. This is to say that the reactions above take place only to an insignificant extent. The complex is formed mainly without releasing protons, perhaps according to equation (3), or with the participation of chloride ion, according to (4):

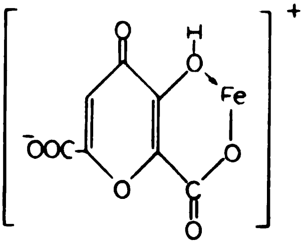
$$Fe\,(OH)^{2+} + HR^{2-} \rightleftarrows [FeR] + H_2O \tag{3}$$

$$Fe^{3+} + HR^{2-} + Cl^{-} \rightleftarrows [FeHRCl] \tag{4}$$

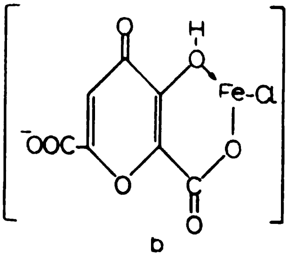
The formation of a neutral ferric ion complex in the presence of chloride ion was determined by Mannelli and Biffoli(2) for meconic acid, and a similar complex has been found with kojic acid(6).

In the 2.12—2.90 pH range ($n = 0.66$), when the ion HR^{2-} predominates, it is possible that the (FeR) complex forms as well as the ($FeHRCl$) complex, according to eqs. (2) and (3).

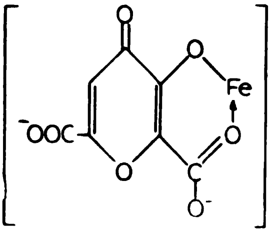
From our results and comparisons with kojic acid, it was concluded that the meconic acid complexes arise by closing of the six-membered ring of the phenol group in position 3 and the carboxyl group in position 2 with the participation of ferric ion. Accordingly, the structures of the red complexes ($FeHR^{+}$), ($FeHRCl$) and (FeR) can be represented by formulas a, b and c:



a



b



c

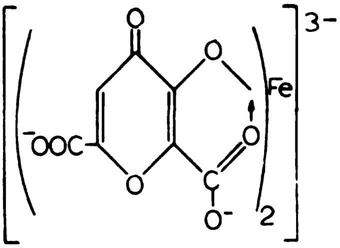
An analysis of the behavior of $\log \frac{A}{A_0 - A}$ in the pH range 2.90—3.50 showed that the number of protons (n) released in the reaction comes to 0.66. Since in the $pH > 2.90$ range in which the $Fe : R = 1 : 2$ complex forms, the second degree of dissociation of meconic acid is virtually complete, the reactions involving the formation of the prange-red complex can proceed according to these equations:

$$[FeR] + HR^{2-} \rightleftarrows [FeR_2]^{3-} + H^{+} \tag{5}$$

$$Fe(OH)^{2+} + 2\,HR^{2-} \rightleftarrows [FeR_2]^{3-} + H_2O + H^+ \tag{6}$$

$$Fe(OH)_2{}^{+} + 2\,HR^{2-} \rightleftarrows [FeR_2]^{3-} + 2\,H_2O \tag{7}$$

During the formation of this complex two six-membered rings occur with the participation of one ferric ion. The structural formula of this complex could be



In the $pH > 6.2$ range the orange-yellow complex forms. The number of protons released, the composition and formation constant of this complex could not be determined because of ferric ion hydrolysis. However, the capacity of meconic acid to complex ferric ion is about the same as that of kojic acid$^{(6)}$. Depending on pH, this acid form: complexes in which the ferric ion to kojic acid ratio is either 1 : 1, 1 : 2, or 1: 3. Presumably the composition of the orange-yellow complex of meconic acid is $(FeR_3)^{6-}$.

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A SYNTHESIS OF FLUORENE-2,7-DICARBOXYLIC ACID

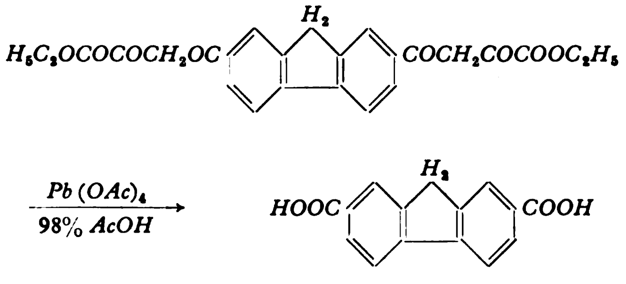
by

BOJAN D. PODOLEŠOV and DRAGANA S. PETROVA

The formation of aryl carboxylic acids by oxidative cleavage of ethyl esters of aroylpyruvic acid with lead tetraacetate was first reported by Jančulev and Podolešov(1). They also established that oxidative cleavage of ethyl 2-fluorenoylpyruvate gives fluorene-2-carboxylic acid. Since very little is known about fluorene-2,7-dicarboxylic acid, the purpose of this communication is to report the synthesis of this compound.

Sheldrick *et al.*(3) have shown that fluorene-2,7-dicarboxylic acid can be obtained by hydrolyzing (with strong acid or alkali reagents) the corresponding *N*-alkyl-*N*-phenylamides, which are prepared by treating fluorene with alkylphenyl-carbamyl halides in the presence of anhydrous aluminum chloride. The same diacid has also been prepared(3) by the Wolff-Kishner-Huang-Minlong reduction of 9-fluorenone-2,7-dicarboxylic acid. We used the oxidative cleavage of γ,γ-fluorene-2, 7-di(α,γ-diketobutyric acid) diethyl ester with lead tetraacetate.

First γ,γ-fluorene-2,7-di(α,γ-diketobutyric acid) diethyl ester (I), yellow crystals m.p. 195—196°, was obtained by acylation of 2,7-diacetylfluorene with diethyl oxalate (1 : 2 molar ratio) in the presence of sodium ethoxide:



I

II

By oxidative cleavage of γ,γ-fluorene-2,7-di (α.γ-diketobutyric acid) diethyl ester (I) by means of lead tetraacetate, a product was obtained in the form of a light yellow powder (II), which had no definite melting point, but which upon heating to above 300°C partly carbonized and partly sublimed. No suitable solvent was found for recrystallization. The properties of product (II) were in agreement with those described by Ishikava *et al.*(3).

For characterization of the oxidation product, i.e. fluorene-2, 7-dicarboxylic acid, its dimethyl and diethyl esters were prepared. The dimethyl ester consists of light yellow needles which melt at 190—192°C, and the diethyl ester crystallizes in the form of light yellow platelets which melt at 165—167°C.

The fact that fluorene-2,7-dicarboxylic acid (II) is obtained by lead tetraacetate oxidation of the acylation product of 1,7-diacetylfluorene confirms that this compound is γ, γ-fluorene-2,7-di(α,γ-diketobuturic acid) diethyl ester (I), i.e. that acylation of 2,7-diacetylfluorene with diethyl oxalate takes place on the acetyl groups in positions 2 and 7 rather than on the methylene group of fluorene in position 9.

EXPERIMENTAL

1. γ,γ-*Fluorene*-2,7-*di* (α,γ-*diketobutyric acid*) *diethyl ester* [*or* γ, γ-2,7-*flurenylenedi* (α, γ-*diketobutyric acid*) *diethyl ester*] — Anhydrous sodium ethoxide was prepared in the usual manner, in a 500 *ml* round-bottom flask fitted with a reflux condenser and drying tube. 0.92 *g* (0.04 mole) of sodium and 1.84 *g* (0.04 mole) of anhydrous ethanol in 100 *ml* of anhydrous benzene were used. A hot solution of 5.006 g (0.02 mole) 2,7-diacetylfluorene and 5.85 g (0 .04 mole) freshly distiled diethyl oxalate in 300 ml anhydrous benzene was added to sodium ethoxide with shaking. The reaction mixture was heated on a water bath for an hour and then allowed to stand for 24 hours: a dark orange precipitate was obtained. In order to remove unreacted 2,7-diacetylfluorene, the reaction mixture was filtered hot and the product washed with 100 ml hot benzene.

The sodium derivative was treated by rubbing with hydrochloric acid (1 : 1), then filtered and washed with water. The yield was 8.5 *g* (94.4%) of crude, yellow-orange product. Recrystallization from acetic acid and benzene gave yellow cristals melting at 195—196°C.

Anal. Calc. for $C_{25}H_{22}O_8$: C 66.66 H 4.92%
Found : C 66.85 H 4.68%

2. *Fluorene-2,7-dicarboxylic acid* — Oxidative cleavage of γ, γ-Fluorene-2,7-di (α, γ-diketobutyric acid) diethyl ester.

1.126 *g* (0.0025 mole) of γ, γ-fluorene-2,7-di (α, γ-diketobutyric acid) diethyl ester was dissolved in 250 *ml* of 98% acetic acid and 11.06 *g* (0.025 mole) of powdered lead tetraacetate was added to the solution. The reaction mixture was gradually heated with stirring and a yellow precipitate began to appear at about 62°C.

The reaction mixture was heated and stirred for another 6 hours at 61—65°C. The light yellow precipitate was filtered off and washed with acetic acid. The yellow powder (210 *mg*, 33%) had no definite melting point; when heated above 300°C it gradually carbonized and sublimed. The product was practically insoluble in all common organic solvents. Its properties corresponded to those of fluorene-2,7-dicarboxylic acid$^{(3)}$. For characterization its dimethyl and diethyl esters were prepared.

3. *2,7-Fluorene-dicarboxylic acid dimethyl ester* — 0.4 *g* of the oxidation product (II) was heated under reflux with 15 ml thionyl chloride for 5 hours. The thionyl chloride was then evaporated *in vacuo* and the yellow residue was heated under reflux on a water bath with 50 ml methanol for 3 hours.

The methanol was evaporated and the residue was recrystallized from acetic acid. 0.3 *g* of light yellow needles, melting at 190—192°C, was obtained. The melting point was in good agreement with that given in the literature.$^{(3)}$

Anal. Calc. for $C_{17}H_{74}O_4$: C 72.33 H 5.00%
Found : C 72.52 H 5.10%

4. *2,7-Fluorene-dicarboxylic acid diethyl ester* — 200 *mg* of the oxidation product (II) was heated under reflux with 150 *ml* anhydrous ethanol and 4 *ml* concentrated sulfuric acid for 10 hours, and 100 ml of water was then added to the reaction mixture. Extraction with ether, washing with water, drying and removal of the solvent by distillation left a solid which, upon four recrystalizations from acetic acid gave light yellow platelets, melting at 165—167°C. (Lit. $^{(3)}$ 166—167°C).

Anal. Calc. for $C_{19}H_{18}O_4$: C 73.53 H 5.85%
Found : C 73.25 H 6.05%

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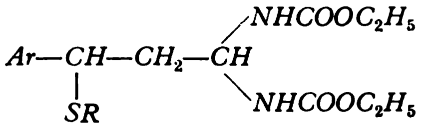
ADDITION OF MERCAPTANS TO UNSATURATED ALDEHYDES. II.

ADDITION OF ETHYLMERCAPTAN, AMYLMERCAPTAN AND BENZYLMERCAPTAN TO UNSATURATED AROMATIC ALDEHYDES

by

KSENIJA D. SIROTANOVIĆ and MILKA M. BAJLON-PASTOR

Continuing our study on the addition of thiophenol to the unsaturated aromatic aldehydes in the presence of urethane and hydrochloric acid[(1)], at which the carbonyl group of the aldehyde simultaneously condenses with urethane, we have also developed bisurethanes of β-phenylmercapto-m-nitro-hydrocinnamaldehyde and of β-phenylmercapto-p-nitro-hydrocinnamaldehyde (1):



$$Ar-\underset{\displaystyle SR}{\underset{|}{CH}}-CH_2-CH\left\langle\begin{matrix}NHCOOC_2H_5\\NHCOOC_2H_5\end{matrix}\right. \qquad (I)$$

Where: $R = C_6H_5$-, $Ar = m\text{-}NO_2C_6H_4$-, $p\text{-}NO_2C_6H_4$-

Thus all the seven unsaturated aldehydes used (cinnamaldehyde, ortho-, meta- and para-nitrocinnamaldehyde, and ortho-, meta-, and para-chlorocinnamaldehyde) have given bisurethanes of addition products with thiophenol. In these reactions the nitro-cinnamaldehydes produced better yields (51—60%) than the chlorocinnamaldehydes (32—53%). With cinnamaldehyde itself a bisurethane of the addition compound with thiophenol was produced in a yield of 50%.

Aside from employing thiophenol, under the same conditions and starting from an unsaturated aromatic aldehyde, mercaptan and urethane (1 : 1 : 2 ratio) in the presence of hydrochloric acid, addition of other mercaptans, notably ethylmercaptan, amylmercaptan and benzylmercaptan to α, β-unsaturated aromatic aldehydes was also tried. The unsaturated aromatic aldehydes used in this study were: cinnamaldehyde, ortho-, meta- and para-nitrocinnamaldehyde and ortho-, meta- and para-chlorocinnamaldehyde. However, not all the addition product bisurethanes were obtained as expected. Five of the seven theoretically possible compounds were isolated when ethylmercaptan was added, and 4 each with amylmercaptan and benzylmercaptan (Table 1). This could have been expected, as it also agrees with the observations of other authors(2, 3, 4) concerning the property of thiophenol to combine with the double bond of unsaturated compounds (some unsaturated carbohydrates and aliphatic unsaturated aldehydes) more easily than is the case with aliphatic mercaptans and benzylmercaptan. This may be attributed to the greater acidity of thiophenol.

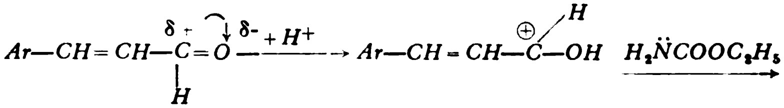
In all these additions it was noted that the aldehydes behaved differently depending on the type and position of the substituent. More compounds was obtained from nitro-cinnamaldehydes (11 of the possible 12) and in better yields (31—60%) than from chloro-cinnamaldehydes with which 8 of the possible 12 were obtained in yields of 10—53%.

As for the position of the substituent, the most reactive were metasubstituted cinnamaldehydes with which all the compounds expected were obtained, followed by para-substituted with which 7 out of the possible 8 were obtained (all four with the nitro-substituted and three with chloro-substituted), while the weakest reaction was with the ortho-substituted cinnamaldehydes, from which only 4 compounds were obtained (3 with nitro-substituted and 1 with chloro-substituted cinnamaldehyde). With cinnamaldehyde itself only one of the possible four bisurethanes of β-mercapto-aldehydes, bisurethane addition compound with thiophenol, was obtained.

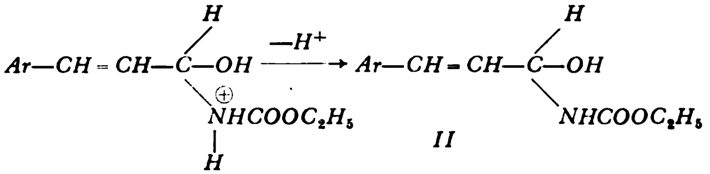
As was reported in Part I(1) of this study, when mercaptan acts on α, β-unsaturated aliphatic aldehydes it is easily added to the double $>C=C<$ bond of the aldehyde producing the -mercapto-aldehyde. However, when mercaptan acts on an aromatic unsaturated aldehyde, cinnamaldehyde, addition to the ethylene bond does not take place. Instead, the carbonyl group reacts and the corresponding mercaptals of cinnamaldehydes form. This behavior of cinnamaldehyde under the action of mercaptan can be explained by the presence of a benzene ring, which because of a positive resonance effect $(+R)$ diminishes the addition capacity (electrophilicity) of the double bond, i.e. the partial positive charge on the β-C-atom and thus renders reaction with mercaptans impossible.

In our additions using urethane as well as mercaptan, resulting in 20 out of the possible 28 bisurethane β-mercapto-aldehydes, the reaction mechanism might be as explained below.

In the presence of concentrated hydrochloric acid a urethane molecule, via its free electron pair, is first added to the positive carbon atom in the carbonyl group producing compound (II):



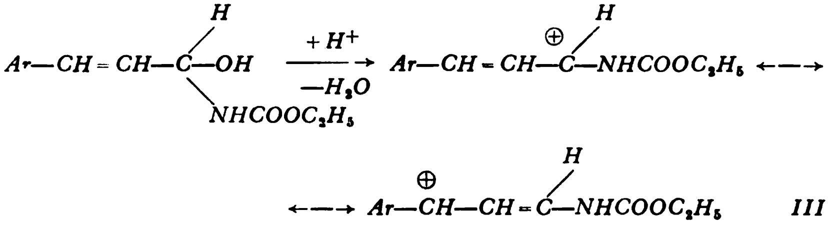
$$Ar-CH=CH-\underset{H}{\overset{\delta+}{C}}=\overset{\delta-}{O}\xrightarrow{+H^{+}}Ar-CH=CH-\overset{\oplus\,/H}{C}-OH\xrightarrow{H_2\ddot{N}COOC_2H_5}$$



$$Ar{-}CH{=}CH{-}\underset{\underset{H}{|}}{\overset{\oplus}{N}HCOOC_2H_5}{\setminus}\overset{H}{C}{-}OH \xrightarrow{-H^+} Ar{-}CH{=}CH{-}\overset{H}{\underset{NHCOOC_2H_5}{C}}{-}OH$$

II

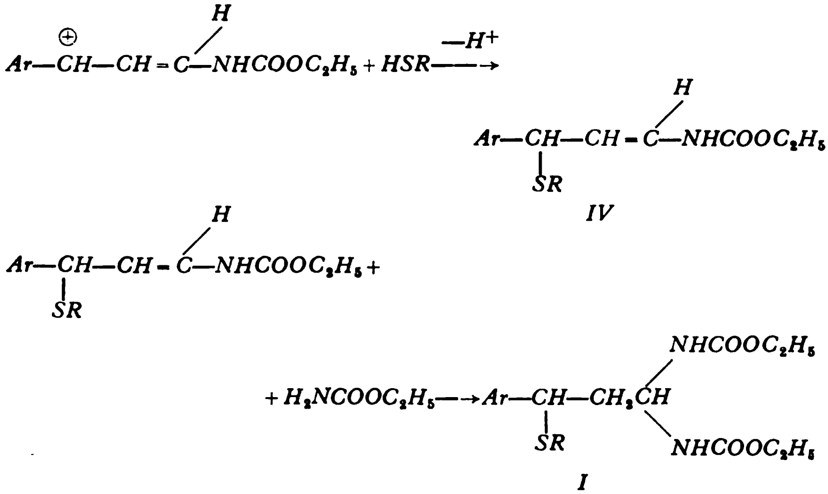
By the further action of acid and elimination of water the cation (III) is obtained:



$$Ar{-}CH{=}CH{-}\overset{H}{\underset{NHCOOC_2H_5}{C}}{-}OH \xrightarrow[-H_2O]{+H^+} Ar{-}CH{=}CH{-}\overset{\oplus}{\overset{H}{C}}{-}NHCOOC_2H_5 \longleftrightarrow$$

$$\longleftrightarrow Ar{-}\overset{\oplus}{C}H{-}CH{=}\overset{H}{C}{-}NHCOOC_2H_5 \qquad III$$

to which mercaptan or its anion is then added. To the compound (IV) thus obtained, another urethane molecule binds producing a bis-urethane of β-mercapto-hydrocinnamaldehyde:



$$Ar{-}\overset{\oplus}{C}H{-}CH{=}\overset{H}{C}{-}NHCOOC_2H_5 + HSR \xrightarrow{-H^+} Ar{-}\underset{SR}{CH}{-}CH{=}\overset{H}{C}{-}NHCOOC_2H_5 \quad IV$$

$$Ar{-}\underset{SR}{CH}{-}CH{=}\overset{H}{C}{-}NHCOOC_2H_5 + H_2NCOOC_2H_5 \longrightarrow Ar{-}\underset{SR}{CH}{-}CH_2CH(NHCOOC_2H_5)_2 \quad I$$

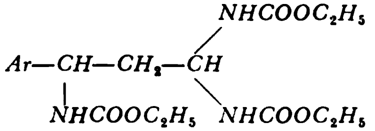
The yields and number of addition products with nitrocinnamaldehydes being better than those with chloro-cinnamaldehydes can be ascribed to the nitro group which attracts electrons and thus augments the positive character of the β-C-atom and enables addition of mercaptan to the double bond. Chlorine bound to the benzene ring is a substituent which repels electrons when in the ortho- or para-position and thus diminishes the reactivity of the double bond, as confirmed by our findings.

Hydrolysis of all bisurethanes of β-mercapto-aldehydes obtained took place in the presence of 2, 4-dinitrophenylhydrazine, from which

2, 4-dinitrophenylhydrazones of β-mercapto-aldehydes were obtained (Table 2), except for two cases, the hydrolysis of bisurethanes of β-ethylmercapto-p-chloro-hydrocinnamaldehyde and of β-phenylmercapto-p-chloro-hydrocinnamaldehyde, in which the excess mercaptan was eliminated and the 2, 4-dinitrophenylhydrazone of p-chloro-cinnamaldehyde itself obtained. In the same way, besides 2,4-dinitrophenylhydrazone of β-mercapto-aldehydes, in some cases small amounts of 2, 4-dinitrophenylhydrazones of the unsaturated aromatic aldehydes themselves were obtained.

In cases when mercaptan did not add to the double bond of the aldehyde, bisurethanes of the unsaturated aldehydes(1) were obtained, while the mercaptan of the unsaturated aldehyde (Table 4) was obtained as well as the bisurethane of the β-mercapto-aldehyde in two cases.

Apart from bisurethanes and mercaptans, compounds containing three urethane residues in a molecule were isolated. They are assumed to be 1,1,3-tris (carbetoxy-amino)-compounds (V) originating from the unsaturated aldehyde by addition of urethane to the double bond and by the condensation of urethane and the carbonyl group, analogous to the reaction of certain aliphatic α, β-unsaturated aldehydes with urethane(5, 6).



$$Ar{-}\underset{\displaystyle NHCOOC_2H_5}{CH}{-}CH_2{-}CH(NHCOOC_2H_5)_2$$

V

EXPERIMENTAL

1. *Bisurethanes of β-alkylmercapto-β-aryl-propionaldehydes and β-arylmercapto-β-aryl-propionaldehydes.* — The unsaturated aromatic aldehyde, mercaptan and urethane are mixed in a 1 : 1 : 2 molecular ration and if the mixture is not homogeneous double the quantity of ether is added. Next a drop of concentrated hydrochloric acid is added per 0.01 mole aldehyde and the mixture is kept at room temperature until hardening (three days to three months). The hardened mixture is treated with ether or petroleumether and then filtered. The crude product is recrystallized from ethyl alcohol or an acetone-petroleum ether mixture. Samples of 0.01 or 0.02 mole aldehyde were used. Yields, melting points and analysis results for the bisurethanes of β-mercapto-aldehydes obtained are shown in Table 1.

2. *2,4-Dinitrophenylhydrazones of β-alkylmercapto-β-aryl-propionaldehydes and of β-arylmercapto-β-aryl-propionaldehydes.* — One millimole of the bisurethane of the β-mercapto-aldehyde, 1 millimole 2,4-dinitrophenylhydrazine and 15 ml of ethyl alcohol are heated to the boiling point, 0.4 ml of concentrated hydrochloric acid is added, and the mixture is cooled off and filtered. The crude product is treated with warm alcohol. The undissolved 2,4-dinitrophenylhydrazone of

TABLE 1

Bisurethanes: $ArCH(SR)CH_2CH(NHCOOC_2H_5)_2$

	Ar	R	Yield %	M. P. C°	Formula	Analysis for C calc. %	Analysis for C found %	Analysis for H calc. %	Analysis for H found. %	Analysis for N calc. %	Analysis for N found. %	Analysis for S calc. %	Analysis for S found. %
1	o-NO_2-C_6H_4-	C_2H_5-	38	153.5	$C_{17}H_{25}N_3O_6S$	51.13	50.74	6.27	6.23	10.53	10.30		
2	m-NO_2-C_6H_4-	C_2H_5-	40	162.5	»	51.13	51.08	6.27	6.50	10.53	10.54		
3	p-NO_2-C_6H_4-	C_2H_5-	50	124	»	51.13	51.14	6.27	6.26	10.53	10.56		
4	m-Cl-C_6H_4-	C_2H_5-	28	143	$C_{17}H_{25}ClN_2O_4S$	52.51	52.58	6.43	6.63	7.20	7.03		
5	p-Cl-C_6H_4-	C_2H_5-	10	133.5	»	52.51	52.32	6.43	6.46	7.20	7.55		
6	o-NO_2-C_6H_4-	C_5H_{11}-	47	118	$C_{20}H_{31}N_3O_6S$					9.52	9.47	7.20	6.45
7	m-NO_2-C_6H_4-	C_5H_{11}-	50	153	»	54.42	54.21	7.03	6.91	9.52	9.48		
8	p-NO_2-C_6H_4-	C_5H_{11}-	31	125.5	»	54.42	54.20	7.03	6.94	9.52	9.36	7.20	6.68
9	m-Cl-C_6H_4-	C_5H_{11}-	24	123	$C_{20}H_{31}ClN_2O_4S$					6.50	6.88	7.43	7.34
10	C_6H_5-	C_6H_5-	50	114	*								
11	o-NO_2-C_6H_4-	C_6H_5-	53	118	*								
12	m-NO_2-C_6H_4	C_6H_5-	51	136	$C_{21}H_{25}N_3O_6S$					9.39	9.38	7.15	7.08
13	p-NO_2-C_6H_4-	C_6H_5-	60	135	»					9.39	9.60	7.15	6.73
14	o-ClC_6-H_4-	C_6H_5-	40	126	*								
15	m-ClC_6-H_4-	C_6H_5-	53	141	*								
16	p-Cl-C_6H_4-	C_6H_5-	32	116	*								
17	m-NO_2-C_6H_4-	$C_6H_5CH_2$-	34	154	$C_{22}H_{27}N_3O_6S$	57.34	57.00	5.85	6.02	9.11	9.11	6.94	6.83
18	p-NO_2-C_6H_4-	$C_6H_5CH_2$-	50	139	»	57.34	57.34	5.85	5.86	9.11	9.03	6.94	6.89
19	m-Cl-C_6H_4-	$C_6H_5CH_2$-	30	120	$C_{22}H_{27}ClN_2O_4S$					6.22	6.50	7.11	7.09
20	p-Cl-C_6-H_4-	$C_6H_5CH_2$-	27	142	»					6.22	6.31	7.11	7.20

* Analytical data given in a the previous paper(1)

the unsaturated aldehyde remains. When the solution is cooled or when some of the solvent is removed, the 2,4-dinitrophenylhydrazone of β-mercapto-aldehydes separates out. It is crystallized from ethyl alcohol and brought to constant m.p. Melting points and analysis results for the 2,4-dinitrophenylhydrazones of β-mercapto-aldehydes are presented in Table 2.

TABLE 2

2.4-Dinitrophenylhydrazones:

$$\underset{SR}{\underset{|}{ArCH}}CH_2CH{:}NNHC_6H_3(NO_2)_2$$

	Ar	*R*	M. P. °C	Formula	Analysis for *N*	
					calc. %	found %
1	o-NO_2-C_6H_4-	C_2H_5-	89.5	$C_{17}H_{17}N_5O_6S$*	16.70	16.81
2	m-NO_2-C_6H_4-	C_2H_5-	133.5	„	16.70	17.03
3	p-NO_2-C_6H_4-	C_2H_5-	128.5	„	16.70	16.14
4	m-Cl-C_6H_4-	C_2H_5-	102	$C_{17}H_{17}ClN_4O_4S$	13.71	14.06
5	o-NO_2-C_6H_4-	C_5H_{11}-	87	$C_{20}H_{23}N_5O_6S$	15.18	15.38
6	m-NO_2-C_6H_4-	C_5H_{11}-	91	„	15.18	15.60
7	p-NO_2-C_6H_4	C_5H_{11}-	102	„	15.18	15.42
8	C_6H_5-	C_6H_5-	139	**		
9	o-NO_2-C_6H_4-	C_6H_5-	114	$C_{21}H_{17}N_5O_6S$	14.99	15.29
10	m-NO_2-C_6H_4-	C_6H_5-	122	„	14.99	15.15
11	p-NO_2-C_6H_4-	C_6H_5-	136	„	14.99	15.50
12	o-Cl-C_6H_4	C_6H_5-	105	$C_{21}H_{17}ClN_4O_4S$	12.26	12.38
13	m-Cl-C_6H_4-	C_6H_5-	101	„	12.26	12.38
14	m-NO_2-C_6H_4-	$C_6H_5CH_2$-	114	$C_{22}H_{19}N_5O_6S$	14.55	14.60
15	p-NO_2-C_6H_4-	$C_6H_5CH_2$-	155	„	14.55	14.70
16	m-Cl-C_6H_4-	$C_6H_5CH_2$-	117	$C_{22}H_{19}ClN_4O_4S$	11.91	12.50
17	p-Cl-C_6H_4-	$C_6H_5CH_2$-	103	„	11.91	12.29

* Analysis for *C* and *H* : *C*, calc. 48.69%, found 48.39%; *H*, calc. 4.08%, found 4.03%.

** Analytical data given in a previous paper(1).

Dinitrophenylhydrazones of unsaturated aldehydes are recrystallized from toluene or xylene. They do not show depressed melting points with the products obtained from unsaturated aldehydes. Table 3 shows m.p. values for 2,4-dinitrophenylhydrazones of unsaturated aldehydes other than those already reported(1, 7, 8).

3. *1,1,3-Tris (carbetoxy-amino)-compounds.* — 1,1,3-Tris (carbetoxy-amino)-3-(2-chlor-phenyl)-propane was obtained when the procedure described under 1 above was applied in an attempt to isolate bisurethanes of β-alkylmercapto-o-chlorohydrocinnamaldehydes. The

TABLE 3

2,4-Dinitrophenylhydrazone of	M. P. °C	Formula	Analysis for *N*	
			calc. %	found %
o-nitrocinnamaldehyde	258	$C_{15}H_{11}N_5O_6$	19.60	19.63
m-nitrocinnamaldehyde	247	,,	19.60	18.23
o-chlorocinnamaldehyde	260	$C_{15}H_{11}ClN_4O_4$	16.16	16.23
p-chlorocinnamaldehyde	257	,,	16.16	16.14

hardened mass, washed with ether and recrystallized from ethyl alcohol, melted at 193°C.

Anal. Calc. for $C_{15}H_{26}N_3O_6$: C 51.98%; H 6.25%; N 10.10%.
Found : C 51.85%; H 6.09%; N 9.89%.

1,1,3-Tris(carbetoxy-amino)-3-(4-chlor-phenyl)-propane was obtained in an attempt to isolate the bisurethane of β-amylmercapto-p-chloro-hydrocinnamaldehydes (procedure under 1 above). The hardened mass dissolved in ether and after 5 months a solid substance had separated out m.p. 147°C. Recrystallized from ethyl alcohol its m.p. was 158°C.

Analysis Calc. for $C_{15}H_{26}N_3O_6$: N 10.10%
Found : N 10.24%.

4. *Benzylmercaptals.* — Benzylmercaptals of *p*-chlorocinnamaldehydes (10%) and of p-nitrocinnamaldehydes (44%) in the form of white crystals separated out during the evaporation of ether with which crude bisurethanes of β-benzylmercapto-*p*-chlorocinnamaldehydes and of β-benzylmercapto-*p*-nitrohydrocinnamaldehydes were

TABLE 4

Benzylmercaptal of	M. P. °C	Formula	Analysis	
			calc. %	found %
p-nitrocinnamaldehyde	93	$C_{23}H_{21}NO_2S_2$	C, 67.82 H, 5.16 N, 3.44	C, 67.45 H, 5.16 N, 3.50
p-chlorocinnamaldehyde	91	$C_{23}H_{21}ClS_2$	C, 69.61 H, 5.29	C, 69.16 H, 5.29

washed. They were recrystallized from alcohol. Melting points and analysis are given in Table 4. The benzylmercaptal of *p*-chlorocinnamaldehyde was also obtained by the condensation of 0.01 mole aldehyde with 0.02 molmercaptan in the presence of gaseous *HCl* after Baumann(9) (yield 23%).

Analyses for sulfur were done according to Gasparini's method(10). For other microanalyses our gratitude is due to Ruža Tomović, and Radmila Dimitrijević. We are indebted to Stana Tanasijević for practical assistance.

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ADDITION OF MERCAPTANS TO UNSATURATED ALDEHYDES. III.

PREPARATION OF BISURETHANES AND BISAMIDES OF β-ALKYLMERCAPTO-ALDEHYDES AND β-ARYLMERCAPTO-ALDEHYDES

by

KSENIJA D. SIROTANOVIĆ and MILKA M. BAJLON-PASTOR

A previous study(1) dealt with the preparation of bisurethanes of β-phenylmercapto-propionaldehydes, and of bisamides of β-phenylmercapto-propionaldehydes and β-phenylmercapto-butyraldehydes.

In continuing this study the preparation of other bisurethanes and bisamides was investigated, starting from: first, α, β-unsaturated aliphatic aldehydes with the simultaneous action of the mercaptans and urethane or acetamide; second, from β-mercapto-aldehydes by condensation with urethane or acetamide.

The β-mercapto-aldehydes with which the condensations were done were obtained by the addition of the mercaptans to the α, β-unsaturated aldehydes:

Aldehydes	*Mercaptans*
1. — Acroleine	1. — Ethyl-mercaptan
2. — Crotonaldehyde	2. — Amyl-mercaptan
3. — α-Methylpentenal	3. — Phenyl-mercaptan
4. — 2-Hexenal	4. — Benzyl-mercaptan

With these aldehydes and mercaptans all the addition products expected were obtained (Table 1) and in good yields (50—80%), except for the addition of amyl-mercaptan to α-methylpentenal whose compound yield was only 28%. Additions were done in the presence of organic bases as catalysts — when ethyl-mercaptan and amyl-mercaptan were used the catalyst was triethylamine, while for thiophenol (phenyl-mercaptan) and benzylmercaptan it was piperidine. To each mole of aldehyde 1.1 mole mercaptan was used, with heating of 0 to 3 h.

Of the 16 β-mercapto-aldehydes obtained only 5 are described in the literature, the addition products of acroleine with ethyl-mercaptan(2, 3) and benzyl-mercaptan(2, 3, 4), and of crotonaldehyde with ethyl-mercaptan(5), thiophenol(6, 7), and benzyl-mercaptan(2, 8, 9).

TABLE 1

Aldehyde: $R'CHCHR''CHO$ (with SR''' on the first CH)

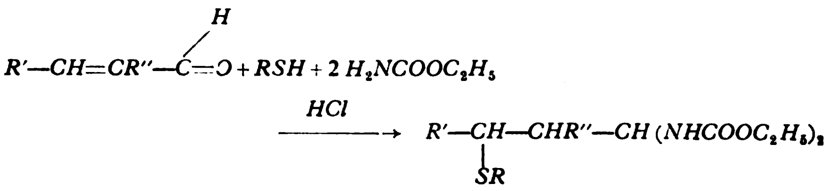
	R'	R''	R'''	Heated at 100° hours	Yield %	B. P. °C	M. P. °C	Formula	2,4—Dinitrophenylhydrazone							
									calc. C%	found C%	calc. H%	found H%	calc. N%	found N%	calc. S%	found S%
1	C_2H_5-	CH_3-	C_2H_5-	2	68	99°/20 mm	87°	$C_{14}H_{20}N_4O_4S$	49.41	49.73	5.88	5.54	16.47	16.32	—	—
2	n-C_3H_7-	H-	C_2H_5-	2	77	111°/20 mm	52°	$C_{14}H_{20}N_4O_4S$	—	—	—	—	16.47	16.72	—	—
3	H-	H-	n-C_5H_{11}-	—	67	110°/20 mm	104°	$C_{14}H_{20}N_4O_4S$	49.41	49.06	5.88	5.86	16.47	16.75	—	—
4	CH_3-	H-	n-C_5H_{11}-	—	81	116°/13 mm	43°	$C_{15}H_{22}N_4O_4S$	—	—	—	—	15.82	15.72	9.04	8.51
5	C_2H_5-	CH_3-	n-C_5H_{11}-	2	28	135°/14 mm	71°	$C_{17}H_{25}N_4O_4S$	—	—	—	—	14.65	15.01	—	—
6	n-C_3H_7-	H-	n-C_5H_{11}-	2	76	138°/15 mm	42°	$C_{17}H_{25}N_4O_4S$	—	—	—	—	14.65	14.53	—	—
7	H-	H-	C_6H_5-	—	49	128° 139°/18 mm	126°	*	*							
8	C_2H_5-	CH_3-	C_6H_5-	3	59	126°/ 3 mm	121°	$C_{18}H_{20}N_4O_4S$	55.67	55.90	5.15	4.98	14.43	14.59	—	—
9	n-C_3H_7-	H-	C_6H_5-	3	59	133°/ 4 mm	89°	$C_{18}H_{20}N_4O_4S$	—	—	—	—	14.43	14.41	8.24	8.42
10	C_2H_5-	CH_3-	$C_6H_5CH_2$-	1	60	134°/ 3 mm	76°	$C_{19}H_{22}N_4O_4S$	56.71	56.95	5.47	5.56	13.93	14.13	—	—
11	n-C_3H_7-	H-	$C_6H_5CH_2$-	3	66	144°/ 3 mm	71°	$C_{19}H_{22}N_4O_4S$	—	—	—	—	13.93	13.70	7.96	8.10

* Analytical data were given in a previous paper (1)

The β-mercapto-aldehydes obtained are relatively stable liquids of an unpleasant odor, and high boiling point. They distill in vacuum without decomposing. All the products not described in the literature were classified as 2,4-dinitrophenylhydrazones and were analyzed as such (Table 1).

As described earlier two methods were employed to prepare bisurethanes of β-mercapto-aldehydes:

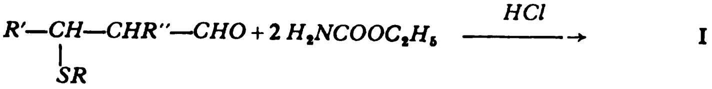
A. From the corresponding α, β-unsaturated aliphatic aldehyde by the simultaneous action of mercaptans and urethane (1 : 1 : 2) in the presence of hydrochloric acid and on standing at room temperature for a considerable time(1):



$$R'\text{—}CH\text{=}CR''\text{—}\overset{H}{C}\text{=}O + RSH + 2\,H_2NCOOC_2H_5 \xrightarrow{HCl} R'\text{—}\underset{SR}{CH}\text{—}CHR''\text{—}CH(NHCOOC_2H_5)_2$$

I

B. By condensation of the β-mercapto-aldehydes (II) with urethane (1 : 2) after Bischoff(10) in the presence of concentrated hydrochloric acid:



$$R'\text{—}\underset{SR}{CH}\text{—}CHR''\text{—}CHO + 2\,H_2NCOOC_2H_5 \xrightarrow{HCl} \text{I}$$

Table 2 shows that of the 16 bisurethanes of β-mercapto-aldehydes expected, method *A* gave only six, four from acroleine with the best yields (45—85%), and one from crotonaldehyde and hexenal each, with yields of 36% and 22% respectively; no product was obtained from α-methylpentenal. Three products were obtained with thiophenol and one each with ethyl-mercaptan, amyl-mercaptan, and benzylmercaptan.

Starting from β-mercapto-aldehydes (method *B*), 11 bisurethanes were obtained including all the four products with β-mercapto-propionaldehydes (yields 57—94%), three products with β-mercapto-butyraldehydes (63—87%) and three with β-mercapto-n-capronaldehydes (56—99%), and only one product with α-methyl-β-mercapto-valeraldehyde and in a very low yield (7%). With regard to the mercaptans, here again the largest number of products (four) was obtained with β-phenylmercapto-aldehydes, followed by three products each with β-ethylmercapto-aldehydes and β-amylmercapto-aldehydes, and only one product with β-benzylmercapto-aldehyde.

It is seen that the number of products is higher and yields better if the addition products (β-mercapto-aldehydes) are taken as

TABLE 2

Bisurethane: $$R'\underset{\substack{|\\ SR'''}}{CH}CHR''CH(NHCOOC_2H_5)_2$$

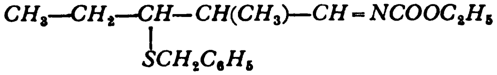
	R'	*R''*	*R'''*	Yield %	M. P. °C	Formula	calc. *N* %	found *N* %	calc. *C* %	found *C* %	calc. *H* %	found *H* %	calc. *S* %	found *S*%
1	*H*-	*H*-	C_2H_5-	85 94 (79)	124	$C_{11}H_{22}N_2O_4S$	10.07	10.07	47.48	47.30	7.91	7.99	11.51	11.62
2	CH_3-	*H*-	C_2H_5-	— 79 (51)	69	$C_{12}H_{24}N_2O_4S$	9.59	9.82	49.31	48.94	8.22	8.02	—	—
3	*n*-C_3H_7-	*H*-	C_2H_5-	— 99 (76)	94.5	$C_{14}H_{28}N_2O_4S$	8.75	8.76	52.50	52.14	8·75	8.95	—	—
4	*H*-	*H*-	*n*-C_5H_{11}-	47 87 (58)	105	$C_{14}H_{28}N_2O_4S.{}^1/{}_2H_2O$	8.51	8.46	51.06	51.46	8.81	8.58	—	—
5	CH_3-	*H*-	*n*-C_5H_{11}-	— 63 (51)	69	$C_{15}H_{30}N_2O_4S$	8.38	8.32	53.89	54.09	8.98	8.90	—	—
6	*n*-C_3H_7-	*H*-	*n*-C_5H_{11}-	— 98 (74)	67	$C_{17}H_{34}N_2O_4S$	7.74	7.63	56.35	56.48	9.40	9.90	—	—
7	*H*-	*H*-	C_6H_5-	45 57 (28)	145	*								
8	CH_3-	*H*-	C_6H_5-	36 87 (45)	77	$C_{16}H_{24}N_2O_4S$	8.24	8.33	56.47	56.05	7.05	7 02	—	—
9	C_2H_5-	CH_3-	G_6H_5-	— 7 (4)	139	$C_{18}H_{28}N_2O_4S$	7.61	7.72	58.71	58.34	7.61	7.93	—	—
10	*n*-C_3H_7-	*H*-	C_6H_5-	22 56 (33)	83	$C_{18}H_{28}N_2O_4S$	7.61	7.53	—	—	—	—	8.77	8.82
11	*H*-	*H*-	$C_6H_5CH_2$-	79 79 (48)	95	$C_{16}H_{24}N_2O_4S$	8.24	8.51	—	—	—	—	9.41	9.70

* Analytical data were given in a previous paper (1)

the starting point rather than the unsaturated aldehydes themselves. However, if the yields are calculated with respect to the starting aldehydes from which the β-mercapto-aldehydes were obtained then the values for method *B* bisurethanes are considerably lower (bracketed figures, Table 2).

The bisurethanes of β-mercapto-aldehydes obtained are crystalline substances with relatively low melting points (67—145°C). They do not dissolve in water and petroleum ether, hardly dissolve in alcohol and ligroin, and quite readily in ether. They crystallize from dilute alcohol, ligroin or benzol.

In trying to obtain bisurethanes of β-mercapto-aldehydes by both methods, compounds of a different structure were isolated in some cases. Thus benzyl-mercaptan and urethane acting on α-methyl-pentenal gave the monourethane of α-methyl-β-benzylmercapto-*n*-valeraldehyde (III):

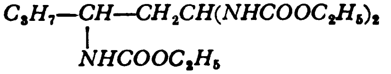


$$CH_3—CH_2—\underset{\displaystyle SCH_2C_6H_5}{\underset{|}{CH}}—CH(CH_3)—CH=NCOOC_2H_5$$

III

This compound was also obtained by method *B*, i.e. the condensation of α-methyl-β-benzylmercapto-*n*-valeraldehyde with urehane.

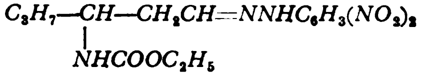
The action of ethyl-mercaptan and urethane and of amyl-mercaptan and urethane on hexenalin both cases yielded 1,1,3-tris (carbetoxy-amino)-*n*-hexane (IV):



$$C_3H_7—\underset{\displaystyle NHCOOC_2H_5}{\underset{|}{CH}}—CH_2CH(NHCOOC_2H_5)_2$$

IV

which means that urethane added onto the double bond of hexenal and condensed with the carbonyl group. The structure of this compound was proved by hydrolysis in the presence of 2,4-dinitrophenylhydrazine — 2,4-dinitrophenylhydrazone of β-carbetoxyamino-n-capron-aldehyde was obtained (V):



$$C_3H_7—\underset{\displaystyle NHCOOC_2H_5}{\underset{|}{CH}}—CH_2CH=NNHC_6H_3(NO_2)_2$$

V

Bisamides of β-mercapto-aldehydes (VI) were also obtained by both methods:

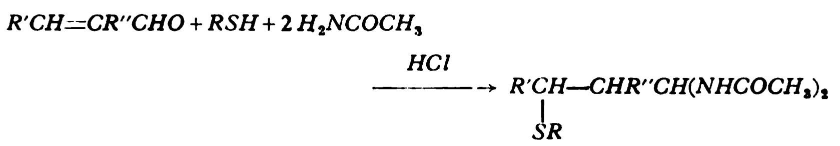
A. From the corresponding unsaturated aldehydes, mercaptans, and acetamide (1 : 1 : 2) in the presence of hydrochloric acid, at room temperature⁽¹⁾:

TABLE 3

Bisamide: $R'\underset{\displaystyle SR'''}{\underset{|}{C}}HCHR''CH(NHCOCH_3)_2$

	R'	R''	R'''	Yield % A	Yield % B	M. P. °C	Formula	calc. N %	found N%	calc. C%	found C%	calc. H%	found H%	calc. S%	found S%
1	H-	H-	C_2H_5-	79	65 (55)	176	$C_9H_{18}N_2O_2S$	12.89	12.63	49.54	49.10	8.26	8.26	14.68	14.47
2	n-C_3H_7-	H-	C_2H_5-	—	16 (12)	134	$C_{12}H_{24}N_2O_2S$	10.77	10.57	55.38	54.73	9.23	9.42	—	—
3	H-	H-	n-C_5H_{11}-	23	51 (34)	145	$C_{12}H_{24}N_2O_2S$	10.77	10.62	—	—	—	—	—	—
4	H-	H-	C_6H_5-	61	41 (21)	202	*								
5	CH_3-	H-	C_6H_5-	39	48 (25)	128	*								
6	n-C_3H_7-	H-	C_6H_5-	19	26 (16)	123	$C_{16}H_{24}N_2O_2S$	9.12	8.98	—	—	—	—	10.29	10.41
7	H-	H-	$C_6H_5CH_2$-	73	61 (37)	159	$C_{14}H_{20}N_2O_2S$	10.00	10.30	—	—	—	—	11.42	11.39
8	CH_3-	H-	$C_6H_5CH_2$-	37	65 (46)	134	$C_{15}H_{22}N_2O_2S$	9.52	9.64	—	—	—	—	10.88	10.73
9	C_2H_5-	CH_3-	$C_6H_5CH_2$-	—	8 (5)	176	$C_{17}H_{26}N_2O_2S$	8.70	8.72	63.35	62.74	8.07	8.05	—	—
10	n-C_3H_7-	H-	$C_6H_5CH_2$-	—	20 (13)	107	$C_{17}H_{26}N_2O_2S$	8.70	8.85	—	—	—	—	—	—

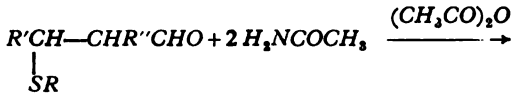
*Analytical data were given in a previous work.



$$R'CH{=}CR''CHO + RSH + 2\,H_2NCOCH_3 \xrightarrow{HCl} R'\underset{SR}{\underset{|}{CH}}{-}CHR''CH(NHCOCH_3)_2$$

VI

B. By condensation of β-mercapto-aldehydes (II) with acetamide in the presence of acetic acid anhydride[(11)]:



$$R'\underset{SR}{\underset{|}{CH}}{-}CHR''CHO + 2\,H_2NCOCH_3 \xrightarrow{(CH_3CO)_2O}$$

VII

The bisamides are reviewed in Table 3. Here again the number of compounds obtained from the already prepared β-mercapto-aldehydes was larger (ten) than that from the unsaturated aldehydes (seven). Yields were better (23—79%) from the unsaturated aldehydes, especially if method *B* yields are calculated with respect to the unsaturated aldehyde (bracketed figures, Table 3), than those (8—65%) from the prepared β-mercapto-aldehyde. Method *A* again yielded all four products with acroleine (23—79%), two with crotonaldehyde (37% and 39%), one with hexenal (19%) and none with α-methylpentenal. Method *B* produced all four compounds with β-mercapto-propionaldehydes (41—65%), three with β-mercapto-capron-aldehydes (16—26%), two with β-mercapto-butyraldehydes (48—65%) and only one with β-mercapto-valeraldehydes (yield of 8%).

The bisamides obtained from β-mercapto-aldehydes are white crystalline substances with melting points between 107 and 202°C. They do not dissolve in petroleumether, ether or water. They were crystallized from acetone or an acetone-petroleumether mixture.

Bisurethanes and bisamides of β-mercapto-aldehydes are obtained in about the same numbers starting from either the unsaturated aldehydes (6 bisurethanes, 7 bisamides) or from the β-mercapto--aldehydes (11 bisurethanes, 10 bisamides). The yields of bisurethanes are considerably better than those of bisamides (Table 2 and 3).

With regard to the reactivity of the unsaturated aldehydes, all 8 products were obtained with acroleine (4 bisurethanes, 4 bisamides), 3 with crotonaldehyde (1 bisurethane, 2 bisamides), 2 with hexenal (1 bisurethane, 1 bisamide), and none with α-methylpentenal. The most compounds (6) were obtained with thiophenol, followed by benzyl-mercaptan (3), and ethyl-mercaptan and amyl-mercaptan (2 each).

Starting from β-mercapto-aldehydes, all 8 compounds were obtained with β-mercapto-propionaldehydes (4+4), 6 with β-mercapto--n-capronaldehydes (3+3), 5 with β-mercapto-*n*-butyraldehydes (3 + 2), and only 2 with α-methyl-β-mercapto-valeraldehydes (1+1). Of the β-mercapto-aldehydes used, the most reactive were the β-phenyl-mercapto-aldehydes which yielded 7 out of the 8 compounds expected

(4 + 3), followed by β-benzylmercapto-aldehydes and β-ethylmercapto-aldehydes which gave 5 products each (1+4; 3+2), and β-amylmercapto-aldehydes which gave only 4 compounds (3+1).

EXPERIMENTAL

1. *β-ethylmercapto and β-amylmercapto-aldehydes* were obtained after Catch *et al.*⁽²⁾. 0.1 mole of unsaturated aldehyde is cooled to 0°C, slightly more than 0.1 mole of mercaptan and 3 or 4 drops of triethylamine are added and then the mixture left at room temperature for several hours, or heated to 100°C and then distilled in vacuum.

2,4-dinitrophenylhydrazones of β-mercapto-aldehydes were prepared with well-cooled solutions of the 2,4-dinitrophenylhydrazines in a mixture of phosphoric acid and alcohol⁽¹²⁾.

The times of heating the reaction mixtures, yields, and boiling points for the aldehydes not described in the literature, and the melting points and analyses of the 2,4-dinitrophenylhydrazones of these aldehydes are shown in Table 1 ($R'''=C_2H_5$—, n-C_5H_{11}—).

2. *β-Phenylmercapto- and β-benzylmercapto-aldehydes* were obtained as under 1 above, except that 3 or 4 drops of piperidine were added instead of diethylamine (*sic.*).

The times of heating the mixture, yields and boiling points of the aldehydes not described in the literature, and the melting points and analyses of their 2,4-dinitrophenylhydrazones are shown in Table 1 ($R'''=C_6H_5$—, $C_6H_5CH_2$—).

3. *Bisurethanes of β-alkylmercapto- and β-arylmercapto-aldehydes*

A. — After Sirotanović⁽¹⁾. A mixture of 0.02 mole unsaturated aldehyde, 0.04 mole urethane, 0.02 mole mercaptan and a drop of concentrated hydrochloric acid* is kept at room temperature for several days (5—15). Then the hardened or semihard mass is treated with water and petroleumether and filtered.

B. After Bischoff⁽¹⁰⁾. 0.01 mole β-mercaptoaldehyde and 0.02 mole urethane are mixed, fused by mild heating in a water bath and left at room temperature for a few hours. Next a drop of hydrochloric acid is added and the mixture is left to harden (overnight). The hardened mass is treated with water or petroleumether and filtered.

Crude bisurethanes were recrystallized from dilute ethyl alcohol or petroleumether, except for the bisurethanes of β-phenylmercapto-propionaldehydes and β-phenylmercapto-butyraldehydes (recrystallized from benzene) and β-benzylmercapto-propionaldehydes (from an ether-petroleum ether mixture). Melting points of mixtures of the products obtained by *A* and the corresponding products obtained by *B* did not show depression.

Yields, melting points and analyses of the bisurethanes obtained are given in Table 2.

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* When ethylmercaptan is used, aldehyde and urethane are first mixed, the mixture is colled in ice, cooled mercaptan is added and hydrochloric is added at the end.

4. *Bisamides of β-alkylmercapto- and arylmercapto-aldehydes.*

A. After Sirotanović$^{(1)}$. To a mixture of 0.02 mole of unsaturated aldehyde, 0.04 mole acetamide and slightly over 0.02 mole mercaptan*, a drop of hydrochloric acid is added and the mixture left at room temperature for 5—15 days to harden. The hard or semi-hard mass is treated with ether (except for bisamide of β-phenylmercapto--capronaldehydes which is first treated with water and then kept under ether for a few days) and then filtered.

B. After Stefanović *et al.*$^{(11)}$. A mixture of 0.02 mole of β-mercapto-aldehyde, 5 g acetamide and 5 ml acetic acid anhydride is heated at 100°C for 3 h. The anhydride of acetic acide is removed in vacuum and the residue is cooled, washed with cold water and treated with ether or ether-petroleum ether mixture until hardening (except for bisamides of β-phenylmercapto-*n*-capronaldehydes, which are only treated with water and petroleum ether) and then filtered.

Crude products are recrystalized from acetone, acetone-petroleum ether mixture, or ethyl alcohol. The melting points of mixtures of products obtained by *A* and the corresponding products of *B* do not show depression.

Yields, melting points and analyses of the bisamides obtained are shown in Table 3.

5. *Monourethane of α-methyl-β-benzylmercapto-m-valeraldehyde.*

A. Obtained from α-methylpentenal, benzylmercaptan and urethane while trying to prepare the corresponding bisurethane as under 3*A*. The reaction mixture, which remains syrupy even after standing at room temperature for a month, is treated with water and petroleum ether until partial hardening, and then with methyl alcohol on a porcelain plate. 0.3 *g* (5%) of crude substance (M.P. 87—94°C) was obtained. Recrystallized from ligroin, it melted at 96°C.

B. Obtained from α-methyl-β-benzylmercapto-*n*-valeraldehyde and urethane in an attempt to obtain bisurethane as under 3 *B*. 1.1 g (37%) of crude substance (M.P. 92°C) was obtained. Recrystallized from ligroin, it melted at 96°C.

Melting points of a mixture of the substances obtained under *A* and *B* did not show depression.

Analysis Calc. for $C_{16}H_{23}NO_2S$: *C* 65.53%; *H* 7.85%; *N* 4.78%.
Found : *C* 65.26%; *H* 7.75%; *N* 4.75%.

6. *1,1,3-tris (carbetoxy-amino)-hexane* was obtained while trying to prepare bisurethanes of β-ethylmercapto and β-amylmercapto--n-capronaldehydes as under 3*A*. The hardened mass is treated with ether and filtered. 28% and 25% of crude substance were obtained (m.p. 122—127°C), respectively. Recrystallized from an acetone-petroleum ether mixture, it melted at 128°C.

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* When using ethyl-mercaptan the mixture is cooled to 0°C.

Analysis Calc. for $C_{15}H_{29}N_3O_6$: C 51.90%; H 8.35%; N 12.10%.
Found : C 52.12%; H 8.46%; N 11.82%.
M.W. Calculated 347
Found 315

Hydrolysis of 1,1,3-tris(carbetoxy-amino)-hexane with hydrochloric acid in the presence of 2,4-dinitrophenylhydrazine. 0.35 *g* (1 millimole) of the above compound, 0.2 *g* 2,4-dinitrophenylhydrazine and 15 ml alcohol are heated until boiling. 0.2 ml of concentrated hydrochloric acid is added and heating continued for 2 m until boiling. On cooling the yellow 2,4-dinitrophenylhydrazone of β-(carbetoxy--amino)-n-capronaldehyde separates out (m.p. 156°C). Recrystallized from absolute ethanol, it melted at 162—163°C.

Analysis Calc. for $C_{15}H_{21}N_5O_6$: C 49.00%; H 5.69%; N 19.07%.
Found : C 49.07%; H 5.66%; N 19.15%.

Analysis for sulfur was done by Gasparini's method(13).

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STABILIZATION OF *L*-ASCORBIC ACID WITH COMPLEXON III IN SOLUTIONS OF SOME ORGANIC ACIDS

by

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JELENA V. BANJAC

In aqueous solutions, *L*-ascorbic acid undergoes auto-oxidation. Its concentration falls with time, though at different rates depending on a number of factors, such as light, temperature, *p*H, presence of metallic ions, etc.

The stabilization of *L*-ascorbic acid in solution is highly important theoretically and practically. Though many authors have been studying it for years, a satisfactory solution to this problem has not yet been found.

Originally the possibility of stabilizing L-ascorbic acid with some acids or their mixtures was explored. The best results, but only for the determination of *L*-ascorbic acid, were obtained with oxalic and metaphosphoric acid(1, 2).

More recently, studies have been made with ethylenediaminotetraacetic acid and its disodium salt (complexon III) with a view to use in the food and pharmaceutical industries, since complexon III is not poisonous and its calcium salt is already used in therapy(3, 4, 5).

In this study the stabilizing effect of acetic, citric, tartaric, and lactic acid on *L*-ascorbic acid with complexon III have been investigated. These acids are frequent in natural products or they are added in processing, so that they could be decisive factors for the application of complexon III in some preserving techniques.

EXPERIMENTAL

Solutions. — The principal solutions for the preparation of samples were of these concentrations:

— 5% solution of acetic, citric, tartaric, and lactic acids, whose precise concentration was determined by titration with 0.2*N* solution of sodium hydroxide using phenolphthalein as indicator.

— 0.1*M*, 0.01*M*, and 0.001*M* solutions of complexon III (the reagent was first dried at 105°C).

— Precisely 0.1% solution of *L*-ascorbic acid.

Preparation of samples. — Samples were prepared by putting known volumes of the principal solutions in a measuring vessel which was then filled with distilled water up to the mark.

The samples examined were:

(a) *L*-ascorbic acid in distilled water;
(b) *L*-ascorbic acid and complexon III in concentrations: $2.5 \times 10^{-5} M$; $2.5 \times 10^{-4} M$; $2.5 \times 10^{-3} M$; $2.5 \times 10^{-2} M$;
(c) *L*-ascorbic acid and one of the said acids in concs. of: 0.25%, 1.0%, 3.0%,
(d) *L*-ascorbic acid and a mixture of complexon III with one of the said acids in each of the concentrations under (*b*) and (*c*).

To all the samples the same amount of *L*-ascorbic acid (8.8 mg%) was added. As soon as the vessel had been filled with distilled water up to the mark, the true concentration of *L*-ascorbic acid was determined by titration and taken as 100% for later calculations of the L-ascorbic acid remaining.

Method. — The stability of *L*-ascorbic acid in the samples of the above compositions at 29 ± 1°C was followed for 96 h. Determinations were made at the 24th, 48th, 72nd, and 96th hour. One hour before each determination of the remaining *L*-ascorbic acid the samples were taken out of the thermostat and brought up to room temperature. For each determination two 10 ml samples were taken.

L-ascorbic acid was determined volumetrically after Tillmans, using 2,6-dichlorphenolindophenol(1). Tillmans' reagent was also employed in the titration of solutions (*b*) and (*c*), but without *L*-ascorbic acid; it was established that these acids do not absorb the reagent in solutions of the given concentrations.

It was assumed that under the given reaction conditions *L*-ascorbic acid does not change into *n*-diol compounds which absorb Tillmans' reagent, the more so because complexon III binds copper which usually accelerates these reactions.

RESULTS AND DISCUSSION

Percentages of the *L*-ascorbic acid remaining in the solutions after 96 h at 29+1°C are presented in Table 1. The same results are presented as curves in graphs *a* and *b*, Figs. 1—4. The graphs give:

(a) The relationship between the percentage of *L*-ascorbic acid remaining and the concentration of the acid present at constant concentration of complexon III;

(b) The relationship between the percentage of *L*-ascorbic acid remaining and the concentration of complexon III at constant concentration of the given acid.

From the curves *a* it may be seen that complexon III considerably improves the stability of *L*-ascorbic acid in solutions of these acids. While after 96 h only 1.1—2.3% L-ascorbic acid was found in 0.25 solutions of the acids, in the same solutions with complexon III there was between 76 and 98%, depending on the type and concen-

TABLE 1

% *L-ascorbic acid in samples thermostated for 96 hours at 29 ± 1°*

Complexon (moles)	Water	Acetic acid %			Citric acid %			Tartaric acid %			Lactic acid %		
		0.25	1.0	3.0	0.25	1.0	3.0	0.25	1.0	3.0	0.25	1.0	3.0
0	0	1.12	1.13	1.07	2.33	3.38	2.11	1.91	1.13	1.24	1.72	1.03	1.18
2.5×10^{-5}	94.94	95.69	95.53	94.24	95.42	78.64	74.68	94.58	91.71	53.85	94.27	91.10	4.04
2.5×10^{-4}	95.25	97.32	98.53	97.83	96.87	96.46	91.63	94.38	94.56	79.75	98.53	95.49	82.47
2.5×10^{-3}	91.49	97.60	97.42	97.06	98.39	98.11	94.52	96.91	96.21	89.40	98.22	96.53	89.09
2.5×10^{-2}	22.83	77.06	89.17	89.81	87.01	92.31	94.12	75.00	94.50	93.71	86.82	88.75	91.26

tration of the acid and the concentration of complexon III. The stability was highest in weakly acid solutions of complexon III, and decreased with increasing acidity, except in solutions with 2.5×10^{-2}M complexon III in which the stability rose continuously. It may be further noted that $2.5 \times 10^{-2}M$ complexon III better stabilizes *L*-ascorbic acid in solutions of the acids than in aqueous solution.

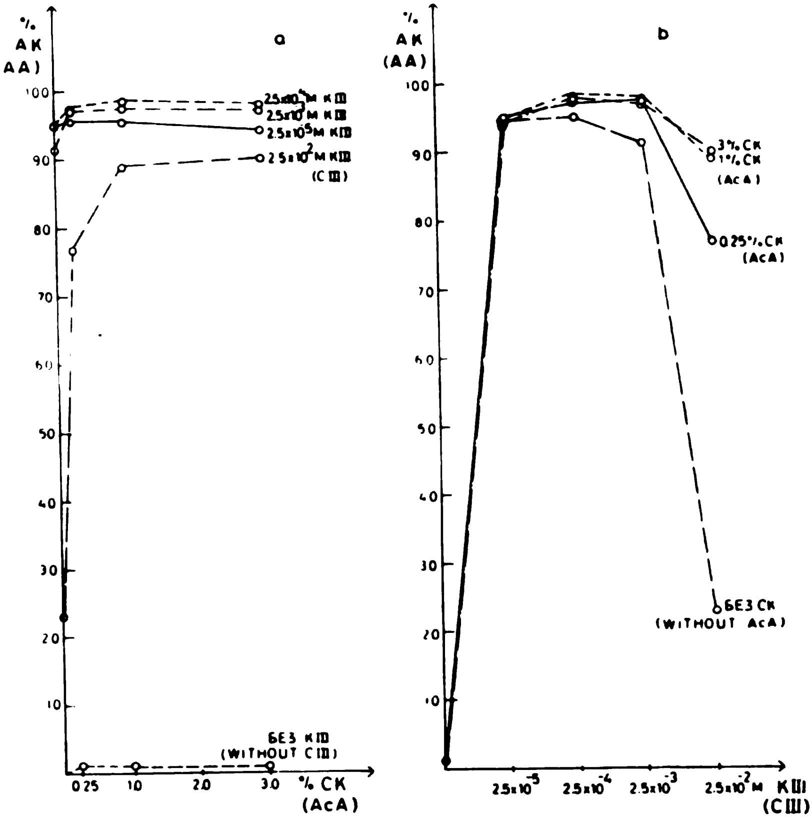

Figure 1

(a) Change of *L*-ascorbic acid (*AA*) concentration as a function of acetic acid (*AcA*) concentration at constant concentration of complexon III (CIII)

(b) Change of *L*-ascorbic acid (*AA*) concentration as a function of complexon III (CIII) concentration at constant acetic acid (*AcA*) concentration

In the solutions containing $2.5 \times 10^{-5}M$ complexon III, the stability of *L*-ascorbic acid fell with increasing acid concentration. The decrease was different for each of the acids. Thus after 96 h at 29+1°C in 3% solutions of acetic, citric, tartaric, and lactic acid, percentages of 94.24, 74.68, 53.85, 4.04% were found, respectively.

Graphs *b* show that the stability of *L*-ascorbic acid usually increases and then decreases with increasing complexon III concentration. Exceptions are 3% solutions of tartaric and lactic acid in which the stability rises continuously.

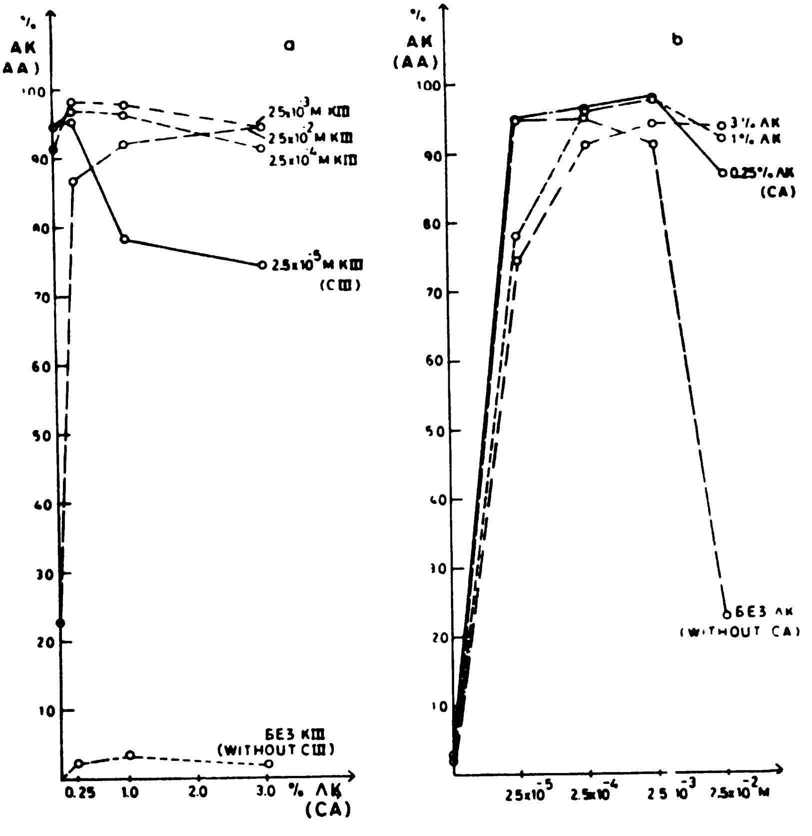

Figure 2

(a) Change of *L*-ascorbic acid (*AA*) concentration as a function of citric acid (*CA*) concentration at constant complexon III (CIII) concentration

(b) Change of *L*-ascorbic acid (*AA*) concentration as a function of complexon III (CIII) concentration at constant citric acid (*CA*) concentration

It is generally known that metal ions, especially copper ions, catalytically accelerate the oxidation of *L*-ascorbic acid, and that complexon III binds metallic ions into very stable complexes. The chelating power of complexon III depends on the *pH*; the optimum for copper ions in dilute solutions is around 3.5(6).

Our experiments show that the maximum stability of *L*-ascorbic acid does not always correspond to the same *p*H. For example, in the solution of *L*-ascorbic acid which contain 3% citric, tartaric, and lactic acid and $2.5 \times 10^{-4} M$ complexon III, the *pH* is about 2.15, while maximum stability was achieved only in the solution with citric acid. In the solutions containing lactic or tartaric acid, as may be seen from graphs *b* in Figs. 3 and 4, the maximum stability of *L*-ascorbic acid does not fall within the range of complexon III concentrations examined and the corresponding *pH* values. For maximum stability considerably a higher *pH* is required.

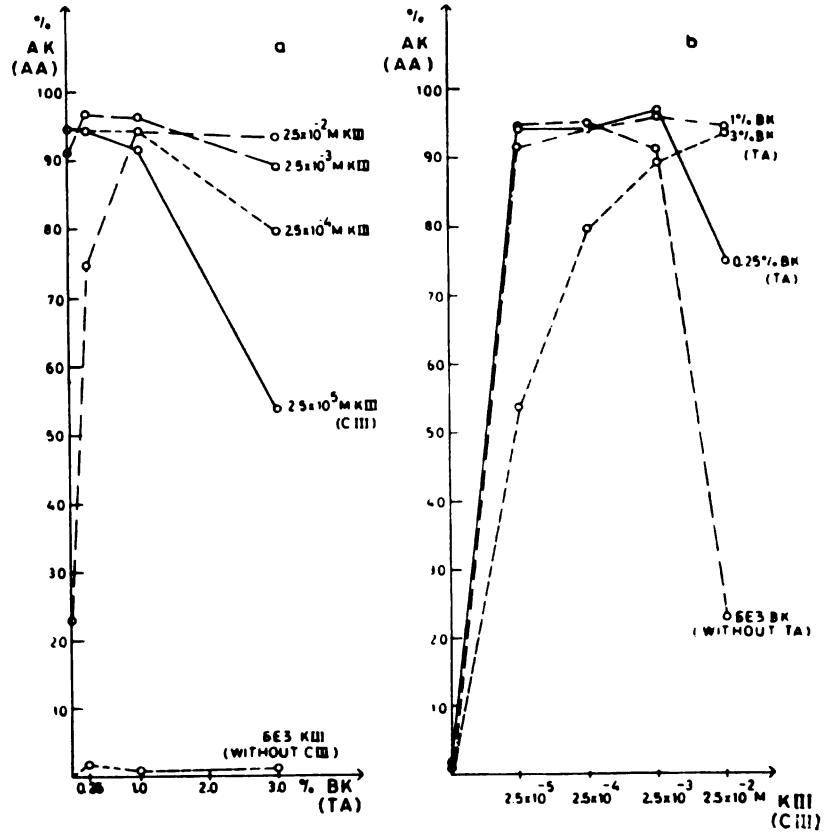

Figure 3

(a) Change of *L*-ascorbic acid (*AA*) concentration as a function of tartaric acid (*TA*) concentration at constant complexon III (CIII) concentration

(b) Change of *L*-ascorbic acid (*AA*) concentration as a function of complexon III (CIII) concentration at constant tartaric acid (*TA*) concentration

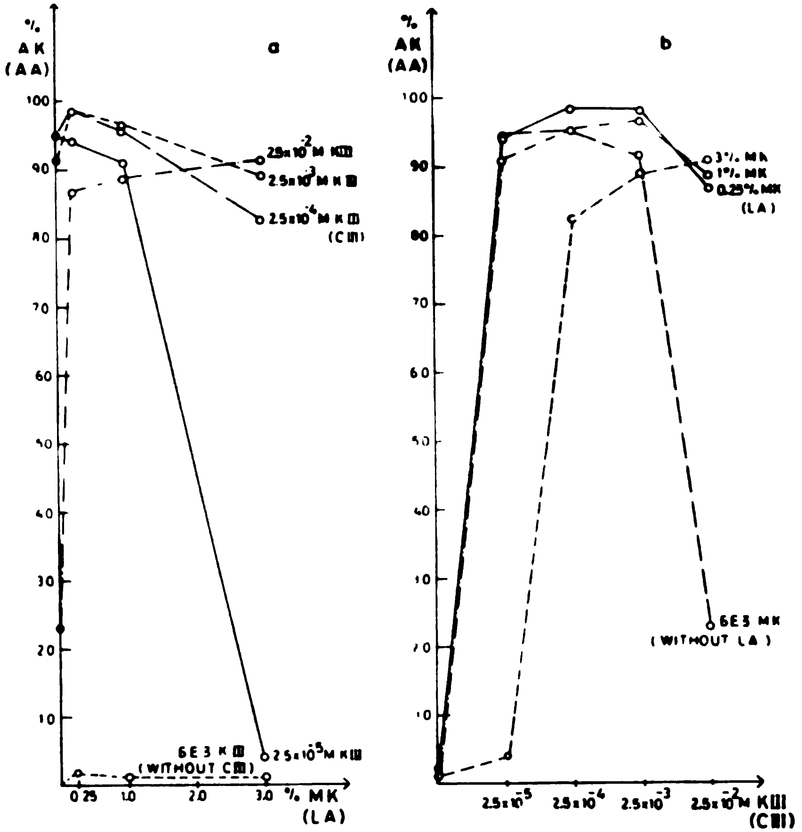

Figure 4

(a) Change of *L*-ascorbic acid (*AA*) concentration as a function of lactic acid (*LA*) concentration at constant complexon III (CIII) concentration

(b) Change of *L*-ascorbic acid (*AA*) concentration as a function of complexon III (CIII) concentration at constant lactic acid (*LA*) concentration

It can be concluded that the rate of increase or decrease of the stability of *L*-ascorbic acid and the conditions for its maximum stability principally depend on the nature of the acid present.

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INFLUENCE OF TEMPERATURE ON THE TREHALOSE CONTENT OF *S. CEREVISIAE* DURING CONTINUOUS GROWTH AT 16—44°C

by

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The content of trehalose in cells of *Saccharomyces cerevisiae* has been studied since 1925, when E. M. Koch and F. C. Koch(1) isolated trehalose from baker's yeast. In view of the fact that *S. cerevisiae* can contain a considerable amount of trehalose (up to 15% of the dry cell substance according to K. Myrbäck and B. Oertenblad(2), and T. Sato and Sh. Thumura(3, 4), K. M. Brandt(5) concludes the trehalose (like glycogen) is a reserve carbohydrate. Brandt(5) was the first to study the effect of a short heating at 50°C on the trehalose content of a suspension of *S. cerevisiae* cells. Later, many authors studied various factors which affect the biosynthesis and the dissimilation of trehalose in cells of *S. cerevisiae* (see papers reviewed by W. E. Trewelyan(6) and more recent publications by A. Panek(7, 8, 9) and M. Erlander(10, 11, 12). Moreover, the trehalose, being a cell component, is an indicator of yeast quality. The storage quality of baker's yeast and the preparation of active dry yeast of good quality depend on the trehalose content (G. Butschek and R. Kautzmann(13). The trehalose content in cells of *S. cerevisiae* can be increased by anaerobic cultivation in a mash containing a small amount of nitrogen compounds relative to sugar content. Under these conditions cells poor in proteins and rich in trehalose are formed. This was used by F. Hayduck(14) over fifty years ago.

Investigating the continuous growth of *S. cerivisiae* we have observed that the cellular trehalose content, inspite of the presence of considerable amounts of appropriate nitrogen compounds in the mash, depends upon the temperature of cell multiplication. In our experiments we studied a strain of *S. cerivisiae* cultivated in our laboratory at 30°C (denoted as Š-30) and thermo-tolerant strains obtained by adaptation of this strain to 40°C (strain Š-40) and to 43°C (Š-43).

This study was financed through a contract with the Institute for Chemical, Technological and Metallurgical Research, Belgrade (Topic No. 34) concluded in April 1963.

Since there are no data in the literature on the effect of the temperature on the trehalose content, we believe that our results might be of some interest.

EXPERIMENTAL

The strains of *S. cerevisiae (S. cerevisiae Š-30, S. cerevisiae Š-40* and *S. cerevisiae Š-43)* were left to grow continuously in Kluyver's vessels of 1.25 and 2.25 lit, in which air was introduced by means of a glass spray of G-3 density. The vessels were closed with bossed rubber stoppers. Each stopper had four holes: one for an upright bulb condenser, closed with sterilized cotton, one for a thermometer, one for a tube through which the initial suspension of cells was poured into the vessel, and one for a T-tube whose one end was connected via a tap with a vessel containing sterilized oleic acid (for the removal of foam), and the other with a burette containing 10% sodium hydroxide solution (for the adjustment of *pH*). The vessel with oleic acid and the burette with sodium hydroxide solution were closed with sterilized cotton. The upper part of the Kluyver's vessel had a side arm with a rubber stopper with a jacket, through which a coiled glass capillary tube for adding nutrient solution was inserted, reaching almost to the air spray.

The constant inflow through the capillary tube was regulated by means of a level regulator consisting of a metallic vessel with a scew cover and an unright tube. In the vessel there was a sharp-pointed float which functioned as a needle valve for the inlet tube in the vessel cover, thus ensuring a constant level in the regulator. The conical bottom of the regulator was connected with the outlet tube. The inlet tube was connected with a vessel containing sterilized nutrient solution, and the outlet tube with the capillary tube of the Kluyver's vessel. The rate of inflow was regulated by means of the capillary tube and by the difference in level in the Kluyver's vessel and in the regulator. The temperature in the Kluyver's vessel was regulated by means of water of suitable temperature which sprayed out from a circular glass tube containing many holes. The volume rate of inflow into the vessel was determined by measuring the time required to fill up vessels of 25, 50 and 100 *ml*, respectively. The rate of inflow of the nutrient solution was so adjusted that the Kluyver's vessel got filled up in 12 hrs 30 min to 13 hours. In some experiments the average time was somewhat longer.

One liter of the nutrient solution contained 50 *g* of the dry matter of corn-steep liquor, 50 g of glucose, 12.5 g of $(NH_4)_2SO_4$, 2.5 *g* of $(NH_4)_2HPO_4$, 2.5 *g* of K_2SO_4, 0.5 *g* of $MgSO_4$, 5.0 *g* of $CaCl_2$ and 2 *ml* of biotic solution (0.2 *mg* of aneurine + 0.10 *mg* of riboflavine + 5.0 *mg* of nicotinic acid + 0.3 *mg* of *p*-benzoic acid + + 1.0 *mg* of pyridoxine + 0.5 *mg* of *Ca*-pantothenate + 0.01 *mg* of biotin + 0.2 g of inositol). The solution was prepared in the following way: the solution of glucose and the solution of corn steep liquor with salts were sterilized separately; the mixture of biotics was sterilized in sealed ampullae. All three solutions were mixed just before use. The bottle containing the solution was of 10 lit capacity.

Cultures of the strains were grown in the fluid of baker's yeast (150 g/lit, *pH* = 5.3), to which 100 *g* of saccharose per lit and 1.5 *g* of $(NH_4)_2HPO_4$ per lit were added after filtration. The biomass obtained was separated under sterilized conditions (filtration and centrifugation). For continuous growth experiments 40 to 45 *g* was mixed with 800 ml of baker's yeast fluid and the mixture put into a Kluyver's vessel in which it was fed with the nutrient solutions for 6—10 hours. A current of sterilized air was passed through at a rate of 300 or 600 *lit*/hour, depending on the vessel capacity. Then the rate of inflow of nutrient solution was accurately adjusted in the course of 1—2 hours, and continuous growth allowed to proceed for a further 96 hours.

In the course of the experiments the necessary physical and chemical parameters were determined and monitored, viz:

1. The temperature of the mash in the Kluyver's vessel; 2. the discharge rate of the mash; 3. air flow rate was measured by means of a rotameter and regulated manully; 4. the concentration of the dry biomass (*g*/*lit*) was determined by filtering 10—25 *ml* of the mash through a glass filter funnel whose bottom was covered with fine asbestos, and drying the precipitate at 110°C for 4—5 hours; 5. the *pH* was determined by a suitable indicator paper and electrometrically, and was adjusted with 10% sodium hydroxide solution; 6. trehalose was separated quantitatively after W. E. Trewelyan and J. S. Harrison(15, 16) and determined using anthrone (Seifter *et al.*(17). The anthrone solution was prepared from 500 *ml* of H_2SO_4, 200 *ml* of water and 0.7 *g* of anthrone; 7. reducing sugars (glucose, etc.) in the mash were determined with Fehling's solution and by titration of Cu_2O after Bertrand; 8. percentage of nitrogen in the cell was determined by the Kjedahl method.

The specific rate of growth (*g* of dry cell substance 1, *g* of dry cell substance/hour) of *S. cerevisiae* in the steady state was calculated from the dry cell substance and the mean time.

RESULTS AND DISCUSSION

a. *Experiments with strain Š-30.* Thirty experiments were performed with strain Š-30, at temperatures of 16°, 20°, 30°, 35°, 38°, 39°, 40° and 42°C. The temperature during filling of the Kluyver's vessel (6—10 hrs) was 30°C, and then it was raised to the temperature of the experiment. Figure 1 shows the change of dry cell substance concentration (g/100 ml) in the course of growth at 16°, 30°, 38°, 39°, 40° and 42°C (dashed lines) and the change of the trehalose concentration (T%) in dry cell substance (full lines) (Experiments 24, 10, 17, 25, 13 and 16).

From curves the following may be concluded.

The initial concentration of dry cell substance was approximately the same at the beginning of all experiments (upper part of Fig. 1). However, its change during the experiments was characteristic for the temperature. The concentration increased the most rapidly at 30°C, levelling off after 30—36 hours. It increased much slower at

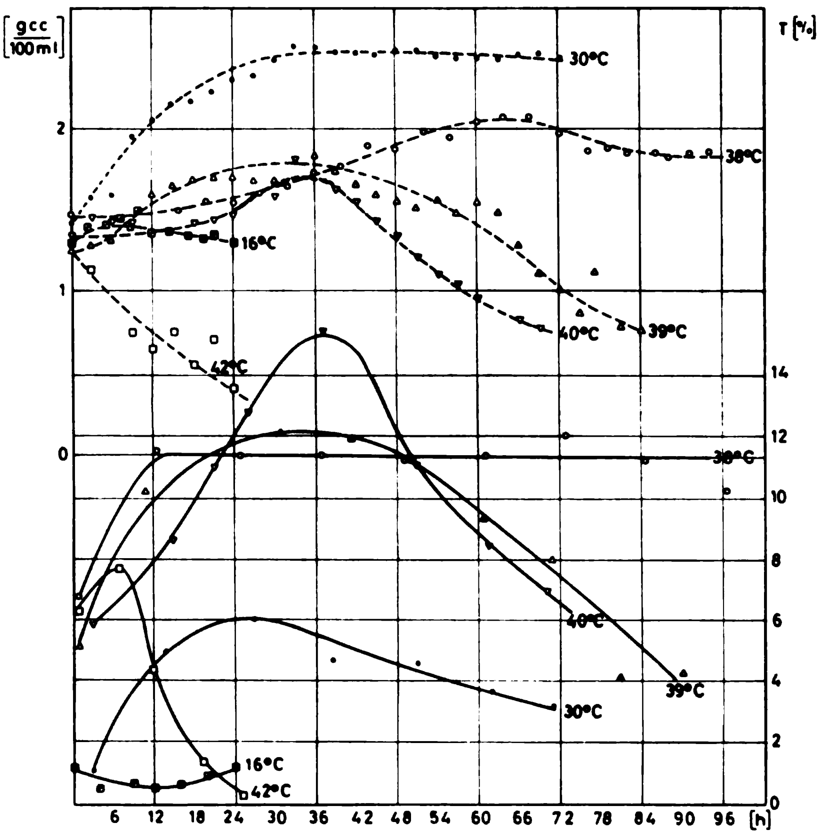

Figure 1

Continuous growth of *Saccharomyces cerevisiae* Š.30 at 16°, 30°, 38°, 40° and 42°C. Dashed lines: concentration of cell dry substance, *g* (100 ml); full lines: concentratin of trehalose in cell dry substance, T%.

(Experiments No: 24,10,17,25,13,16).

the beginning of growth at other temperatures (except 42°C); it reached a maximum and then either decreased constantly (39°, 40°, 42°, 16°) or levelled off (38°C). This might be ascribed to an unfavorable effect of the temperature and to the reduced solubility of oxygen in the mash (39°, 40°, 42°), on account of which the specific rate of growth continuously decreased. The stimulatory effect of the temperature before its supressing effect began, was not observed at 42°C. At this temperature the outward appearance of cells suddenly altered and the growth rate rapidly decreased; the damaged cells showed greater and greater affinity for methylene blue. The effect of a low temperature, 16°C, was due to slow enzymatic reactions, i.e. slow physiological processes in the cell.

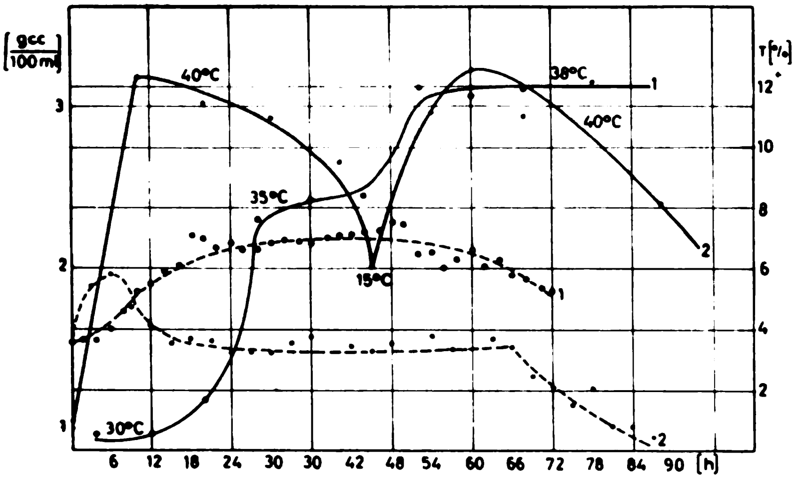

Figure 2

The effect of a change of temperature in the course of an experiment. Dashed lines: cell dry substance (g/100 ml); full lines: concentration of trehalose in cell dry substance (T%). Curves 1: growth at 30°C (24 hrs), 35°C (24 hrs) and 38°C (24 hrs). Curves 2: growth at 40°C (42 hrs); growth temperature decreased to 15°C (2 hrs); growth temperature increased to 40°C (42 hrs).

The behavior of the trehalose concentration (lower part of Fig. 1) was very similar. With increased cell growth it also increased reaching its maximum (15.54%) at 40°. After the maximum was attained the trehalose concentration constantly decreased except at the growth temperature of 38°C. It decreased most rapidly at the temperature of 42°C on account of cell thermolysis, whereby trehalose, being a soluble substance, leaves the cell.

The effect of temperature change in the course of an experiment is shown in Fig. 2 (experiment 4 and 33). These experiments confirm that the temperature of growth affects considerably the concentration of trehalose in dry cell substance. The trehalose concentration increased with increasing temperature up to a certain limit, then decreased the faster the more unfavorable was the effect of the increased temperature on the growth rate. When the temperature was decreased from 45°C to 15°C (in the course of two hours) the concentration of trehalose decreased to 6%, but after the temperature was again raised to 40°C it increased to 12.54%. The latter value was also obtained when the temperature of 30°C was raised to 40°C (see Fig. 2). This dependence of trehalose concentration on temperature of growth indicates that the rate of synthesis of trehalose in the cells rises when the growth rate of cells is increased by increased temperature. However, when the growth rate begins to decrease on account of too high a temperature, trehalose synthesis also slows down and its concentration begins to decrease. The numerical values

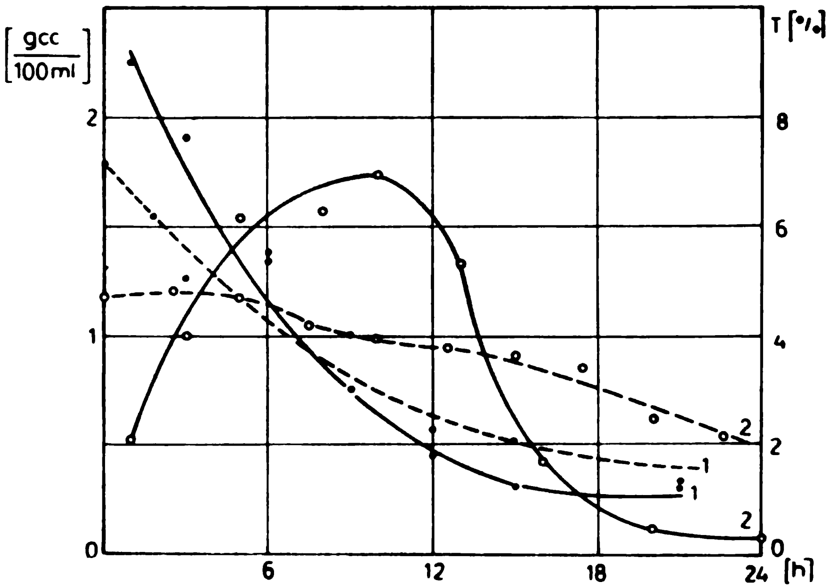

Figure 3

Continuous growth of *S. cerevisiae* Š-40 at 44°C (curve 1, experiment 39) and *S. cerevisiae* Š-30 at 42°C (curve 2, experiment 34). Full line: trehalose concentration (T%); dashed line: dry cell substance concentration (g/100 ml).

of trehalose concentration refer to experiments in which the cells stayed in the Kluyver's vessel a mean of 12 hrs and 30 minutes to 13 hours.

b. *Experiments with thermo-tolerant strain Š-40.* This strain was obtained by adaptation of the strain Š-30 to 40°C. Figure 3 shows the change of trehalose concentration in dry cell substance and the change of dry cell substance concentration per 100 ml for strain Š-30 adapted to 40°C, i.d. the behavior of Š-40 in 24 hours of continuous growth at 44°C (experiment 39), and the behavior of strain Š-30 in continuous growth at 42°C (experiment 34). These experiments exhibit a specific behavior of the thermo-tolerant strain whose growth rate and rate of trehalose synthesis decreased abruptly with increasing temperature. However, no thermolysis of cells was observed by means of methylene blue absorption. The strain Š-30 behaves as shown in Fig. 1. It is worth mentioning that at the beginning of the experiment the trehalose in cells of Š-40 was rather high.

The thermo-tolerant strain showed another interesting property. When the culture was grown in a thermostat at 40°C and then in a Kluyver's vessel at 30°C, the cells contained a relatively small amount trehalose (5.6%), which rapidly increased (above 11.5%) when the temperature was raised to 40°C and then rapidly decreased (Fig. 4 —

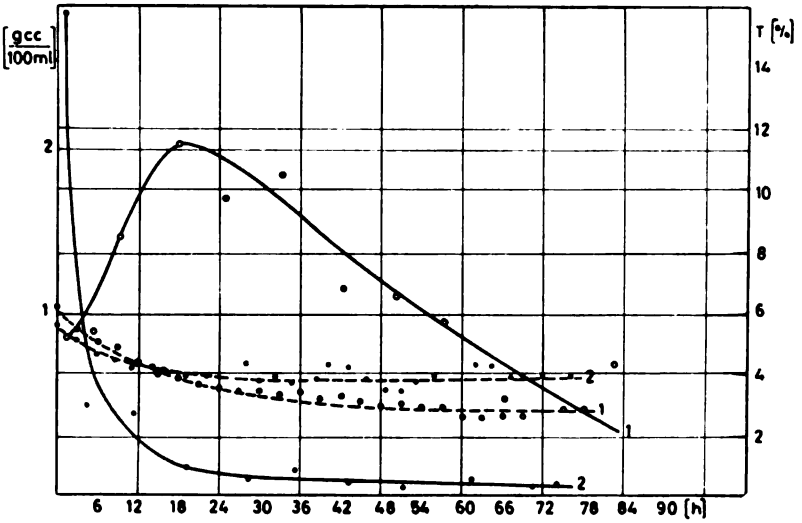

Figure 4

Continuous growth of *S. cerevisiae* Š-40 at 40°C (curves 1, experiment 29) and at 30°C (curves 2, experiment 44).

full curve 1). The concentration of dry cell substance levelled off to a constant value in a relatively short time. This means that this strain had adapted to 40°C (dashed line in Fig. 4). When the same strain was grown in the Kluyver's vessel at 40°C the trehalose concentration in the cells was high (15.8%), but during continuous growth at 30°C it rapidly decreased (Fig. 4, full line). After a short time period the concentration of dry cell substance levelled of to a constant value (Fig. 4, dashed line).

In all these experiments the sugar content in the mash was between 50 and 300 *mg/lit*, indicating that the cells were not fasting and that the dry cell substance concentration depended on the concentration of oxygen and the mean time the cells stayed in the Kluyver's vessel. The nitrogen of the dry cell substance of Š-30 was 7.15—8.15% at growth temperatures ranging from 16° to 38°C, and only 6.15—7.00% at 40°C. This means that the protein content ($N\% \times 6.25$) in the former case amounted to 45—50% and in the latter only 38—43%. A similar decrease of nitrogen content in dry cell substance of *Torupopsis utilis* at a growth temperature of 49°C was observed by M. Lorenz$^{(18)}$.

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A NEW FURNACE FOR DETERMINING THE IGNITION TEMPERATURE OF COAL

by

I. Đ. BAJALOVIĆ, V. V. ALMAŽAN and N. K. JOVANOVIĆ

Data on the ignition temperature of coal are often needed for technical and scientific purposes. Thus, for example, in the construction of the fire-beds of a steam-boiler it is necessary to know the ignition temperature of the coal to be used, especially when the furnace is fed with coal dust. The ignition temperature is of great importance in the study of spontaneous combustion and in the study of self-oxidation, used for the classification of coals according to their spontaneous-ignition indexes.

One of the earliest important methods for the determination of the ignition temperature of coal was invented by Bunte, Büchner and Bender(1). It consists in the following: a test tube with a sintered glass bottom is placed in a tricresyl-phosphate bath, and 2 *g* of the coal to be examined (grain size 0.088 mm) is placed in the bottom of the tube. One end of a thermocouple is inserted into the coal and the other into the bath, the temperature of the latter being measured by a thermometer. The ignition temperature is determined graphically; it lies at the intersection of the curves of bath temperature and coal temperature. Ignition temperatures by this apparatus are very low, ranging between 150° and 210°C for all types of coal.

Among the furnace in use today we will mention that produced by the firm Fedeler, after Moore and Krup. The furnace is heated electrically via a rheostat and contains a massive metal block *A* (Fig. 1) with a small coal dish *Z* to which a thermocouple T is welded. In the course of heating a current of air or oxygen is passed through. At a heating rate of 2° per minute, 0.1 g of coal to be examined is put into the dish through the opening 0 each five minutes, until a temperature is reached at which the coal sample ignites. At the moment of ignition the instrument shows a sudden rise of temperature which indicates the ignition temperature. However, the accuracy is very low. By several repetitions it can be reduced to ±10°C. Another disadvantage of the furnace is that the procedure is very slow, since after each determination one has to wait until the massive metal block cools off.

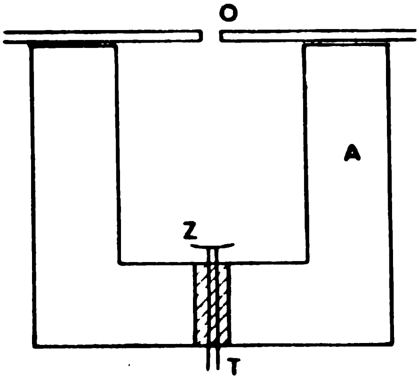

Figure 1

The Moore-Krupp's stove. (*A*) metal block, (*Z*) coal dish, (*T*) thermocouple, (*O*) opening for feeding coal.

PRINCIPLE OF THE NEW FURNACE

The determination of the temperature at which a process takes place often involves many technical difficulties, since irregular flow or radiation from heated surfaces, or different rates of heat conduction in different media can cause considerable temperature variations over very short distances. Thus for example, differences in the rate of heating of coals of different grain size, or the rate at which the thermometer reacts when the temperature changes, can cause considerable lag of the temperature readings.

In this paper a new furnace (Fig. 2) for determining the ignition temperature of coal is described. It avoids many sources of error and the coal can be examined under the conditions prevailing in a fire-bed.

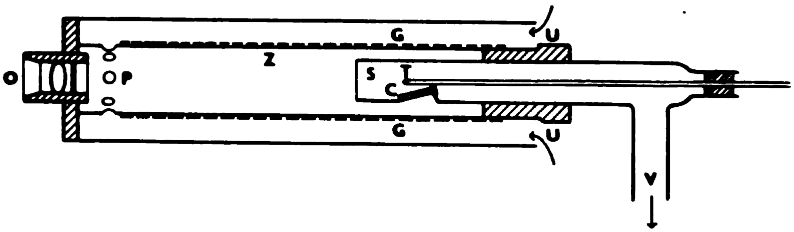

Figure 2

The stove for determining ignition temperature in hot air current. (*U*) air inlet, (*G*) heater wire, (*P*) openings for introduction of hot air, (*S*) glass tube with crucible for coal *C*, *T*— thermocouple, (*V*) connection for vacuum, (*O*) peep hole.

The coal sample is heated by a current of hot air. The tube *V* is connected to vacuum pump which maintains constant air flow. The air enters the furnace through the opening *U*, passes over the noninsulated wires of the heater *G* and, in the small space between the heater and the outer casing, easily gets heated to the required temperature. The hot air then enters the inner metallic tube *Z* through the opening *P*, and finally passes through the glass tube *S* where there is a small coal dish *C* and a thermocouple *T*. It leaves the furnace through tube *V*. The heater is adjusted so that at a constant air flow the temperature of the air gradually increases. The glass (or quartz) tube *S* acts as an insulator which prevents the coal and the thermocouple getting heated by radiations from the walls of the tube *Z*, since this would interfere with the determination of the ignition temperature. Under the described conditions the coal and the thermocouple have the temperature of the hot air entering tube *S*.

The coal is put in a small rectangular dish (10 × 5 *mm*) made of this nickel plate (thickness 1 *mm*) titled (at an angle of 18°) towards the air current so that the vertical projection of the exposed surface is 3 *mm*. In this way the coal gets better exposed to the air current. The junction of the thermocouple is placed above the fourth of the dish, 2 *mm* above the coal surface. The peep hole *O* allows observation of the surface of the coal for the flash point.

The ignition temperature is determined in the following way: the vacuum pump and the heater are switched on simultaneously. Since the temperature of the heater rises gradually, the air current passing over the coal also gets gradually hotter, and hence the coal too. The temperature is monitored on meter *G* (Fig. 3). The temperature at the moment when the slightest flash of light is observed is taken as the ignition temperature.

The temperature distribution in the air in the tube containing the coal sample was examined by means of two thermocouples at

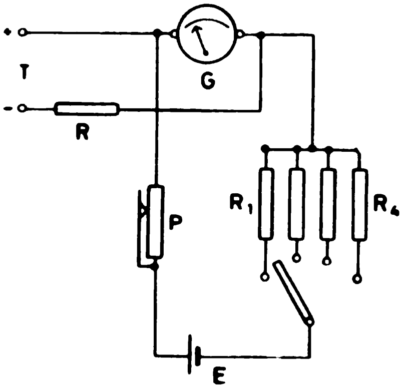

Figure 3

Scheme of the measuring instrument. (*E*) contragalvanic cell, (*P*) potentiometer for zero correction, R_1, R_2, R_3 and R_4 measuring resistors.

various positions. One thermocouple was placed in the position of the thermocouple during determination, and the second 25 mm downstream in the air current. The maximum difference under conditions identical with those of a determination was 2.5°C. In our opinion this small drop in the direction of the air current is of no significance, and therefore no correction was made.

Regardless of the precision required in practice, the apparatus is adjusted to register changes of 1°C. This is made possible by means of the equipment shown in Fig. 3. By means of a bridge circuit E the needle of a sufficiently sensitive measuring instrument is zeroed at each 100° via resistors R_1, R_2, R_3, or R_4, so that the meter shows temperatures from 100° to 200°, from 200° to 300°, from 300° to 400°, or from 400° to 500°, depending which resistor is connected.

With the apparatus described it was possible to study with sufficient accuracy the effect of various factors on the ignition temperature of coal and other materials.

EFFECT OF GRAIN SIZE OF COAL ON IGNITION TEMPERATURE

The grain size of the coal sample affects the accuracy of the ignition temperature determination and the reproducibility of the results. The effect of the grain size was studied with samples of Plevlje and Miljevina coal (grain size: —0.50 + 0.25, —0.25 + 0.063, and —0.063 + 0). A piece of Plevlje coal of 3 × 3 × 3 mm was examined as well.

TABLE 1

Effect of grain size of coal on the reproducibility of the ignition temperature

Grain size:	—0.25 + 0.063	—0.063 + 0	
	Coal — Miljevina		
	252	226	220
	264 max	223	221
	252	227 max	220 min
	245 min	226	223
	249	225	226
	261	225	225
			224
Mean value:	254	224	
	Plevlje Coal		
	289	250	251
	280 min	253	250
	282	251	250 min
	298	256 max	
	302 max	252	
	292	253	
	287	251	
Mean value:	290	252	

In a series of measurements of which the results with two grain sizes are shown in Table 1, it was found that the greater the grain size the wider was the range of ignition temperatures obtained. For a large grain size the readings ranged over an interval of approximately +10° (±9.5° and ±11°), and for small grain size about ±3.5°.

In both cases shown in Table 1 (and in those not shown) the effect of grain size on the ignition temperature is apparent. For the larger grain size the ignition temperature was higher by 30° and 25°.

The piece of Plevlje coal ignited at 332°, and the mean ignition temperature obtained for coal of grain size —0.315 + 0.25 was 321°.

THE EFFECT OF AIR FLOW RATE ON THE IGNITION TEMPERATURE OF COAL

In our first experiments this was a big problem since changes in the flow rate affected the value of the ignition temperature by as much as 100°. The ignition temperature of Aleksinac coal (grain size: 0.25 + 0.063) at different air flow rates is shown in Table 2. This grain size was selected since at this value the effect of the air flow rate was pronounced, i.e. the variations of the temperatures were great.

TABLE 2

Ignition temperature at different air flow rates

lit/min	t^0	*lit/min*	t^0
8.7	338	0.9	268
8.3	348	0.7	293
8.2	333	0.6	297
3.6	308	0.6	299
3.1	303		

TABLE 3

Effect of air flow rate on the ignition temperature of coal at different grain sizes

lit/min	t^0	t^0
	—0.25 + 0.063	—0.063 + 0
0.25	—	—
0.50	—	—
0.75	285	222
1.00	265	223
1.50	260	217
2.00	258	218
2.50	255	220

The results show that at high flow rates the ignition temperature was high, but also at quite low rates the values are too high. We are of the opinion that the lowest temperature obtained under various operating conditions should be taken as the actual ignition temperature. The effect of different air flow rates on the ignition temperature of a coal (Banja Luka, Novi revir) at two different grain sizes is shown in Table 3.

For the smaller grain size the lowest temperature i.e. the ignition temperature was obtained at a flow rate of 1.5 *lit/min.* However, for the larger grain size the lowest temperature was not reached even at flow rate of 2.5 *lit/min.* At flow rates of 0.25 and 0.50 *lit/min* none of the coal samples ignited at 300°, indicating that at this flow rate the amount of oxygen present is not sufficient.

In view of the given definition of the ignition temperature, and the data shown in Table 2 and 3, and other measurements, it may be concluded that the optimum air flow rate is between 1 and 3 liters per minute, depending on the coal.

EFFECTS OF LOOSENESS OF COAL SAMPLE ON THE IGNITION TEMPERATURE

In addition to the air flow rate and the grain size, the looseness of coal also has some effect. It does make some difference whether the coal in the dish is loose and just spread evenly over the surface, or is compacted during charging. The error due to differences in looseness can be as high as 20°. Seven successive measurements of the ignition temperature of a sample of Plevlje coal are shown in Table 4. The sample was spread loosely in the dish and the excess of coal scraped off by a plate which slides across the dish and is tilted at about 20° in the direction of motion. The sample is thereby slightly compacted and the looseness is sufficiently reproducible. The error of ±2° shows that sufficiently reproducible results can be obtained without a stricly defined way of compacting the sample.

TABLE 4

Reproducibility of the ignition temperature with samples of the same looseness

t^0		
248	248	248
249		
250	250	
251	251	
252	252	252

By means of this sensitive instrument it was found that the temperature of the beginning of the exothermic reaction does not always coincide with the temperature registered by the visual effect.

This difference can amount to several degrees, depending on the kind of coal. A temperature rise is observed on the instrument before ignition of the coal surface can be seen. This difference is usually greater for coals of a low ignition temperature, whereas it is almost zero when the ignition temperature is close to 300°C. The curve in

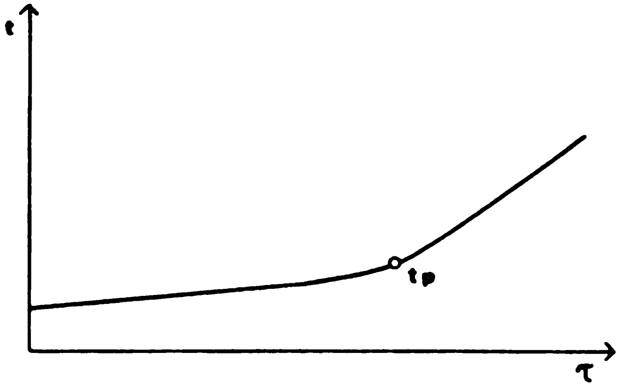

Figure 4

Time-temperature diagram. (t_p) ignition temperature.

Fig. 4 shows the rise of sample temperature with time; a sudden change of slope (faster rise of temperature) before the visual ignition temperature t_i can be clearly seen.

OPTIMUM OPERATING CONDITIONS

From the aforesaid it may be seen that the lowest temperature obtained in a series of experiments under different experimental conditions was taken as the ignition temperature. To obtain reproducible results it was necessary to determine the optimum operating conditions as regards air flow rate, rate of heating, and grain size and looseness of the sample. It is worth mentioning that different amounts of moisture in the coal sample can also cause considerable errors in the determination of the ignition temperature. Therefore the rate of heating should be so adjusted that all the whole moisture is driven off before a temperature of 150—160° is reached. The time required for heating up to this temperature should be about three minutes, otherwise the ignition temperature obtained will be too high, and the results will not be reproducible.

Experiments have shown that the duration of one determination is 4 to 6 minutes. This short duration and the low thermal capacity of the furnace permit a great number of measurements to be made in a short time.

VERIFICATION OF THE RESULTS BY MEANS OF A THERMOBALANCE

Figure 5 shows a typical curve obtained by means of a thermobalance. The segment *ab* represents the loss of moisture, which is completely removed by approximately 140°C; the part *bc* shows that the loss of weight is very small until the beginning of the curvature at *c*. This point may be considered as the beginning of the exothermic reaction, when the weight begins to fall rapidly. Visible ignition of the coal sample is usually detected at the end of the curvature, at *d* (for coals with a low ignition temperature) and this temperature was taken as the ignition temperature. The rest of the curve represents combustion, where for a small change of temperature there is rapid loss of weight.

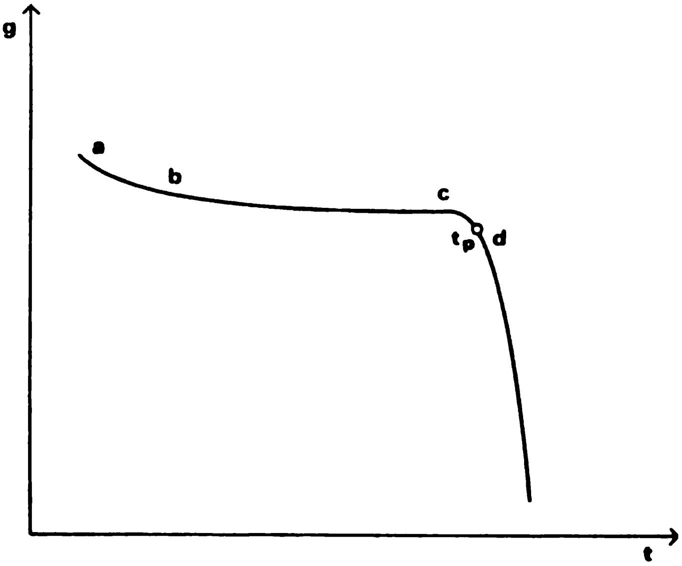

Figure 5

Temperature — weight diagram, obtained by thermobalance. (*ab*) drying period, (*c*) beginning of exothermal reaction, (t_p) ignition temperature.

The drying of the sample should be completed before the ignition temperature is reached (first part of the curve *ab*), since the presence of moisture would increase the temperature at which the exothermic reaction begins. The results of seven measurements on Plevlje coal (grain size —0.063 + 0) are given in Table 5.

The results are consistent with those obtained by means of the new furnace (Tables 4 and 5; mean value of the ignition temperature: 250° and 251°).

TABLE 5

Ignition temperature of Plevlje coal (grain size: —0.063+0) *obtained by thermobalance*

240	245	250	255	260	265
	245				

PROPERTIES AND OPERATION OF THE NEW FURNACE

The basic difference between our furnace and apparatuses described in the literature (including the newest model of the firm Feddeler) is that in our case the sample is heated by means of hot air, and not by radiation or conduction from the heater to the sample. With heating by heat or conduction one can never be certain that the thermocouple or the thermometer is at the same temperature as the coal sample. However, the hot air conveys sufficient heat to heat a thin layer of coal and the thermocouple, although their specific heats are different.

The low specific heat of the furnace permits repetition of measurement after ten minutes, since the apparatus does not have to be cooled below 100°.

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DETERMINATION OF THE ANGLE BETWEEN PLANES SURROUNDING THE ETCHING PITS AND THE (III) PLANE OF GERMANIUM SINGLE CRYSTALS

by

ANDREJA V. VALČIĆ and MILAN G. BREKIĆ

INTRODUCTION

When a well worked-up and polished slice of germanium single crystal is chemically etched, a number of etching pits appear on its surface. In the case of the (111) plane the etching pits have the shape of the frustum of a trigonal pyramid. Figure 1 shows a microphotograph of etching pits on a germanium single crystal surface (magnification approximately 450 ×).

When a beam of parallel light falls on the etched surface of the reflected beam splits up into components whose number is equal to the number of planes surrounding the etching pit. This fact was used for the determination of the angle between the planes surrounding the etching pit and the (111) plane of germanium single crystal. Figure 2 shows the reflectrogram obtained from the (111) plane of a germanium single crystal.

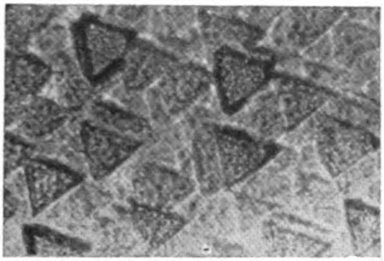

Figure 1

Etching pits on a (111) surface of germanium single crystal 450 ×

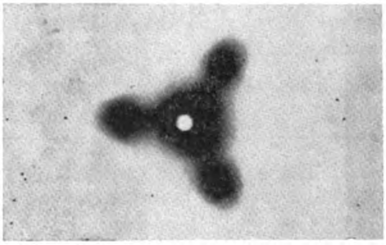

Figure 2

Reflectogram of germanium single crystal from (111) plane

APPARATUS AND METHOD

The apparatus used in the determination consisted of a light source, a screen and a holder for the single crystal slice, all mounted on a rail which acted as an optical bench. At one end of the rail there was a 30 W lamp whose filament was positioned at the focus of a lens, giving a parallel beam. The beam width was adjusted by means of a slit. In the middle of the apparatus there was a screen with an opening for the passage of the light beam. On the other end of the rail there was a goniometer with a holder for the crystal slice.

The determinations were carried out with slices of p-type germanium single crystals with specific resistence of 2—3 ohms per cm and a dislocation density of about 3000/cm². All slices were cut along (111) plane.

The determination consisted in mechanical treatment of slices, etching with chemical reagents, and measurements of the distance between the spots on the screen and the surface of the crystal slice.

The crystal slices were ground with emery-paper and polished with alumina (Al_2O_3), sieved through 100 DIN mesh. A number of different etchants was tried. The best etching pits were obtained under the experimental conditions given in Table 1 (the reflectograms were the sharpest). In the course of etching the reaction mixture was stirred vigorously and continuously.

TABLE 1

Experiment No.	Composition of etchant	Time (min)	Temperature °C
1	1 HF 2 H_2O_2 4 H_2O	6	22
2	1 g of KOH 4 g of $K_3Fe(CN)_6$ 50 ml of H_2O	15	Boiling temp. of the mixture

The etchant compositions in Table 1 are given in volume ratios. The concentration of the hydrofluoric acid was 49% and that of hydrogen peroxide 30%.

The etched single crystal slice was then placed on the goniometer and the light beam from the light source (A) passing through the opening on the screen was alowed to fall on its surface (Fig. 3). The light was reflected from planes formed on the crystal surface by etching. Each plane surrounding the etching pit reflected a spot (F) on the screen (C).

When the crystal slice is oriented along the (111) plane, the spots on the reflectogram lie on straight lines intersecting at an angle of 120°, and their distances from the centre are equal (Fig. 2). The lengths d and G are easily measurable and the ratio d/G gives $\tan \alpha$. The length $\triangle$ 6 can be neglected with respect to d and G. It can be concluded that the ratio of the angles α and α', is $\alpha : \alpha' = 2 : 1$. Figure 4 shows a schematic representation of an etching pit and the angle which was determined.

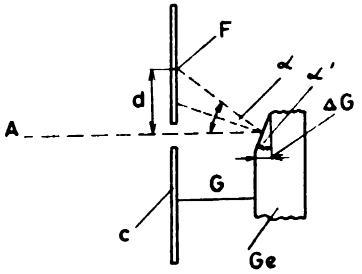

Figure 3

Scheme of the apparatus

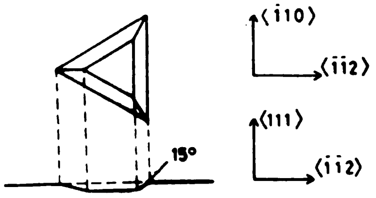

Figure 4

Shape and orientation of etching pits after etching (111) oriented germanium crystals

Using the above data we calculated the angle between the planes of the etching pit and the (111) plane; it was found to be 15°. The results are consistent with those obtained by Batterman$^{(1)}$, and Bloem and van Vessem$^{(2)}$, who determined this angle by different methods.

It is known that the etching rate of single crystals is different in different directions, and it may be concluded that $\tan \alpha'$ represents the ratio etching rates in the directions A $<\bar{1}1\bar{1}>$ and B $<\bar{1}\bar{1}2>$. To verify this conclusion we carried out a series of experiments. Samples were prepared by cutting a slice of germanium single crystal along the direction $< \bar{1}\bar{1}0 >$ (Fig. 5) and protecting the slice with paraffin except in the directions A $<\bar{1}\bar{1}\bar{1}>$ and B $<\bar{1}\bar{1}2>$. The samples were etched according to Table 1 for different times. Etching took place only on planes which were not protected by paraffin. After etching, the paraffin was removed and variations in sample thickness in direction $A <\bar{1}\bar{1}\bar{1}>$ and direction B $<\bar{1}\bar{1}2>$ were examined. The results are given in Table 2.

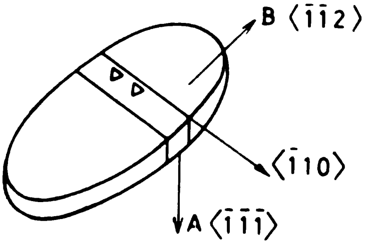

Figure 5

Slice of the germanium single crystal

TABLE 2

Composition of etchant	$HF:H_2O_2:H_2O$			1 g of KOH + 4 g of $K_3Fe(CN)_6$ in 50 ml of H_2O
	1:2:4	1:4:4	3:4:4	
Etching time (min)	15	15	15	15
Thickness variations in direction A (*microns*)	21.9	14.1	14.8	10.05
Thickness variations in direction B (*microns*)	85.7	52.2	60	35.7
Ratio A/B	0.268	0.27	0.264	0.281

Echant compositions are given in volume ratios.

From the above results it was concluded that the ratio of etching rates in directions A $(\bar{1}\bar{1}\bar{1})$ and B $(\bar{1}\bar{1}2)$ is equal to tan α'.

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NEW FLUORESCENT INDICATORS*

by

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In a study on the fluorescent properties of quinoline and its derivatives S. Šljivić(1) observed that the fluorescence intensity of these compounds was dependent on the pH of the solution. On the basis of these optical properties quinoline and methylquinolines were used as fluorescent indicators(2, 3).

In our study on the optical properties of quinoline derivatives we found that the fluorescence intensity, in the case of quiline bases, was dependent on the changes taking place at the nitrogen atom, as established from the absorption spectra. The absorption spectra were different in acid and basic media, and extended to longer wavelengths going from basic to acid solutions. These findings indicated that the extension of the spectra was due to the acceptance of protons by nitrogen.

Correlating the structure of quinoline derivatives with their fluorescent properties we established that an alkoxy group in position 6 of the quinoline nucleus considerably affected the intensity of the fluorescence. On the basis of this observation the following compounds were tried analytical indicators: 6-methoxyquinoline, 6-ethoxyquinoline, 6-ethoxy-2-methylquinoline, 8-methoxyquinoline and 4-cyano-6-methoxyquinoline.

All these compounds with the exception of the last exhibit an intense fluorescence in acid solutions, whereas in basic media they show no fluorescence. The compound possessing a cyano group in position 4 as well as the alkoxy group, exhibited a very intense fluorescence both in acid and basic media. However, the fluorescence in basic solution was found to be more intense than in acid media and this compound might also be used as an indicator. On account of the presence of the cyano group the acid-basic properties of this compound are slightly different from those of quinoline derivatives possessing only an alkoxy group; the cyano group decreases the basicity of the quinoline nucleus so that the pH-interval in which the fluorescence intensity is changed is shifted to more acid values.

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* Communicated at the IInd Yugoslav Congress for Pure and Applied Chemistry, Beograd, 1966.

EXPERIMENTAL

Fluorescence intensity was measured on a Kipp fluorometer with two photo-cells. The photo-current was measured with a Multiflex galvanometer whose sensitivity was 10^{-9} A. A Radiometer 22 *pH*-meter was used for *pH* determinations. All the measurements were done at room temperature.

The substances were synthesized according to procedures described in the literature and their physical constants were the same as those reported. Solutions with different pH-values were made without buffering since the buffer substances might quench the fluorescence; acid solutions were made with sulphuric acid, and basic solutions with sodium hydroxide. All the solutions were made up just before use.

TABLE I

Indicator	pH-interval in which the fluorescence intensity varies *pH*	Concentration % *g/v*	Amount of indicator in 10 *ml* of the solution drops
6-Methoxyquinoline	4.6 — 7.1 intense blue fluorescence 4.6 no-fluorescence (7.1)	10^{-3} %	5—6
4-Cyano-6-methoxyquinoline	1.5 — 3.8 intense blue fluorescence (3.8) green-yellow fluorescence (1.5)	10^{-3} %	5—6
6-Ethoxyquinoline	4.0 — 6.6 intense blue fluorescence (4.0) no-fluorescence (6.6)	10^{-3} %	5—6
6-Ethoxy-2-methylquinoline	4.5—6.8 intense blue fluorescence (4.5) no-fluorescence (6.8)	10^{-3} %	5—6
8-Methoxyquinoline	3.8 — 6.7 intense blue fluorescence (3.8) no-fluorescence (6.7)	10^{-3} %	5—6

RESULTS AND DISCUSSION

pH-intervals in which the fluorescence intensity varies are shown in Table I.

Curves of fluorescence intensity against *pH* are given in Fig. 1 and Fig. 2.

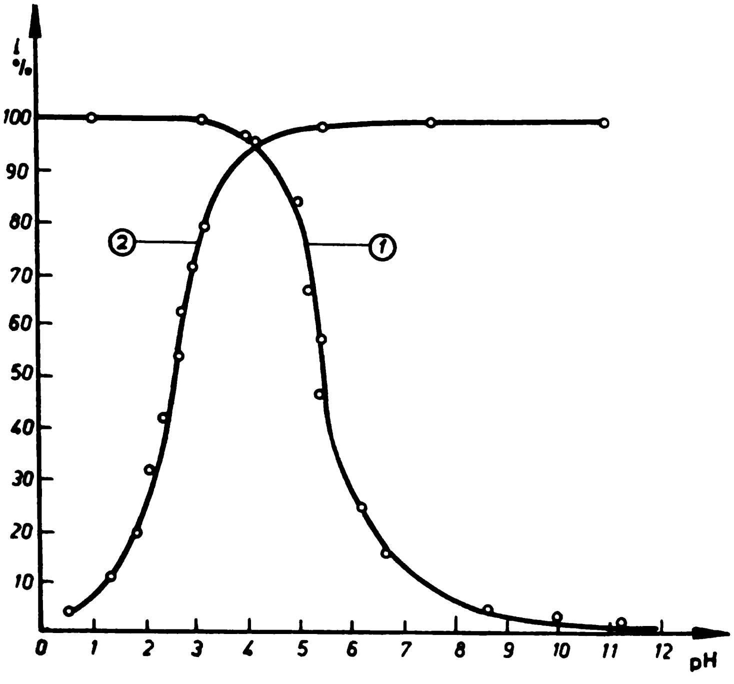

Figure 1

Plots of fluorescence intensity against *pH*

1 6-methoxyquinoline ($c = 0.01\%$)

2 4-cyano-6-methoxyquinoline ($c = 4 \times 10^{-4}\%$)

Since the fluorescence intensity of these indicators is very strong, they can be used in very small amounts. In addition, they can be used for the determination of small amounts of acids and bases since their presence does not affect the pH of the solution. They are convenient for titrations of turbid and colored solutions. However, in yellow solutions they cannot be used since the yellow color acts as an optical filter and quenches the fluorescence.

We investigated factors which change the fluorescence intensity. We established that the intensity is decreased in the presence of the following inorganic compounds: $HgCl_2$, K_2SO_4, $AgNO_3$, CH_3COOK, CH_3COOAg, $K_2C_2O_4$, KCl, $NaCl$, $LiCl$, $RbCl$, $LaCl_3$, KBr, $KCHS$, and KI. These compound quench the fluorescence but the indicators can still be used since a change of intensity is still observed.

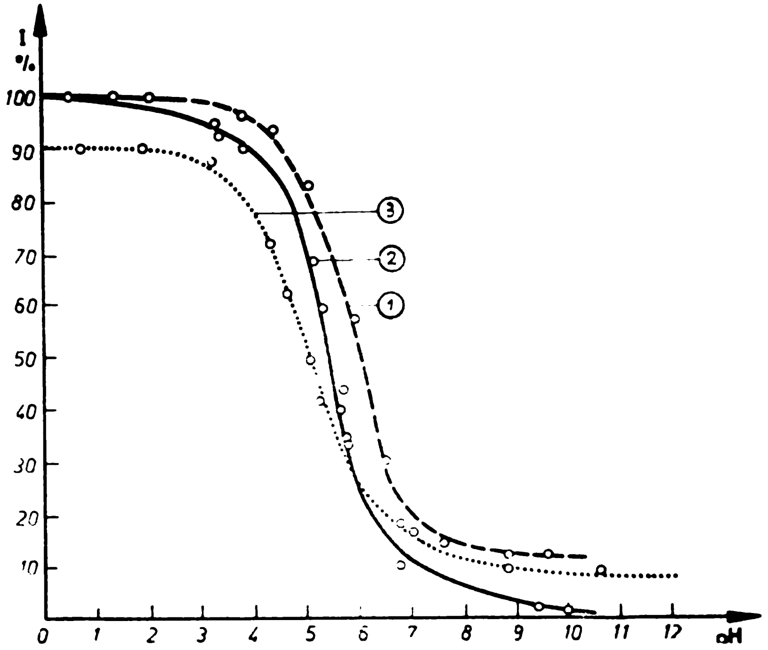

Figure 2

Plots of fluorescence intensity against pH

1 6-ethoxy-2-methylquinoline ($c = 3 \times 10^{-4}$%)
2 6-ethoxyquinoline ($c = 5 \times 10^{-3}$%)
3 8-methoxyquinoline ($c = 4 \times 10^{-4}$%)

By using polaroids(6) these indicators can be applied in fluorescent solutions as well.

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ANALYTICAL ASPECT OF THE REACTION OF HYDROCIMTHYDROXAMIC ACID WITH FERRIC ION

by

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and BRANISLAVA S. STANKOVIĆ

Hydrocimthydroxamic acid was first synthesized by Thiele and Pickard in 1899(1). However, since then there have been no studies of the reactions of this reagent with metal ions. We undertook to investigate the reactions of hydrocimthydroxamic acid with different metals. The property of hydrocimthydroxamic acid to form poorly soluble compounds with some metals was used for their gravimetric determination(2). In reaction with ferric ion a coloured soluble complex is formed. We paid particular attention to this reaction and investigated the optimal conditions for the formation of a complex of given composition and satisfactory stability. Our studies have shown that the complex of hydrocimthydroxamic acid with ferric ion can be of value for analysis under certain conditions.

The reaction in which the complex of ferric ions is formed was studied by spectrophotometry. The influence of solution *pH* on the formation of the complex was investigated and the composition and formation constant of the complex in acid medium were determined stoichiometrically.

EXPERIMENTAL

Reagents. — 1) Hydrocimthydroxamic acid (hydroxam β-phenylpropionic acid, $C_6H_5.CH_2.CH_2.CONHOH$) was obtained by the method of Thiele and Pickard(1) and recrystalized from benzol. Melting point 77.8° (uncorr.) (lit. 78°).

2) The initial solution of ferric chloride was obtained by dissolving $FeCl_3.6H_2O$ (E. Merck p.a.) in double-destilled water and standardized by the gravimetric and volumetric methods.

3) The ionic strength was adjusted with 2 *M* solution of $HClO_4$.

4) 0.01 *M* and 0.05 *M EDTA* solutions were made by dissolving the necessary amount of complexon III ($Na_2H_2Y.2H_2O$) and standardizing.

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Apparatus. — 1) Beckman model DU spectrophotometer with 10 mm absorption cells.

2) Radiometer 22 *pH*-meter.

RESULTS AND DISCUSSION

Absorption curve of hydrocimthydroxamic acid (Fig. 1).

The literature(3, 4) only gives information on the absorption curves of hydrocinnamonic acid in water and alcohol solutions. We have recorded the absorption curve of the water solution of hydrocimthydroxamic acid at *pH* 4.80 and 0.91 in the 225—300 mμ wavelength range.

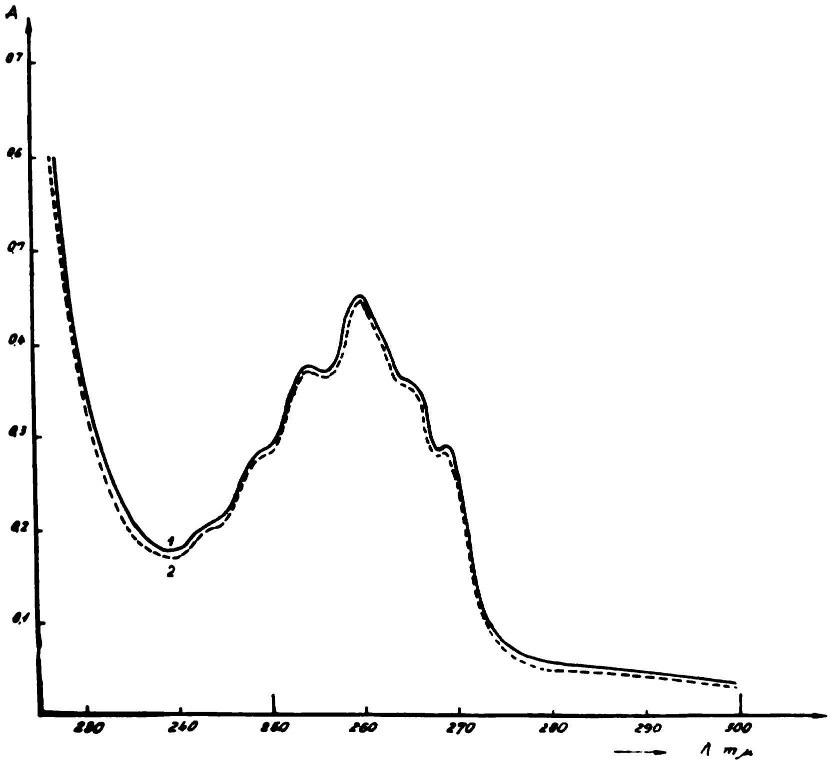

Figure 1

Absorption curve of hydrocim'hydroxamic acid

Curve: 1 $pH = 4.80$; Curve: 2 $pH = 0.90$

$C_{HR} = 2 \cdot 10^{-3}\,M$; $\mu = 0.20$ ($NaClO_4$) and ($HClO_4$)

It may be seen that the curves obtained at *pH* 4.80 and 0.91 coincide within the limits of experimental error. The maximum is at 260 mμ, and the molar absorptivity a_M is 225 ± 1. Solutions of hydrocimthydroxamic acid are very stable and the absorption values do not change even after three months.

A comparison of the absorption curves of water solutions of hydrocimthydroxamic acid and hydrocinnamonic acid showed them to be practically identical, to have the same λ_{max} and approximately the same molar absorptivity.

Absorption curves of hydrocimthydroxamic acid in the presence of ferric ion at different pH (Fig. 2)

Depending on the *pH* solutions of hydrocimthydroxamic acid in the presence of ferric ion have different colors. This shows that hydroxamic acid reacts with ferric ion forming soluble complexes of different composition depending on the *pH*. At *pH* in the range 0.65—1.60 the color is violet-red, with increasing *pH* gradually changing

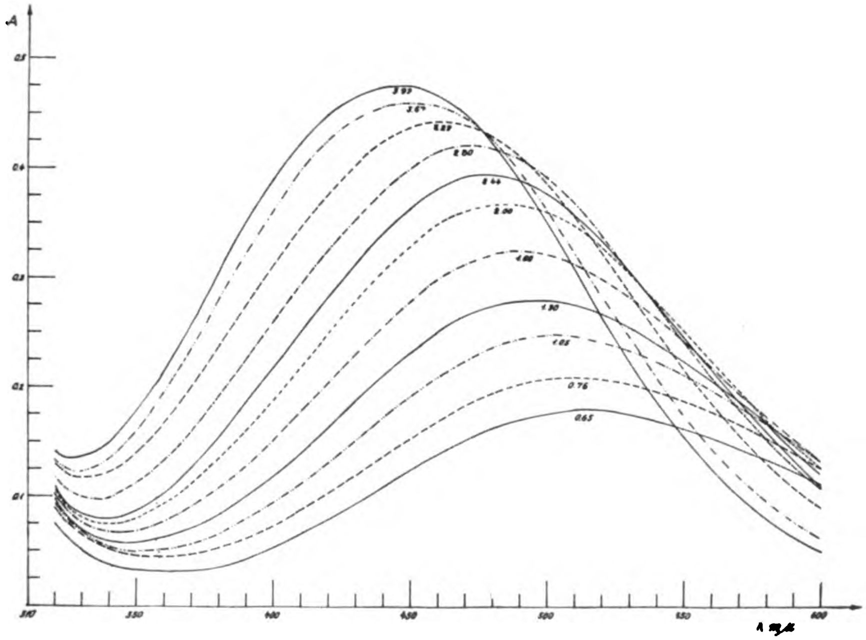

Figure 2

Influence of *pH* on the absorption curve of hydrocimthydroxamic acid solution with ferric ion. The number on the curve indicates *pH*. $c_{HR} = 10^{-2}\ M$; $c_{Fe^{3+}} = 2 \cdot 10^{-4}\ M$; $\mu = 0.20$ ($HClO_4$).

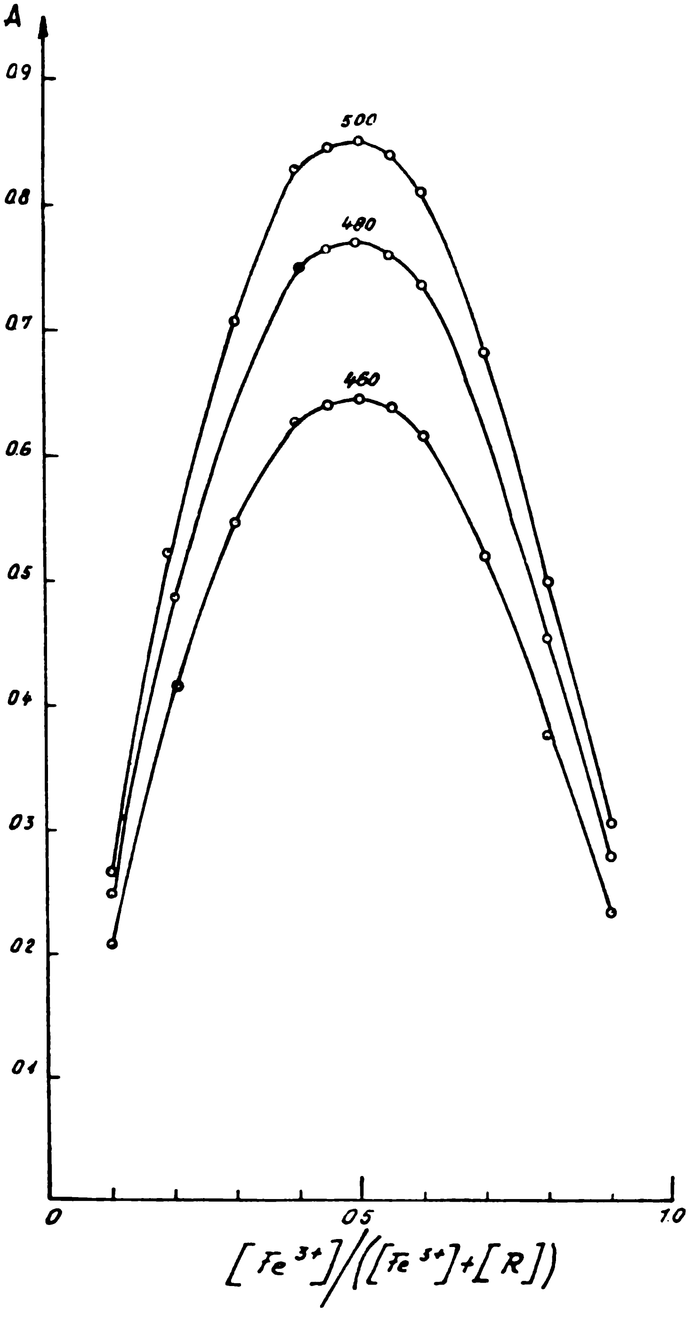

Figure 3

Job's curves of equimolecular solutions.

$c_{HR} + c_{Fe^{3+}} = 4 \cdot 10^{-3}$ *M*; $\mu = 0.20$ ($HClO_4$); $pH = 0.80 \pm 0.03$

into a reddish-orange (*pH* 2.00—2.44), and at higher *pH* becoming orange. At *pH* 0.65—2.44 the solutions are stable, but at $pH \geqq 3.00$ they become turbid after standing and iron precipitates in the form of hydroxide.

We have studied the influence of *pH* on the absorption curve of hydrocimthydroxamic acid solutions in the presence of ferric ion in the *pH* range 0.65—3.92 at constant ionic strength ($\mu = 0.20$).

It may be seen from Fig. 2 that with increasing pH there the absorption increases and the maximum of the curve moves towards shorter wavelengths. In a highly acid medium, at pH 0.65—1.05, the absorption maximum is at 520 mμ. In this pH range the absorption does not change even after standing for several weeks, i.e. the violet-red complex is stable.

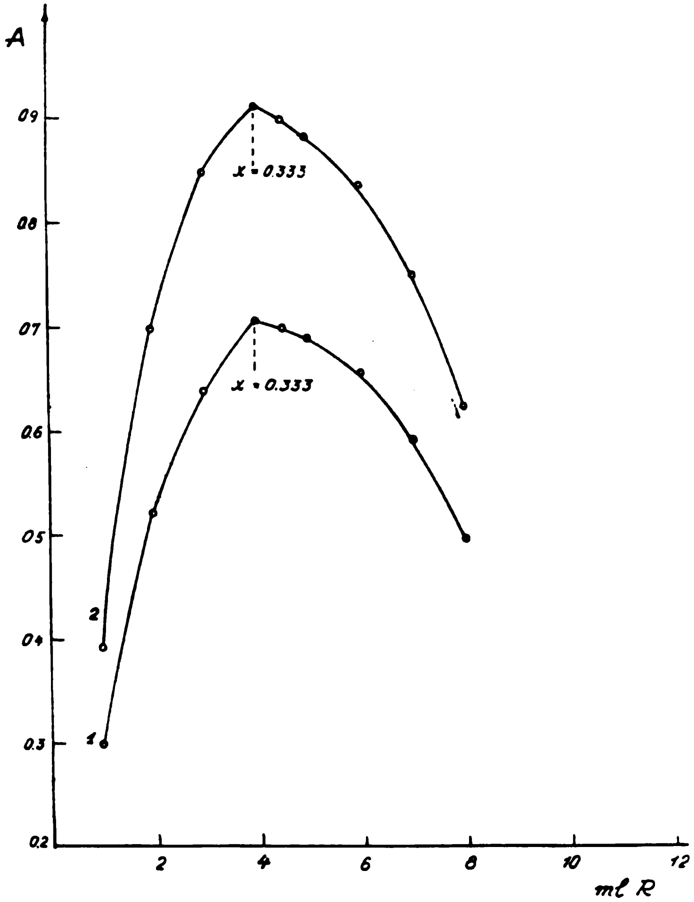

Figure 4

Job's curves for non-equimolecular solutions

$c_{Fe^{3+}} = 2 \cdot 10^{-3}\ M$; $p = 5$; $pH = 0.90 \pm 0.03$; $\mu = 0.20$ ($HClO_4$)

Curve 1 : 460 mμ; Curve 2 : 500 mμ

Determination of the composition and formation constant of the violet-red complex

The composition of this complex was determined by Job's method of equimolecular solutions at $pH = 0.80$⁽⁵⁾. The Job's curves obtained are shown in Fig. 3.

The same results were obtained at different wavelengths. All the Job's curves show the same maximum whose position corresponds to the values on the apscissa $[Fe^{3+}]/[(Fe^{3+}] + [R]) = 0.50$. Therefore the ratio of ferric ion to hydrocimthydroxamic acid in the violet-red complex is 1 : 1 (FeR).

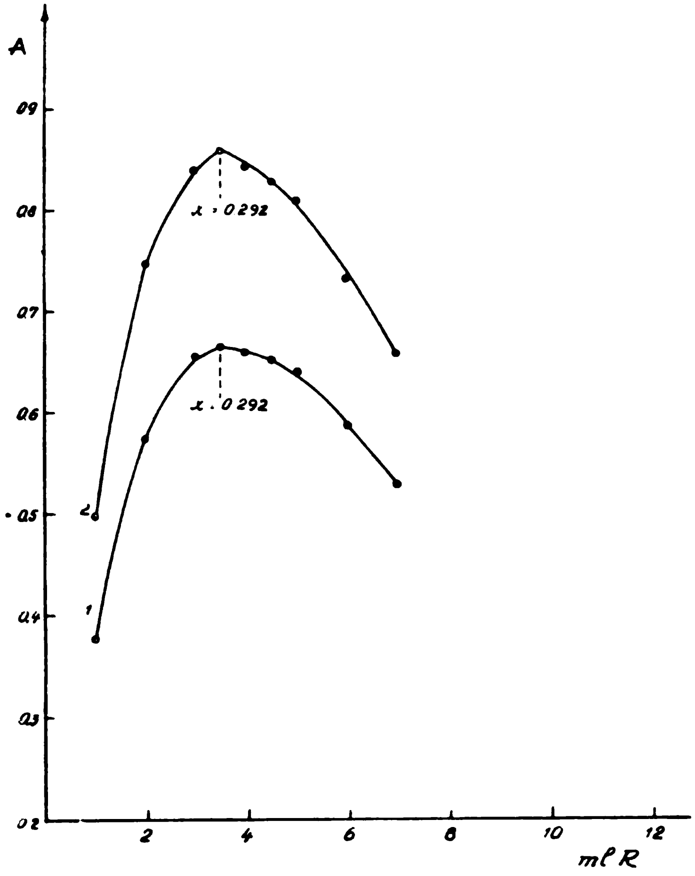

Figure 5

Job's curves for non-equimolecular solutions

$c_{Fe^{3+}} = 1.5 \cdot 10^{-3}$; $p = 10$; $pH = 0.90 \pm 0.03$; $\mu = 0.20$ ($HClO_4$)

Curve 1 : 460 $m\mu$; Curve 2 : 500 $m\mu$

For the determination of the constant of formation of the *FeR* complex we used Job's method on non-equimolecular solutions⁽⁵⁾. The determinations were performed at five ($p = 5$) and tentimes ($p = 10$) higher concentrations of the reagent but at the same *pH* and ionic strength. The absorption was measured at 420, 440, 450, 460, 480, 500 and 580 mμ.

Job's curves for non-equimolecular solutions obtained at $p = 5$ are shown in Fig. 4, and the curves obtained at $p = 10$ in Fig. 5.

The constant of formation was calculated by means of Job's formula:

$$K' = \frac{(p-1)\cdot(1-2\,X_{max})}{c_{Fe^{3+}}\cdot p\cdot[(1+p)\cdot X_{max}-1]^2}$$

The details and results are shown in Table 1.

TABLE 1

$c_{Fe^{3+}}$	pH	μ	p	X_{max}	$\log K'$
$2\cdot10^{-3}\,M$	0.90±0.03	0.20	5	0.333	2.83
$1\cdot5\cdot10^{-3}\,M$	0.90±0.03	0.20	10	0.292	2.71
Mean value	$\log K' = 2.77\pm0.06$				

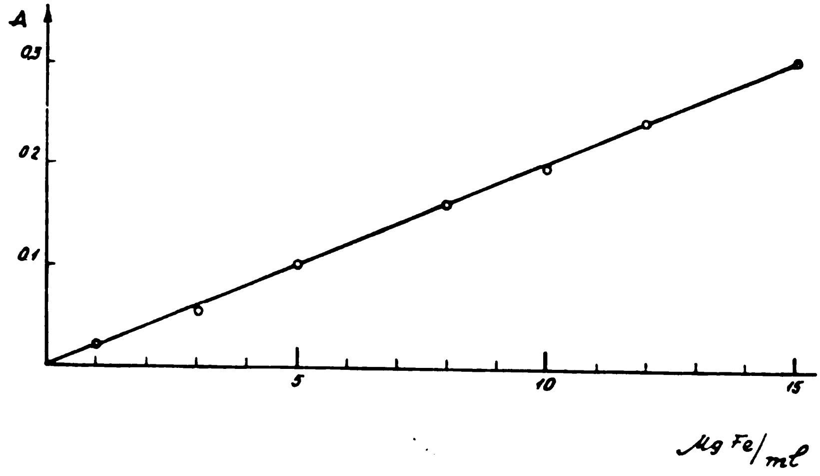

Figure 6
Calibration curve
$c_{HR} = 1.5\cdot10^{-2}\,M$; $pH = 0.88\pm0.03$; λ 500 mμ

Beer's Law

In order to apply spectrophotometric methods to study the complex of ferric ion with hydrocimthydroxamic acid it was necessary to check the validity of Beer's law. The investigations were performed in an acid medium in the presence of a large excess of the reagent in the concentration range 1—15 μg *Fe*/ml (Fig. 6).

Within the investigated range the color obeys Beer's law, the absorption being a linear function of concentration. However, although the measurements were made at $\lambda_{max} = 500$ mμ, the molar absorption was low, $a_M = 1129$. This means that the reaction is not sufficiently sensitive for spectrophotometric determination of iron.

Direct Titration of Iron (III) with EDTA in the Presence of Hydrocimthydroxamic Acid as the Indicator

As the ferric ion forms a violet-red complex with hydrocimthydroxamic acid ($pH < 1.7$) which is less stable than the ferricomplexonate ($\log K' = 2.77$ or $\log K' = 25.1$(6), the possibility of determining iron (III) by direct titration with complexon III in the presence of hydrocimthydroxamic acid as the indicator was studied.

Certain hydroxamic acids, such as *N*-phenylhydroxamic, *N*-sulphophenylhydroxamic(7) and cimthydroxamic (8), have recently been used as metalic indicators in the complexometric determination of iron. In these methods titration was done in acid medium with heating to 50°—60°C or 45°—50°C. Our studies have shown that the titration of ferric ion with *EDTA* in the presence of hydrocimthydroxamic acid as the indicator can be done at room temperature. The reproducibility of the titration was very good and the method is suitable for the determination of semimicro amounts of iron (III).

Procedure. The solution containing 1 to 10 mg of iron (III) is put into an Erlenmeyer flask of pyrex glass, which is then filled with double-distilled water up to 50 ml. The *pH* is adjusted two 1, by adding hydrochloric acid, and then 2—3 drops of 0.05% solution of hydrocimthydroxamic acid are added. The solution is titrated with 0.01 *M* or 0.05 *M EDTA* solution from a 10 ml burette. In the final phase of titration the violet-red color of the solution changes to pale yellow. The results are shown in Table 2.

Iron cannot be determined in the presence of *Ti*, *Zr*, *Th*. However, under the given conditions ($pH < 2$) small quantities of *Co*, *Ni*, *Cu*, $V_{(V)}$, $U_{(VI)}$, rare earths and Al do not interfere with the determination of iron.

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Analytical Chemistry, Belgrade

Received July 1 1966

TABLE 2

mg Fe		
Taken	Found	Mean value
1.005	1.000 1.000 1.005 1.011 1.005	1.004 ± 0.003
2.011	2.011 2.005 2.005 2.011 1.999	2.006 ± 0.005
3.016	3.016 3.016 3.016	3.016 ± 0
5.027	4.999 4.999 4.999 5.027 4.999 5.027	5.008 ± 0.006
10.053	9.997 9.997 10.053 10.053 10.053 10.025 10.025 9.969 10.025 10.053	10.025 ± 0.023

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SPECTROPHOTOMETRIC DETERMINATION OF PALLADIUM WITH EDTA AND SODIUM SALT OF THIOGLYCOLIC ACID

by

VILIM J. VAJGAND and MILETA D. JAREDIĆ

Palladium forms stable complex compounds with a number of substances, and in most cases, like its salts, they are yellow, and only exceptionally colorless like palladium-tetraamine complex.

Mac Nevin and Kriege(1) investigated the complex formation of palladium ion with *EDTA* and found four kinds of complex at various *pH* values. At *pH* 1.8 H_2PdY was formed, at 2.5 *HPdY*, in the *pH* range 3.7—9 PdY^{2-}, and from 10.5 to 13 $Pd(OH)Y^{3}$. All these complexes absorbed in the near ultraviolet region and had absorption maximums at the following wavelengths (λ_{max}): 377 mμ in the *pH* region 1.6 to 2, 377 mμ from 4.5 to 9.5, and 356 from 11.5 to 13.5. The logarithm of the stability constant at *pH* from 3.7 to 8.9 was 18.5 ± 0.6.

On the other hand Ezerskaia, Filimonova and Solovikh(2) found that in aqueous solutions *EDTA* bound with palladium ion only as a bidentate ligand. Shlonskaia *et al.*(3) found that in the presence of chloride or perchlorate a complex was formed which contained the above anions as well as palladium and *EDTA*.

In investigating the stability constants of palladium complexes with different ligands Fasman, Kutiukov and Sokol'skii(4) proved that a large number of these complexes were stable. For the tetraamine complex it was found that $Ks = 10^{30}$.

For direct determination of palladium by complexometric titration there are no metal indicators for determining the titration end point. Indirect titration is performed by adding an excess of the disodium salt of *EDTA* (Complexon III) to the solution of palladium ion, and retitrating the excess with Zn^{2+} at *pH* 10 with eriochrome *T* as indicator. Since a regulator containing ammonium or an ammonium salt must not be used, the *pH* is maintained at the desired value by adding potassium hydroxide solution which causes difficulties in titration. Good results are obtained by adding complexon III in excess, which in general can be easily adjusted.

Our aim was to try to determine palladium by direct titration using complexon III with spectrophotometric end point determination. The greatest *pH* range in which wavelength of the absorption maximum does not change is *pH* 4.5 to 9.5, so the spectrophotometric measurements were performed in an acetate regulator at approximately *pH* 5.

To determine microgram amounts of palladium ion in solution we investigated the possibility of using *Na* salt of thioglycolic acid as complexing agents. The sodium salt of thioglycolic acid forms a yellow complex with palladium ions both in alkaline and acidic media. It is important that this complex is also formed in a solution containing NH_4^+-ions despite the fact that the palladium tetraamine complex is very stable.

Since palladium chloride is yellow, like the palladium-thioglycolate complex (*PdTGC*), for spectrophotometric investigation of the latter the palladium chloride must be decolorized with ammonia solution, becoming the colorless palladium-tetraamine complex. Therefore all the spectrophotometric investigations of the palladium-tetraglycolic complex were performed in a solution containing 10^{-2} mol/l NH_4OH.

EXPERIMENTAL

Spectrophotometric titration of palladium with complexon III solution

The standard 0.1 *M* complexon III solution was prepared by precise measurements of the corresponding quantity of the substance and dissolving it in the required amount of water. A 0.01 *M* solution was prepared by diluting 0.1 *M* solution. The concentration of the pallado-chloride solution was determined gravimetrically using dimethylglyoxime(5), and thence a 0.01 *M* solution was made by dilution.

Pallado-chloride was dissolved in water with a small quantity of hydrochloric acid to help dissolution. The excess acid was neutralized with potassium hydroxide to $pH = 3$. Care was taken not to obtain an alkaline solution because insoluble palladium hydroxide would be formed.

Spectrophotometric measurements were made on an SF-4 spectrophotometer in 4 ml quarz cells.

The verification of Beer's law for the *Pd-EDTA* complex is shown in Fig. 1. The graph shows a positive discrepancy for concentrations higher than 3.10^{-4} *M* complex per liter. These measurements were carried out at the wavelength 337 mμ, in a solution whose *pH* was adjusted to be 5.

These preliminary experiments defined the optimum conditions for photometric titration of palladium. A measured amount of 0.01 *M* palladium chloride was diluted to about 100 ml, and the *pH* increased to 5—5.5 by adding sodium acetate since the palladium chloride solution was acidic. The spectrophotometric titration of palladium was performed with a 0.01 *M* solution of complexon III at a wavelength of 332 mμ. The titration curve is shown in Fig. 2, and the results in Table I.

TABLE I

Results of spectrophotometric titration of palladium with *EDTA*

Pd^{2+} taken in *mg*	*Pd* found in *mg*	*Pd* found, in %
3.39_6	3.39_4	99.9
”	3.40_5	100.3
”	3.40_5	100.3
”	3.38_4	99.6
”	3.42_5	100.9
”	3.41_5	100.6
”	3.40_5	100.3
”	3.40_5	100.3
	Mean value: 100.3±0.3%	

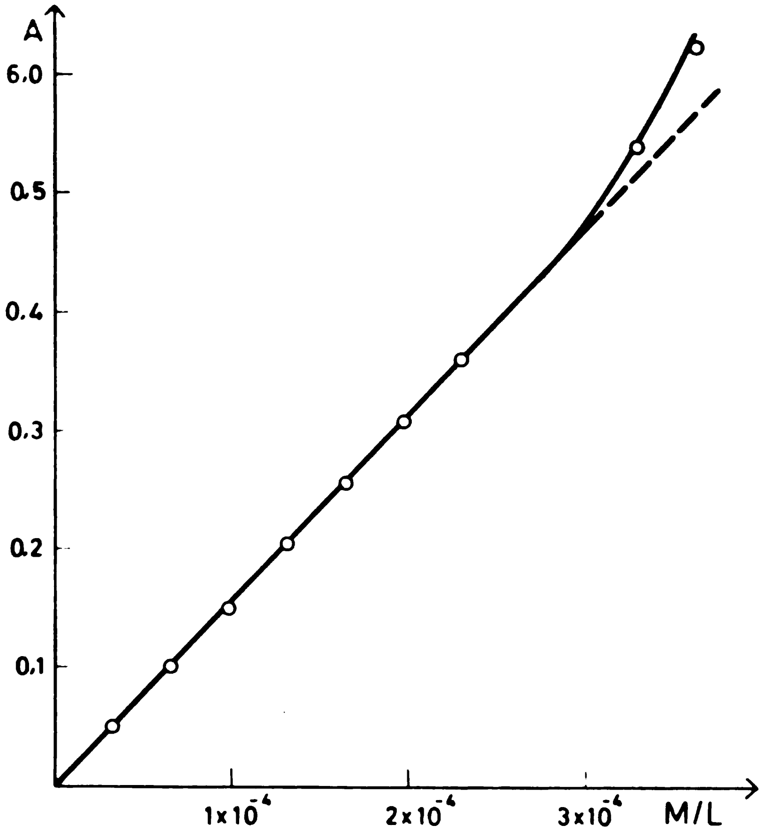


Figure 1

Verification of Beer's law for the *Pd-EDTA* complex at *pH* 5

The mean value of 8 determinations is 100.3%, and the average discrepancy ±0.3%. The results obtained by spectrophotometric titration are more precise than those obtained with the calibration curve by applying Beer's law. Using Beer's law Mac Nevin and Kriege([6]) got 99.0 ± 0.5% with 6 determinations for quantities of *Pd* of 1—1.5 mg.

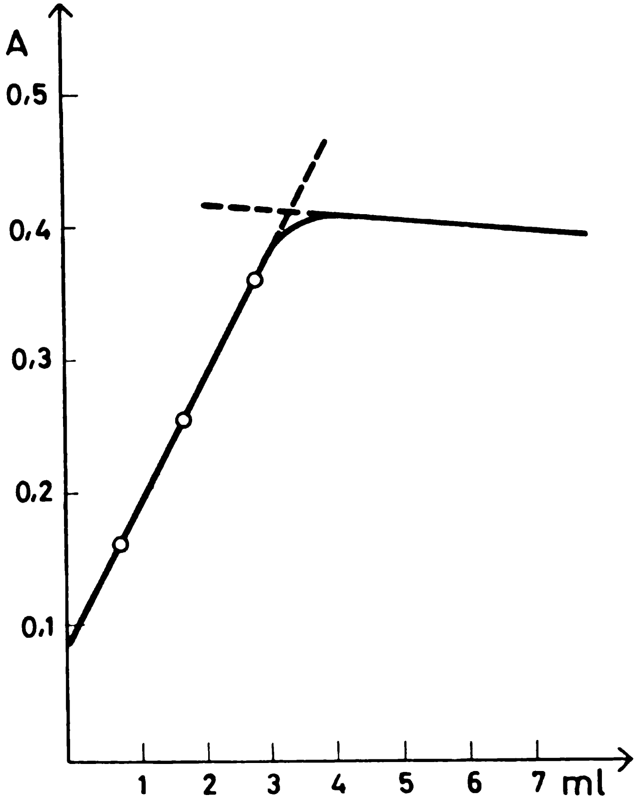
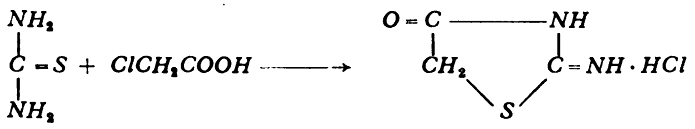


Figure 2

Titration curve of 3.10^{-4} *M* $PdCl_2$ with 0.01 *M EDTA*

Determination of microgram quantities of palladium with Na-thioglycolate (Na-TGC) obtained from pseudothiohydantoin

Pseudothiohydantoin was synthesized by mixing thiocarbamide and monochloracetic acid in molar ratio(7). The reaction is as follows:



From the product obtained *HCl* was easily separated and was neutralized by adding sodium carbonate or sodium acetate.

Pseudothiohydantoin is a white crystalloid powder insoluble in cold water, alcohol and ether. It is soluble in sodium hydroxide solution and concentrated hydrochloric acid.

A standard 0.01 *M* solution of sodium thioglycolate was prepared by dissolving the required quantity of pseudothiohydantoin in a determined volume. Since it is insoluble in water, sodium hydro-

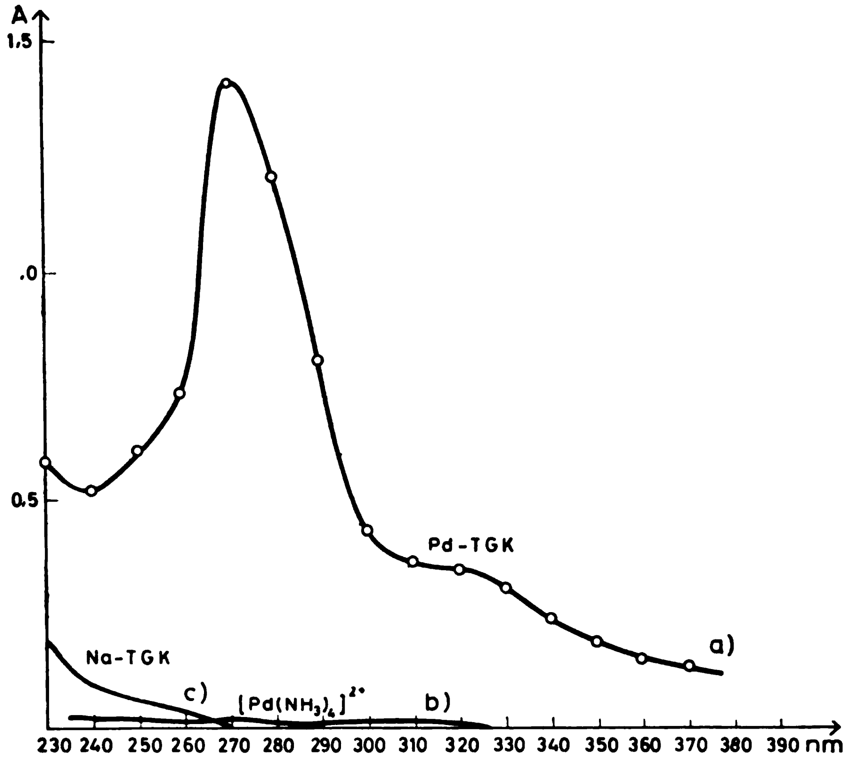


Figure 3

a) Absorption curve of 10^{-5} *M*/1 palladium-complex in 10^{-2} *M* NH_4OH

b) Absorption curve of 10^{-5} *M*/1 palladium-tetraamine complex in 10^{-2} *M* NH_4OH

c) Absorption curve of 10^{-4} *M*/1 sodium salt of thioglycolic acid in 10^{-2} *M* NH_4OH

xide solution was gradually added until it all dissolved. During this process the pseudothiodantoin changed into the sodium salt of thioglycolic acid (*Na-TGA*). The *pH* of the solution obtained was 11—11.5.

To find the region of the absorption maximum of the palladium-thioglycolate complex (*Pd-TGC*), we registered the absorption spectrum of a solution containing 10^{-5} *M*/1 $PdCl_2$, 10^{-4} *M*/1 *Na-TGA* and 10^{-2} *M*/1 ammonium hydroxide. Ammonium was used for reasons mentioned earlier. The absorption curve of *Pd-TGC* complex is shown in Fig. 3. The absorption curves of 10^{-5} *M*/1 palladium-tetraamine complex and 10^{-4} *M*/1 *Na-TGA* are also shown in Fig. 3. The graph shows that the absorption of *Pd-TGC* complex is at 270 mμ.

Using the molar ratio method the curve shown in Fig. 4 was obtained indicating that under the given conditions in the *Pd-TGC* complex palladium combines with *Na-TGA* in the ratio 1 : 2.

Beer's law was verified at 420 mμ where the absorption of the complex was low, permitting the investigation of higher concentrations. The graph in Fig. 5 shows positive deviations for concentrations exceeding 6 . 10^{-5} *M*/1.

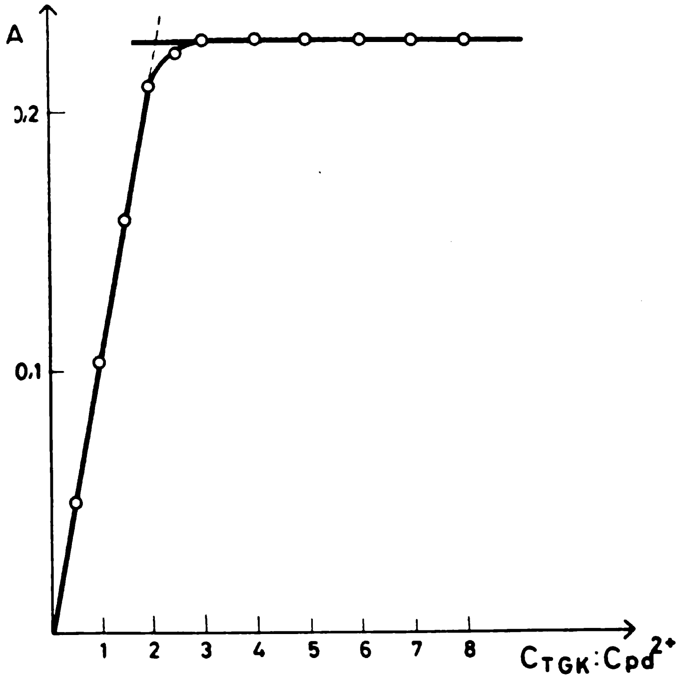


Figure 4

The molar ratio method for mixtures of 0.01 *M*/1 $PdCl_2$ and 0.01 *M*/1 sodium salt of thioglycolic acid

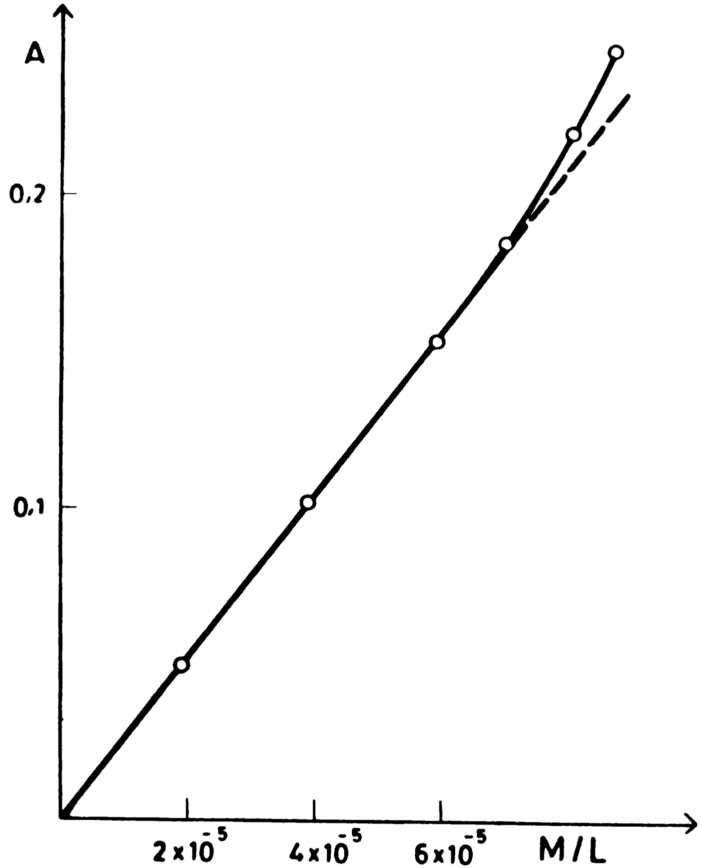


Figure 5

Verification of Beer's law for the palladium-thioglycolate complex

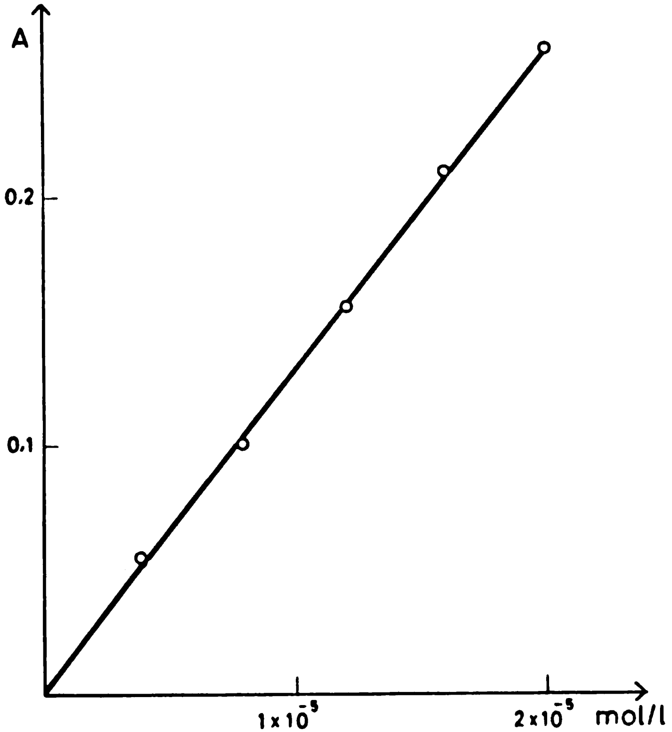


Figure 6

Calibration curve for the determination of microquantities of palladium with *Na*-salt of thioglycolic acid

To determine microgram quantities of palladium in solution a calibration curve of *Pd-TGC* complex was recorded at a wavelength of 320 mμ (Fig. 6). Palladium was determined in ten samples containing 30 to 100 γ palladium in 50 ml solution. To each sample one milliliter of 0.01 *M Na-TGA* was added. The solution contained 10^{-2} $M/1$ NH_4OH.

The results are presented in Table II.

TABLE II

Determination of microquantities of palladium using Beer's law

Pd taken, in micrograms	*Pd* found, in micrograms	*Pd* found, in %
106.4	106.4	100.0
85.1	85.2	100.1
63.8	64.4	100.9
63.8	63.5	99.5
58.5	58.1	99.3
53.0	53.0	100.0
47.8	47.5	99.3
42.6	42.6	100.0
31.9	32.2	100.7
31.9	31.7	99.3
	Mean value:	99.9±0.5%

The mean value from ten determinations was 99.9% with an average discrepancy of 0.5%.

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INDIRECT COMPLEXOMETRIC DETERMINATION OF SILVER

by

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In practical analysis the need often arises for rapid titrimetric determination of silver. The complexometric titration with metal indicators, which is successfully used for the determination of a number of metals(1), cannot be directly applied in this case as silver ions cannot be directly titrated with *EDTA* in the presence of metal indicators. Direct complexometric titration of silver ions is possible using potentiometric end point determination, as shown by Štrafelda(2). Flaschka and Huditz(3, 4) have developed a method for indirect complexometric titration of silver in the presence of metal indicators using the fact that silver ions in ammonium solution liberate nickel ions from the complex tetracyanonickel (II) ion:

$$[Ni(CN)_4]^{2-} + 2\,Ag^+ \longrightarrow 2[Ag(CN)_2]^- + Ni^{2+}$$

The nickel ions can then be easily titrated with *EDTA* in the presence of murexide. However, despite the very accurate results, this method has certain disadvantages, of which we shall cite the following: (*a*) it cannot be used when the solution analyzed contains other cations which interfere with the determination of nickel; (*b*) the preparation of potassium tetracyanonickelate (II) is time consuming and relatively complicated, the product is not quite pure and its solutions are unstable.

By using the phenomenon of spontaneous electrochemical deposition (cementation) on liquid amalgams of some metals in indirect complexometric determinations of a number of cations, Scribner and Reilly(5) opened up a new field for the application of complexometric titration. Through cementation on liquid amalgams of zinc, cadmium, lead and bismuth they were able to get normal accuracy in the indirect complexometric analysis of solutions containing various cations in different combinations including silver ions.

The process of cementation on liquid amalgams is relatively well defined, which offers a number of advantages when it is to be used for indirect complexometric determinations. In the first place, in choosing the conditions necessary for the determination to be quantitative, it is possible to use the ample polarographic data and potential-*pH* curves(5). Besides, the fact that the process takes place on the surface between the two phases — amalgam and solution — allows the continuous regeneration of the reaction surface and the achievement of intimate contact of the reactants.

However, the liquid amalgams also have a number of serious disadvantages as well. In the first instance there is the limitation due to the fact that the number of metals which readily soluble in mercury is relatively small. There is also the fact that the liquid amalgam in contact with the solution is a very unstable system. Because of the action of oxygen present in the solution, the amalgam undergoes rapid corrosion, which can lead to great errors in analysis. Therefore it is necessary(5) to remove oxygen from the test solution by introducing purified nitrogen, and the determination itself should be performed in a special apparatus in an atmosphere of purified nitrogen. If it is desired to avoid this relatively complicated procedure, it is necessary to do a parallel dummy test, but the results in this case are not quite reliable.

The above disadvantages could be avoided if metal powders could be used instead of liquid amalgams, the corrosion stability of the former being much greater. This possibility was pointed out by Budesinsky(6) who used cadmium powder for indirect complexometric determination of some nitro- and nitroso-compounds. The main drawback is that during the determination inactivation of the reaction surfaces and slowing down of cementation takes place, as the metal powder particles get coated with a layer of the separated metal. However, if powder of special characteristics is used in great excess, it seems logical that the quantitative product of the cementation and the reproducibility of the results should not be affected.

The aim of our study was to investigate the possibility of using cementation on metal powders for indirect complexometric determination of silver. Experiments were performed with powder of nickel, copper, cadmium and zinc. Besides the fact that according to thermodynamic criteria for reversible processes cementation on these powders is possible, this choice was also dictated by the fact that the determination of silver in the presence of these metals is of analytical interest and by the fact that these powders are obtainable with defined characteristics.

EXPERIMENTAL TECHNIQUE

Preparation of the solution. 0.1 *M EDTA* solution was prepared by dissolving a precisely measured quantity of the substance, quality p.a., dried at 80°C, in double-distilled water. 0.01 and 0.05 *M EDTA* solutions were prepared by diluting this solution. 0.01 *M* solutions of copper, zinc and cadmium sulphate and silver nitrate were prepared by dissolving measured amounts of the *p.a.* quality salt in double-distilled water. 0.01 and 0.05 *M* solutions were prepared by diluting the initial solutions. The silver solution was standardized electrogravimetrically(7) and the other solutions by titration with *EDTA* according to known methods(1, 8, 9).

Preparation of metal powders. Powders of *p.a.* copper, nickel, cadmium and zinc were rounded(10) and fractionated to obtain spherical particles 50—100 μ in diameter. Just before determination they were treated for a short time with dilute (1 : 4) nitric acid and then washed well with double-distilled water.

Determination procedure. A precisely measured volume of the standardized silver solution (or mixture of measured volumes of the silver solution and the copper, nickel, cadmium or zinc solutions) is diluted with double-distilled water in an Erlenmeyer flask up to 50 ml. If necessary the *pH* is adjusted (6—6.5). The metal powder is added in 4—5 portions to a total amount of 1.5 g with vigorous shaking. Twenty minutes after the beginning of adding the metal powder, the contents of the flask are filtered and the corresponding cation determined in the filtrate by titration with *EDTA*.

Methods of titration. Copper and nickel were determined by titration with *EDTA* in the presence of murexide(8). Cadmium and zinc were determined by titration with *EDTA* in the presence of eriochromium black *T*(8, 9).

In a series of determinations parallel dummy runs were made and it was found that under the given conditions there was no corrosion of the powder to such a degree as to influence the results.

RESULTS AND DISCUSSION

(a) *Determinations on copper powder.* — The results with and without the presence of copper ions in the test solution are shown in Table 1. It may be seen that silver can be indirectly determined with the usual accuracy for complexometric titration.

TABLE 1

Indirect determination of silver using Cu powder

Sample	Taken *mg*		Found *Cu* total *mg*	Calculated *Ag mg*	Error *mg*
	Ag	*Cu*			
1	54.22	—	15.98	54.30	0.08
2	54.22	—	15.93	54.10	—0.12
3	54.22	—	16.03	54.44	0.22
4	54.22	—	15.97	54.24	0.02
5	54.22	—	15.94	54.16	—0.06
6	54.22	31.75	47.65	54.00	—0.22
7	54.22	31.75	47.67	54.06	—0.16
8	54.22	31.75	47.68	54.10	—0.12
9	54.22	31.75	47.77	54.42	0.20
10	54.22	31.75	47.73	54.30	0.08

(*b*) *Determinations on nickel powder* — The results are shown in Table 2. It can be said that in this case, too, the accuracy of the indirect determination was satisfactory.

TABLE 2

Indirect determination of silver using Ni powder

Sample	Taken *mg*		Found *Ni* total *mg*	Calculated *Ag mg*	Error *mg*
	Ag	*Ni*			
1	54.22	—	14.89	54.50	0.28
2	54.22	—	14.75	54.20	—0.02
3	54.22	—	14.81	54.46	0.24
4	54.22	—	14.69	54.00	—0.22
5	54.22	—	14.71	54.08	—0.14
6	54.22	29.38	44.19	54.44	0.22
7	54.22	29.38	44.08	54.04	—0.18
8	54.22	29.38	44.22	54.54	0.32
9	54.22	29.38	44.08	54.04	—0.18
10	54.22	29.38	43.64	53.62	—0.60

(c) *Determinations on cadmium powder* — It can be concluded from the results presented in Table 3 that cadmium powder is also suitable for indirect complexometric determination of silver. The mean error is somewhat greater in this case, and it was noted as well that the time necessary for quantitative cementation is slightly longer than with the preceding powders.

TABLE 3

Indirect determination of silver using Cd powder

Sample	Taken *mg*		Found *Cd* total *mg*	Calculated *Ag mg*	Error *mg*
	Ag	*Cd*			
1	54.12	—	28.33	54.40	0.28
2	54.12	—	28.33	54.40	0.28
3	54.12	—	27.98	53.72	—0.40
4	54.12	—	27.94	53.64	—0.48
5	54.12	—	28.05	53.86	—0.26
6	54.12	33.68	61.20	52.84	—1.28
7	54.12	33.68	60.98	54.60	0.48
8	54.12	33.68	60.37	53.38	—0.74
9	54.12	33.68	60.51	53.66	—0.46
10	54.12	33.68	60.85	54.34	0.22

(d) *Determinations on zinc powder* — The results indicate negative systematic errors (which range from —3 to —10%), for which reason this powder is not suitable for indirect complexometric determination of silver. It seems that the cementation of silver on zinc powder, although energetically most favorable from the thermodynamic point of view, is not complete. The explanation for this should probably be sought in the character and kinetic parameters of the cathode and anode processes.

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COMPLEX COMPOUNDS OF *L*-ASCORBIC ACID AND METAL IONS. V.

INVESTIGATION OF THE COMPOSITION OF URANIUM, LEAD AND ALUMINUM COMPLEXES IN WEAK ACID AND ALKALINE MEDIA BY *pH*-METRIC TITRATION

by

DRAGAN S. VESELINOVIĆ and MILENKO V. ŠUŠIĆ

The composition of ascorbic acid and UO_2^+, Pb^{++} and Al ion complexes was investigated by *pH*-metric titration in the same way as in our previous study(1) of other cations. The titration curves are shown in Figs. 1, 2 and 3. Number 1 denotes ascorbic acid solution, and numbers 2, 3 and 4 mixtures of ascorbic acid and metal salts. The concentration of ascorbic acid was the same in all titrations. Number 5 denotes the solutions of metal salts without ascorbic acid.

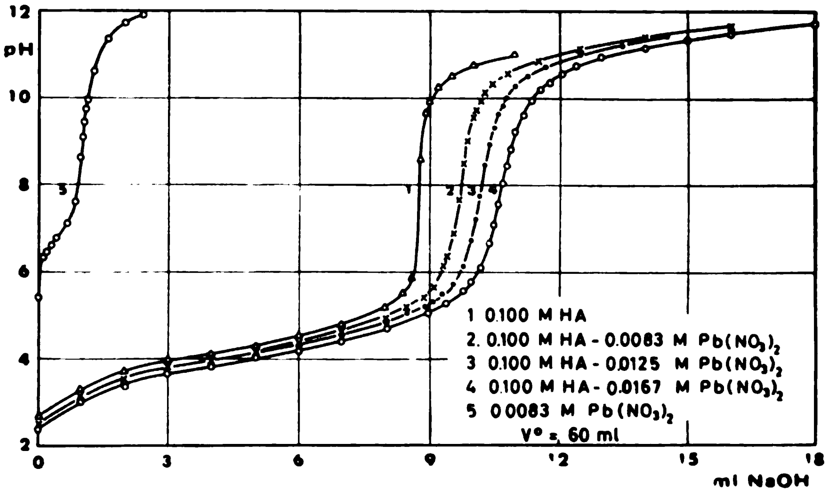

Figure 1

pH-metric titration curves of ascorbic acid (HA), ascorbic acid-$UO_2(NO_3)_2$ mixtures and $UO_2(NO_3)_2$ solution with 0.6857 *M NaOH.*

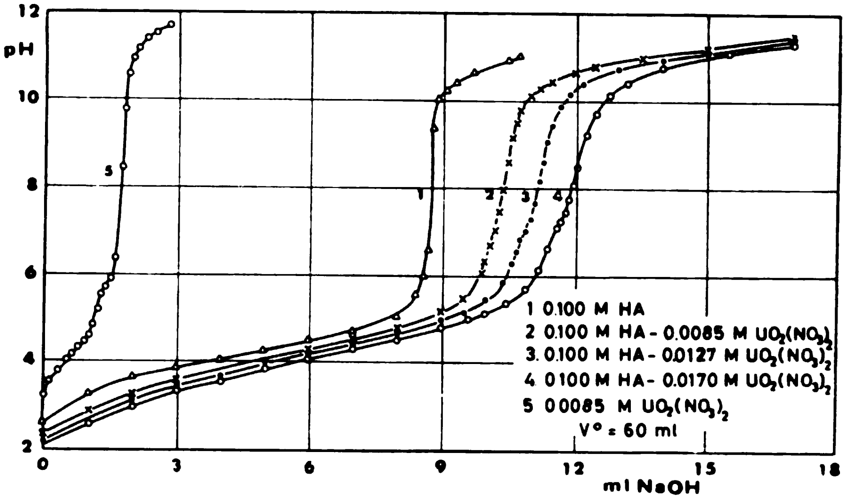

Figure 2

pH-metric titration curves of ascorbic acid (*HA*), ascorbic acid-$Pb(NO_3)_2$ mixtures and $Pb(NO_3)_2$ solution with 0.6857 *M NaOH.*

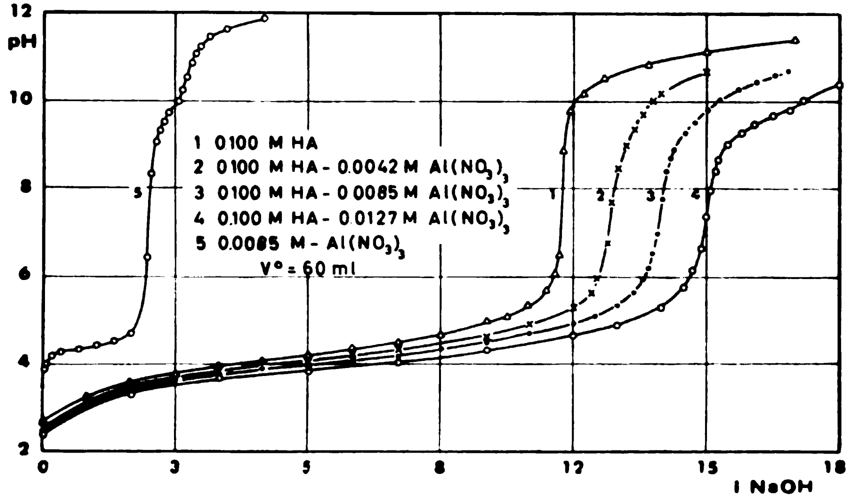

Figure 3

pH-metric titration curves of ascorbic acid (*HA*), ascorbic acid-$Al(NO_3)_3$ mixtures and $Al(NO_3)_3$ solution with 0.5096 *M NaOH.*

All the curves obtained by titrating mixtures of ascorbic acid and aluminum or lead show a single, marked step, which is somewhat drawn out. However, the mixture of ascorbic acid and uranium salts gave a curve with first a small rise followed by a more marked step which is also drawn out. The smaller step corresponds to the formation of the hydrolysis products, as seen from a comparison with curve 5 in Fig. 1, and will not be considered further. The amount of hydroxide consumed up to the equivalence point increases with increasing amount of metal salt. This is definite proof that with higher *pH* OH^- ions take part in the formation of the complexes. This is further supported by the fact that there is no separation of either lead or aluminum hydroxide or $Na_2U_2O_7$. Besides there is the characteristic yellow color of the solution which is particularly intense with uranium.

The absence with these three elements of the potential rise corresponding to neutralization of ascorbic acid, in contrast to the others previously studied(1), can be explained by the fact that hydroxo-ascorbic complexes are already formed in acid medium, before the end of neutralization of the acid, this causing overlapping of the rise due to the formation of hydroxo-complex with that due to neutralization, giving a broadened single step.

The downward shift of *pH* at which the hydroxo-complexes of these three elements are formed is due to hydrolysis of the metal ions. This is best seen from the titration curves No. 5, which show that the formation of hydrolysis products begins already in acid medium ($pH = 4$—6). As the formation of hydroxo-complexes can be identified with the hydrolysis of the cation complex $(MeA)^{+}$(2), it is evident that the hydrolysis capacity of a cation is not significantly changed by the introduction of ascorbic acid into this cation complex. This means that the *pH* of the solution at which the ascorbic-hydroxo-complex is formed will be lower the higher the degree of hydrolysis of the metal cations. This also explains why two kinds of titration curve are obtained, those with two steps (neutralization of the acid and formation of hydroxocomplexes) recorded in our previous study with cations which do not hydrolyse in acid medium(1), and curves without a step corresponding to neutralization of the acid with cations which hydrolyse in acid medium (UO_2^{++}, Pb^{++} and Al^{3+}).

For calculation of the excess *NaOH* used in the titration with respect to the amount necessary for neutralization of the acid the volume of base read from curve 1 was subtracted from that from curves 2, 3 and 4. The results for the ratio of metal and OH^- ions in the complex are shown in Table I. It can be seen that uranium and aluminum form complexes with two OH^- ions, lead with one.

The ratio of hydroxide and metal salts was not calculated from the results of *pH*-metric titration was not performed, as various hydrolysis products are formed.

TABLE I

Potentiometric titrations of Ha + Me mixture with NaOH

Me	*mmol Me*	Equivalent point (*ml NaOH*)	*NaOH mol/1*	*ml NaOH* for neutralization of acid	Difference *ml NaOH*	Ratio *Me* : *NaOH* (*mmol*)	Molar ratio *Me* : OH^- in the complex
U	0.500	10.40	0.6857	8.75	1.65	1: 2.26	1 : 2
U	0.750	11.20	"	"	2.45	1: 2.25	1 : 2
U	1.000	12.00	"	"	3.25	1: 2.23	1 : 2
Pb	0.500	9.75	"	"	1.00	1: 1.32	1 : 1
Pb	0.750	10.25	"	"	1.50	1: 1.38	1 : 1
Pb	1.000	10.55	"	"	1.80	1: 1.33	1 : 1
Al	0.250	12.65	0.5096	11.75	1.10	1: 2.23	1 : 2
Al	0.500	13.95	"	"	2.20	1: 2.22	1 : 2
Al	0.750	14.95	"	"	3.20	1: 2.16	1 : 2

DISCUSSION

The results show that the ascorbic-hydroxy-complex of uranium can be presented by the general formula $(MeA_n(OH)_2)^{n-}$, and that of lead by the formula $(MeA_nOH)^{1-n}$. The general formula which corresponds to the ascorbic-dihydroxy-complex of aluminum is $/MeA_n(OH)_2/^{1-n}$. Considering the results obtained earlier for other cations(1) which correspond to these general formulae, we can conclude that ascorbic acid forms two kinds of hydroxo-complex with metal cations: monohydroxo and dihydroxo. Possible general formulas for these complexes for bivalent cations formed at different *pH*'s by successive incorporation of OH^- ions into cation complexes, would be $(MeAOH)$ and $(MeA\,(OH)_2)^-$, since that $n = 1$. By analogy, the general formulas for monohydroxo- and dihydroxo-complexes for the trivalent cations are: (MeA_2OH) and $(MeA_2(OH)_2)^-$. These formulas containing two anions of ascorbic acid $(n = 2)$(2), are confirmed by the fact that hydroxo-complexes of bivalent cations are formed from cation complexes with the maximum number of bound anions of ascorbic acid, so we expect this to be the case with polyvalent cations too. For aluminum, and we think that this is the case with all trivalent cations, the maximum number of ligands is $n = 2$, from which the above general formulas follow. This is supported by the fact that the ascorbic acid complex of iron (trivalent)(2) in which $Fe^+ : A^- = 1 : 2$ has been isolated. However, because of the scarcity of experimental evidence, the general formulas for ascorbic-hydroxo-complexes of trivalent cations can only be taken as the most likely.

Experiments have so far revealed that one cation forms only one kind of hydroxo-complex, either a monohydroxo- or a dihydroxo-complex. However, we can generalize our conclusions from the previous study⁽¹⁾ to all hydroxo-complexes of metal cations, viz.: all cations form monohydroxo- and dihydroxo-complexes with ascorbic acid by successive incorporation of one and then two OH^- ions into the cation complex.

The *pH* range in which the hydroxo-complexes are formed depends on the metal cations; with uranium, aluminum and lead they are already formed in acid medium, with the other cations studied only in alkaline medium. As the uranyl, plumbo and aluminum ions hydrolyse already in acid medium, unlike the other cations studied, it is clear that the range of formation of the hydroxo-complexes depends on the hydrolysis constant of the metal cation itself. As we observed different metal cations in the preceding study, this conclusion can be applied to all cations and their hydroxo-ascorbic complexes.

APPARATUS AND REAGENTS

We used $UO_2(NO_3)_2$, $Pb(NO_3)_2$ and $Al(NO_3)_3$, *p.a.* quality, produced by Merck, *BDH* and Kemika. Everything else was the same as in our previous study(1).

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* Available in English translation from: Clearinghouse for Federal Scientific and Technical Information, Springfield, Virginia 22151.

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THE INFLUENCE OF SOME ADMIXTURES ON THE ACTIVITY OF CONTACT MASSES FOR THE DIRECT SYNTHESIS OF METHYLCHLOROSILANES*

by

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The reaction of methyl chloride with silicon in the presence of copper gives a mixture of methylchlorosilanes of a very complex composition. As is well known, minimal quantities of various elements or compounds present in the contact mass can have an appreciable effect on the course of methylchlorosilane synthesis. Therefore, it was of interest to examine the action of some admixtures on the activity of the contact mass. Many papers dealing with the influence of admixtures on the activity and selectivity of the contact mass, especially using a silicon-copper alloy, have been reported.(1) This paper is concerned only with the influence of admixtures on the activity of a contact mass prepared from ferrosilicon and copper (I) chloride; similar observations have already been reported.(2)

EXPERIMENTAL

Contact masses were prepared from 170 g of ferrosilicon powder and 35 g of powdered copper (I) chloride. The ferrosilicon was of the following composition: *Si* 95.32%, *Fe* 2.44%, *Al* 1.55%, and *Ca* 0.36%.

Copper (I) chloride was obtained by the reduction of copper (II) salt with sodium sulphite, and contained about 0.001% of calcium and magnesium. Methyl chloride produced from methyl alcohol was of the quality used for refrigerators. In all experiments the contact mass was prepared by mixing ferrosilicon with copper (I) chloride in a porcelain ball mill, and drying in a reactor with a stream of methyl chloride at 220°C. After drying the temperature was raised to 300°C in order to initiate the reaction.

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* Communicated at the XXXIV-th International Congress of Industrial Chemistry — Beograd, September 1963. Summary of this communication published in *Chimie & Industrie* 90: 213, 1963.

TABLE I

Influence of $AlCl_3$, $TlCl$, $LiCl$, $B(OCH_3)_3$, $TiCl_4$ and $HgCl_2$
on the activity of the contact mass

No.	Admixture	1st Period			2nd Period			Overall		
		a	b	c	a	b	c	a	b	c
1	none	$22^{5}/_{6}$	184.50	8.06	$19^{1}/_{4}$	140.00	7.27	42	324.50	7.72
2	none	$19^{5}/_{6}$	126.65	6.39	24	183.30	7.63	44	309.95	7.04
3	none	$9^{1}/_{2}$	88.50	9.32	36	240.50	6.68	$45^{1}/_{2}$	329.00	7.23
4	2.6 g $AlCl_3$	$19^{1}/_{2}$	213.95	11.24	24	186.00	7.75	$43^{1}/_{2}$	399.95	9.19
5	0.6 g „	$18^{1}/_{6}$	208.00	11.47	24	176.20	7.35	$42^{1}/_{6}$	384.20	9.10
6	0.6 g „	$24^{1}/_{2}$	210.50	8.60	24	173.00	7.21	$48^{1}/_{2}$	383.50	7.98
7	1.08 g $TlCl$	20	174.10	8.71	24	119.50	4.98	44	293.60	6.67
8	» »	20	149.10	7.46	21	64.40	3.07	41	213.50	5.20
9	» »	$20^{1}/_{4}$	187.00	9.24	$23^{1}/_{2}$	136.00	5.79	$43^{3}/_{4}$	323.00	7.38
10	» »	20	219.00	10.95	$9^{1}/_{2}$	89.40	9.40	$29^{1}/_{2}$	308.40	10.44
11	1.52 g $LiCl$	$20^{5}/_{6}$	103.95	4.99	$19^{1}/_{3}$	77.68	4.02	$40^{1}/_{6}$	181.63	4.52
12	0.77 g „	$17^{3}/_{4}$	120.52	6.79	24	91.35	3.81	$41^{3}/_{4}$	211.87	5.06
13	» »	$15^{1}/_{2}$	113.42	7.32	12	62.00	5.17	$27^{1}/_{2}$	175.42	6.37
14	3 ml $B(OCH_3)_3$	18	153.00	8.51	29	189.90	6.54	47	342.90	7.30
15	3 „ „	18	189.70	10.53	25	191.50	7.66	43	381.20	8.85
16	5 „ „	$17^{5}/_{6}$	182.64	10.22	24	199.55	8.31	$41^{5}/_{6}$	382.19	9.13
17	5 „ „	$24^{1}/_{2}$	225.50	9.20	$24^{1}/_{2}$	188.54	7.69	49	414.04	8.45
18	10 „ „	$18^{1}/_{6}$	153.05	8.43	24	174.40	7.27	$42^{1}/_{6}$	327.45	7.76
19	10 „ „	22	177.30	8.06	$19^{1}/_{2}$	128.85	6.60	$41^{1}/_{2}$	306.15	7.37
20	0.5 ml $TiCl_4$	20	184.00	9.20	24	162.50	6.77	44	364.50	7.86
21	» »	$20^{5}/_{6}$	168.80	8.10	$12^{1}/_{6}$	104.92	8.63	33	273.72	8.28
22	1.0 „ „	18	142.70	7.92	24	156.10	6.51	42	298.80	7.12
23	1.3 „ „	$19^{1}/_{3}$	164.40	8.50	22	168.50	7.65	$41^{1}/_{3}$	334.90	8.11
24	0.49 g $HgCl_2$	23	210.00	9.13	24	46.50	1.93	47	256.50	5.45
25	1.50 g „	22	182.00	8.27	23	61.50	2.67	45	243.50	5.41
26	5.0 g „	21	149.00	7.09	24	121.00	5.04	45	270.00	6.00
27	» »	20	165.00	8.25	14	62.00	4.43	34	277.00	6.68

a) Duration of synthesis in hours
b) Quantity of methylchlorosilanes in grams
c) Yield of methylchlorosilanes in grams per hour

* *TlCl* was melted with *CuCl* in inert atmosphere.

All experiments were carried out in a horizontal glass tube reactor at 300°C, and the feed of methyl chloride was regulated so that it was almost consumed in the reaction with silicon, e.g. 1.1 part wt. of methyl chloride per 1.0 part wt. of methylchlorosilanes obtained.

Admixtures were either mixed in mechanically with the contact mass during its preparation or were deposited on it from the gaseous phase at the beginning or during the synthesis. Some admixtures were previously fused with the copper (I) chloride in an inert atmosphere.

The following admixtures were added by mechanical mixing with the contact mass in a porcelain ball mill: anhydrous aluminum chloride, thallium (I) chloride, lithium chloride and mercury (II) chloride.

Mercury and compounds of titanium and boron were deposited on the contact mass from the gaseous phase. Measured quantities of titanium tetrachloride or methyl borate were put into the reactor before the beginning of the reaction of methyl chloride with silicon, e.g. at a temperature of about 220°C. Mercury was introduced into the reactor in the form of vapor by means of the methyl chloride stream which passed through a wash-bottle containing heated mercury, the mercury load of the stream depending on the temperature.

DISCUSSION

The results are presented in Tables I, and II. Experiments Nos. 1, 2, and 3 are of a greater number of experiments obtained without admixtures. From the results the following can be concluded:

TABLE II

Influence of mercury on the activity of the contact mass

No.	Temp. of *Hg*	1st Period			2nd Period			Overall		
		a	b	c	a	b	c	a	b	c
28	100	20	233.00	11.65	20	148.00	7.40	40	381.00	9.53
29	120	19	226.00	11.89	$12^1/_3$	115.70	9.37	$31^1/_3$	341.70	10.90
30	220	23	309.60	13.45	22	198.50	9.02	45	508.10	11 29
31	320	18	196.80	10.91	24	236.20	9.84	42	433.00	10.31

a) Duration of synthesis in hours
b) Quantity of methylchlorosilanes in grams
c) Yield of metylchlorosilanes in grams per hour

Anhydrous aluminum chloride showed a positive influence on the activity of the contact mass and increased the yield of methylchlorosilanes, especially in the first twenty hours of the synthesis. It was established increasing the quantity added from 0.6 g to 2.6 g did not affect the yield.

Contact masses to which thallium (I) chloride was added by mechanical mixing did not show increased activity. However, contact masses containing thallium (I) chloride fuse together with copper (I) chloride beforehand in an inert atmosphere, showed an increased activity. Addition of lithium (I) chloride in quantities ranging from 0.77 g to 1.52 g had an unfavorable effect on the activity of the contact mass.

In the case of methyl borate admixtures larger than 5 ml added to the contact mass after drying at 220°C, did not produce any considerable change, while 10 ml produced a slight decrease of the yield.

Addition of small quantities of titanium tetrachloride did not produce any significant improvement.

When small quantities of mercury (II) chloride were added a slight increase of the yield was observed in the first period of the synthesis, but later there was a sudden decrease. This suggested that a continual supply of small quantities of mercury vapor could have a positive effect. Therefore we carried out experiments introducing mercury vapor throughout the synthesis(3).

In these experiments mercury was heated from 100°C to about 320°C. When the temperature of the mercury in the wash-bottle was between 100°C and 120°C, no increase of the yield was observed. However, when it was heated to 220°C, there was a considerable increase of yield. Under these conditions the quantity of mercury introduced into the reactor was almost negligible. The activity of the contact mass was considerably increased in the course of the first twenty hours of the synthesis. When the temperature of mercury was increased to about 320°C considerable quantities of mercury were carried into the reactor so that when the synthesis was over condensed mercury drops were found in it. However, the yield of methylchlorosilanes was no greater than in the case when the mercury was at 220°C. These results indicate that increasing the quantity of mercury fed into the reactor did not cause a proportional increase of methylchlorosilane yield. The maximum yield is independent of the quantity of mercury introduced.

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THERMOGRAVIMETRIC AND DIFFERENTIAL THERMAL ANALYSIS OF NICKEL (II) CHLORIDE ADDUCTS WITH DIMETHYLSULFOXIDE*

by

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INTRODUCTION

Adducts of the same salt with dimethylsulfoxide (*DMSO*) can, depending on the conditions of synthesis, contain a different number of *DMSO* molecules(1, 2). The most important factors are the temperature of the saturated solution from which the adduct crystalizes, and the temperature and the partial pressure of *DMSO* when drying the adduct. Schläfer and Opitz(3) showed that under equilibrium conditions $NiCl_2.8DMSO$ comes out of a solution of $NiCl_2$ in *DMSO* below 48.5°C, and above that temperature $NiCl_2 . 3DMSO$. They dried the adducts relatively high in *DMSO* at several successively rising temperatures in a water-pump vacuum, and for a number of adducts found that certain intermediate products of thermal degradation of the initial adducts were formed. The synthesis of adducts with different *DMSO* contents is due either to the fact that the equilibrium forms which crystalize out from the solution differ in *DMSO* content, or to thermal degradation of the already isolated solid adduct which can proceed step by step with the formation of intermediate products.

The question arises whether thermal degradation of adducts high in *DMSO* under conditions of continuously rising temperature, in *TGA* and *DTA*, proceeds successively with the formation of definite intermediate products.

Weaver and Keim(4) performed *DTA* of several complex salts of transition elements with *DMSO*, including $NiCl_2.3DMSO$. On their *DTA* curves successive liberation of *DMSO* is not visible, which they explain by a too low melting point of the complex and insufficient volatility of *DMSO*.

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* Communicated at the 2nd Yugoslav Congress for Pure and Applied Chemistry, Beograd, 1966.

The adducts of salts with *DMSO* are indeed far from being ideal substances for *TGA* and *DTA* as *DMSO* boils at 189°C and the majority of adducts break down before this temperature. However, we nevertheless performed *TGA* and *DTA* of a number of complexes transition element of salts with *DMSO* and were able in some cases to observe the successive degradation of the adduct. The most typical examples are precisely adducts of $NiCl_2$. Studying the thermal behavior of $NiCl_2.8DMSO$ and $NiCl_2.3DMSO$ we were able to demonstrate the existence of a very stable adduct $NiCl_2.DMSO$ which was isolated and studied by *TGA* and *DTA*. By quantitative *DTA* we determined the enthalpy of the formation of this compound and estimated the activation energy of its degradation.

In order to compare the process of liberation of *DMSO* from these adducts with the dehydration of the hydrate of nickel (II) chloride, we performed *TGA* and *DTA* of $NiCl_2.6H_2O$.

EXPERIMENTAL

Chemicals: Industrial *DMSO* from the firm "Union Rheinische Braunkohlen Kraftstoff AG", Wesseling, was purified by fractional column distillation under low pressure(2).

Synthesis: $NiCl_2.8DMSO$ and $NiCl_2.3DMSO$ were synthesized according to the procedure of Schläfer(3). $NiCl_2.DMSO$ was obtained by thermolysis of $NiCl_2.3DMSO$.

Analysis: Ni^{+2} was determined by complexometry, and the composition of the adducts was also checked via the thermogravimetric data.

TGA was performed with a Chevenard-type thermo-balance of the firm Amsler. A 100 mg sample of the adduct was thermolysed in an open quartz vessel in an air atmosphere, with a heating rate of 150°C/h.

DTA was performed in an apparatus of the firm Linseis with optical recording, with a heating rate of 300°C/h. Three techniques were applied: a) *DTA* in air under conditions of free diffusion; b) *DTA* with diffusion prevented; c) *DTA* in vacuum (on average 0.5 mm Hg). The sample weight was 300 mg, and baked Al_2O_3 was used as the reference substance. For *DTA* under conditions *a* we used nickel "sample-holders". For *b* and *c* the samples were packed in layers. 300 mg of sample was put into cylindrical platinum calorimetric containers between two equal layers of Al_2O_3 of 100 mg each. The powdered adduct was always well tamped with a glass rod.

Calibration

For quantitative *DTA* the apparatus was calibrated by Wendlandts procedure(5) using $CuSO_4.5H_2O$, $CaSO_4.2H_2O$ and $BaCl_2.2H_2O$. The areas under the peaks were determined by measuring on an analytical balance. The callibration factors were: 39.3 ± 3.9 kcal/0.1 g of paper with nickel sample holders, 34.6 ± 3.8 kcal/0.1 g of paper for the vacuum technique.

RESULTS AND DISCUSSION

TGA

The *TGA* curve of $NiCl_2.8DMSO$ (Fig. 1) shows that thermolysis of this compound is a gradual process.

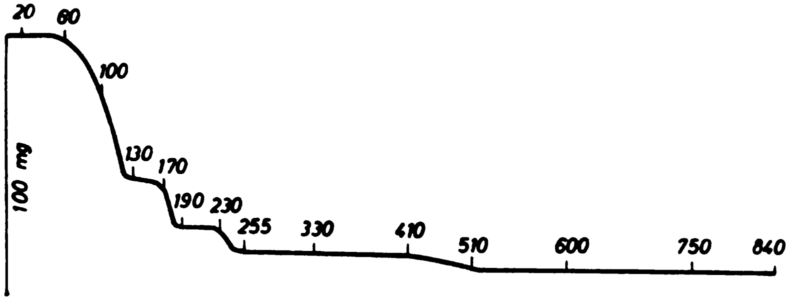

Figure 1

TGA of $NiCl_2 \cdot 8\,DMSO$

The first horizontal plateau corresponds to the region of stability of the intermediary triadduct, and the second to the monoadduct. The overal thermolysis therefore is composed of three phases:

1. $NiCl_2.8DMSO \rightarrow NiCl_2.3DMSO + 5DMSO$
2. $NiCl_2.3DMSO \rightarrow NiCl_2.DMSO + 2DMSO$
3. $NiCl_2.DMSO \rightarrow NiCl_2 + DMSO$

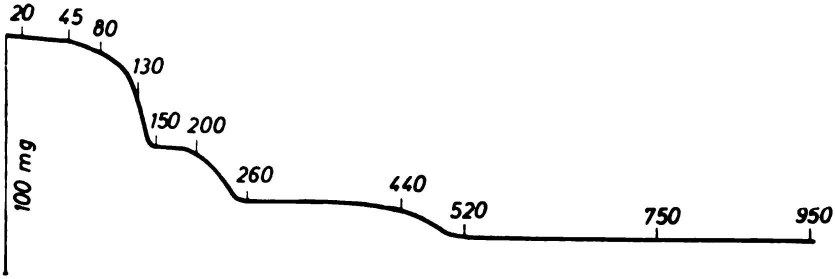

Figure 2

TGA of $NiCl_2 \cdot 3\,DMSO$

The *TGA* curve of $NiCl_2.3DMSO$ (Fig. 2) confirms the above conclusion. The intermediary product — the monoadduct — is obviously formed. Reactions 2 and 3 take place here, the horizontal parts of the curve representing the areas of stability of the monoadduct and $NiCl_2$.

The formation of the monoadduct as a very stable intermediary product during thermolysis of $NiCl_2.8DMSO$ and $NiCl_2.3DMSO$ made possible its isolation. The thermal stability of this adduct is demonstrated by the curve shown in Fig. 3. *DMSO* is liberated within the same temperature range as during thermolysis of $NiCl_2.8DMSO$ and $NiCl_2.3DMSO$.

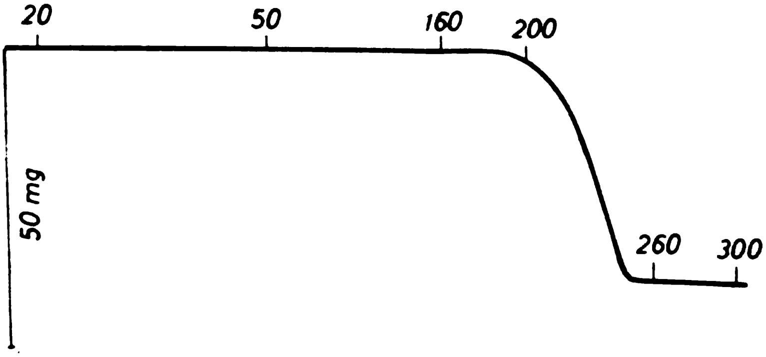

Figure 3
TGA of $NiCl_2 \cdot DMSO$

TGA of $NiCl_2.6H_2O$ is shown in Fig. 4. During the first phase of dehydration 4 molecules of water are liberated, and the stability plateau of 90°—150°C corresponds to the dihydrate thus formed.

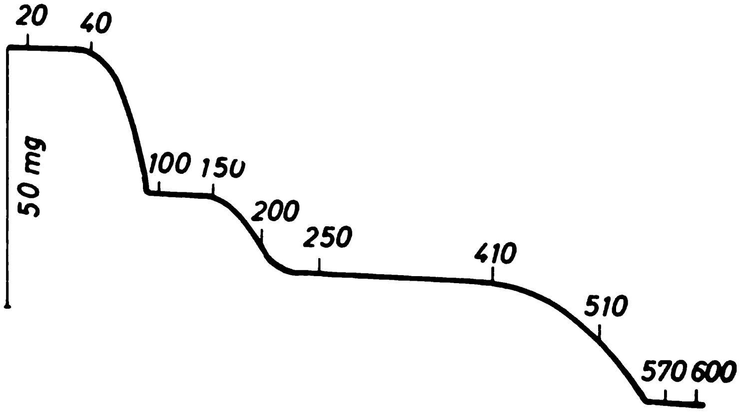

Figure 4
TGA of $NiCl_2 \cdot 6H_2O$

The bend in the curve at approximately 200°C shows that during the liberation of the last molecules of water a hemihydrate is formed as an intermediate.

It is interesting that the process of liberation of water from the hydrate ends at approximately the same temperature (about 250°C) as the liberation of *DMSO* from its complexes with $NiCl_2$.

DTA

The *DTA* curves of $NiCl_2.8DMSO$ in vacuum (Fig. 5), in air with (Fig. 6) and without diffusion (Fig. 7) are in complete agreement with the conclusions from the *TGA* curve (Fig. 1) and supplement it in as much as they show incongruent melting of the adduct. This is the cause of the first endothermic peak with a maximum at about 50°C. In the case of vacuum *DTA* the rate of liberation of *DMSO* vapor depends on the rate of formation; with the techniques in air the rate of evaporation is rate-determining. For that reason the area under the first peak with this technique is small, and the peak relatively sharp: the octaadduct melts and disintegrates. With the vacuum technique the area under the peak is relatively large and the peak itself broad: the octaadduct melts and disintegrates and the 5 molecules of *DMSO* produced are given off immediately.

The *DTA* curve in vacuum, in contrast to the curves in air, shows a clear peak with a maximum at 105° which corresponds to the disintegration of the triadduct and liberation of two more molecules of *DMSO* (reaction 2). On curves 5 and 6 the liberation of *DMSO*, which is produced according to reactions 1 and 2 appears as a single entity. The evaporation of *DMSO* finally becomes boiling, which is represented in Fig. 5 by the sharp peak with a maximum at 205°C*. The difference is entirely due to the fact that in the vacuum technique the adduct $NiCl_2.3DMSO$ gets heated alone, while with the other techniques it is heated in the presence of excess *DMSO* (solution). Therefore in this case the liberation of *DMSO* from the solution and the disintegration of the triadduct are combined into a single process.

At first glance it might appear odd that the thermolysis in *TGA* in air is nearer to that in *DTA* in vacuum than to that in *DTA* in air. The basic difference is that in *TGA* the *DMSO* formed is given off much more easily than in *DTA* in air (a high and narrow column, and with one of the techniques, layered packing).

The existence and disintegration of the monoadduct is practically identically manifested on all three curves. Here the *DMSO* vapor pressure is already so great that in any case the rate of the process is determined by the rate of *DMSO* formation.

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* N. B.: The maximums of the peaks are not the basic characteristic of the effect. At the maximum only the rates of inflow and absorption of energy are equal. Nevertheless we speak of the peak with the maximum at 205°C to facilitate reference to the figure and for the sake of brevity.

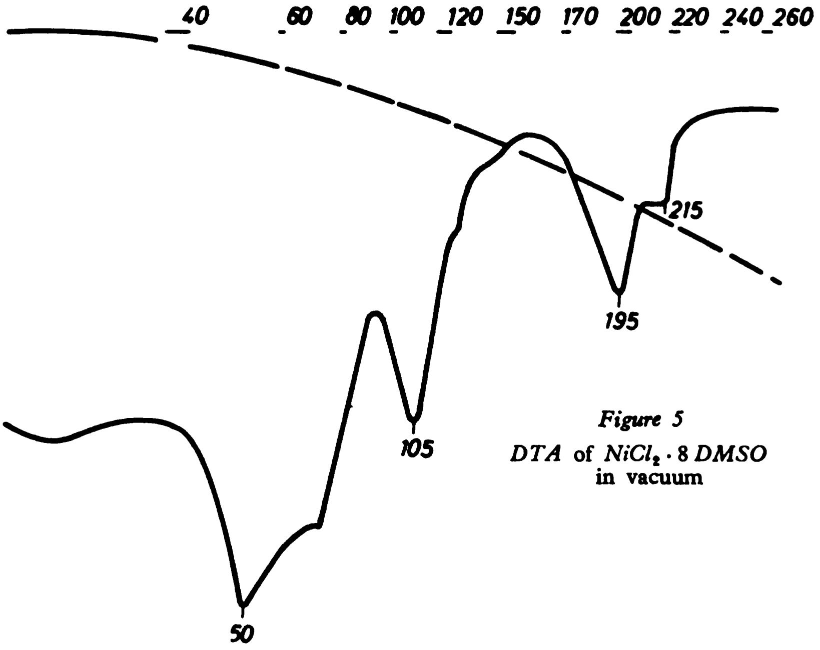

Figure 5
DTA of *NiCl*$_2$ · 8 *DMSO*
in vacuum

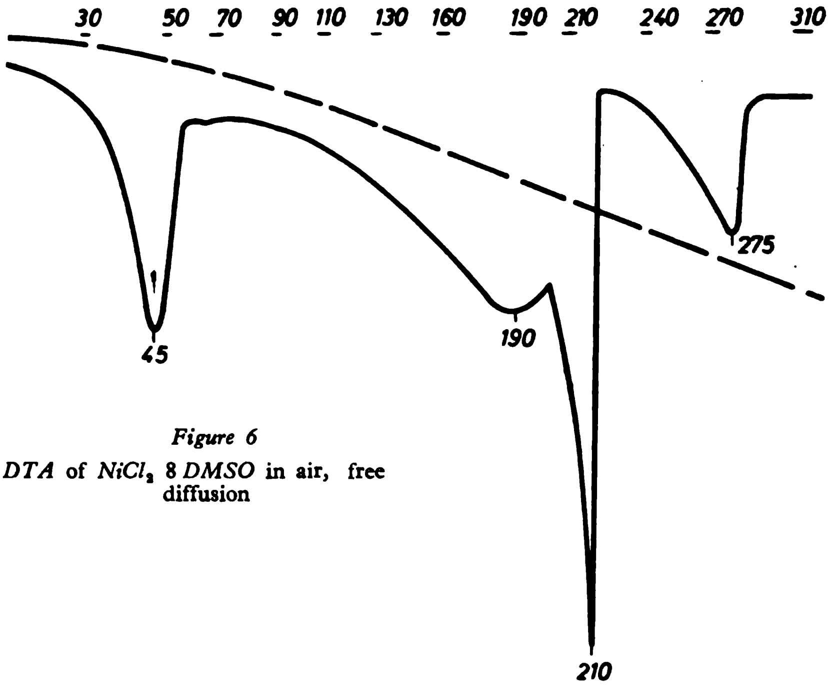

Figure 6
DTA of *NiCl*$_2$ 8 *DMSO* in air, free diffusion

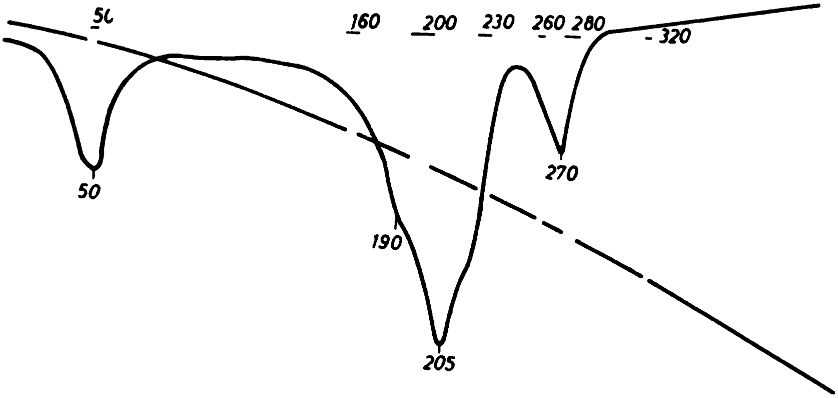

Figure 7

DTA of $NiCl_2 . 8DMSO$ in air, diffusion prevented.

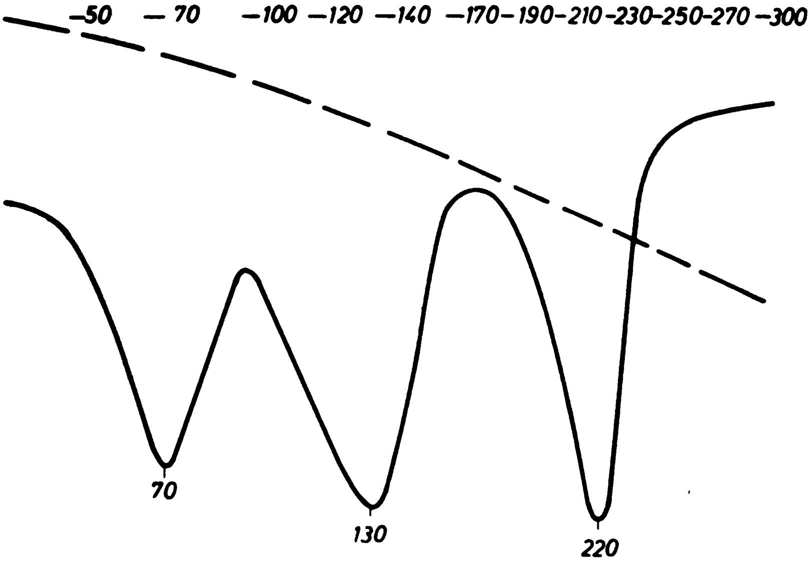

Figure 8

DTA of $NiCl_2 . 3DMSO$ in vacuum.

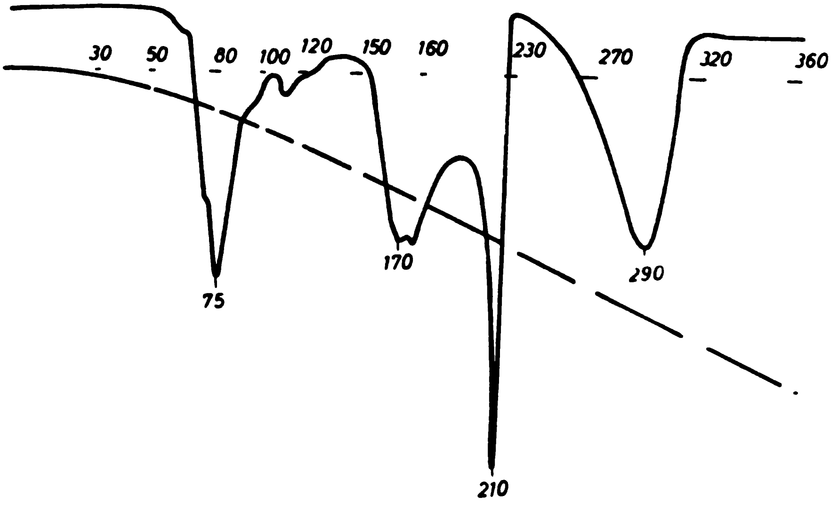

Figure 9

DTA of *NiCl₂*. 3*DMSO* in air, free diffusion.

The *DTA* curves of $NiCl_2$.3*DMSO* in vacuum (Fig. 8), in air (Fig. 9) and with diffusion prevented (Fig. 10) show three effects: the first peak at 75°C corresponds to the congruent melting of the triadduct. There is here as yet no real disintegration of the adduct,

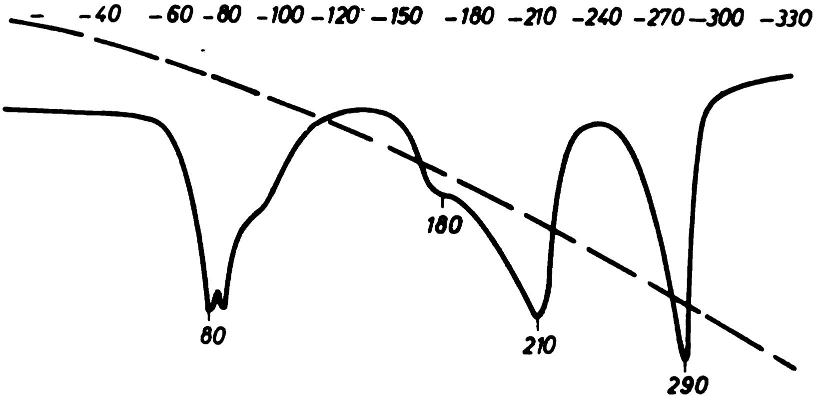

Figure 10

DTA of $NiCl_2$. 3*DMSO* in air, diffusion prevented.

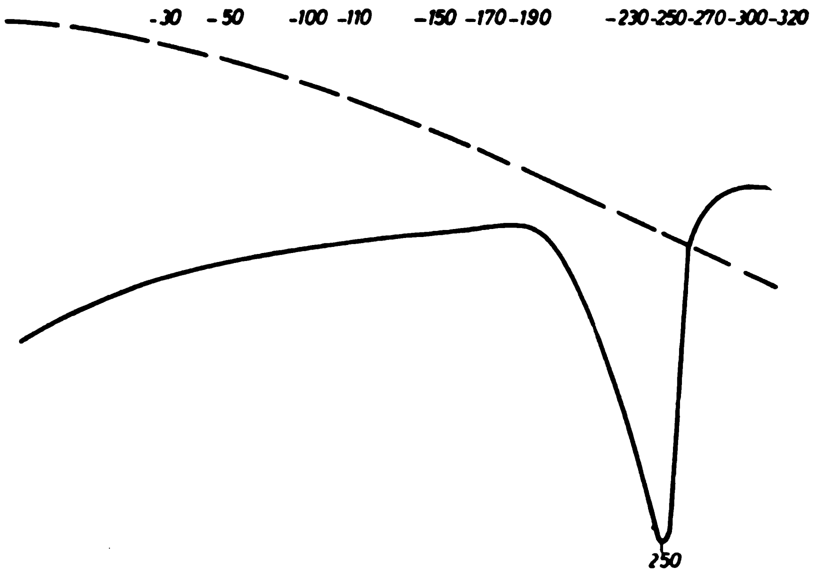

Figure 11

DTA of *NiCl*$_2$. *DMSO* in vacuum.

as is evident from the fact that in all three cases 2 *DMSO* molecules are given off after this peak, which is also the case with the vacuum technique. The middle peak reflects the liberation of 2 *DMSO* molecules and has in Fig. 8 a clear and in Fig. 9 a less pronounced doublet character, due to boiling. The third peak corresponds to the disintegration of the monoadduct and the giving off of a molecule of *DMSO*.

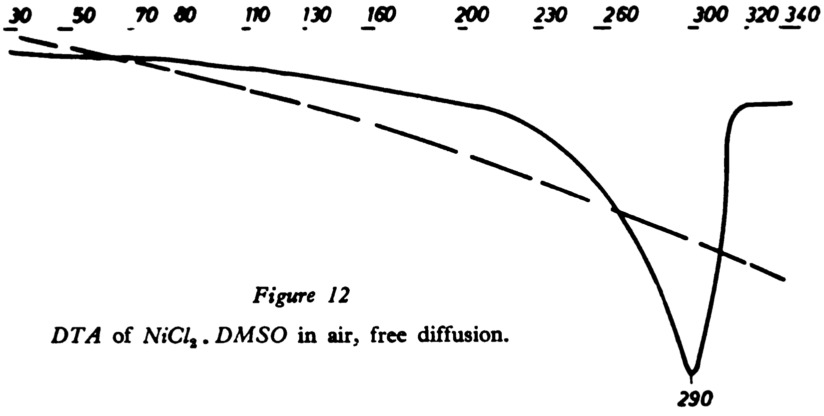

Figure 12

DTA of *NiCl*$_2$. *DMSO* in air, free diffusion.

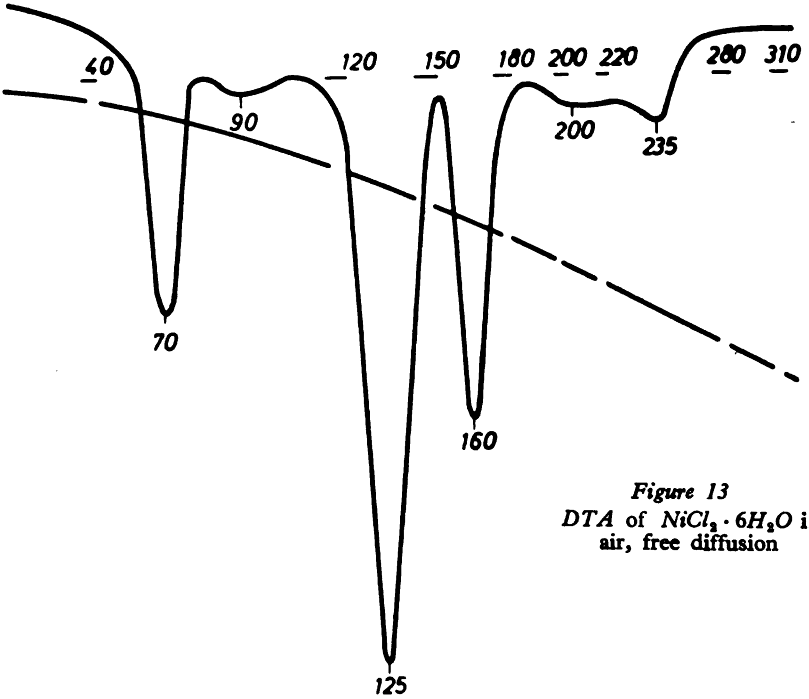

Figure 13
DTA of $NiCl_2 \cdot 6H_2O$ in air, free diffusion

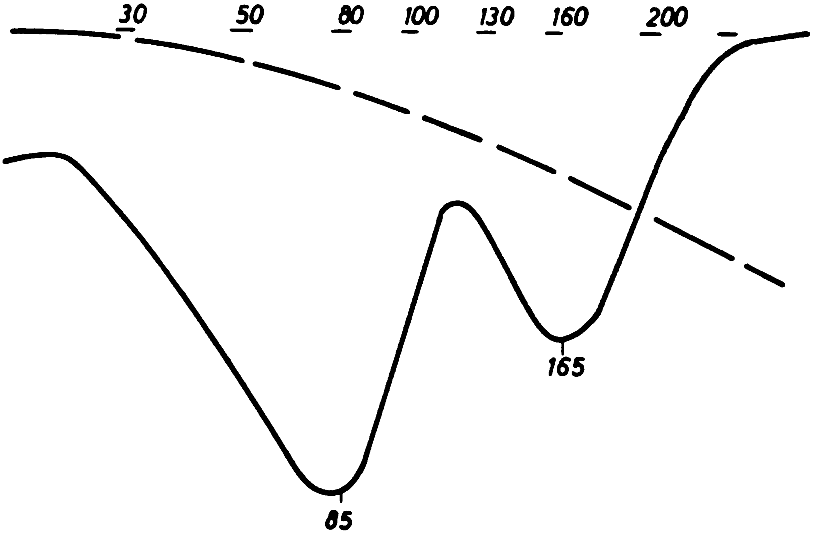

Figure 15
DTA of $NiCl_2 . 6H_2O$ in vacuum.

DTA of $NiCl_2.DMSO$ in vacuum (Fig. 11) and in air (Fig. 12) proceed practically identically, the sole difference being that the only peak present appears at a slightly lower temperature in vacuum. It corresponds to the disintegration of the adduct and complete liberation of *DMSO*.

A comparison with the thermal behaviour of $NiCl_2 . 6H_2O$ in *DTA* is interesting. In *DTA* in air (Fig. 13) the main peaks correspond to melting (at 70°) and the liberation of 4 (at 125°) 11/2 (at 160°) molecules of H_2O, and 1/2 molecules of H_2O from the hemiadduct (235°). The cited temperatures always correspond to the maximums of the peaks, although the effect itself always starts earlier.

With *DTA* of $NiCl_2 . 6H_2O$ in vacuum (Fig. 14) the melting is followed immediately by the giving off of 4 molecules of water, jointly manifested by the first peak, the liberation of the remaining two molecules of water by the second.

Temperature of Disintegration of $NiCl_2 . DMSO$

The last peak on the *DTA* curves of the $NiCl_2$ adducts, which corresponds to reaction 3, is due to a single reaction, which makes it possible to estimate the reaction enthalpy by means of Speil's formula⁽⁵⁾:

$$\int_{t_1}^{t_2} \Delta\ T dt = \frac{\Delta h \cdot m}{g \cdot k}$$

(t_1 and t_2 are the temperature limits of the peak, $\Delta\ T$ is the temperature difference, $\int_{t_2}^{t_1} \triangle\ Tdt$ = the area under the peak on the *DTA* curve, $\Delta\ h$ = heat of reaction per g of sample, m = sample mass, k = thermal conductivity of the sample, and g = a constant which depends on the furnace and on the geometry of the sample holder).

The reaction enthalpy of the liberation of *DMSO* from $NiCl_2.$ $. DMSO$, determined by means of quantitative *DTA*, is 23.6 ± 0.5 kcal/mol in an air atmosphere, and 21.1 ± 1.1 kcal/mol in vacuum.

The accurace of this data was checked by the calorimetric method. The value of 24.06 ± 0.04 kcal/mol obtained is in agreement with the results of *DTA*.

Estimation of the Activation Energy of Disintegration of $NiCl_2 . DMSO$

On the assumption that the disintegration of the monoadduct is a first order reaction we have applied the approximated Borchardt-Daniels method⁽⁶⁾ for the calculation of the constant k:

$$k = \frac{\Delta\ T}{(A - a)}$$

(ΔT = temperature difference, A = total peak area, a = peak area up to time t).

The areas A and a were obtained by integrating the peaks on transparent paper and by measurement on a torsion-microbalance with a sensitivity of 0.02 mg. T (expressed in mm) was measured at four points of the peak.

In order to obtain the true dimensions of the constant k, the areas would have to be measured in time × temperature units, but considering that a condition of quantitative *DTA* is that the temperature rises linearly with time, instead of time, temperature is taken as the abscissa. This changes the numerical value of the constant but not the activation energy, which is determined by Arrhenius's equation from the slope of the curve $d\ln k/d(1/T)$, as shown in Fig. 15. The activation energy was found to be $Ea = 35 \pm 1$ kcal/mol in an atmosphere of air, and 32 ± 1 kcal/mol in vacuum.

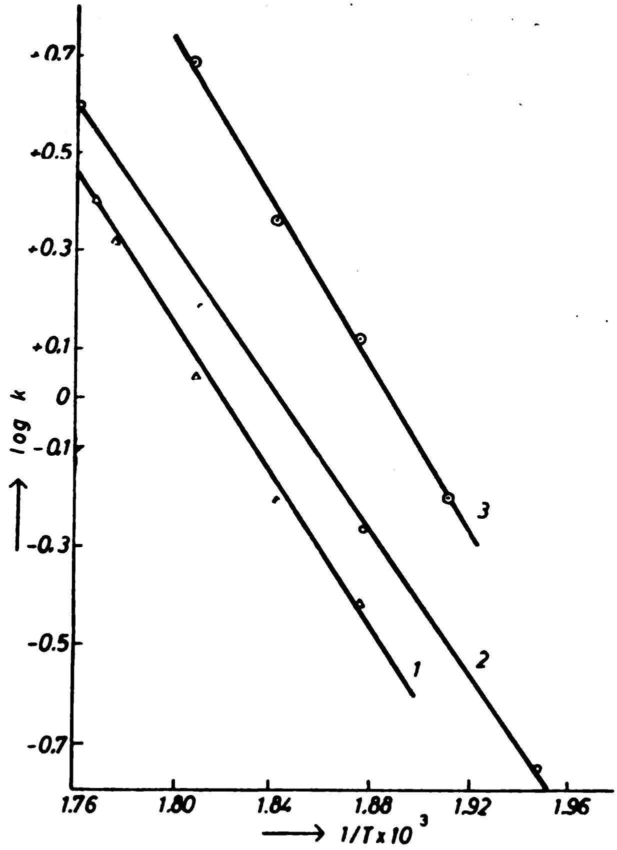

Figure 15

Arrhenius's diagram for the activation energy of disintegration of $NiCl_2 \cdot DMSO$

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School of Sciences,
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Sarajevo

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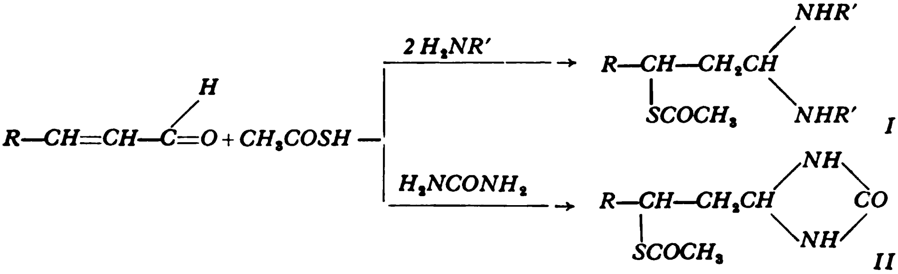
THE ADDITION OF THIOLACETIC ACID TO UNSATURATED ALDEHYDES. II.

BISAMIDES AND BISURETHANES OF β-ACETYLTHIO-ALDEHYDES*

by

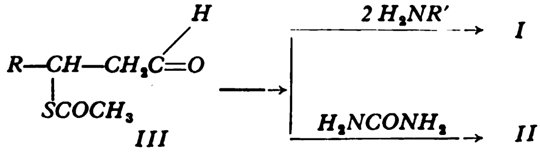
KSENIJA D. SIROTANOVIĆ and MILKA M. BAJLON-PASTOR

In a previous paper⁽¹⁾ we reported that by the action of thiolacetic acid on α, β-unsaturated aldehydes (cimtaldehyde and crotonaldehyde) in the presence of cetamide, urethane or carbamide, there is a good yield of bisamides or bisurethanes (I) and of monocarbamide (II) of the β-acetylthio-aldehydes, which means that thiolacetic acid adds onto the double bond of aldehyde, and the carbonile radical reacts with acetamide, urethane or carbamide:



(where $R = -CH_3$, $-C_6H_5$; and $R' = -COCH_3$, $-COOC_2H_5$).

The same compounds were obtained starting from previously prepared addition products with thiolacetic acid, or from the β-acetylthio-aldehydes (III) via condensation with acetamide, urethane or carbamide, but yields were smaller:



(where $R = -CH_3$, $-C^6H_5$; and $R' = -COCH_3$, $-COOC_2H_5$).

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* Communicated at the XXXIVth International Congress on Industrial Chemistry, Belgrade, September 1963.

In the present study we extended our investigations to a greater number of α, β-unsaturated aliphatic, aromatic and heterocyclic aldehydes, viz., besides cimtaldehyde and crotonaldehyde, the following unsaturated aldehydes:

acroleine
2-methyl-2-pentenal
2-hexenal
ortho-, meta- and para-nitrocimtaldehyde
ortho-, meta- and para-chlorcimtaldehyde
furylacroleine
thiopheneacroleine.

The aldehydes were treated with thiolacetic acid and acetamide or urethane (in the molecular ratio 1 : 1 : 2) in the presence of concentrated hydrochloric acid as a catalyst. The reaction took place at room temperature.

We obtained a great number of bisamides and bisurethanes of β-acetylthio-aldehydes which so far have not been described in the literature, as seen from the tables (I—IV).

Some of the bisamides and bisurethanes were also obtained by other paths — condensation of the β-acetylthio-aldehydes with acetamide, or urethane. The β-acetylthio-aldehydes were formed by adding thiolacetic acid to unsaturated aliphatic aldehydes after Brown, Jones and Pinder(2). Of the aldehydes obtained α-methyl-β-acetylthio-aldehyde and β-acetylthio-n-capronaldehyde have not been described in the literature.

From the products and yields of these reactions one can see that with the unsaturated aromatic aldehydes all the bisurethanes of the β-acetylthio-aldehydes were obtained in good yields (from 39% to 71%), while of the bisamides we obtained five of the expected seven products, and in low yields (from 26% to 57%).

With regard to the aliphatic unsaturated aldehydes, the bisamides of the β-acetylthio-aldehydes were obtained from acroleine, croton-aldehyde and hexenal, while the bisurethanes were obtained from acroleine and 2-methyl-2-pentenal.

Starting from the addition products of the unsaturated aliphatic aldehydes with thiolacetic acid, or the β-acetylthio-aldehydes, condensation products with acetamide and urethane were obtained from β-acetylthio-propionaldehyde, β-acetylthio-butyraldehyde and β-acetylthio-capronaldehyde. None of the products were obtained with α-methyl-β-acetylthio-valeraldehyde.

With the used heterocyclic aldehydes (furylacroleine and thiopheneacroleine), the bisamide and bisurethane of the addition product were only obtained with thiopheneacroleine. In all attempts to obtain them with furylacroleine only resins was obtained.

All the products obtained are solid crystalline substances with a sharp melting point. They are soluble in acetone and warm alcohol, and insoluble in ether and petroleumether.

EXPERIMENTAL

(The melting points and boiling points are uncorrected)

1. *β-acetylthio-aldehydes* were obtained after Brown, Jones and Pinder(2).

a) *α-methyl-β-acetylthio-valeraldehyde.* A mixture of 10 g (0.1 mol) of 2-methyl-2-pentenal, 11.5 g (0.15 moles) of thiolacetic acid and a few milligrams of benzoil-peroxide was heated in a flock with an upright condensor for 2 hours in a water bath, and then distilled in vacuum. 11.5 g (66%) of α-methyl-β-acetylthio-valeraldehyde was obtained, b.p. 115°/20 mm*Hg*.

2, 4-dinitrophenylhydrazone of α-methyl-β-acetylthio-valeraldehyde, recrystallized from ethyl alcohol, melted at 124—5°.

Analysis: Calculated for $C_{14}H_{18}N_4O_5S$ 15.82% *N*
found 15.74% *N*

b) *β-acetylthio-n-capronaldehyde.* A mixture of 5 g (0.05 mol) of hexenal, 5 g (0.07 mols) of thiolacetic acid and a few milligrams of benzoil-peroxide was heated 3 hours in a water bath and then distilled in vacuum. 5.3 g (61%) of β-acetylthio-*n*-capronaldehyde was obtained, b.p. 96—7°/4 mm.

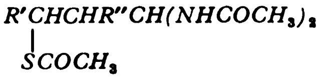
2. *Bisamides of aliphatic β-acetylthio-aldehydes* were obtained in two ways.

A. From the unsaturated aldehyde, thiolacetic acid and acetamide in the molecular ratio 1 : 1 : 2(1). A drop of concentrated hydrochloric acid was added to the mixture for each 0.02 moles of aldehyde and the mixture left for several days at room temperature. The hardened mass was treated with ether and filtered.

B. Obtained from the β-acetylthio-aldehyde with excess of acetamide (3—4 mol per mol) in the presence of acetic acid anhydride(3). The mixture was heated in a flask with an upright condensor 3—4 hours at 100°, acetic acid anhydride removed in vacuum, ether added to the residue which was then left to stand until the bisamide crystallized out.

TABLE I

Bisamides:



$$\underset{\displaystyle SCOCH_3}{R'CH}CHR''CH(NHCOCH_3)_2$$

R′	*R″*	Yield %		M. P. °C	Formula	Analysis	
		A	*B*			Calc. *N*%	Found *N*%
H	*H*	68	74	191	$C_9H_{16}N_2O_3S$	12.07	12.31
CH_3	*H*	20*	20*	149			
C_3H_7	*H*	47	27	165	$C_{12}H_{22}N_2O_3S$	10.22	10.44

* Analytical data given in the previous work(1).

The raw products were crystallized from ethyl-alcohol, acetone or a mixture of acetone and petrolium ether. The melting points of mixtures of products obtained by *A* and of the corresponding products obtained by *B* did not show depression.

The yields, melting points and analyses for the bisamides are shown in Table I.

3. *Bisurethanes of the aliphatic β-acetylthio-aldehydes* were obtained in two ways.

A. From the unsaturated aldehyde, thiolacetic acid and urethane in the molecular ratio 1 : 1 : 2(1). A drop of concentrated hydrochloric acid was added to the mixture for each 0.02 moles of aldehyde, which was then left at room temperature for several days. The hardened mass was then treated with ether and filtered.

B. From the β-acetylthio-aldehyde and urethane in the molecular ratio 1 : 2(4). A few drops of concentrated hydrochloric acid was added to the mixture which was then left overnight at room temperature. It was then treated with ether and filtered.

The raw bisurethanes were recrystallized from ethylalcohol or from a mixture of acetone and petrolium ether. The melting points of mixtures of corresponding products obtained by *A* and *B* did not show depression.

TABLE II

Bisurethanes:

$$\underset{\displaystyle SCOCH_3}{R'CH}CHR''CH(NHCO_2C_2H_5)_2$$

R′	R″	Yield %		M. P. °C	Formula	Analysis	
		A	*B*			Calc. *N* %	Found *N* %
H	*H*	27	92	143	$C_{11}H_{20}N_2O_5S$	12.07	12,31
CH_3	*H*	—	48*	89			
C_2H_5	CH_3	47**	—	149	$C_{14}H_{26}N_2O_5S$	8.38	8.47
C_3H_7	*H*	—	37	110	$C_{14}H_{26}N_2O_5S$	8.37	8.67

* Analytical data given in the previous work(1).

** Reaction mixture left 90 days at room temperature.

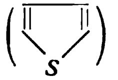
The yields, melting points and analyses for the bisurethanes are shown in Table II.

4. *Bisamides of aromatic and heterocyclic β-acetylthio-aldehydes* were obtained after K. Sirotanović(1). A drop of concentrated hydrochloric acid was added to a mixture of 0.01 mol of the unsaturated aldehyde, 0.01 mol of thiolacetic acid, 0.02 mol of acetamide and

TABLE III

Bisamides:

$$R-\underset{\substack{|\\ SCOCH_3}}{C}HCH_2CH(NHCOCH_3)_2$$

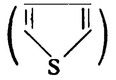
R	Yield %	M. P. °C	Formula	Analysis			
				Calc. N %	Found N %	Calc. S %	Found S %
C_6H_5	27*	206					
m-NO_2-C_6H_4	26	209	$C_{15}H_{19}N_3O_5S$	11.89	12.27		
p-NO_2-C_6H_4	26	216	,,	11.89	11.88	9.06	9.38
m-Cl-C_6H_4	57	202	$C_{15}H_{19}ClN_2O_3S$	8.17	8.37		
p-Cl-C_6H_4-	35	178	,,	8.17	8.45	9.34	9.33
C_4H_3S 	32	203	$C_{13}H_{18}N_2O_3S$	8.91	8.83	20.38	19.85

* Analytical data were given in the previous work[1]

TABLE IV

Bisurethanes:

$$R-\underset{\substack{|\\ SCOCH_3}}{C}HCH_2CH(NHCO_2C_2H_5)_2$$

R	Yield %	M. P. °C	Formula	Analysis			
				Calc. N %	Found N %	Calc. S %	Found S %
C_6H_5	39*	148					
o-NO_2-C_6H_4	48	169	$C_{17}H_{23}N_3O_7S$	10 17	9.99	7.74	7.87
m-NO_2-C_6H_4	57	174	»	10.17	9.82	7.74	7.79
p-NO_2-C_6H_4	50	160	»	10.17	10.24	7.74	7.79
o-Cl-C_6H_4	65	142	$C_{17}H_{23}ClN_2O_5S$	6.94	7.14	7.95	7.82
m-Cl-C_6H_4	71	174	»	6.94	6.96	7.95	8.01
p-Cl-C_6H_4	53	157	»	6.94	7.24	7.95	8.03
C_4H_3S 	27	120	$C_{15}H_{22}N_2O_5S$	7.48	7.65	17.11	16.52

* Analytical data given in the previous work[1].

a few milliliters of absolute ether. The mixture was then left to stand for a few days at room temperature (until it hardened). The product was washed with ether filtered and crystallized from ethylalcohol or a mixture of acetone and petrolium ether. The yields, melting points and analyses for the bisamides are shown in Table III.

5. *Bisurethanes of aromatic and heterocyclic* β-*acetylthio-aldehydes* were obtained in the same as the bisamides under 4, except that urethane was used instead of acetamide. The raw products were recrystallized from ethylalcohol. The yields, melting points and analyses for the bisurethanes are shown in Table IV.

The microanalyses for nitrogen mentioned were done by Ruža Tasovac of the Institute of Chemistry of the School of Sciences. The analyses for sulphur were done by Gasparini's method(5).

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STABILIZATION OF *L*-ASCORBIC ACID WITH COMPLEXON III IN SOLUTIONS OF SOME ORGANIC AND INORGANIC ACIDS

by

VERICA D. RAJKOVIĆ, JELENA V. BANJAC
and JELISAVETA D. ĐORĐEVIĆ

This is a continuation of the study of the stabilization of *L*-ascorbic acid with ethylendiaminotetraacetic acid (*EDTA*) and its disodium salt (complexon III) in the presence of some acids, within the context of preliminary studies on: using complexon III in processing natural products;

— the determination of *L*-ascorbic acid in natural and processed products.

The possibility of stabilizing of *L*-ascorbic acid with complexon III in the presence of oxalic, metaphosphoric, trichloroacetic and hydrochloric acid has been systematically investigated in the present study. Earlier authors used these acids, pure or mixed with other acids, for the extraction and stabilization of *L*-ascorbic acid for its determination(2, 3).

The studies of H. T. Freebairn(4) with trichloroacetic, metaphosphoric and oxalic acid do not give a complete picture of the stabilization of *L*-ascorbic acid with *EDTA* in the presence of these acids, but only data on 2% oxalic, 5% metaphosphoric and 0.3 and 3.3% trichloroacetic acid in the presence of 2.5×10^{-3} *M EDTA*.

Our studies were aimed at examining whether is justified to oxalic, metaphosphoric, trichloroacetic or hydrochloric acid during the stabilization of *L*-ascorbic acid with complexon III in the course of extraction and determination, and if so in what concentrations.

EXPERIMENTAL

The preparation of the basic solutions and samples and determination of *L*-ascorbic acid at pre-determined time-intervals was the same as in our previous study(1).

The acids studied in the present investigation were oxalic, metaphosphoric, trichloroacetic and hydrochloric.

TABLE 1

% L-ascorbic acid in samples kept for 96 hours at 29 ± 8°C

Complexon (moles)	Water	% Metaphosphoric acid			% Oxalic acid			% Trichloroacetic acid			% Hydrochloric acid		
		0.25	1.0	3.0	0.25	1.0	3.0	0.25	1.0	3.0	0.25	1.0	3.0
0	0	76.38	75.97	65.54	81.61	83.32	80.89	2.25	0	0	4.18	20.77	26.50
2.5×10^{-5}	94.94	77.12	34.54	39.76	78.00	83.58	78.04	87.42	17.95	1.35	74.68	26.75	36.57
2.5×10^{-4}	95.25	94.02	77.31	64.64	81.13	84.03	78.63	94.06	28.93	15.79	82.46	24.56	29.30
2.5×10^{-3}	91.49	95.58	78.54	69.00	83.64	82.67	79.57	96.54	72.64	55.99	88.53	40.33	31.75
2.5×10^{-2}	22.83	85.27	93.46	85.62	89.32	80.31	75.24	87.71	93.43	46.80	85.26	38.31	33.56

RESULTS AND DISCUSSION

The effects of oxalic, metaphosphoric, trichloroacetic and hydrochloric acid on the stabilization of *L*-ascorbic acid with complexon III during 96 hours at 29 ± 1° are shown in Table 1 expressed in terms of the percentage of *L*-ascorbic acid remaining in the solution. The same results are shown in Fig. 1—4 in the form of curves which represent:

a) the dependence of the percentage of *L*-ascorbic acid remaining on the concentration of the given acid at a constant concentration of complexon III;

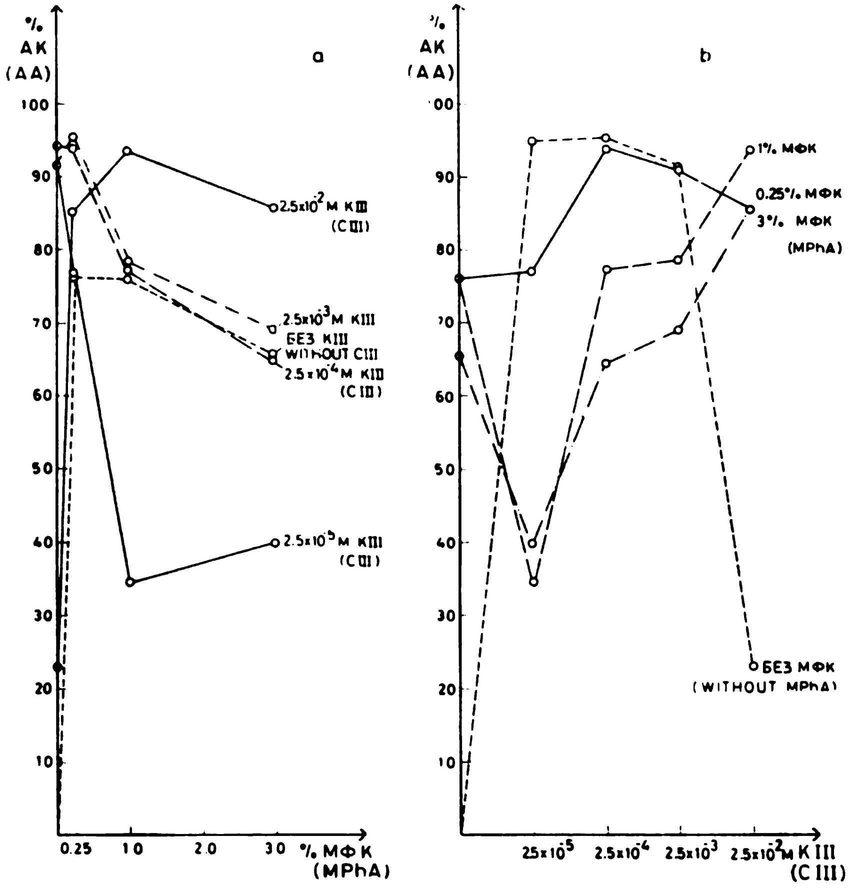

Figure 1

a. Concentration of *L*-ascorbic acid (*AA*), as a function of metaphosphoric acid (*MPhA*) concentration at constant complexon III (CIII) concentration.

b. Concentration of *L*-ascorbic acid (*AA*) as a function of complexon III (CIII) concentration at constant metaphosphoric acid (*MPhA*) concentration.

b) the dependence of the percentage of *L*-ascorbic acid remaining on the concentration of complexon III at a constant concentration of the given acid.

It may be seen from Table 1 and from Graph *a* that of the four acids, oxalic and metaphosphoric stabilize quite well even without complexon III, that hydrochloric acid does so rather poorly, and that in solutions of trichloroacetic acid, after 96 hours at 29 ± 1°, there was little or no *L*-ascorbic acid left. The diagrams also show a regularity common to the majority of the curves: the stability of *L*-ascorbic acid falls with increasing concentration of the acid from 1—3%.

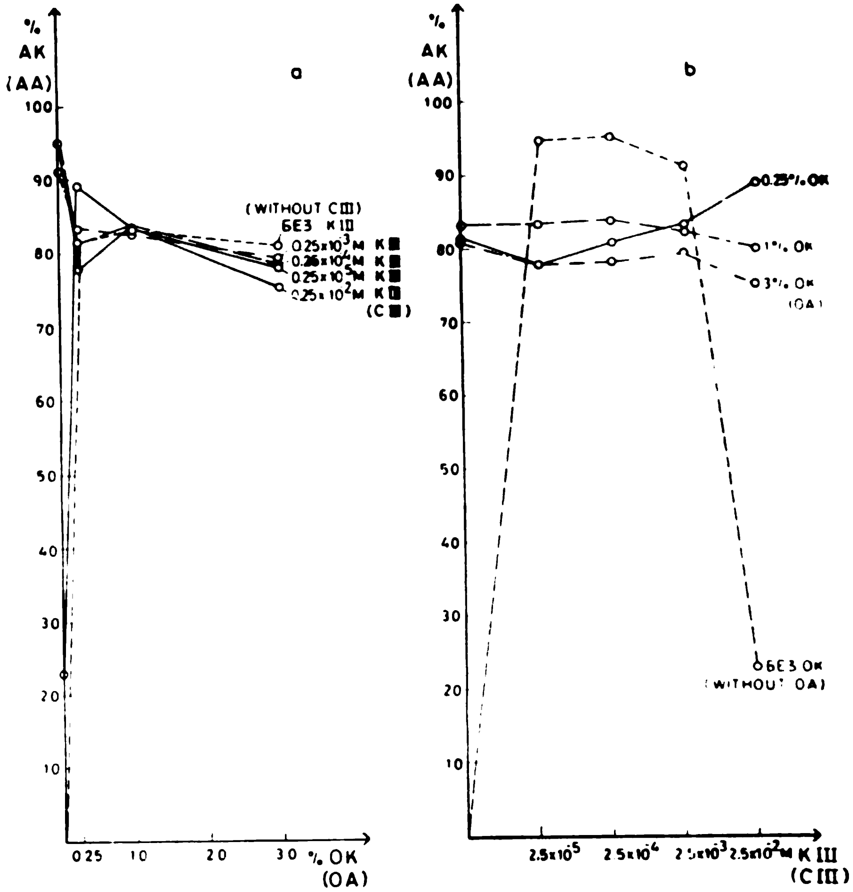

Figure 2

a. Concentration of *L*-ascorbic acid (*AA*), as a function of oxalic acid (*OA*) concentration at constant complexon III (CIII) concentration.

b. Concentration of *L*-ascorbic acid (*AA*) as a function of complexon III (CIII) concentration at constant oxalic acid (*OA*) concentration.

It is obvious from Graph *b* that the stability of *L*-ascorbic acid is usually greater in water solutions of complexon III (2.5×10^{-5}—2.5×10^{-3}) than in the corresponding solutions of the four acids. Most of the curves show some sort of maximum which corresponds to the greatest stability of *L*-ascorbic acid or the optimum concentration of complexon III in the presence of the given concentration of the acid. Exceptions are the 1 and 3% oxalic acid solutions in which changes of the concentration of complexon III did not produce a significant change in stability (78—84%). Changes of the concentration of complexon III in 1 and 3% solutions of hydrochloric acid also produced smaller changes in stability than in the solutions of meta-

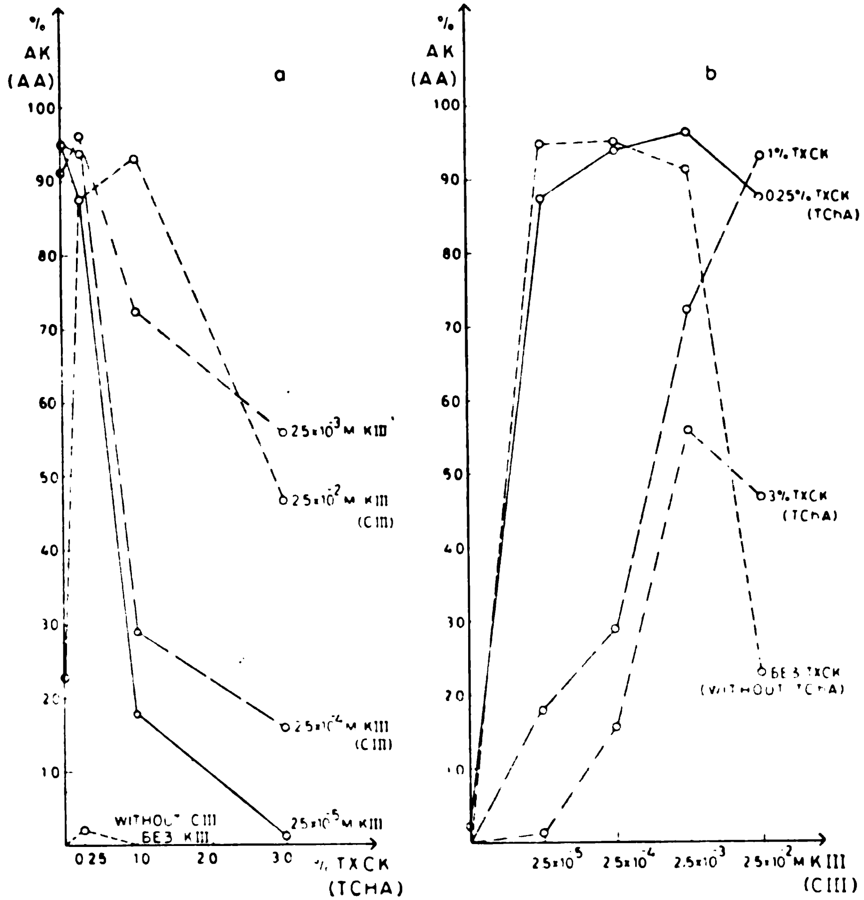

Figure 3

a. Concentration of *L*-ascorbic acid (*AA*), as a function of trichloroacetic acid (*TChA*) concentration at constant complexon III (CIII) concentration.

b. Change in the concentration of *L*-ascorbic acid (*AA*) as a function of complexon III (CIII) concentration at constant trichloroacetic acid (*TChA*) concentration.

phosphoric and trichloroacetic acid, but this was of no importance in view of the fact that the values anyway ranged between 20 and 40%.

These results confirm the findings of Freebairn that a mixture of 0.3% trichloroacetic acid and 2.5 × 10- *EDTA* has a much better stabilizing effect than a mixture of 3.3% trichloroacetic acid and 2.5×10^{-3} *M* complexon. Our experiments have shown that a mixture of 0.25% trichloroacetic acid and a 10 times lower concentration of complexon III has almost as good a stabilizing effect.

Freebairn further found that pure oxalic acid, or a mixture of it with *EDTA*, has a poor stabilizing effect. He attributed this to

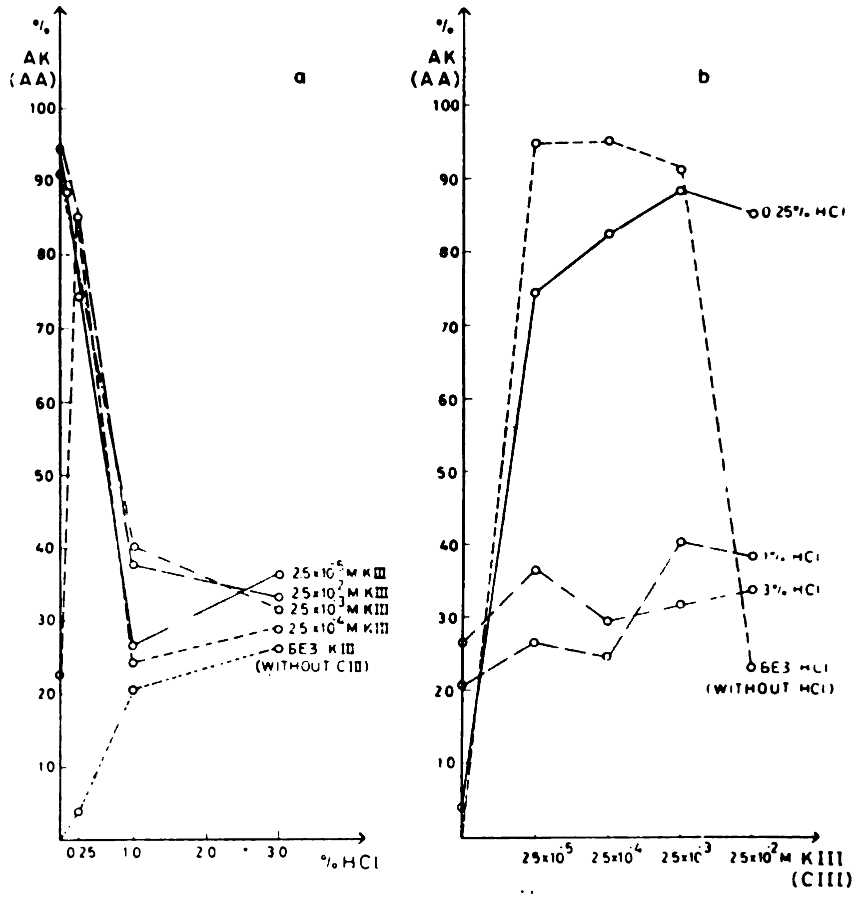

Figure 4

a. Concentration of *L*-ascorbic acid (*AA*), as a function of hydrochloric acid (*HCl*) concentration, at constant complexon III (CIII) concentration.

b. Concentration of *L*-ascorbic acid (*AA*) as a function of complexon III (CIII) concentration, at constant hydrochloric acid (*HCl*) concentration.

the low *pH* of the mixture with 2% oxalic acid. Our studies have shown that mixtures of oxalic acid and complexon III cannot be considered as exceptionally good but are still quite good stabilizers, considering that in these samples there was 78—84% of the initial *L*-ascorbic acid left after 96 hours at 29 ± 1°. The advantage of mixtures of oxalic acid and complexon III lies in the fact that with changing concentrations of the acid or complexon the stability of *L*-ascorbic acid is little changed.

It can be concluded from the above that in stabilizing *L*-ascorbic acid with complexon III none of the acids here studied should be added, or if this is inavoidable (for instance in order to precipitate proteins or inactivate enzymes, or for some other reason) then it should be added in the smallest possible quantity.

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CHEMICAL COMPOSITION OF ETHERIC OIL FROM NEEDLES OF BLACK PINE (*PINUS NIGRA* ARN.)

by

DOBRILA M. KARAPANDŽIĆ

The needles and young branches of black pine are used in Yugoslavia as a source of etheric oil. We have found no data in the literature on the chemical composition and physical and chemical constants of the etheric oil from the domestic black pine. The first report on the chemical composition of this oil abroad was recently published by I. Ognjanov and E. Cankova(1). These authors studied the oil from the needles of Bulgarian black pine (*Pinus nigricans*).

We analyzed the oil obtained by steam distillation at the firm "Kotroman" (Mokra Gora). The needles and young branches were taken from black pine trees in the nursery on the slopes of Šargan.

EXPERIMENTAL

The oil under study had the following physical and chemical constants: $n_D^{20} = 1.4721$, $\alpha_D^{20} = 29.7°$, $d_{20}^{20} = 0.8658$, acid. no. = 0.23, est. no. = 5.13, est.no. after acet. = 14.01.

In distillation under normal pressure most of the oil (about 76%) distilled over below 165°.

The etheric oil (995 g) was submitted to fractional vacuum distillation on a column produced in Yugoslavia whose efficiency was 25 *T.P.* Each 10 ml of the distillate was caught. The physical constants were determined for each fraction. The course of distillation and the physical constants of the different fractions are shown in the distillation diagram (Fig. 1).

Identification of the components

l-α-pinene. Fractions 2—41 had constants close to α-pinene. They were mixed, redistilled and then distilled over metallic sodium. The α-pinene thus purified had the following constants: $n_D^{20} = 1.4667$,

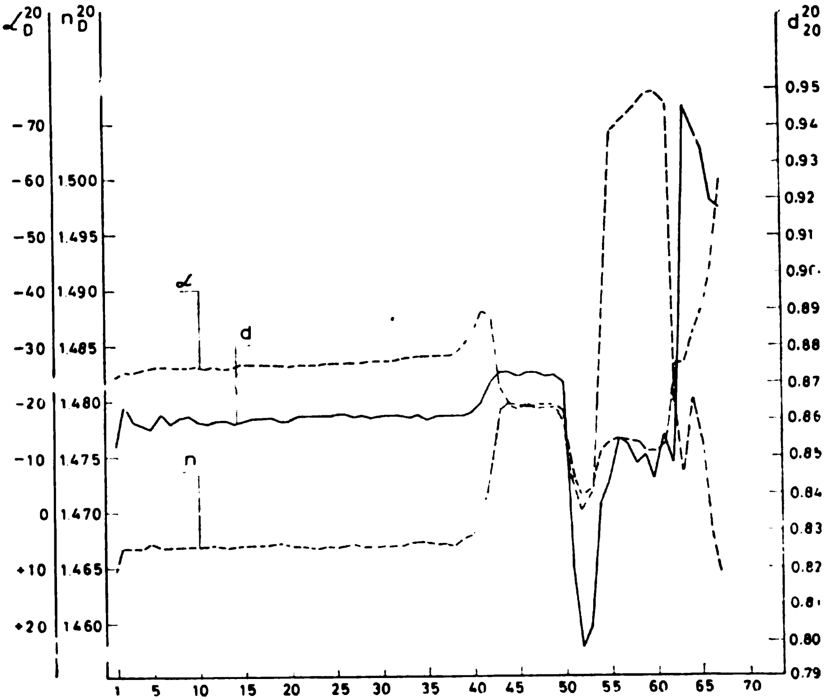

Figure 1

Distillation diagram

$[\alpha]_D^{20} = -31.8°$, $d_{20}^{20} = 0.8590$. The nitrosochloride, prepared by the method of Wallach⁽²⁾, melted at 103°.

l-β-pinene. The fractions 43—50 were composed mainly of β-pinene. After purification by redistillation and distillation over metallic sodium, the β-pinene had the following constants: $n_D^{20} =$ $= 1.4795$, $[\alpha]_D^{20} = -23.56°$, $d_{20}^{20} = 0.8721$.

The β-pinene was oxidised by the method of Wallach⁽³⁾ with $KMnO_4$ in alkaline medium. In this way a hardly soluble sodium salt of nopinic acid was obtained. The acid was liberated from its salt by means of dilute H_2SO_4 and then extracted with ether. After removing the solute crystals of nopinic acid separated out. After recrystallization the crystals melted at 126—127°.

β-*mircene*. Fraction no. 52 had constants similar to mircene. An adduct with maleic anhydride was prepared by the method of Diels and Adler⁽⁴⁾; after purification this anhydride melted at 33°. The presence of mircene was proved both by means of the UV spectrum (maximum at 224 mμ) and by the IR spectrum.

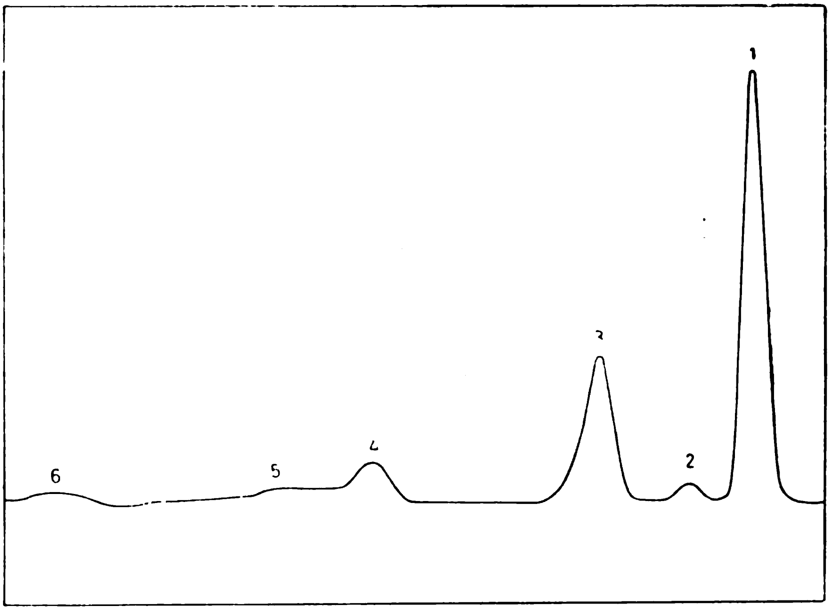

Fig. 2. Chromatogram of monoturpene hydrocarbons from the etheric oil of black pine.

1. α-pinene, 2. camphene, 3. β-pinene + mircene,
4. limonene, 5. *p*-cimol, 6. unidentified component.

l-limonene + dipentene. Fractions 55—61 had the constants similar to limonene. After purification, redistillation and distillation over metallic sodium, the limonene had the following constants: $n_D^{20} = 1.4740$, $[\alpha]_D^{20} = 99.21$, $d_{22}^{20} = 0.8446$. By bromification after Baeyer(5) a tetrabromide was obtained, which melted at 123°. This shows that the limonene isolated is present in the mixture with dipentene whose tetrabromide is less soluble.

By gas-liquid chromatography of the monoturpene fraction of the oil (Fig. 2) the presence of camphene, *p*-cimol and an unidentified component was proved. The quantitative ratio of the monoturpene hydrocarbons was as follows: l-α-pinene (69.3%), camphene (1.78%), l-β-pinene + mircene (17.3%) l-limonene (5.7%), *p*-cimol (4.1%) and the unidentified component (1.8%).

The higher fractions did not yield crystal derivatives. Fractions 66 and 67 with acetic acid anhydride and bromine vapor gave the coloured reaction typical of proazulenes. Dehydrogenation with selenium yielded some blue oil. A closer identification of these proazulenes was not successful.

The IR spectrum analysis of mircene was carried out by Dr. Dragan Jeremić of the Institute of Technology in Belgrade. The gas-liquid chromatography was done by Dr. Nestor Kobilarov, also of the Institute of Technology. The analysis was done on a column with di (2-ethylhexil) sebacate on celite as the static phase, H_2 as the carrier-gas, $t = 120°$, test sample 5 μl. The different components were identified by comparison with relatively pure compounds isolated from other oils, and by the IR spectrum.

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CHEMICAL COMPOSITION OF ETHERIC OIL FROM NEEDLES OF BALKAN PINE (*PINUS HELDREICHII* CHRIST.)

by

DOBRILA M. KARAPANDŽIĆ

Pinus Heldreichii, white pine or Balkan pine, is a relicht endemic species from the Tertiary and is found exclusively in the Balkan peninsula, except for some small areas in South Italy.(1) The chemical composition of etheric oil from its needles has not been studied. The turpentinic oil was investigated by B. Okrajinov-Rotović(2) who found that it contained 1-α-pinene (30.13%) and 1-limonene (57.38%).

Balkan pine, from the morphological point of view, bears certain similarities to the black pine. For that reason we considered it of interest to study the chemical composition of the etheric oil from the needles and to determine its physical and chemical constants. The oil was obtained by steam distillation in mobile distilleries belonging to the firm "Kotroman". The needles were taken from Balkan pine trees on the Prokletije mountains.

EXPERIMENTAL

The oil had the following characteristics: $n_D^{20} = 1.4753$, $\alpha_D^{20} = -74.4°$, $d_{20}^{20} = 0.8533$, acid no. = 0.37, est.no. = 4.34, est. no. after acet. = 12.8.

In distillation under normal pressure most of the oil (74.4%) distilled over below 180°.

In order to isolate the components of the oil we performed fractional vaccum distillation of 68 g of oil. Fractions of 10 ml of the distillate were caught. The physical constants were determined for each fraction. The course of distillation and the physical constants of the fractions are shown in the distillation diagram (Fig. 1).

Identification of the components

1-α-pinene. Fractions 1—14 consisted mainly of α-pinene. By oxidation of these fractions with $KMnO_4$ after Thurber(3) pinonic acid was obtained. The semicarbazone of the pinonic acid, after re-

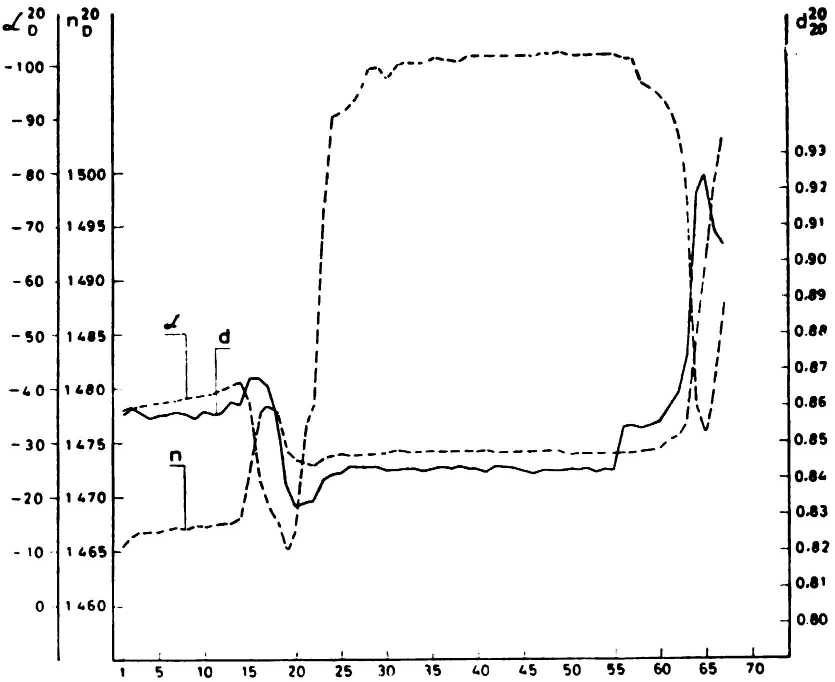

Fig. 1. Distillation diagram

crystallization from dilute methyl alcohol, melted at 204°. The nitrosochloride, prepared by the method of Wallach⁽⁴⁾, melted at 102°. It was then transformed into nitrolpiperidine, m.p. 118—119°.

l-β-pinene. Fractions 16—18 had constants close to β-pinene. The presence of β-pinene was proved by oxidation of these fractions with $KMnO_4$ in alkaline medium by the method of Wallach⁽⁵⁾ : a hardly soluble sodium salt of nopinic acid was obtained. Nopinic acid liberated from its salt by means of dilute H_2SO_4 melted at 126—127°.

β-mircene. Fraction 19 showed an abrupt fall of the angle of rotation and of specific gravity, and because of that we assumed that it contained mircene. The presence of mircene was demonstrated by IR spectrum analysis of this fraction.

l-limonene. Fractions 21—26 consisted mainly of limonene with a high optical activity. The specific rotation of the majority of fractions was in the range 119—120°. By bromification of these fractions after Baeyer⁽⁶⁾ limonene-tetrabromide was prepared which after crystallization from ethyl acetate melted at 103—104°.

Analysis of the monoturpene fraction of this oil by means of gas-liquid chromatography (Fig. 2) showed also the presence of camphene (peak 4) and of three unidentified components (peaks 1,

Fig. 2. Chromatogram of monoturpene hydrocarbons from etheric oil of Balkan pine needles

1 and 2 — unidentified components, 3 — α-pinene, 4 — camphene, 5 — β-pinene, 6 — mircene, 7 — unidentified component, 8 — limonene.

2 and 7). The chromatogram also showed some unmarked peaks of unidentified components present in small quantities.

According to the gas-liquid chromatography the percentage composition of the monoturpene fraction was: unidentified components (1.74%), (8.74%) and (0.87%), α-pinene (23.60%), camphene (2.04%), β-pinene (1.74%), mircene (1.09%) and limonene (60.08%).

A comparison of the analyses of etheric oil from black pine and Balkan pine shows considerable differences in the main components. The oil of black pine contains a large proportion of α-pinene, that from Balkan pine l-limonene.

Because of the high content of limonene the etheric oil of Balkan pine could be used as a source of limonene. This hydrocarbon is otherwise obtained by the distillation of *Abies alba* fir cones.

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