

An International Journal of Analytical Chemistry

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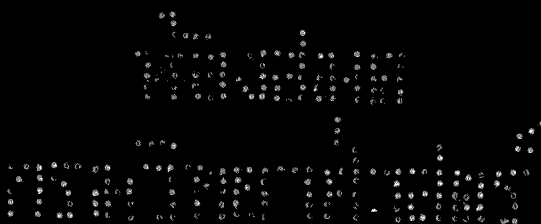
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# Talanta

An International Journal of Analytical Chemistry



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## EFFECT OF PRECIPITATE AND COMPLEX FORMATION ON THE DETERMINATION OF SILVER BY ATOMIC-ABSORPTION SPECTROSCOPY

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**Summary**—In the determination of silver, by atomic-absorption spectroscopy, the presence of small amounts of precipitating agents in the solution to be analysed can result in significant changes in the absorbance at 328.1 nm. The controlling factor is the physical form of the precipitated material. The presence of some complexing agents also causes variable absorption readings, and with ligands such as thiosulphate and cyanide ions the interference can be attributed to secondary reactions associated with the sparingly soluble compounds formed under specific conditions.

MANY interference effects in atomic-absorption studies are considered to arise from variations in the tendency of small solid particles to decompose into atoms. These particles are initially formed in the flame through desolvation of aerosol droplets, their size depending, *inter alia*, on the composition of the solution and the droplet size. Accordingly, a number of investigations have been made of the influence of nebulization factors,<sup>1-4</sup> desolvation rates,<sup>5-7</sup> and thermal stability of the solid residue.<sup>5-13</sup>

Some interference effects disappear on use of high temperature flames, and in these cases it is accepted that the extent of interference is related to the thermal stability of the solid. It is normally assumed that the rate of heat transfer through the ultrafine particles is sufficient to ensure complete volatilization within the selected zone of the flame, although it is recognized that the height of observation above the burner top is extremely important, especially with compounds of low volatility.

The feasibility of introducing finely ground powders directly into the flame has been investigated and it was shown<sup>14</sup> that satisfactory results can be obtained provided that the test samples are diluted with an excess of solid base material.

This approach is somewhat analogous to using a system in which suspended matter is dispersed in an aqueous phase. Such suspensions may arise through precipitate formation during sample dissolution or appear in indirect methods of anion analysis.

In order to elucidate the influence of precipitated matter on radiation absorption, a study has been made of the behaviour of the silver system. This element was chosen because it forms a series of sparingly soluble compounds having properties which are well documented, and because its determination by atomic-absorption spectroscopy is comparatively free from interference problems, even in cool flames.

Other interference effects originate in the initial solution phase. Sastri *et al.*<sup>11</sup> have shown, for example, that where metals form oxides, of high dissociation energy, sensitivity is enhanced if the metals in solution are not bonded to oxygen. In this particular study a change in bond type was achieved through the formation of metallocenes or fluoro complexes. The addition of hydrofluoric acid to the solution

to be analysed is known to enhance the sensitivity of several systems<sup>12,15-17</sup> and the possible role of solution equilibria in relation to some observed interference effects has been outlined by Thomas and Pickering.<sup>17</sup>

Hartlage<sup>18</sup> observed that the addition of ethanolic solutions of amines to transition metal solutions could result in decreased absorption and it was suggested that the interference effect might be caused by the formation of metal amine complexes which do not dissociate at the temperatures of the flames used (air-acetylene and nitrous oxide-acetylene).

Since these effects could be more general, a study of the influence of complexing agents on the atomic absorption of silver solutions was included in the investigation.

## EXPERIMENTAL

### *Reagents*

Analytical reagent grade chemicals and demineralized water were used to prepare standard solutions (molarity shown in Tables I and II) of silver nitrate, sodium chloride, potassium bromide, sodium iodide, potassium thiocyanate, sodium sulphide, sodium hydroxide, ammonia, methylamine, ethylenediamine, sodium salt of ethylenediaminetetra-acetic acid, sodium sulphite, sodium thio-sulphate, sodium cyanide and thiourea.

### *Apparatus*

The output from a Techtron Model AA-3 Atomic Absorption Spectrophotometer was fed to a Riken-Denshi SP-G3 recorder to permit monitoring of radiation absorption over a period of time.

Absorption measurements were based on the 328.1 nm emission line derived from a silver hollow-cathode lamp run at 4 mA. The slitwidth was fixed at 250  $\mu\text{m}$ , which yielded a half-intensity bandwidth of 0.7 nm.

The 0.10-m flat-top burner was fed either by an air-coal gas or air-acetylene mixture. The air pressure in both cases was 72 kN/m<sup>2</sup> (15 lb/in.<sup>2</sup>) (flow-rate, 6.2 l./min) while the rotameter settings adopted were 2.5 for coal gas and 1.5 for acetylene (corresponding to 1.0 and 1.3 l./min respectively).

### *Procedure*

Standard silver nitrate solutions were prepared by adding appropriate aliquots of a stock solution to clean volumetric flasks. Varying amounts of solutions containing precipitating or complexing agents were then added to these flasks before final dilution to the mark. In some cases, two drops of a 1% gelatin or gum arabic solution were added to help stabilize the colloids formed. The concentration ranges studied are summarized in Tables I and II.

For each study at least three control solutions (*i.e.*, no precipitant or added ligands) were included in the series and the absorbance of the test solutions was compared with that of these controls. All solutions were aspirated for a period of at least one minute, and the stability of experimental conditions was checked by random insertion of the controls. The uptake rate was similar for all solutions, *viz.* 7 ml/min.

The effect of burner height was investigated, but most measurements were made with the burner top 6 mm below the centre of the lamp beam.

Repetitive tests with standard solutions showed that the reproducibility of the absorbance readings was better than  $\pm 1\%$ , hence test deviations greater than this were considered to be significant. With the sample concentrations used, an absorbance change of 1% corresponds to a variation of about 3% in apparent silver content.

## RESULTS AND DISCUSSION

The decreases in absorbance observed in these investigations (Figs. 1-9) can be attributed to

- (i) reduced uptake rates into the flame;
- (ii) physical exclusion of precipitated material (*i.e.*, solid matter is not drawn into the capillary tube or is left in the nebulizer chamber);
- (iii) incomplete conversion of suspended solids into gaseous atoms;

TABLE I.—EXPERIMENTAL CONDITIONS USED IN PRECIPITATION STUDY

[Ag <sup>+</sup> ] 10 <sup>-5</sup> M	Precipitating ion added	Concentration of added solution 10 <sup>-3</sup> M	Concentration of additive in final solution 10 <sup>-6</sup> M	Comments
3.7	Cl <sup>-</sup>	1.85	3.7-740	White precipitate visible in solutions where added concentration < 5 × 10 <sup>-5</sup> M
3.7	Br <sup>-</sup>	1.85	7.4-740	White precipitate visible in solutions where added concentration < 5 × 10 <sup>-5</sup> M
3.7	I <sup>-</sup>	0.925	3.7-740	White precipitate visible in solutions where added concentration < 5 × 10 <sup>-5</sup> M
3.7	SCN <sup>-</sup>	1.85	7.4-740	White precipitate visible in all solutions
1.85	S <sup>2-</sup>	1.85	7.4-1110	Yellow-brown colour visible in most solutions
3.7	S <sup>2-</sup>	1.85	7.4-1110	
3.7	OH <sup>-</sup>	3.25	3.25-1630	All solutions appeared clear
1-8.98	OH <sup>-</sup>	0.1	310	All solutions appeared clear
0.92-9.25	OH <sup>-</sup>	0.185	584	All solutions appeared clear
0.55-9.99	OH <sup>-</sup>	0.185	1324	High mole-ratio solutions contained visible dark precipitate on standing

TABLE II.—EXPERIMENTAL CONDITIONS USED IN COMPLEX FORMATION STUDY

[Ag <sup>+</sup> ] 10 <sup>-5</sup> M	Complexing agent added	Concentration of added solution, 10 <sup>-3</sup> M	Concentration of additive in final solution, 10 <sup>-6</sup> M	Comments
3.7	NH <sub>3</sub>	7.40	3.70-1850	Clear solutions
3.7	CH <sub>3</sub> NH <sub>2</sub>	7.40	7.40-3700	Clear solutions
3.7	H <sub>2</sub> NCH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub>	3.70	1.85-1850	Clear solutions
3.7	EDTA	3.70	1.85-1850	Clear solutions
3.7	SO <sub>3</sub> <sup>2-</sup>	3.70	3.7-1850	Clear solutions
1.85	S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>	0.60	1.19-677	Yellow-brown colour visible at mole-ratios less than about 6:1
3.7				
3.7	H <sub>2</sub> N—C—NH <sub>2</sub>    S	3.70	7.40-1850	Light brown colour visible at mole-ratios less than about 3:1. Thin dark film on sides of some flasks
1.85	CN <sup>-</sup>	3.70	3.7-1850	White precipitate visible at mole-ratios less than about 2:1
3.70				
5.55				

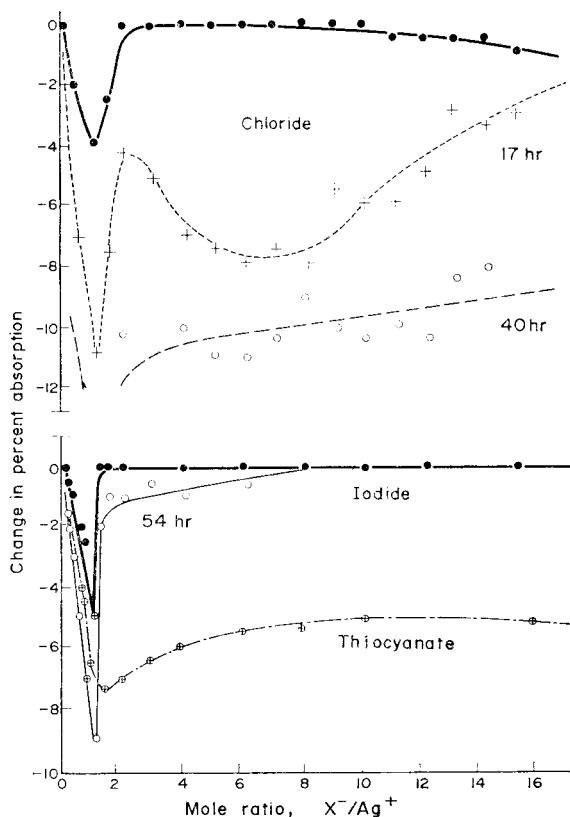


FIG. 1.—Comparison of the behaviour of silver solutions containing varying amounts of precipitating agents. The dotted lines in the chloride and iodide segments show the variation observed on allowing the solutions to stand for different periods of time.

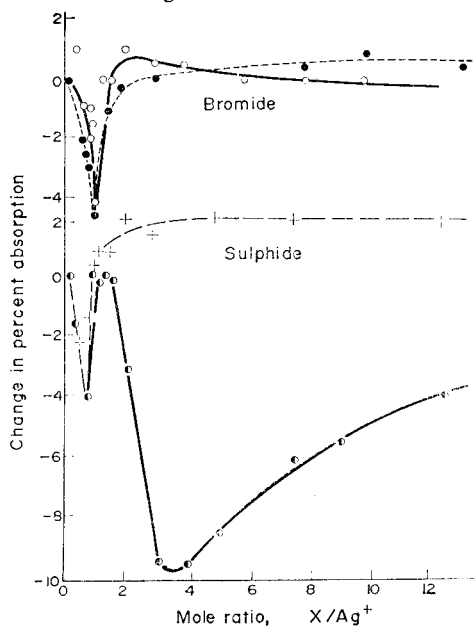


FIG. 2.—Interference effects observed when bromide or sulphide ions were added to silver solutions.  
Full lines—air, coal gas flame; dotted lines—air, acetylene flame.



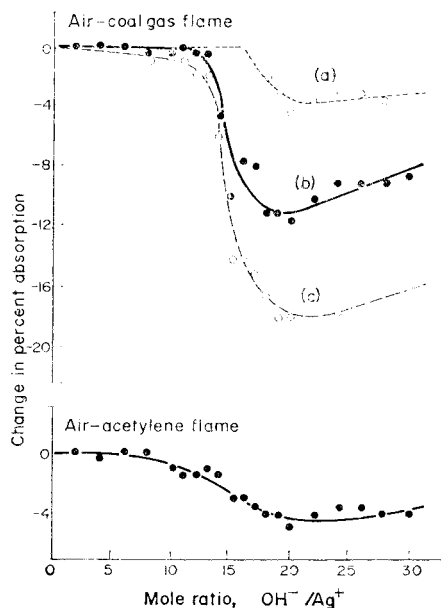


FIG. 3.—Curves showing the effect of added hydroxide ions and flame stoichiometry on the absorption of a silver solution.

Air, coal gas flame: (a) fuel-lean, (b) normal, (c) fuel-rich,

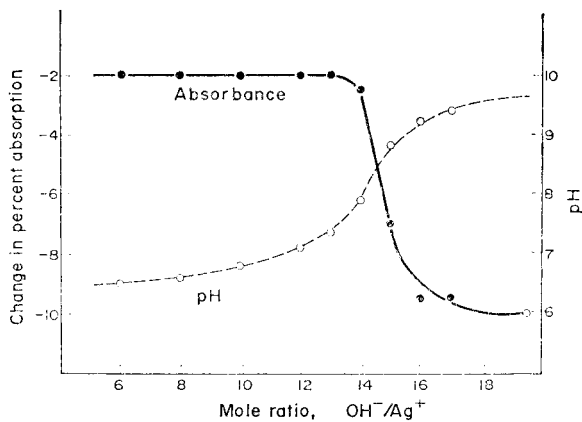


FIG. 4.—Graph showing the relationship between the pH of the test solution and the observed change in atomic absorbance of silver solutions containing added hydroxide ions.

- (iv) incomplete dissociation of stable complexes or polymerized species;
- (v) changes in non-specific absorption or flame background absorption;
- (vi) a combination of two or more of these effects.

Comparison tests with precipitant and ligand solutions indicated that spectral effects (v) were insignificant and uptake rates (i) varied little from solution to solution, except where larger particles caused temporary blockage of the capillary. The presence of these larger particles was made apparent by irregular fluctuations on the chart record and occurred mainly in conditions corresponding to the sharp absorbance

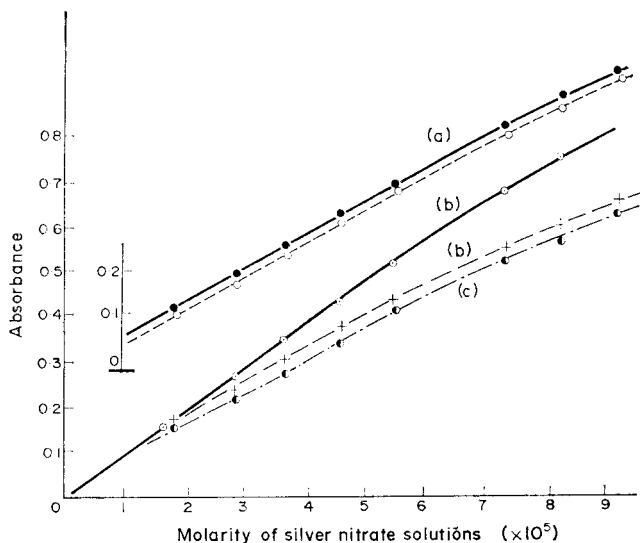


FIG. 5.—Curves showing the effect of hydroxide ion on the absorbance of silver solutions.  
Full lines—no hydroxide present; dotted lines—initial hydroxide concentration  $5.8 \times 10^{-5}M$ ; (a) air, acetylene flame; (b) air, coal gas flame; (c) air, coal gas—fuel-rich.

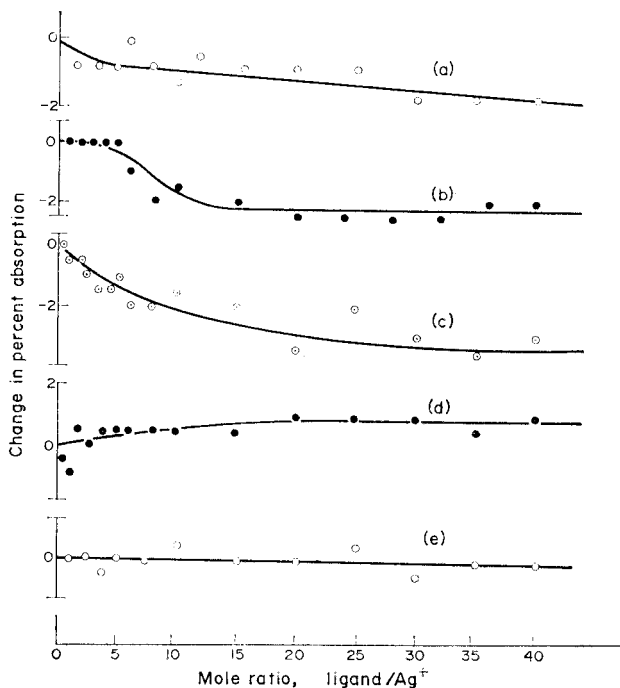


FIG. 6.—Comparison of the behaviour of silver solutions containing varying amounts of complexing agents using an air-coal gas flame: (a) ammonia; (b) methylamine; (c) ethylenediamine; (d) EDTA; (e) sulphite.

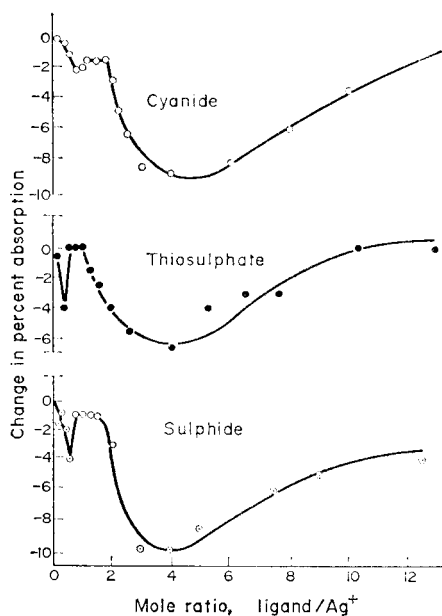


FIG. 7.—Comparison of the effects observed when varying amounts of cyanide, thio-sulphate or sulphide ion are added to  $3.7 \times 10^{-5} M$  silver nitrate solutions. Air, coal gas flame.

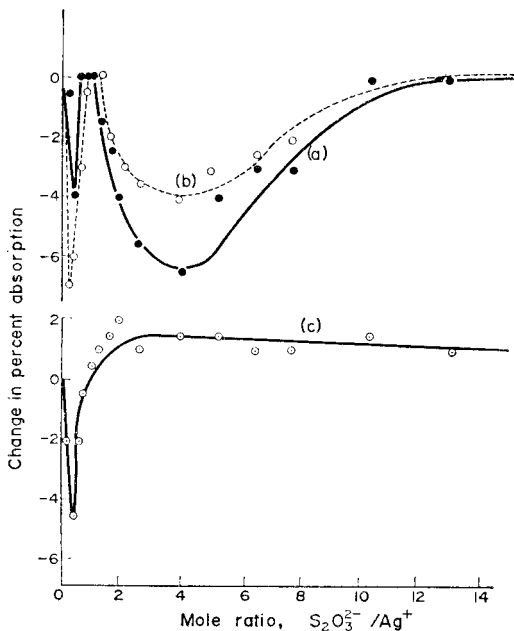


FIG. 8.—Comparison of the behaviour of silver solutions containing varying amounts of sodium thiosulphate. (a) Air-coal gas flame, freshly prepared solutions; (b) air-coal gas flame, solutions retained for 50 hr; (c) air-acetylene flame, freshly prepared solutions.

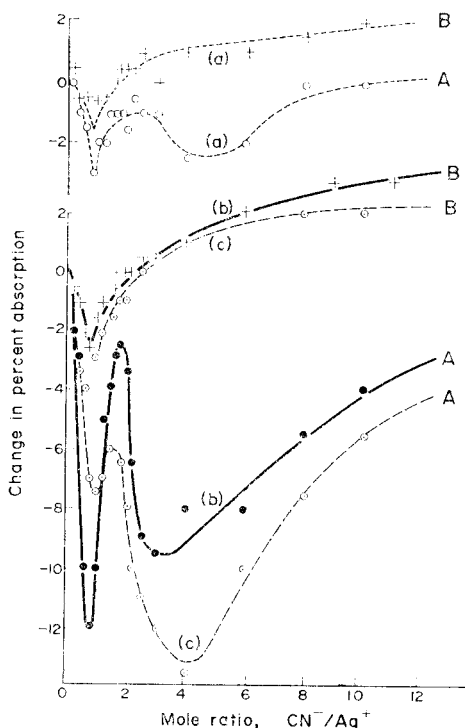


FIG. 9.—Graphs showing the effect of sodium cyanide additions on the behaviour of silver solutions in (A) air-coal gas flames and (B) air-acetylene flames. Silver solutions (a)  $1.85 \times 10^{-5}M$ ; (b)  $3.70 \times 10^{-5}M$ ; and (c)  $5.55 \times 10^{-5}M$ .

peaks (*cf.* Figs. 1, 2, 7–9). Many of the colloidal suspensions gave results similar to the control standards, hence it may be concluded that the efficiency of the nebulization process is not significantly altered by the presence of a true colloidal suspension.

Thermal effects (*iii* and *iv*) should be less significant in higher temperature flames and it can be observed from Figs. 2, 5, 8 and 9 that the substitution of acetylene for coal gas as the fuel component caused the virtual elimination of several interference effects.

The hotter flame, however, did not eliminate all the interference effects and it can be argued that the remaining effects are caused by physical exclusion of flocculated particles from the flame. The degree of coagulation of colloidal suspensions tends to vary from system to system, because of differences in the adsorption of preferred ions, and can be time-dependent.

Consider the behaviour of the halide and thiocyanate systems (Figs. 1 and 2). The particles initially formed are of colloidal dimensions, but where the initial silver ion concentration exceeds the added precipitant ion concentration, silver ions become incorporated in the Stern layer. This leads to a lowering of repulsive forces between particles, so favouring flocculation. After the 1:1 stoichiometric point, the specific adsorption of negative ions acts to maintain the sol as a stable dispersion.

Studies of the adsorption of surplus ions by silver halides and thiocyanate<sup>19</sup> have shown that although AgBr and AgSCN have about the same solubility, the negative AgSCN sol has a much smaller adsorption affinity for the thiocyanate ion than the

AgBr has for the bromide ion. This difference in behaviour is reflected in the atomic-absorption studies. Owing to the meagre adsorption of thiocyanate ions, the AgSCN floc does not disperse readily in the presence of excess of anion and the physical loss remains high. In contrast, the halide systems are sufficiently dispersed in the presence of excess of anion to yield normal absorbance values.

In the sulphide, thiosulphate and cyanide systems (Figs. 7–9), decreases in absorbance at low anion:silver ion ratios can also be attributed to the formation, in the solution to be nebulized, of colloidal flocs. It is interesting to note that in the case of iodide, cyanide and sulphide precipitates, the coagulating effect of excess of silver ions could be inhibited by adding gum arabic as a protective colloid.

With the low concentration of reactants employed, a large excess of chloride ion is required to achieve complete precipitation of the silver ion, and equilibrium is slowly achieved, as indicated by the time effect recorded in Fig. 1. With the less soluble silver iodide, time effects are less marked and the absorption peak is much sharper.

The influence of precipitate solubility is most clearly marked in the silver-hydroxide ion system (as shown in Fig. 3). In this case a large excess of hydroxide ion has to be present to cause any significant effect. The reduction in absorbance changes slightly with time but varies little with height of observation in the flame.

Measurement of the pH of the solutions yielded the results recorded in Fig. 4, and from this it can be suggested that the depression effect coincides with the formation of some species in solution at mole ratios  $> 13:1$ . If this ratio represents onset of precipitation and if the species formed is AgOH, the solubility product is given by  $[Ag^+][OH^-]$  or  $(3.7 \times 10^{-5})(4.8 \times 10^{-4})$ . This gives an experimental value of about  $1.8 \times 10^{-8}$  mole<sup>2</sup>/l.<sup>2</sup> which compares favourably with the value of  $1.7 \times 10^{-8}$  quoted<sup>20</sup> in the literature. The validity of this interpretation was tested by adding varying amounts of silver ion to a solution of fixed hydroxide ion concentration. The results obtained with use of an air-coal gas flame are summarized in Fig. 5. The product of the reactant concentrations corresponding to the apparent onset of interference (intersection point) equals  $0.9 \times 10^{-8}$  mole<sup>2</sup>/l.<sup>2</sup> which is again of the order expected if AgOH precipitation is responsible for the change. Silver hydroxide is unstable, and decomposes rapidly to yield Ag<sub>2</sub>O and H<sub>2</sub>O, hence the solid phase actually entering the flame is more likely to be the oxide rather than the hydroxide.

The interference effects shown in Figs. 3 and 5 virtually disappeared if air-acetylene flames were used. The need for a hot flame was unexpected since Ag<sub>2</sub>O readily decomposes on heating, its standard heat of formation being nearly an order of magnitude less than those for most common silver compounds. This suggests that the lower concentration of silver atoms in the flame arises from kinetic effects rather than from high thermal stability.

Three factors which may be important are the size of the particle, efficiency of heat transfer, and the heat of vaporization of molten silver particles. The latter has a value of about 280 kJ/mole and to assess the importance of this factor, the absorbance of a series of solutions containing silver metal sols was determined. The readings recorded were slightly less than those observed with corresponding silver nitrate standards but the effect was not large enough to explain the interference observed in the silver-hydroxide system.

The variations in absorbance induced by the presence of complexing agents in the silver solution are summarized in Figs. 6–9. It may be observed from Fig. 6 that the

presence of sulphite and EDTA ions produced no observable effect, while the presence of amines had a small influence on the absorption signal.

At 25° the  $\beta_2$  values for the silver complexes formed with ammonia, methylamine and ethylenediamine are  $10^{7.2}$ ,  $10^{6.8}$  and  $10^{7.7}$  l.<sup>2</sup>/mole<sup>2</sup> respectively. With stability constants of this order a tenfold excess of ligand is required to convert half the metal into the complex form AB<sub>2</sub>, and a much larger excess is needed to ensure a predominance of the complex form. The decrease observed with molar ratios of 30 or 40:1 may therefore represent an effect similar to that recorded by Hartlage.<sup>18</sup> The substitution of an air-acetylene flame for the coal gas flame slightly diminished the apparent interference but the cause of the effect is not necessarily solely thermal stability of the complex, since the addition of the organic reagents will alter slightly both the solution viscosity (*i.e.*, nebulizer effects) and flame chemistry. Excess of thiourea, which reacts with silver ions to form soluble complex ions of the type  $\text{Ag}[\text{SC}(\text{NH}_2)_2]_x^+$  (where  $x = 2, 3, 4$ ) also had no significant effect on the magnitude of the absorption signal, although small amounts of this compound (*e.g.* mole ratios of < 3:1) yielded variable results, owing to the deposition of some of the silver as a precipitate on the flask walls.

The type of behaviour observed when varying amounts of thiosulphate or cyanide ions were added to the silver solutions is clearly shown in Fig. 7. The second or larger valley could be eliminated by using a hotter flame (*cf.* Fig. 8) hence it may be concluded that it is because of the formation of a species of reasonable thermal stability. The nature of this second species is somewhat difficult to postulate.

As noted in Table II, the addition of sodium thiosulphate to silver nitrate solutions yielded yellow-brown colloidal suspensions in all cases where the mole ratio ( $\text{S}_2\text{O}_3^{2-}/\text{Ag}^+$ ) was less than 6:1. Positive identification of the sol was not attempted, since it could be  $\text{Ag}_2\text{S}_2\text{O}_3$  (which hydrolyses to  $\text{Ag}_2\text{S}$ ) or  $\text{NaAgS}_2\text{O}_3$  or a combination of all three compounds.

In the presence of excess of thiosulphate, silver is reported<sup>21,22</sup> to form several thiosulphate complexes, the actual nature depending upon the relative concentrations of silver and thiosulphate ions. With mole ratios above 5:1 the predominant species is  $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$ . Reference to Figs. 7 and 8 shows that in coal gas flames signal depression becomes less with increasing excess of thiosulphate or time of standing, hence it is unlikely that  $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$  is responsible for the reduced concentration of silver atoms in the flame. Subsequent tests with other initial silver concentrations confirmed that the maximum effect corresponds to a mole ratio of about 4:1. In this respect, the behaviour of the thiosulphate system resembles that observed for silver sulphide systems (*cf.* Figs. 2 and 7).

One explanation for the position of the maximum interference effect is four co-ordination of silver, and this idea is supported by the observation that silver exhibits a co-ordination number of four in some species, including the ion  $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$ .

Alternatively, on desolvation of the nebulized solution in the flame the solid species formed could be one of the double salts described in the phase-rule study by Basset and Lemon.<sup>23</sup> It was found that at 25° the system  $\text{Na}_2\text{S}_2\text{O}_3\text{-Ag}_2\text{S}_2\text{O}_3\text{-H}_2\text{O}$  yields a series of solid phases or double salts, the composition changing with increasing  $\text{Na}_2\text{S}_2\text{O}_3:\text{Ag}_2\text{S}_2\text{O}_3$  ratios.

The validity of these explanations is challenged by the results obtained in the presence of cyanide ions (Fig. 9). The addition of gum arabic to this system eliminated

both interference effects, that is, it stabilized the  $\text{Ag}[\text{Ag}(\text{CN})_2]$  sol and served to eliminate the larger effect centred on mole ratios of about 4:1. Gum arabic had a similar (if not quite as effective) influence on the silver-thiosulphate system. This suggests that the interference effect arises from colloidal aggregates which are small enough to be effectively dispersed in the nebulizer unit, but large enough to create heat transfer problems. While this hypothesis is attractive, it conflicts with the known stability of the complex anion  $[\text{Ag}(\text{CN})_2]^-$ . On the basis of equilibrium calculations this species should predominate at all mole ratios greater than two.

### CONCLUSIONS

Several points of practical significance become apparent from this study.

(i) The formation of a precipitate in aqueous solution does not necessarily prevent the determination of the precipitated element by atomic-absorption spectroscopy. However, to prevent mechanical loss of material at the nebulization stage, the particle size should approach colloidal dimensions.

(ii) For solids of low thermal stability and limited solubility, it could prove convenient to introduce finely ground material directly into the flame as an aqueous suspension. The degree of atom formation may depend, however, on factors other than thermal stability, *e.g.*, particle size, thermal conductance, flame composition *etc* and careful calibration will be essential. This approach has been recently used for the determination of tin.<sup>24</sup>

(iii) In screening systems for interference effects, false impressions may be gained by making single tests with excess of interferent ion. The results recorded in this paper clearly demonstrate that the absorbance observed can vary widely over a range of mole ratios of reactants.

(iv) Because of the comparatively low thermal stability of most silver compounds, complex formation should have little effect on the absorbance of silver solutions. However, where insoluble intermediates can be formed, the effects of colloidal aggregates can persist even though calculations show that soluble complex species should predominate. From the behaviour of the silver system with several ligands (sulphide, thiosulphate and cyanide) it may be proposed that some polymolecular species in which the mean ratio of ligand to silver is about 4:1 is formed. The existence of such a species has not been predicted from solution studies, hence one could suggest that the use of atomic absorption in conjunction with a cool flame provides a technique which may prove useful for detecting odd solution phenomena.

**Zusammenfassung**—Bei der Bestimmung von Silber durch Atom-absorptions-Spektralanalyse kann die Gegenwart kleiner Mengen von fallenden Reagentien in der Analysenlösung beträchtliche Änderungen in der Extinktion bei 328.1 nm hervorrufen. Wesentlicher Faktor ist die physikalische Form des ausgefällten Materials. Die Gegenwart einiger Komplexbildner verursacht ebenfalls veränderliche Extinktionswerte. Mit Liganden wie Thiosulfat- und Cyanidionen kann man die Störung auf Sekundärreaktionen zurückführen, die mit den unter den jeweiligen Bedingungen gebildeten schwerlöslichen Verbindungen zusammenhängen.

**Résumé**—Dans le dosage de l'argent, par spectroscopie d'absorption atomique, la présence de petites quantités d'agents de précipitation dans la solution à analyser peut avoir pour résultat des changements importants dans l'absorption à 328,1 nm. Le facteur prédominant est la

forme physique de la matière précipitée. La présence de quelques agents complexants cause aussi des lectures d'absorption variables, et avec des ligands tels que les ions hyposulfite et cyanure, on peut attribuer l'interférence à des réactions secondaires associées aux composés faiblement solubles formés dans des conditions spécifiques.

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## CHROMATOGRAPHIC SEPARATION OF COPPER WITH AN $\alpha$ -HYDROXYOXIME\*

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**Summary**—Two aliphatic  $\alpha$ -hydroxyoximes have been synthesized and characterized. These reagents are highly selective for the extraction of copper(II) from weakly acidic aqueous solution. A column containing a hydroxyoxime on a solid support effects a quantitative separation of copper(II) from most other metal ions.

SEPARATION of metal ions by reversed-phase chromatography is a useful procedure when an organic substrate is available that will retain only a limited number of metal ions. The  $\alpha$ -hydroxyoximes appear to have this specificity for copper(II).

$\alpha$ -Benzoinoxime was introduced in 1923 by Feigl<sup>1,2</sup> and Strebinger<sup>3</sup> for the micro-determination of copper in ammoniacal solutions. Azzalin<sup>4</sup> and Shik<sup>5</sup> improved the initial method. They reported interference from small amounts of iron, aluminium, lead, tin and zinc in the copper determination. Langer<sup>6</sup> used  $\alpha$ -benzoinoxime in the amperometric titration of copper and reported an interference by small amounts of nickel.

The use of aliphatic  $\alpha$ -hydroxyoximes for copper was not stressed until 1965 when Swanson<sup>7,8</sup> reported that these oximes selectively extracted copper(II) from acidic liquors in the leaching of low grade ores. His work applied specifically to the recovery of copper on an industrial scale. The conditions reported in these patents are not necessarily those required for quantitative removal of copper from analytical samples in the laboratory. In the industrial process the organic solution can be recycled through the process without being completely stripped of its copper content.

A liquid for large-scale copper recovery is now marketed by General Mills under the name LIX-64. The composition of this material has been kept secret by the manufacturer. Cerrai and Ghersini<sup>9</sup> did some analytical work with LIX-64 and speculated that it was a mixture of substituted hydroxybenzophenone oximes and 5, 8-diethyl-7-hydroxy-6-dodecanone oxime. They employed a column containing LIX-64 on a solid support to separate copper(II) from five other metal ions. With a 0.5 M ammonium sulphate eluent considerable tailing was observed with iron(III), manganese(II), chromium(III) and vanadium(IV). Except for iron(III), the use of 0.5 M ammonium chloride reduced this tailing. Ammonium hydrogen fluoride was finally used to complex iron(III) and eliminate its tailing.

Two samples of LIX-64 examined in our laboratory had different copper(II) capacities and somewhat different physical properties. Fractionation under reduced pressure and gas chromatographic analysis indicated the presence of at least 9 different constituents. We separated copper(II) quantitatively from several other metal ions, using a column packed with LIX-64 on a solid support. However, because of the impure nature of LIX-64 and the uncertainty regarding its composition, it was

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decided to synthesize pure  $\alpha$ -hydroxyoximes, to characterize them, and to evaluate them for the quantitative chromatographic separation of copper(II) from other metal ions.

## EXPERIMENTAL

### Apparatus

A Bausch and Lomb spectrophotometer was used for all spectrophotometric measurements. A VOM-8 recorder and a 10-mm Bausch and Lomb flow-through cell were used in the continuous monitoring of the vanadium-copper separation.

A Nuclear Chicago anti-walk, single-channel analyser, model 27352 spectrometer was used to isolate gamma radiation in all radiometric analysis. A Nuclear Chicago decade scaler, model 27104, was used to count the emissions from the spectrometer. The detector was a  $75 \times 75$  mm NaI scintillation crystal.

The chromatographic columns were made in 9-mm glass tubing. The top of the tube was enlarged to 15 mm to provide a reservoir for the eluent. The bottom of the tube was restricted to 2 mm to provide control for the effluent flow.

### Reagents and solutions

All solvents, eluents and metal salts were of analytical reagent grade quality obtained from our laboratory stock. All radioactive isotopes except  $^{113}\text{Sn}$  were made in the Ames Laboratory Research Reactor. The  $^{113}\text{Sn}$  was obtained from the Ames Laboratory stock of commercial isotopes.

A sodium acetate-acetic acid solution (pH 5) was used as an eluent in all column separations. This solution was equilibrated with toluene by shaking in a separatory funnel and separating the layers. The organic solutions used in the batch extractions were the same as the column eluent except for the adjustment of the pH.

The 0.05M solutions of most metals were made by dissolving appropriate metal salts in distilled water. Tartaric acid was added to the antimony, tin, titanium and tungsten sample solutions to prevent hydrolysis at a pH of 5. Tartaric acid was also added to the iron solution to minimize tailing during the column separations and increase its velocity through the column bed.

### Synthesis of the $\alpha$ -hydroxyoximes

The 10-hydroxyicosan-9-one (I) and 5,8-diethyl-7-hydroxydodecan-6-one (II) needed for the synthesis of the  $\alpha$ -hydroxyoximes were prepared according to the procedure of Hansley.<sup>10</sup> I was purified by crystallization from acetone (m.p.  $51^\circ$ ) and II was purified by vacuum distillation (b.p.  $110$ – $115^\circ$  at 0.06 mbar). The methyl esters used in the preparation of the  $\alpha$ -hydroxyketones were prepared by the procedure of Vogel.<sup>11</sup>

The  $\alpha$ -hydroxyoximes were prepared by a procedure similar to that of Swanson.<sup>8</sup> A mixture of 0.2 mole of the  $\alpha$ -hydroxyketone, 0.4 mole of hydroxylamine hydrochloride, 125 ml of pyridine and 125 ml of absolute ethanol were refluxed for 3 hr. The reaction mixture was cooled, diluted with about 500 ml of water and extracted with ether. The aqueous layer was discarded. The ether layer was washed 4 times with water, twice with 3% hydrochloric acid and 4 more times with water. The ether layer was dried and the ether removed by evaporation.

Two products were isolated from the residue obtained from the oximation of I. The residue from the ether evaporation step was dissolved in petroleum ether and cooled in an ice-bath. The solid compound had an analysis of C, 70.7%; H, 11.6%; N, 8.1% [calculated C, 70.54%; H, 11.84%; N, 8.28% for 9,10-eicosandionedioxime, (EDO)]. The NMR spectrum showed a triplet at  $\delta$  1.08, a broad singlet at  $\delta$  1.64 and a singlet at  $\delta$  4.42. The proton integration of these peaks gave a ratio of 6:32:2. The melting point was  $151$ – $2^\circ$ . This *vic*-dioxime was a result of the oximation of the *vic*-diketone by-product of the acyloin condensation.<sup>12</sup>

Further cooling of the residue in a "dry-ice"-acetone bath yielded a solid compound having an analysis of C, 73.3%; H, 12.2%; N, 4.0% [calculated C, 73.56%; H, 12.34%; and N, 4.29% for 10-hydroxyicosan-9-oxime (HEO)]. The NMR spectrum had a triplet at  $\delta$  1.08, a broad singlet at  $\delta$  1.61, a singlet at  $\delta$  3.96 and a broad singlet at  $\delta$  4.46. The proton integration of these peaks showed a ratio of 6:33:1:1. The melting point was  $48$ – $9^\circ$ .

Purification of the oximation product from II was obtained by the distillation of the residue from the ether evaporation step. The product, 5,8-diethyl-7-hydroxydodecan-6-oxime (DHDO), was a viscous liquid having a boiling point of  $133$ – $4^\circ$  at 0.03 mbar. The analysis was C, 70.7%; H, 12.2%; N, 5.2% (calculated C, 70.80%; H, 12.25%; and N, 5.16% for DHDO). The NMR spectrum had a triplet at  $\delta$  1.08, a quintet at  $\delta$  1.64, a broad singlet at  $\delta$  2.84, and a sharp singlet at  $\delta$  4.98. The proton integration of these peaks gave a ratio of 12:19:1:1. The peak at  $\delta$  1.64 is due to the superimposing of the 16-methylene hydrogens upon the 3 methine hydrogens. This explains the additional splitting within the peak.

### Analytical methods

Palladium was determined by the absorbance of the yellow chloride complex at 290 nm. Molybdenum was determined by the absorbance of the yellow complex formed with thiolactic acid, measured at 330 nm. Trace amounts of copper were determined by the absorbance of the bathocuproine complex, measured at 479 nm.<sup>13</sup>

Chromium, silver, antimony, tungsten, uranium and tin were determined by the gamma emissions from their radioactive isotopes as compared to the background radiation. All other ions, including the larger amounts of copper were determined by standard EDTA titration procedures.<sup>14</sup>

### Paper chromatography

Whatman No. 1 chromatographic paper was impregnated with the oxime by dipping it into a 10% toluene solution of the oxime. After the paper had been air-dried, spots of the metal ions were placed 25 mm from the bottom edge of the paper.

After elution with the acetate or tartrate buffer solution of desired pH, the position of the metals was determined by spraying with either a 50% solution of ammonium polysulphide or a 0.1% ammoniacal solution of alizarin.

$R_f$  values were calculated, using the centre of the spots as reference.

### Column preparation

Amberlyst XAD-2, an inert styrene-divinylbenzene, macroreticular resin was obtained from the Rohm and Haas Chemical Company. The beads were ground and sieved to obtain an 80–100-mesh fraction. The support was back-washed to remove any adhering fines, washed with 6M hydrochloric acid, water and acetone, and air-dried before use. The XAD-2 support (1.50 g) was slurried in water, poured into the glass columns (9 × 62 mm) and retained by a glass-wool plug. The column was gently tapped while the excess of liquid drained from the bed. This aided the settling of the resin. A small plug of glass-wool was placed on top of the resin bed to hold it in place.

A 20% w/w solution of the oxime in toluene (0.64M DHDO or 0.54M HEO) was passed through the column to replace the water. The column was allowed to equilibrate for at least 1 hr before flushing the excess of toluene solution with water. From 8 to 10 column volumes of the acetate eluent were flushed through the column bed to prepare it for the separation step.

### Separation procedure

A known amount of each metal ion to be separated was mixed in the reservoir above the resin bed and allowed to drain onto the column. The sides of the reservoir were rinsed with 1–2 ml of the acetate eluent (pH 5). When this had drained onto the column, the sample was eluted with the required amount of acetate solution at a flow-rate of 4–5 ml/min. All metals except copper, palladium and silver were eluted with the acetate solution. Copper was then stripped from the column with 30 ml of 6M hydrochloric acid.

In the palladium-copper separation, the resin bed was equilibrated with 0.1M sulphuric acid instead of the acetate buffer solution. The copper was eluted first with the 0.1M acid while the palladium was retained by the oxime substrate. The palladium was then eluted with 6M hydrochloric acid as the yellow chloride complex. Gold and molybdenum also appear to be retained by the oxime when 0.1M sulphuric acid is used as the eluent.

### Isolation of copper from National Bureau of Standard samples

Sample no. 124-d, a high copper (83.60%) low tin (4.56%) alloy was dissolved in *aqua regia*. Tartrate solution was added to prevent the interference of tin. Sodium hydroxide (1M) was added until the solution turned dark blue (pH 5.2). An aliquot was placed on a column of 20% (w/w) DHDO where the copper was separated from all other metals by the procedure described previously.

Sample no. 54-d, a high tin (88.57%) low copper (3.62%) was treated as above except that hydrofluoric acid was used to prevent the interference of tin. Tartrate solutions did not prevent this interference at high concentration of tin.

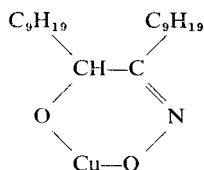
### Distribution ratios

A 5-ml portion of toluene containing a known amount of oxime was shaken in a closed tube for 1 hr with 5 ml of a buffered aqueous phase containing a known amount of copper(II). The copper(II) remaining in the aqueous phase was determined and the distribution ratio,  $D$ , calculated.

## RESULTS AND DISCUSSION

*Characterization of copper(II)-oxime complexes*

Extraction of copper(II) in aqueous solution with solid HEO dissolved in toluene produces a green complex in the organic layer. A plot of  $\log D$  as a function of oxime concentration results in a straight line with a slope of 0.98. This indicates that a 1:1 HEO-copper complex is formed. A plot of  $\log D$  vs.  $\log$  of hydrogen ion concentration yields a straight line with a slope of 1.96, representing the loss of 2 protons during the formation of the complex. The lack of NMR peaks at  $\delta$  3.96 and  $\delta$  4.46 indicates a loss of the oxime and hydroxyl protons, respectively, in the formation of the copper complex. The lack of absorption peaks in the 3200–3400  $\text{cm}^{-1}$  infrared region confirms this. From these data the probable structure of the HEO-copper complex is as follows:



Extraction of copper(II) with DHDO in toluene produces two complexes; at oxime concentrations below 0.1M a green complex is formed, and a brown complex is produced at higher oxime concentrations. The green complex gives a slope of close to 1.0 when  $\log D$  is plotted against  $\log$  oxime concentration (Fig. 1), and a slope of 2.0 when  $\log D$  is plotted against  $\log$  hydrogen ion concentration. The NMR spectrum shows no hydroxyl or oxime proton peaks at  $\delta$  2.87 and  $\delta$  4.42, respectively, and the

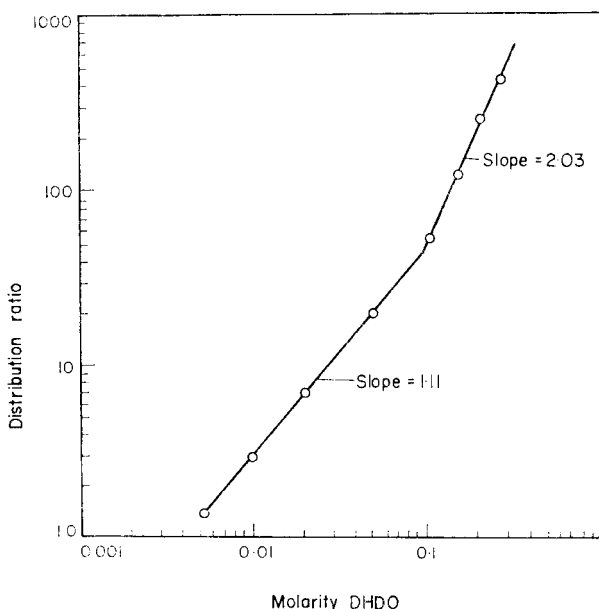
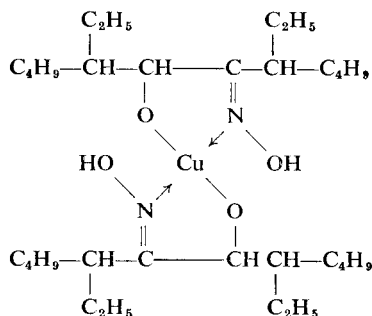


FIG. 1.—The distribution ratio of copper(II) extracted from an acetate solution (pH 4) as a function of the concentration of DHDO in the organic phase.

infrared spectrum substantiates this loss. Thus the green DHDO-copper complex appears to be a 1:1 complex analogous in structure to the green HEO-copper complex.

The brown complex exhibits a slope of approximately 2.0 when  $\log D$  is plotted against  $\log$  oxime concentration (Fig. 3), indicating a 2:1 DHDO-copper complex. The NMR spectrum shows the presence of an oxime hydrogen peak at  $\delta$  2.48 but no hydroxyl hydrogen peak at  $\delta$  4.49. A structure that is consistent with these data is as follows:



### Paper chromatography

Paper chromatography, using paper impregnated with HEO or DHDO, was used to screen the behaviour of a number of metal ions. The results are summarized in Fig. 2. A low  $R_f$  value indicates that the metal ion is complexed by the oxime and would be extracted or retained by the substrate on a chromatographic column.

Iron(III) showed tailing which was eliminated by incorporating tartrate in the eluent. Copper(II), palladium(II), and gold(III) showed strong retention by both oximes. Silver(I) was retained by DHDO but not by HEO, and titanium(IV) was slightly retained by DHDO. Palladium(II) and gold(III) are retained at more acidic pH values than copper(II).

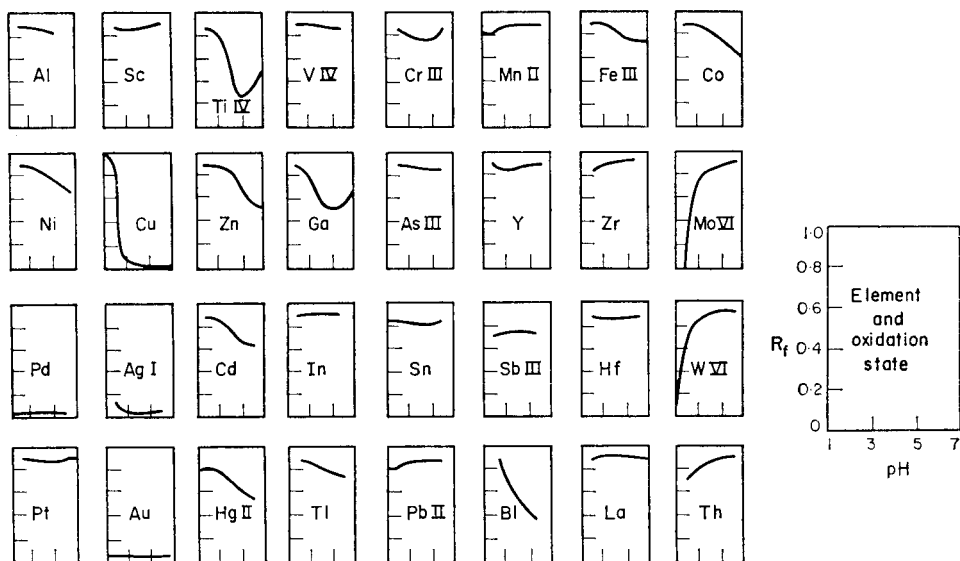


FIG. 2.—The chromatographic behaviour of metal ions on paper impregnated with DHDO.

*Column separations*

From the data for effect of acidity on log *D* an eluent of pH 5 was selected for the separation of copper(II). On a column of HEO, copper was successfully separated from 18 other metal ions with an average recovery of 99.9% for copper and 99.8% for the other metal ions. By using a column of DHDO on a solid support, copper was also separated from the same metal ions except titanium(IV). The average recovery was 99.9% for copper and 99.6% for the other metal ions. Data for individual separations on the DHDO column are given in Table I.

TABLE I.—SEPARATION OF COPPER FROM AQUEOUS SOLUTIONS OF METALS\*

Ion A, <i>mmole</i>	Recovery, %	Volume to complete elution, <i>ml</i>	Cu taken, <i>mmole</i>	Recovery, %	
Co <sup>+2</sup>	0.0225	100.3	15	0.0265	100.3
Ni <sup>+2</sup>	0.0362	99.6	15	0.0265	100.0
Fe <sup>+3</sup>	0.0284	99.6	18	0.0265	100.3
Zn <sup>+2</sup>	0.0222	100.0	15	0.0265	99.4
Cd <sup>+2</sup>	0.0325	100.0	18	0.0284	99.7
Mo <sup>+6</sup>	0.0286	98.9	24	0.0248	99.2
Pd <sup>+2</sup>	0.0278	99.7	30	0.0246	100.0
Pb <sup>+2</sup>	0.0375	100.2	15	0.0265	99.8
Bi <sup>+3</sup>	0.0184	98.6	24	0.0226	99.6
Th <sup>+4</sup>	0.0272	99.2	24	0.0265	99.6
Hg <sup>+2</sup>	0.0286	100.0	24	0.0265	100.8
V <sup>+4</sup>	0.0387	101.7	12	0.0265	99.2
Ti <sup>+4</sup>	0.0200	50.8	20	0.0265	150.5

Ion A, <i>Activity, cpm</i>	Recovery, %	Volume to complete elution, <i>ml</i>	Cu taken, <i>mmole</i>	Recovery, %	
Sb <sup>+3</sup>	53730	97.5	12	0.0265	99.6
U <sup>+6</sup>	770206	100.3	15	0.0265	100.0
Cr <sup>+3</sup>	2795	99.8	9	0.0265	100.0
Sn <sup>+4</sup>	5766	98.6	12	0.0265	99.6
W <sup>+6</sup>	51207	99.6	12	0.0265	100.7

\* 9 × 62 mm column of 20% DHDO on amberlyst XAD-2 support. Acetate solution (pH 5) used as an eluent for ion A and 6*M* hydrochloric acid for copper.

Most metal ions were eluted from these columns with 20 ml or less of the pH 5 eluent, which required only 4–5 min. Copper(II) was then stripped from the column with 30 ml of 6*M* hydrochloric acid (6–8 min). Still faster separations appear to be feasible. In the copper–vanadium separation the effluent was passed through a 10-mm flow-through cell in a spectrophotometer, and the elution curves were recorded as each metal was eluted (Fig. 3). At a flow-rate of approximately 20 ml/min, the entire separation was completed in only 2 min. Use of finer mesh resin would probably reduce the tailing of the copper.

The column method is applicable to samples containing extremely low concentrations of copper(II). Distilled water adulterated with 31 ppm of <sup>64</sup>Cu(II) was adjusted to a pH of 5.0 with acetate buffer, and 200 ml were passed through a 9 × 62 mm

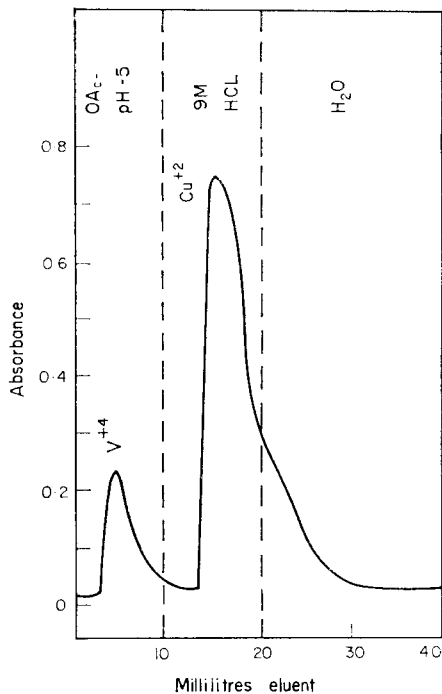


FIG. 3.—Elution of 0.025 mmole of V(IV) and Cu(II) from a  $9 \times 62$  mm column containing 80–100 mesh Amberlyst XAD-2 impregnated with DHDO.

column containing 0.96 mmole of DHDO in toluene. The copper retained by the column was removed with 6M hydrochloric acid and determined radiometrically. The average recovery from duplicate experiments was 100.1%.

Copper was successfully determined in two National Bureau of Standards samples after DHDO column chromatographic separation of the copper from the lead, zinc, tin, nickel, iron and antimony in the samples. Tartrate was added to sample 124-d to prevent interference from tin (4.56%). In sample 54-d where tin was the major component (88.57%) tartrate was ineffective, but interference was prevented by addition of hydrofluoric acid to complex the tin. Results for individual analyses on the samples are summarized in Table II.

TABLE II.—DETERMINATION OF COPPER IN NATIONAL BUREAU OF STANDARD SAMPLES

Sample No.	Copper reported, %	Copper found, %	Difference, %
124d	83.60	83.56	-0.04
124d	83.60	83.61	+0.01
54d	3.62	3.60	-0.02
54d	3.62	3.64	+0.02
54d	3.62	3.56	-0.06
54d	3.62	3.63	+0.01

*Acknowledgments*—The assistance of Dr. O. L. Chapman of Iowa State University in interpreting the NMR data and K. L. Malaby of Ames Laboratory in making and checking the isotopes is gratefully acknowledged.

**Zusammenfassung**—Zwei aliphatische  $\alpha$ -Hydroxy-Oxime wurden dargestellt und charakterisiert. Diese Reagentien sind hochselektiv für die Extraktion von Kupfer(II) aus schwach saurer wäßriger Lösung. Eine Säule, die ein Hydroxyoxim auf einem festen Träger enthält, ist imstande, Kupfer(II) quantitativ von den meisten anderen Metallionen zu trennen.

**Résumé**—On a synthétisé et caractérisé deux  $\alpha$ -hydroximes aliphatiques. Ces réactifs sont hautement sélectifs pour l'extraction du cuivre(II) d'une solution aqueuse faiblement acide. Une colonne contenant une hydroxyoxime sur un support solide effectue une séparation quantitative du cuivre(II) de la majeure partie des autres ions métalliques.

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# ELECTRONIC MODULATION OF MICROWAVE-EXCITED ELECTRODELESS DISCHARGE LAMPS FOR USE IN ATOMIC-FLUORESCENCE SPECTROMETRY

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**Summary**—Electronic modulation of electrodeless discharge lamps has been investigated with respect to frequency of operation and modulation waveform. The optimal frequency of operation was found to be *ca.* 20,000 Hz, using a square waveform, and modulation was best achieved by adding the modulation waveform to the reference of the stabilizing element in the microwave power supply. Optimal operating conditions have been established for d.c. and a.c. modes of operation for several sources.

THERE has been considerable interest recently in the use of microwave-excited electrodeless discharge lamps (EDLs) as high intensity sources for the excitation of atomic fluorescence.<sup>1,2</sup> The principal advantages associated with these sources are the low cost and ease of preparation, and the high line: background intensity ratio of the emitted atomic lines. In previous studies EDLs were operated in the d.c. mode in conjunction with d.c. amplifiers or their radiation was mechanically chopped to match the a.c. amplifier of the flame spectrophotometer used. Recently West *et al.*<sup>3,4</sup> and later Thompson and Wildy<sup>5,6</sup> have described methods of electronically modulating microwave-excited EDLs by transformer-coupling a low voltage (*ca.* 12 V peak to peak) a.c. signal into the anode circuit of the magnetron. Unfortunately this method of modulation has certain disadvantages as indicated by West *et al.*<sup>7</sup> Because the secondary of the transformer is in the anode circuit, the high d.c. magnetron current may cause saturation of the transformer core, resulting in distortion of the modulation waveform applied to the primary of the transformer. Also, because a transformer is generally designed for low frequency sinusoidal waveforms, the frequency and function of the modulation is somewhat limited. These problems can be overcome by injecting the modulation waveform directly at the error-sensing or the reference point of the stabilizing element of the magnetron power supply. This method of modulation was chosen for this investigation and a range of modulation frequencies and functions has been studied in relation to the applications of EDLs for atomic-fluorescence spectrometry.

## EXPERIMENTAL

### *Apparatus*

The modulator used was a function generator (Hewlett Packard, Model 3310A) capable of generating various waveforms (triangular, square, sine, ramp or pulse) of different frequencies ( $1 \times 10^{-4}$ – $5 \times 10^6$  Hz) and amplitude (0–35 V peak to peak). The modulation amplifier was a modified prototype modulation unit (Evans Electro Selenium Ltd., Halstead, Essex, U.K.) used as a voltage amplifier. The microwave generator (Evans Electro Selenium Ltd. Model 245) was current-stabilized and modulation of the magnetron output was provided by injecting the modulation waveform at the error-sensing point of the stabilizing element of the magnetron power supply. The EDLs were operated in a Broida-type three-quarter wave cavity (Evans Electro Selenium Ltd.) fitted with two capacitive tuning stubs. The detector system consisted of a 1-m grating spectrophotometer (Optika Ltd., Walthamstow, London, Model 331/3000) giving a reciprocal linear dispersion of 2.0 nm/mm, coupled to a photomultiplier (E.M.I. Model 9592B) operated at 850 V

supplied by a stabilized power supply (Brandenburg Ltd., Thornton Heath, Surrey, Model 472R). A slit-width of 0.005 mm (10 pm spectral bandpass) was used for all direct-source evaluations, and one of 3.6 mm for all atomic-fluorescence measurements.

The signal from the photomultiplier was amplified by a low-noise wide-band preamplifier, a wide-band amplifier and a variable-frequency, variable- $Q$ , narrow-band amplifier (AIM Electronics Ltd., Cambridge, U.K., Models LNA/133, ACA 123 and TFO 129 respectively). The variable-frequency, narrow-band amplifier was used with a  $Q$  setting of 100 which gave a bandpass (at the 6 db points) of  $f_0/100$  Hz, where  $f_0$  is the frequency of maximum amplification of the narrow-band amplifier and also the frequency of modulation.

The amplified signal was detected by a phase-sensitive detector (AIM Electronics Ltd., Model PSD 122A) which was phase-locked to the modulator.

A fuel-rich premixed air-acetylene flame was used for all atomic fluorescence studies.

#### *Preparation of electrodeless discharge lamps*

The method of preparation was similar to that used by others<sup>1,2</sup> except that the lamp blanks were baked at *ca.* 1000° for *ca.* 12 hr and purged using an intense argon discharge for *ca.* 30 min prior to preparation of the lamp. The purging procedure greatly increased the average lifetime of the lamps and decreased the long-term drift by decreasing the rate of wall discolouration. All lamps were filled to a pressure of between 4 and 5 mbar of argon before sealing.

## RESULTS AND DISCUSSION

#### *Degree of modulation*

The apparatus used in this investigation was capable of producing a maximum modulation of the magnetron current of *ca.* 75%; unfortunately at this level there was a considerable amount of short-term noise (*ca.*  $\pm 8\%$ ) superimposed on the emitted radiation from the modulated EDL. This noise level decreased to below  $\pm 1\%$  when the current modulation was decreased to 63% or below and hence this level of modulation was used because it gave the greatest emitted intensity consistent with low noise. However, the modulation of the coupled microwave power was found to be *ca.* 50% when the current modulation was 63%. This was probably caused by a greater reflection of microwave power from the cavity at the modulation maximum than at the modulation minimum.

#### *The frequency and function of the modulation wavelength*

The effect of the modulation frequency on the intensity of emitted resonance lines was investigated for several different EDLs, *viz.* Cd, Hg, Zn, Sb, Se, As and Pb. All the sources gave a maximum modulated output at a frequency of *ca.* 20,000 Hz (Fig. 1). This maximum would probably have occurred at a higher frequency, but for the drop-off in modulation amplifier response which commences at about 18,000 Hz.

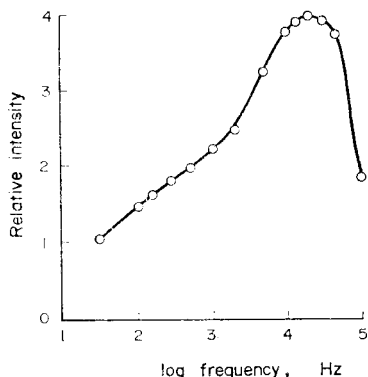






FIG. 1.—Plot of frequency of modulation *vs.* radiation intensity for a mercury EDL (microwave power *ca.* 40 W, measurements made at 253.7 nm).

This investigation was repeated using triangular, sine, square, ramp, and pulse waveforms, and although for each function the optimal frequency occurred at *ca.* 20,000 Hz, each waveform gave a different relative emission intensity (Table I). For all frequencies of operation the square waveform gave the greatest intensity of radiation and was used for all further studies unless otherwise stated.

TABLE I.—EFFECT OF VARIOUS MODULATION WAVEFORMS ON THE RELATIVE INTENSITY OF THE RESONANCE RADIATION FROM A MODULATED EDL MEASURED BY PHASE-SENSITIVE DETECTION SYSTEM

Waveform used	Relative intensity		
	100 Hz	1000 Hz	10,000 Hz
pulse 	1.0	1.8	2.7
pulse 	0.7	1.3	2.0
square wave	3.6	7.0	10.0
sine wave	2.8	5.0	7.2
triangular wave	2.5	4.8	7.0
ramp 	2.4	4.8	6.9
ramp 	2.5	4.8	7.0

### Microwave power

The amplitude of the a.c. component of the resonance atomic fluorescence intensity of a modulated EDL (for a given percentage of modulation) is governed by the gradient of the atomic fluorescence intensity *vs.* microwave power curve obtained from an EDL operating in the d.c. mode. A long (*ca.* 0.25 m) mercury EDL<sup>8</sup> was chosen for the preliminary investigation of this effect because the atomic-fluorescence intensity *vs.* microwave power curve for d.c. mode of operation showed a maximum, thus giving positive, negative and zero gradient portions (Fig. 2a). When this source was used in the a.c. mode, the atomic-fluorescence intensity *vs.* microwave power curve obtained (Fig. 2b) was completely different from that obtained in its d.c. mode of operation. The atomic-fluorescence intensity measured by the phase-sensitive detector system (*i.e.* the amplitude of the a.c. radiation component) was approximately proportional to the gradient of the atomic-fluorescence intensity *vs.* microwave power curve for d.c. operation (N.B. the negative output of the phase-sensitive detector indicates a phase shift of 180°). Figure 3 shows how a triangular modulation waveform produces an a.c. component of the emitted radiation from a modulated EDL. If the EDL had been optimized for d.c. operation (*i.e.*, a microwave power setting of *ca.* 70–80 W) and then modulated, then no signal would be observed on the phase-sensitive detector, for two reasons; the amplitude of the a.c. component of the radiation is very small as a result of the shallow gradient and the frequency of the a.c. component of the emitted radiation is twice that of the modulation frequency (Fig. 3).

The amplitude and the phase relationship of the modulated radiation were compared with the modulated waveform by applying both the modulator and photo-multiplier outputs to the two input channels of a double-beam oscilloscope. This was carried out for a triangular, sine and square waveform with the mercury EDL at

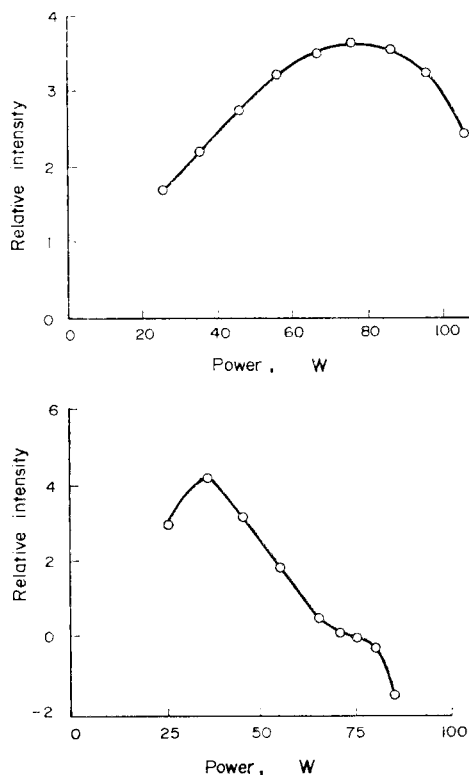


FIG. 2a.—Plot of atomic-fluorescence intensity *vs.* applied microwave power for mercury (microwave power d.c., measurements made at 253.7 nm).

FIG. 2b.—Plot of atomic-fluorescence intensity for mercury *vs.* microwave power (modulation frequency 18 kHz, 50% modulation, measurements made at 253.7 nm).

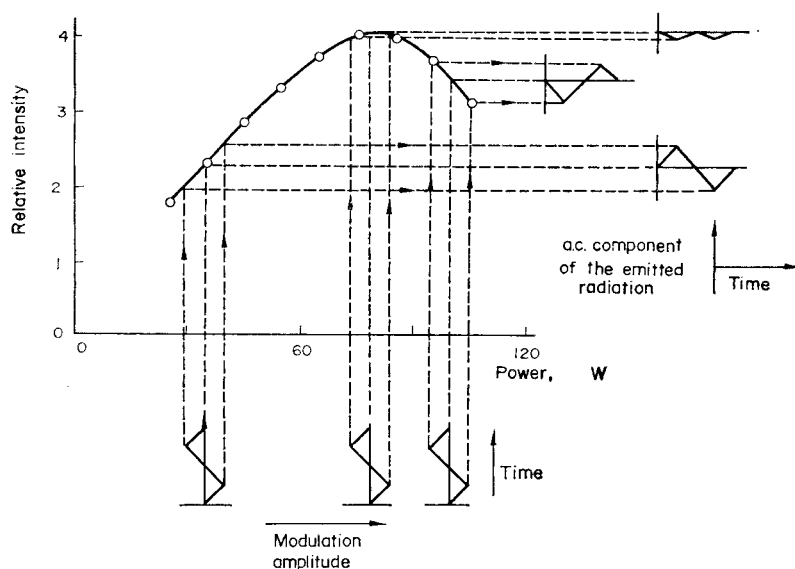


FIG. 3.—Schematic representation of resonance-line modulation, using a triangular modulation waveform at different microwave power levels.

different microwave power settings (Fig. 4). All three waveforms exhibited frequency doubling at the optimal d.c. operating power and a  $180^\circ$  phase-shift at higher microwave powers

Thus, in order to find the optimal microwave operating power for an EDL used in the a.c. mode, it is necessary to investigate experimentally the atomic-fluorescence intensity *vs.* microwave power behaviour in the d.c. mode of operation. The microwave power at which the maximum gradient occurs gives the optimal microwave power for the a.c. mode of operation. In some instances, when self-reversal causes a drop in resonance-line intensity, this maximum gradient may occur at higher microwave powers than the optimal d.c. operating power. However, as long as the detector system is capable of measuring a signal which has a consistent phase shift of  $180^\circ$ , this would be the optimal operational microwave power level for the a.c. mode of operation. This procedure was used for all EDLs investigated.

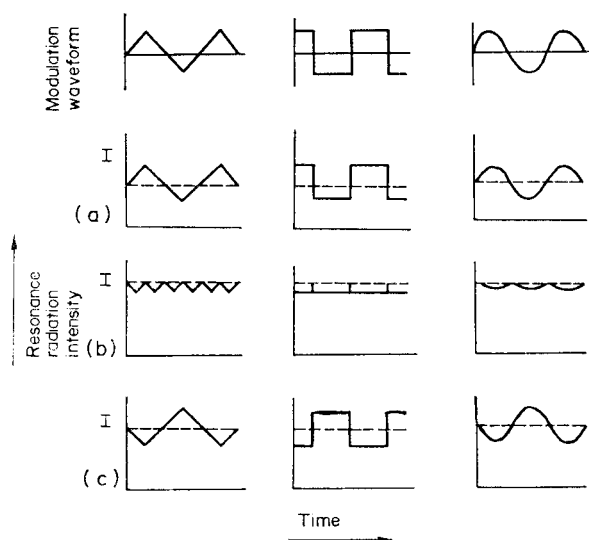


FIG. 4.—Schematic representation of radiation intensity produced with various modulation waveforms at different microwave power levels. (Dotted line indicates d.c. radiation level).

- (a) low power.
- (b) optimal power.
- (c) high power.

### Optimal operating conditions

These conditions, for use in the a.c. mode of operation, were experimentally determined for Cd, Hg, Zn, Sb, Se, As and Pb EDLs (Table II). A comparison of the noise and drift of these sources was then made when operated in the d.c. mode, in the a.c. mode with transformer-coupled modulation and in the a.c. mode with modulation injected at the error-sensing point of the stabilizing element (Table II). In every instance operation in the a.c. mode was found to be superior with respect to noise and drift characteristics. In addition, modulation of the stabilizing circuit was found to produce less noise and drift than transformer-coupled modulation. When operated in the a.c. mode, the mean microwave operating power was always less than

TABLE II.—OPTIMAL OPERATING CONDITIONS, NOISE AND DRIFT FOR EDLS USED IN a.c. AND d.c. MODES

Material	Wavelength, <i>nm</i>	Optimal power, <i>W</i>		Average peak-to-peak noise measured over 30-min period				Drift, %/hr	
		d.c. mode	a.c. mode	d.c. mode	a.c. mode	d.c. mode	a.c. mode	d.c. mode	a.c. mode
Cd	228.8	60	35	2.2	1.3	0.3	—3.6	—1.2	—1.0
Hg	253.7	38	25	2.5	2.6	0.5	—4.6	—1.7	—1.2
Zn	213.9	65	38	1.0	0.4	0.4	—3.5	—1.7	—1.2
Sb/I <sub>2</sub>	231.1	40	25	2.7	1.3	0.5	—4.3	—1.5	—1.2
Se	196.1	38	25	3.1	1.6	0.7	—2.8	—1.3	—1.3
As/I <sub>2</sub>	193.7	40	28	1.8	0.7	0.4	—2.5	—0.9	+0.2
Pb/I <sub>2</sub>	283.3	50	30	3.0	1.7	0.9	—5.8	—2.3	—1.5

that used in the d.c. mode, leading to an increased lifetime of the EDL, owing to a decreased rate of attack of the element in EDL on the quartz walls of the source envelope.

### Conclusion

Less source noise and drift is produced by modulating EDLs at the error-sensing point of a current-stabilization amplifier than by modulation *via* transformer-coupling or by operation in a d.c. mode. Modulation of an EDL leads to a longer lifetime as a result of effective lower microwave operating powers and also allows the use of lock-in, phase-sensitive detector systems which can increase the signal:noise ratio in analytical measurements. The optimum frequency of modulation was found to be *ca.* 20,000 Hz when a square waveform was used.

*Acknowledgements*—We would like to thank the Science Research Council for the award of a studentship to one of us (M. D. S.) and Evans Electro Selenium Ltd. for the loan of some of the apparatus used in this study.

**Zusammenfassung**—Die elektronische Modulation elektrodenloser Entladungslampen wurde bezüglich der Arbeitsfrequenz und der Schwingungsform der Modulation untersucht. Die optimale Arbeitsfrequenz beträgt etwa 20,000 Hz mit Rechteck-modulation. Die Modulation ist am wirksamsten, wenn man die modulierte Schwingungsform zum Bezugssignal des Stabilisierungselements im Mikrowellen-Versorgungsgerät addiert. Für mehrere Lichtquellen wurden die optimalen Arbeitsbedingungen für unmodulierte und modulierte Arbeitsweise ermittelt.

**Résumé**—On a étudié la modulation électronique de lampes à décharge sans électrode par rapport à la fréquence d'opération et à la forme de l'onde de modulation. On a trouvé que la fréquence optimale d'opération est d'environ 20,000 Hz, en utilisant une forme d'onde carrée, et la modulation a été réalisée au mieux en ajoutant la forme d'onde de modulation à la référence de l'élément stabilisateur dans le réseau microondes. On a établi les conditions opératoires optimales pour les modes opératoires en courant continu et courant alternatif pour plusieurs sources.

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## THERMODYNAMICS OF THE PARTITION OF 8-QUINOLINOL BETWEEN SEVERAL ORGANIC SOLVENTS AND AQUEOUS BUFFERS

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**Summary**—The partition coefficients of 8-quinolinol between water and benzene, nitrobenzene, toluene and chloroform have been determined as a function of temperature, and values of  $\Delta H$  and  $\Delta S$  determined for each. Values of the dissociation constant for protonated 8-quinolinol are reported as a function of temperature.

THE DISTRIBUTION of the reagent 8-quinolinol (oxine) and its metal salts (oxinates) between organic solvents and water has been the subject of numerous investigations.<sup>1,2</sup> Recently Mottola and Freiser<sup>3</sup> have studied the distribution of oxine, 2- and 4-methyl oxine, and their copper(II) chelates between a series of organic solvents and water. They interpret their work in terms of solubility parameter, dielectric constant, and mutual solubility of the two phases.

While considerable work has been done on the distribution of these systems as a function of the nature of the immiscible organic solvent and possible correlations, very little has been reported concerning the thermodynamics of the extraction process. Schweitzer and Hellwege<sup>4</sup> have reported the effect of temperature on the extraction of cadmium oxinate into chloroform. They report  $\Delta H = -8.4 \text{ kJ.mole}^{-1}$  and  $\Delta S = 25 \text{ J.mole}^{-1}\text{K}^{-1}$  for the distribution of 8-quinolinol between chloroform and water.

The purpose of this work was to determine the thermodynamic parameters associated with the distribution of 8-quinolinol between water and several closely related organic solvents. The solvents chosen were benzene, toluene and nitrobenzene. Distribution data were obtained with chloroform for use as a basis for comparison.

It became apparent from the literature that the values reported for  $pK_1$  for the acid dissociation of the protonated 8-quinolinol were somewhat varied and that it would be necessary to determine these values as a function of temperature. These values are reported also.

### EXPERIMENTAL

#### *Reagents*

*8-Quinolinol.* A sample obtained commercially was purified by recrystallization from ethanol and by steam distillation. Both products were dried in a vacuum desiccator and showed a melting point of  $73.8^\circ\text{--}74.8^\circ$ . The purity of the preparation was checked by bromination.

*Solvents.* Thiophene-free benzene was distilled through a Vigreux column and a middle cut used. All other solvents were used as received.

*Salts.* All salts were recrystallized from twice distilled water and were oven-dried at  $120\text{--}130^\circ$  for 24 hr.

*Buffer solutions.* The potassium hydrogen phthalate buffer solutions were prepared from dried primary standard grade salt.



### Apparatus

The solutions were equilibrated by means of a tumbling device contained in a large constant-temperature bath. Three thermoregulators with vigorous stirring were used to assure thermal equilibrium. The temperature control as monitored was  $\pm 0.1^\circ$ .

Beckman Model G and a Radiometer pH M4 pH meters were used and standardized with Radiometer buffers and 0.05M potassium acid phthalate buffer solutions. A Beckman DU spectrophotometer was used with thermostatically controlled cells.

### Procedures

*pH measurements as a function of temperature.* For pH measurements at temperatures other than 25, the pH meter was used as a millivoltmeter. The temperature control was set and kept at 25° throughout the series. The meter was standardized at the temperature of interest by using the 0.05M potassium acid phthalate buffer with the appropriate NBS value for that particular temperature. Conversion of the nominal pH reading,  $pH_n$ , into the true pH value was accomplished by means of the equations

$$pH = pH_s + \frac{0.0592}{0.0611} (pH_n - pH_s) \text{ at } 35^\circ$$

$$pH = pH_s + \frac{0.0592}{0.0631} (pH_n - pH_s) \text{ at } 45^\circ$$

where  $pH_s$  is the pH of the 0.05M buffer used for standardization. The validity of these relations was established with respect to the glass-calomel electrode pairs and meters by using known buffers.

*Spectrophotometric determination of  $pK_1$ .* The absorbances of a series of acetic acid-acetate buffers  $2.68 \times 10^{-4}M$  in total 8-quinolinol and containing sufficient sodium chloride to adjust the ionic strength to 0.1, were measured at 358 nm. The results were treated by means of the relationship

$$pK_1 = pH + \log \frac{(A_m - A_0)}{(A_H - A_m)}$$

where  $A_m$  is the measured absorbance in the buffers,  $A_0$  the measured absorbance in  $pH = 7.0$  buffer and  $A_H$  the measured absorbance in 0.1M hydrochloric acid. Initially, the pH of the solutions was calculated from the  $pK_a$  of acetic acid and the known buffer ratio. These measurements were confirmed with the Radiometer pH meter. The pH range of 4.5–4.8 was used to achieve the most favourable values of the ratio of absorbance differences.

*Distribution measurements.* The values of  $K_D$  were determined from the distribution ratio,  $D$ , as a function of pH according to  $D = K_1 K_D / (K_1 + [H^+]) = [\text{total oxine (org)}] / [\text{total oxine (aq)}]$ . The variation of pH was accomplished by using phosphoric acid-sodium dihydrogen phosphate buffers with added sodium chloride to maintain the ionic strength at 0.1. No effect was observed that could be attributed to the absolute concentration of the buffer, indicating no observable formation of extractable ion-pairs. In most cases, equal (25-ml) volumes of the appropriate buffer solution and the pre-equilibrated organic solvent containing a known amount of 8-quinolinol were added to a screw-top flask painted black. The flask was mounted in the thermostatically controlled tumbling device and the samples tumbled for 3 hr to ensure complete equilibration. After tumbling, the flasks were removed and placed in a constant-temperature bath at the appropriate temperature for phase separation. Aliquots were taken from the aqueous phase for pH measurements and spectrophotometric analysis. A positive pressure was exerted on the pipette to prevent incorporation of organic solvent droplets upon passage through the organic layer. The pipette was carefully wiped to remove any adhering organic droplets. The aliquot used for spectrophotometric analysis was added to an appropriate volume of 1M hydrochloric acid contained in a volumetric flask such that upon dilution the final solution was 0.6M in hydrochloric acid. The absorbance was measured at 358 nm and the concentration was calculated from a calibration curve and the appropriate dilution factor. The concentration of the organic phase was usually calculated by difference. The reliability of the difference calculation was checked by spectrophotometric analysis of the organic solution. The molar absorptivity of the protonated form of 8-quinolinol as determined from the calibration curve was  $170 \pm 2 \text{ l.} \cdot \text{mole}^{-1} \cdot \text{mm}^{-1}$  for 358 nm which compares with the reported<sup>3</sup> value of  $165 \pm 3$ .

Aqueous solutions saturated with nitrobenzene showed significant absorbance at 358 nm so a modified procedure was adopted. After addition of the hydrochloric acid, the solution was extracted three times with 10-ml portions of benzene. This technique gave more consistent results than attempts to blank out the absorbance. At 45°, inconsistent results were obtained for the nitrobenzene system and the results for this solvent are therefore not as reliable.

Each reported value of  $D$  is the average of at least two independent measurements.

*Calculation of  $\Delta H$  and  $\Delta S$* 

The values of  $\Delta H$  and  $\Delta S$  were calculated from

$$\log K = -\frac{\Delta H}{2.303 R} \left(\frac{1}{T}\right) + \frac{\Delta S}{2.303 R}$$

with a linear least-squares FOCAL program for  $\log K$  vs.  $1/T$  prepared and run by Dr. P. E. Field of this Department. All results obtained were used in the computations.

## RESULTS AND DISCUSSION

*The temperature dependence of  $pK_1$  of 8-quinolinol*

Values of  $pK_1$  for the reaction  $H_2Ox^+ \rightleftharpoons HOx + H^+$  where  $H_2Ox^+$  and  $HOx$  represent the protonated and neutral forms of 8-quinolinol respectively were determined as a function of temperature. The average  $pK$  values for the several temperatures are; 25°,  $5.030 \pm 0.005$ ; 35°,  $4.892 \pm 0.005$ ; 45°,  $4.778 \pm 0.014$ . Each value is the average of six determinations.

The thermodynamic quantities for 0.1M total ionic strength are  $\Delta H = 20.8 \pm 0.4$  kJ.mole<sup>-1</sup> and  $\Delta S = -19.6 \pm 1.3$  J.mole<sup>-1</sup>.K<sup>-1</sup>. These compare favourably with those obtained for quinoline and isoquinoline, which have similar  $pK$  values as reported by Sacconi *et al.*<sup>6</sup>

The value of  $pK_1$  at 25° reported here agrees well with that of Dyrssen<sup>5</sup> of 5.00 and the value 5.033 obtained from the data of Näsänen *et al.*<sup>7</sup> It does not agree with the value of 4.85 reported by Mottola and Freiser.<sup>3</sup> No reason for this discrepancy could be found.

*The temperature dependence of  $K_D$  for the aqueous-organic solvent pairs*

Values of pH,  $D$  and  $\log K_D$  are summarized for chloroform, toluene, benzene and nitrobenzene in Tables I-IV. Table V summarizes the thermodynamic values calculated from the results.

TABLE I—DISTRIBUTION OF 8-QUINOLINOL BETWEEN CHLOROFORM AND AQUEOUS PHOSPHORIC ACID BUFFERS

pH	$D$	$\log K_D$	$T^\circ C$
2.70	1.84	2.60	25
2.47	1.19	2.64	25
2.32	0.865	2.65	25
2.82	3.41	2.60	35
2.74	2.77	2.59	35
2.39	1.30	2.61	35
2.72	2.94	2.53	45
2.53	1.92	2.53	45
2.38	1.34	2.53	45

Total ionic strength 0.1M.

As previously noted, the chloroform results were taken as a check on the methods used. The values of  $\Delta H = -9.02 \pm 1.4$  kJ.mole<sup>-1</sup> and  $\Delta S = 20.0 \pm 4.6$  J.mole<sup>-1</sup>.K<sup>-1</sup> compare with those of Hellwege and Schweitzer of  $-8.4$  kJ.mole<sup>-1</sup> and 25 J.mole<sup>-1</sup>.K<sup>-1</sup>. At 25°, the  $\log K_D$  value of  $2.63 \pm 0.02$  compares well with the value of 2.66 of Dyrssen<sup>5</sup> and 2.64 of Fresco and Freiser.<sup>8</sup>

$K_D$  values have been obtained at 25° for toluene and benzene. The value of  $2.25 \pm 0.02$  found in this work for  $\log K_D$  for toluene can be compared with 2.21

TABLE II—DISTRIBUTION OF 8-QUINOLINOL BETWEEN TOLUENE AND AQUEOUS PHOSPHORIC ACID BUFFERS

pH	<i>D</i>	log <i>K<sub>D</sub></i>	<i>T</i> °C
2.94	1.52	2.27	25
2.67	0.718	2.22	25
2.47	0.484	2.24	25
2.33	0.358	2.25	25
3.63	9.28	2.20	35
3.19	3.44	2.23	35
2.97	1.91	2.22	35
2.62	0.916	2.23	35
2.44	0.596	2.24	35
3.00	2.76	2.22	45
2.49	0.779	2.18	45
2.33	0.587	2.22	45
2.24	0.414	2.16	45

TABLE III—DISTRIBUTION OF 8-QUINOLINOL BETWEEN BENZENE AND AQUEOUS PHOSPHORIC ACID BUFFERS

pH	<i>D</i>	log <i>K<sub>D</sub></i>	<i>T</i> °C
2.89	1.668	2.36	25
2.60	0.852	2.36	25
2.42	0.565	2.36	25
2.25	0.404	2.38	25
2.16	0.308	2.36	25
2.99	2.49	2.30	35
2.71	1.29	2.29	35
2.52	0.811	2.28	35
2.34	0.593	2.32	35
2.99	3.19	2.28	45
2.68	1.55	2.28	45
2.51	1.06	2.29	45
2.34	0.717	2.29	45
2.24	0.554	2.27	45

TABLE IV—DISTRIBUTION OF 8-QUINOLINOL BETWEEN NITRO-BENZENE AND AQUEOUS PHOSPHORIC ACID BUFFERS

pH	<i>D</i>	log <i>K<sub>D</sub></i>	<i>T</i> °C
2.42	0.98	2.60	25
2.30	0.72	2.59	25
2.29	0.71	2.59	25
2.64	2.1	2.57	35
2.46	1.4	2.58	35
2.29	0.95	2.58	35

TABLE V—SUMMARY OF THERMODYNAMIC DATA

Solvent	$\Delta S$ ,		log <i>K<sub>D</sub></i> (25°C)
	$\Delta H$ , <i>kJ.mole</i> <sup>-1</sup>	<i>J.mole</i> <sup>-1</sup> . <i>K</i> <sup>-1</sup>	
Chloroform	-9.02 ± 1.4	20.0 ± 4.6	2.63 ± 0.02
Toluene	-4.50 ± 1.4	28.0 ± 4.6	2.25 ± 0.02
Benzene	-7.56 ± 0.92	19.6 ± 2.9	2.36 ± 0.01
Nitrobenzene	-2.92 ± 0.84	39.8 ± 2.9	2.59 ± 0.01

reported by Mottola and Freiser. Totally independent replicate measurement yielded  $2.21 \pm 0.01$  for  $\log K_D$ . The thermodynamic data obtained from this second series agree well although the  $\log K_D$  values in the second set are somewhat lower, indicating that systematic errors are involved. For benzene, Umland and Puchelt<sup>9</sup> report  $\log K_D$  of 2.60 whereas the result reported here is 2.36. Their computation of  $\log K_D$  is based upon a  $pK_1$  value of 5.33 which does not agree with the value of other workers. Using the value of  $pK_1$  obtained here the recalculated value of  $\log K_D$  becomes 2.30 which is in better agreement with the results reported here.

For the nitrobenzene system, although results obtained at 45° were not used in the computation, such reliable results as were obtained agree well with the value of  $\log K_D$  calculated from the values of  $\Delta H$  and  $\Delta S$ .

The order for  $\log K_D$  at 25° is nitrobenzene > benzene > toluene. The thermodynamic data support a proximate linear relationship between  $\Delta H$  and  $\Delta S$ . Such a relationship is neither unknown nor unexpected for closely related systems. Rozen<sup>10</sup> has discussed this in some detail, using data for the uranyl nitrate extraction with phosphates and phosphonates.

Although the series is a severely limited one, the trend in  $\log K_D$  values with such functions as Hammett  $\sigma$  values for the  $-\text{CH}_3$  and  $-\text{NO}_2$  groups is also approximately linear. This suggests that the solute-solvent interactions in the hydrocarbon phase are increased by electron-withdrawing groups in the solvent.

**Zusammenfassung**—Die Verteilungskoeffizienten von 8-Hydroxychinolin zwischen Wasser und Benzol, Nitrobenzol, Toluol und Chloroform wurden in Abhängigkeit von der Temperatur gemessen und jeweils  $\Delta H$ - und  $\Delta S$ -Werte ermittelt. Werte für die Dissoziationskonstanten von protoniertem 8-Hydroxychinolin werden in Abhängigkeit von der Temperatur mitgeteilt.

**Résumé**—On a déterminé les coefficients de partage de la 8-hydroxyquinoléine entre l'eau et benzène, nitrobenzène, toluène et chloroforme en fonction de la température, et les valeurs de  $\Delta H$  et  $\Delta S$  ont été déterminées pour chaque solvant. On rapporte les valeurs de la constante de dissociation pour la 8-hydroxyquinoléine protonée en fonction de la température.

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# SPECTROCHEMICAL DETERMINATION OF RARE-EARTH METALS IN URANIUM AND ITS SALTS

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**Summary**—An emission spectrographic procedure is described for the determination of 0.05–4 ppm of rare-earth metals in uranium metal and its salts. Uranium is extracted from the sample with tributyl phosphate, and the impurities are separated by precipitation as hydroxides and oxalates, with yttrium as a carrier. After conversion into the oxides, the rare-earth metals are mixed with graphite and excited in a d.c. arc.

AS THE PERFORMANCE demands on uranium for nuclear reactors grow, it becomes necessary to control impurities of high neutron cross-section, Gd, Eu, Sm and Dy being among the five elements of highest cross-section for neutron absorption. The presence of these elements at concentrations even as low as  $10^{-4}\%$  is undesirable. For this reason attention has been paid to the development of methods for the determination of the rare-earth metals in high-purity uranium at a level of 0.1–100 ppm.

The spectrographic method is the most suitable. Owing to the relatively low sensitivity of the direct spectrographic technique, it is more advantageous to use a prior separation and preconcentration of the rare-earth metals.

Several procedures for preconcentration have been published, involving extraction by ether,<sup>1</sup> ion-exchange<sup>2,3</sup> and paper chromatography.<sup>4</sup> Atwell *et al.*<sup>5</sup> published a concentration procedure which applies extraction of uranium by tributyl phosphate (TBP) from hydrochloric acid, Ni, Co, Mg and Fe being separated by 8-hydroxyquinoline. The rare-earth metals are then precipitated as hydroxides, with lanthanum as a carrier, and their oxides are excited in a d.c. arc. The limit of detection by this procedure is 1 ppm.

The present paper describes a simple, rapid procedure for the determination of rare-earth metals in uranium and its compounds.

## EXPERIMENTAL

### *Sample preparation*

The sample of metallic uranium or its salt is transformed into  $U_3O_8$  by ignition in an oven at 800–900°. If the sample is in the form of  $UF_6$ , it is first converted into  $UO_2$  in an oven for pyrohydrolysis, and then ignited at 800–900° to  $U_3O_8$ . Samples containing 10 g of uranium are dissolved in concentrated nitric acid, 2.5 ml of a solution containing 240  $\mu$ g of Nd/ml are added, and the samples are evaporated to dryness and ignited at 400° for 30 min, thus converting the uranium sample into orange  $UO_3$ .

The  $UO_3$  sample is dissolved in concentrated hydrochloric acid, transferred to a separatory funnel, 25 ml of TBP are added and the mixture is shaken for 3 min. The mixture is allowed to separate into layers, and then the organic phase containing uranium is discarded. Three more extractions, each with 15 ml of TBP, are performed. An inversion occurs at the third extraction, with the TBP layer floating because of the diminishing uranium content. The aqueous layer is transferred to a smaller funnel to which 5 ml of a mixture of kerosene and TBP (5:1) are added, and is shaken for 3 min. The aqueous phase is removed and evaporated to dryness. The organic residues are destroyed by a

mixture of nitric, perchloric and hydrochloric acids. The residue from the aqueous phase is dissolved in dilute hydrochloric acid and 10 ml of a solution containing 1 mg of yttrium/ml are added. The solution is heated, ammonia is added and the precipitate filtered off. The precipitate is dissolved in 10 ml of 0.4M hydrochloric acid and heated to 80° and then 1 g of solid oxalic acid is added. The precipitated oxalates are left overnight and then filtered off. The precipitate is washed with 0.5% oxalic acid solution to which several drops of nitric acid have been added, then dried and ignited at 800°. The oxides obtained by this procedure are weighed to determine the yields, and mixed with graphite in a ratio of 1:1.

The standards are prepared from  $U_3O_8$ , in the range 0.05–10 ppm of rare-earth metal. The  $U_3O_8$  is dissolved in nitric acid and corresponding amounts of rare earth metals, as well as 60  $\mu$ g of Nd/g of uranium are added to this solution. The same procedure is used as for the preparation of the samples.

### *Spectrographic procedure*

Sample and standard replicates are excited in a d.c. arc. The operating conditions are given in Table I.

TABLE I.—APPARATUS AND OPERATING CONDITIONS

Spectrograph	Jarell-Ash with plane grating; 600 grooves/mm
Reciprocal linear dispersion	0.5 nm/mm in first order 0.25 nm/mm in second order
Wavelength region	287.5–412.5 nm (second order)
Slit width	20 $\mu$ m
Analytical gap	4 mm
Excitation source	Jarell-Ash Varisource, d.c. arc
Voltage	250 V
Current	13 A
Electrodes	Sample electrode (anode)—shallow thin-walled graphite electrode, 5.2 mm diam., 2 mm deep crater, wall thickness 0.5 mm. The anode is supported on a 3.1 mm graphite pedestal. Counter-electrode (cathode)—graphite rod, 3.1 mm diam.
Exposure time	30 sec
Photographic emulsion	Kodak SA1, developer D-19, 4 min at 20°

The spectrograms were measured on a Jarell-Ash microphotometer. The emulsion was calibrated by a step-sector method and Seidel correction applied. The concentration of each element was determined from working curves prepared from the synthetic standards and in which logarithmic ratios of analytical line and internal standard line were plotted against logarithmic concentrations. The working curves are based on 15-mg mixtures of rare-earth metals and graphite (1:1). Working curves are given in Figs. 1 and 2.

## RESULTS AND DISCUSSION

### *Parametric studies*

The rare-earth metals were separated from uranium by extraction with TBP in hydrochloric acid solution. The efficiency of the separation was monitored by fluorimetric analysis, which showed that 99.9% of uranium was separated by this procedure.

During the preconcentration a simultaneous concentration of other impurities occurs. These impurities dilute the rare-earth metals and the internal standard, increase the background and the spectral interface and change the excitation performance of the residue. In order to avoid the effects of the impurities, we applied a method of separation of the rare-earth metals hydroxides and oxalates in the presence of yttrium as carrier. The rare-earth oxides obtained after ignition were mixed with graphite at a ratio of 1:1, and 15 mg of this mixture were placed in the electrode shown in Fig. 3. With electrodes of this shape a uniform and fast evaporation of the rare-earth metals from the electrode crater is achieved.

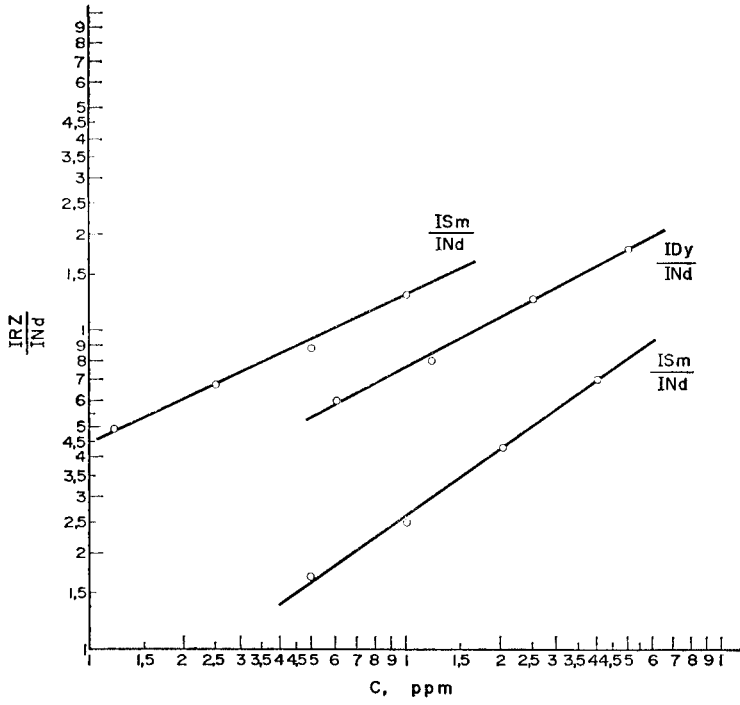


FIG. 1.—Working curves for Sm and Dy.

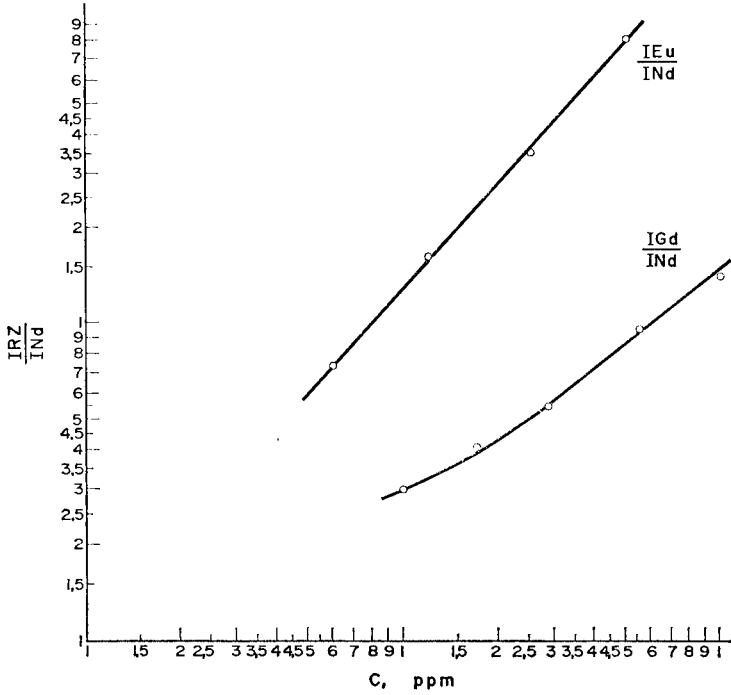


FIG. 2.—Working curves for Eu and Gd.

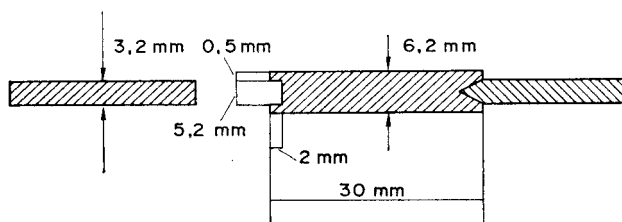


FIG. 3.—Diagram of electrode system.

Neodymium was used as an internal standard since it has similar properties to the elements determined and compensates for eventual losses occurring during the chemical operations. The sensitivity obtained by this procedure is shown in Table II.

TABLE II.—ANALYTICAL LINES AND CONCENTRATION RANGE OF DETERMINATION

Element	Line, nm	Concentration range, ppm
Gd	310.05	0.06-1
Eu	290.67	0.06-1
Sm	323.04	0.5-4
Sm	366.135	0.1-1
Dy	340.78	0.06-0.5
Nd	311.614	internal standard
Nd	344.33	internal standard

#### Reproducibility and recovery

The reproducibility of the method, expressed as relative standard deviation, is  $\pm 5-25\%$  for a concentration range of 0.05-4 ppm.

The recovery was evaluated from measurements on two series of rare-earth metal standards. The first series of standards used rare-earth metals in an yttrium matrix without prior separation, while in the second series samples of rare-earth metals and uranium were prepared. A known amount of a solution of the rare-earth metal was

TABLE III.—RECOVERY OF Gd, Sm, Eu AND Dy ADDED TO URANIUM

Element	Added, ppm	Recovered	
		ppm	%
Gd	0.1	0.12	120
Eu	0.1	0.092	92
Dy	0.1	0.090	90
Sm	0.1	0.11	110

TABLE IV.—ANALYSIS OF URANIUM SALTS

Sample	Concentration found, ppm			
	Gd	Sm	Eu	Dy
$(\text{NH}_4)_2\text{U}_2\text{O}_7$	0.28	1.25	0.1	0.18
$\text{UO}_2$	0.19	0.5	0.08	0.22
U-metal	0.1	0.25	0.06	0.06
$\text{UF}_4$	0.06	0.06	0.06	0.06



added to each sample. The recovery was found to be 90–120% in the concentration range 0.06–4 ppm. Table III illustrates the recovery for a concentration of 0.1 ppm.

Table IV gives analyses of various uranium salts.

**Zusammenfassung**—Ein emissions-spektrographisches Verfahren zur Bestimmung von 0,05–4 ppm seltener Erdmetalle in metallischem Uran und seinen Salzen wird beschrieben. Uran wird aus der Probe mit Tributylphosphat extrahiert, während die Verunreinigungen durch Fällung als Hydroxide und Oxalate mit Yttrium als Träger abgetrennt werden. Nach Überführung in die Oxide werden die seltenen Erden mit Graphit gemischt und in einem Gleichstrombogen angeregt.

**Résumé**—On décrit une méthode spectrographique d'émission pour la détermination de 0,05–4 p.p.m. des métaux des terres rares dans l'uranium métallique et ses sels. On fait l'extraction de l'uranium de l'échantillon au tributylphosphate, tandis que les impuretés sont séparées par précipitation à l'état d'hydroxydes et d'oxalates, avec l'yttrium comme entraîneur. Après conversion en oxydes, les métaux des terres rares sont mélangés au graphite et excités dans un arc à courant continu.

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## ADSORPTION BEHAVIOUR OF A NUMBER OF METALS ON WEAKLY BASIC ION-EXCHANGERS IN METHANOL-HYDROCHLORIC ACID MIXTURES

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**Summary**—Many metals are not strongly adsorbed on DEAE-cellulose from aqueous hydrochloric acid media. However, some metals can be adsorbed on DEAE-cellulose from methanol-hydrochloric acid media. Distribution coefficients of Zn, Cd, Hg(II) and Bi(III), which show pronounced adsorption, are presented as functions of the methanol and the acid concentrations. Differences in the distribution coefficient between the four metals and a considerable number of other metals are large enough to permit good separations on columns. Among the platinum group metals, Pd(II), Ir(IV) and Pt(IV) are adsorbed from the mixed solvents and may be separated from large quantities of base metals such as Fe(III), Co(II), Ni and Cu(II).

THE POTENTIALITY of a weakly basic ion-exchanger, DEAE-cellulose, in inorganic column chromatography in aqueous media has been explored. The adsorption behaviour and separation possibilities of Re(VII), Mo(VI) and W(VI),<sup>1</sup> of Hg(II),<sup>2</sup> and of Pd(II) and Pt(IV)<sup>3</sup> in thiocyanate-chloride media have already been demonstrated. A limited number of metals can adsorb on DEAE-cellulose (abbreviated DEAE) from aqueous solutions, a fact which limits the use of DEAE in inorganic column chromatography.

Muzzarelli and Marcotrigiano<sup>4-8</sup> have investigated the chromatography of many inorganic ions on columns of natural and substituted celluloses, including DEAE. Solvent systems of anhydrous diethyl ether and diethyl ether-90% nitric acid mixtures were used for their investigations. These solvent systems allowed only minute amounts of metal ions to be adsorbed on natural and substituted celluloses.

Recent advances in inorganic chromatography on columns of natural and substituted celluloses, and inorganic ion-exchange involving synthetic resins in organic and aqueous organic solvents, have been reviewed by Muzzarelli,<sup>9</sup> and Moody and Thomas,<sup>10</sup> respectively.

In the present work it was intended to study the anion-exchange behaviour of metal chloro-complexes on a weakly basic ion-exchanger DEAE in methanol-hydrochloric acid mixtures.

### EXPERIMENTAL

#### *Materials*

DEAE (diethylaminoethylcellulose, Serva, Gallard-Schlesinger Chemical Manufacturing Corp.) was placed in a large column and treated with a solution, 1M in sodium chloride and 0.1M in hydrochloric acid. It was then washed with demineralized water by centrifugation until the pH of the supernatant liquid was 2.5, and then with methanol. After drying at 40° for several hours the DEAE was stored in a desiccator for a week over a saturated potassium bromide solution.

Stock solutions of metals were prepared by dissolving appropriate amounts of their salts in hydrochloric acid to yield 1-10 mg of metal per ml. Each stock solution was standardized by a conventional analytical method. Analytical reagent grade chemicals were used throughout the study.

*Determination of distribution coefficients*

The weight distribution coefficients,  $K_d$ , of metals showing pronounced adsorption, *i.e.*, Zn, Cd, Hg(II) and Bi, were determined by a batch equilibrium method. Portions of DEAE (1 g) in the chloride form were placed in glass-stoppered conical flasks containing 1-ml portions of a standard metal solution and 41 ml of an appropriate methanol-hydrochloric acid mixture of varying composition. The mixture was shaken mechanically for 24 hr at  $25.0 \pm 0.1^\circ$ . The two phases were separated by filtration and an aliquot of the filtrate was analysed for the metal concerned, colorimetrically or chelatometrically. The distribution coefficient  $K_d$  was computed by using the formula

$$K_d = \frac{\text{Amount of ion in DEAE phase/g of DEAE}}{\text{Amount of ion in solution phase/ml of solution}}$$

For metals showing lower adsorption ( $K_d < 20$ ) an elution method was used to measure the distribution coefficient. A short column containing 1 g of DEAE was used. The  $K_d$  value is simply given as  $V_{\max} - V_i$ , where  $V_{\max}$  and  $V_i$  are the retention and interstitial volumes respectively.

*Procedure for column separation*

A conventional column (bore 18 mm) containing 1 g of DEAE is used, the bed being 25 mm long. The column should be pretreated before use with methanol-hydrochloric acid mixture. A sample is adjusted to a volume of about 5 ml with hydrochloric acid (1-6*M*), and 45 ml of methanol are added to it and the mixture is loaded onto the top of the column at a flow-rate of  $\sim 1$  ml/min. Zn, Cd, Hg(II) and Bi are strongly retained on the column, while other metals pass through the column. The column is washed with several column volumes of the same methanolic acid mixture. Zn, Cd and Hg(II) remaining on the column can be stripped by elution with about 50 ml of 0.5*M* hydrochloric acid. For the removal of Bi about 25 ml of 1*M* hydrochloric acid are used.

## RESULTS AND DISCUSSION

In order to determine the rate at which DEAE attained equilibrium with metals in mixed solvents, the distribution coefficients for Zn and Pt(IV) were determined at timed intervals and compared with the coefficients at equilibrium,  $(K_d)_{\text{eq}}$ . The results obtained are given in Table I. The rate at which DEAE attains equilibrium with

TABLE I.—RATE AT WHICH DEAE ATTAINS EQUILIBRIUM WITH ZINC AND PLATINUM(IV),  $(K_d)_t/(K_d)_{\text{eq}}$ 

Metal	[HCl],	Time, hr						
	<i>M</i>	0.5	1.0	2.0	3.0	4.0	6.0	24
Zn	1	23	38	84	92	100	100	100
Pt(IV)	3	77	94	100	100	100	100	100

The equilibrium distribution coefficient  $(K_d)_{\text{eq}}$  for Pt(IV) is 800.

metals depends upon the metals and solvent systems used. The rate at which equilibrium is attained is unimportant provided that a flow-rate of eluent of approximately 1 ml/min is maintained.

*Adsorption of metals on DEAE*

$K_d$  values for the four metals showing marked adsorption on DEAE from mixed solvent systems are tabulated in Table II as functions of the methanol and hydrochloric acid concentrations. Both methanol concentration and acidity exercise a pronounced effect on the  $K_d$  values for the four metals. Generally, the  $K_d$  values decrease sharply with decreasing concentration of methanol and with increasing concentration of hydrochloric acid. It is of interest that [except for Hg(II)] Zn, Cd and Bi do not show any marked tendency to adsorb on DEAE in aqueous thiocyanate-chloride media.

TABLE II.—DISTRIBUTION COEFFICIENTS†

Metal	[HCl],	Methanol, % v/v				
	<i>M</i>	95.2	90.4	80.9	71.4	50.0
Zn	1	$8.3 \times 10^2$	$3.7 \times 10^2$	$1.8 \times 10^2$	76	31
	3	$8.3 \times 10^2$	$3.6 \times 10^2$	$1.1 \times 10^2$	47	27
	6	$3.9 \times 10^2$	$2.2 \times 10^2$	73	35	13
	12	$3.9 \times 10^2$	$1.8 \times 10^2$	62	30	11
Cd	1	*	$1.9 \times 10^3$	$5.6 \times 10^2$	$3.6 \times 10^2$	68
	3	*	$9.7 \times 10^2$	$2.6 \times 10^2$	$1.6 \times 10^2$	32
	6	$1.2 \times 10^3$	$4.0 \times 10^2$	$1.2 \times 10^2$	$1.6 \times 10^2$	30
	9	$1.0 \times 10^3$	$3.6 \times 10^2$	84	34	14
	12	$8.7 \times 10^2$	$2.2 \times 10^2$	58	24	11
Hg(II)	1	*	*	$7.3 \times 10^2$	$5.8 \times 10^2$	
	3	*	$1.9 \times 10^3$	$4.3 \times 10^2$	$1.8 \times 10^2$	
	6	*	$1.2 \times 10^3$	$1.5 \times 10^2$	$1.1 \times 10^2$	
	9	*	$8.7 \times 10^2$	$1.3 \times 10^2$	$1.0 \times 10^2$	
	12	$1.6 \times 10^3$	$3.3 \times 10^2$	75	14	
Bi	1	*	*	*	$1.4 \times 10^3$	$7.2 \times 10^2$
	3	*	*	*	$9.6 \times 10^2$	$1.9 \times 10^2$
	6	*	*	*	$4.8 \times 10^2$	$1.0 \times 10^2$
	9	*	*	$1.1 \times 10^3$	$3.3 \times 10^2$	65
	12	*	*	$9.1 \times 10^2$	$3.3 \times 10^2$	32

\*  $K_d$  greater than  $2 \times 10^3$ .

† Loading: Zn 0.19, Cd 0.093, Hg(II) 0.012 and Bi 0.093 meq for 1 g of DEAE.

The presence of methanol also allows Zr, Te(IV), and Tl(I) to be slightly adsorbed on DEAE, their  $K_d$  values ranging from 10 to 20 in a 90% methanol–10% 3*M* hydrochloric acid mixture. Most other metals still do not adsorb on the DEAE to any great extent from the same methanol–acid medium, thus Be, Mg, Ca, Sr, Ba, Sc, Y, the rare earths, Ti(III, IV), Hf, V(IV), Cr(III), Mo(VI), Mn(II), Re(VII), Fe(III), Co(II), Ni, Cu(II), Al, Ga, In, Sn(IV), As(III), Sb(III), Se(IV) and U(VI) exhibit  $K_d$  values lower than 10. Among the platinum group metals, Pd(II), Ir(IV) and Pt(IV) also adsorb strongly on DEAE from methanol–hydrochloric acid media, their  $K_d$  values being greater than  $10^3$  in a 90% methanol–10% 1*M* hydrochloric acid solution. The adsorption of Ru(III) and Rh(III) is much less than that of the three precious metals mentioned above.

DEAE adsorbs more metals from methanol–acid mixtures than from the aqueous thiocyanate–chloride media. The metals which form the most stable chloro-complexes and exhibit the strongest adsorption on strongly basic ion-exchange resins can also show adsorption of DEAE in methanol–acid mixtures. The sequence of adsorption of chloro-complexes according to the ion-exchange systems involved is: strongly basic anion-exchange resin–hydrochloric acid > DEAE–methanol–hydrochloric acid > DEAE–aqueous hydrochloric acid. The numbers of metals adsorbed also decrease in this order.

### Separation of metals

Although the addition of methanol greatly assists the formation of chloro-complexes and causes the reduction of concentration of competitive chloride ions, thus promoting the adsorption of chloro-complexes on DEAE, few metals are sufficiently strongly adsorbed to permit their separation on columns. Therefore, the present ion-exchange system may provide a basis for developing selective methods for

the separation of Zn, Cd, Hg(II), Bi and some platinum group metals from a number of other metals. In order to demonstrate the effectiveness of the separations, each of the first four metals was separated from about 100 mg each of 18 metals including Mg, Ca, La, Sm, Th, U(VI), Mo(VI), Mn(II), Fe(III), Co(II), Ni, Cu(II), In, Sn (IV), As(III), Sb(III), Se(IV) and Te(IV).

Averages for 18 determinations and standard deviations for the four metals were  $44.1 \pm 1.9 \mu\text{g}$  for Zn ( $44.3 \mu\text{g}$  added),  $83.3 \pm 2.0 \mu\text{g}$  for Cd ( $84.9 \mu\text{g}$  added),  $93.0 \pm 0.63 \mu\text{g}$  for Hg(II) ( $93.1 \mu\text{g}$  added) and  $120 \pm 2.5 \mu\text{g}$  for Bi ( $120 \mu\text{g}$  added), indicating satisfactory recoveries. Quantitative recoveries of the 18 metals were also obtained.

The concentration of hydrochloric acid is not critical for separations even on columns involving 1 g of DEAE, as long as the organic to aqueous volume ratio is kept as high as 9:1. A concentration range of 1–10M hydrochloric acid for the aqueous phase may be allowed for Cd, Hg(II) and Bi. For Zn a higher concentration of hydrochloric acid should be avoided.

The strong adsorption of Pd(II), Ir(IV) and Pt(IV) facilitates the concentration of traces of these metals from large quantities of base metals. Thus 1 g of base metal converted into its chloride was taken up in 50 ml of methanol–1.2M hydrochloric acid (9:1) and passed through a column (bore 15 mm, 35 mm long) containing 1 g of DEAE, previously washed with the methanol–acid mixture. The precious metals retained on the column were eluted with 100 ml of 6M hydrochloric acid.

Results for separations of 100  $\mu\text{g}$  each of Pd(II), Ir(IV) and Pt(IV) from 1 g each of Fe(III), Co(II), Ni and Cu(II) were quantitative. With the exception of Ir(IV) the concentration of hydrochloric acid is not critical and a concentration of up to 6M is permissible. The moderate affinity of Pd(II), Ir(IV) and Pt(IV) towards DEAE makes it easy to recover them from the column. This is in contrast to results obtained with conventional anion-exchange resins on which chloro-complexes of platinum group metals are retained irreversibly.<sup>11,12,13</sup> Unfortunately, Ru(III) and Rh(III) are not retained on the column quantitatively as in the case of the three precious metals mentioned above, because of their lower  $K_a$  values. For these metals, increasing the concentration of methanol improves their adsorptions, but variation of the concentration of hydrochloric acid has little effect.

**Zusammenfassung**—Viele Metalle werden aus wässrig salzsauren Medien nicht stark an DEAE-Cellulose adsorbiert. Einige Metalle können jedoch aus methanolisch salzsauren Medien an DEAE-Cellulose adsorbiert werden. Die Verteilungskoeffizienten der stark adsorbierten Ionen Zn, Cd, Hg(II) und Bi(III) werden als Funktionen der Methanol- und der Säurekonzentration angegeben. Die Unterschiede der Verteilungskoeffizienten zwischen den vier Metallen und einer beträchtlichen Anzahl anderer Metalle sind groß genug, um gute Trennungen an Säulen zu erlauben. Von den Platinmetallen werden Pd(II), Ir(IV) und Pt(IV) aus den Lösungsmittelgemischen adsorbiert und können von großen Mengen unedler Metalle wie Fe(III), Co(II), Ni und Cu(II) abgetrennt werden.

**Résumé**—De nombreux métaux ne sont pas fortement adsorbés sur la DEAE-cellulose à partir de milieux acide chlorhydrique aqueux. Toutefois, quelques métaux peuvent être adsorbés sur la DEAE-cellulose à partir de milieux méthanol-acide chlorhydrique. On présente les coefficients de partage de Zn, Cd, Hg(II) et Bi(III) qui montrent une adsorption prononcée, en fonction des concentrations en

méthanol et en acide. Les différences entre les coefficients de partage des quatre métaux et ceux d'un nombre considérable d'autres métaux sont suffisamment grandes pour permettre de bonnes séparations sur colonnes. Parmi les métaux du groupe du platine, Pd(II), Ir(IV) et Pt(IV) sont adsorbés à partir des solvants mixés et peuvent être séparés de grandes quantités de métaux de base tels que Fe(III), Co(II), Ni et Cu(II).

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## IODINE CYANIDE AS VOLUMETRIC OXIDANT

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**Summary**—Iodine cyanide has been developed as an oxidant for the determination of iodide, sulphite, thiosulphate, thiocyanate, arsenic(III), antimony(III), tin(II), mercury(I), iron(II), ascorbic acid and  $\beta$ -naphthol in dilute aqueous mineral acids, glacial acetic acid and 1:1 acetic acid-acetic anhydride mixture, with visual and potentiometric methods of end-point detection.

CERTAIN HALOGENS<sup>1-3</sup> and interhalogen compounds<sup>4-10</sup> have been used as oxidizing agents in volumetric analysis but the oxidizing character of iodine cyanide in different media has not been studied so far. In the present investigation, an attempt was made to develop it as an oxidant for the determination of iodide, sulphite, thiosulphate, thiocyanate, iron(II), arsenic(III), antimony(III), tin(II), mercury(I), ascorbic acid and  $\beta$ -naphthol in dilute aqueous mineral acids, glacial acetic acid and 1:1 acetic acid-acetic anhydride mixture.

### EXPERIMENTAL

#### Reagents

Iodine cyanide,<sup>11</sup> iron(II) perchlorate,<sup>12</sup> mercury(I) perchlorate,<sup>13</sup> arsenic(III) and antimony(III) chlorides<sup>14</sup> were prepared and/or purified according to the procedures reported in the literature. All the other chemicals used were of guaranteed purity.

Iodine cyanide solution (0.025*M*) was prepared in 0.1*M* hydrochloric acid, 0.05*M* sulphuric acid, 0.08*M* nitric acid, glacial acetic acid, and a 1:1 mixture of acetic acid and acetic anhydride. The solutions of various reductants (0.025*M*) in distilled water, glacial acetic acid or 1:1 acetic acid-acetic anhydride mixture were prepared by direct weighing, except for the aqueous solution of  $\beta$ -naphthol (prepared in 0.025*M* sodium hydroxide) and the tin(II) chloride solution (the salt was dissolved in concentrated hydrochloric acid by warming and the solution diluted to 0.1*M* concentration of the acid.). The solutions of various reductants were standardized according to reported methods.<sup>15</sup>

#### Procedures

**Visual titrations.** An aliquot of iodine cyanide solution (5–20 ml) was diluted with distilled water (10 ml) and then titrated, with and without addition of potassium iodide (0.5 g), against sodium thiosulphate, sodium sulphite and tin(II) chloride, with starch (0.5 ml of 1% solution), carbon tetrachloride, benzene, chloroform and carbon disulphide (1–2 ml) as indicators. Iodine cyanide was titrated with ascorbic acid and  $\beta$ -naphthol in the presence of potassium iodide, with starch as indicator. Sodium bicarbonate was added to the iodine cyanide solution before the potassium iodide for titration of arsenic(III), antimony(III) and mercury(I).

**Potentiometric titrations.** In aqueous medium, a known volume of solution (5–10 ml) was taken in a 100 ml titration cell, diluted to about 50 ml with the same solvent, and then titrated as above.

In non-aqueous medium, a known volume of the reductant (5–10 ml) was taken in a dry titration cell and diluted to about 50 ml with the solvent. The cell was fitted with electrodes and a microburette (5-ml) and placed over a magnetic stirrer. After each addition of the oxidant, the contents were thoroughly stirred and the potential noted. Anhydrous sodium acetate (4–5 g) was added to the arsenic(III), antimony(III), iron(II) and tin(II) solutions before the titration.

Typical results are given in Tables I and II.

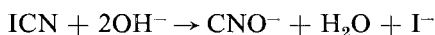
### RESULTS AND DISCUSSION

Iodine cyanide is only slightly soluble in water and its aqueous solution does not react with thiosulphate, sulphite or silver nitrate even on long standing, indicating

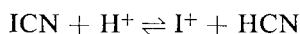
TABLE I.—DETERMINATION OF VARIOUS REDUCTANTS WITH IODINE CYANIDE

Reductant	0.1M HCl medium		0.05M H <sub>2</sub> SO <sub>4</sub> medium		0.08M HNO <sub>3</sub> medium	
	Taken, mg	Found, mg	Taken, mg	Found, mg	Taken, mg	Found, mg
Sodium thiosulphate	134.9	134.7	93.0	93.3	124.0	123.8
	124.7	124.5	74.4	74.2	99.2	99.0
	31.0	31.1	31.0	31.1	62.2	62.3
Sodium sulphite	49.9	50.1	44.1	44.0	52.6	52.7
	32.9	32.8	31.5	31.6	45.5	45.4
	25.2	25.1	18.9	19.0	27.4	27.5
Arsenic(III) oxide	49.7	49.6	87.3	87.5	79.5	79.4
	39.6	39.7	59.4	59.5	49.7	49.6
	22.2	22.3	29.7	29.8	40.0	40.1
Potassium antimonyl tartrate	130.1	130.2	124.5	124.7	99.8	100.0
	97.8	98.4	99.6	99.4	83.6	83.8
	41.5	41.6	83.0	83.1	66.5	66.6
Tin(II) chloride	91.9	91.9	107.5	107.2	64.5	64.6
	55.1	55.2	80.6	80.4	53.5	53.4
	42.9	42.8	53.8	53.7	43.2	43.1
Mercury(I) perchlorate	94.0	93.7	135.2	135.6	122.2	122.0
	75.2	75.3	120.2	120.5	105.9	106.1
	36.5	36.6	88.8	88.6	75.5	75.6
Ascorbic acid	85.0	84.6	79.6	79.8	89.0	88.8
	49.6	49.7	66.2	66.1	54.4	54.5
	44.0	44.2	35.2	35.3	30.8	30.9
$\beta$ -Naphthol	47.0	47.4	57.5	57.7	66.3	66.5
	36.2	36.1	54.0	54.1	43.5	43.4
	23.5	23.6	39.2	39.1	27.5	27.4

that it is a predominantly covalent compound. The behaviour of iodine cyanide in alkaline medium has been reported as:<sup>16</sup>



However, in the presence of hydrochloric, sulphuric, nitric, hydriodic or glacial acetic acid, it reacts with various reductants, owing to the liberation of I<sup>+</sup>:



The removal of I<sup>+</sup> from the solution by a reductant displaces the equilibrium quantitatively to the right. The cyanide ion does not play any part in these titrations, because addition of excess of potassium cyanide does not affect the course of titration with thiosulphate in any way except that a little extra acid has to be added to keep the solution acidic. Iodine(I) halides have already been used as volumetric oxidants in the presence of the corresponding acid,<sup>9,10</sup> the function of the acid being to liberate I<sup>+</sup> from the interhalogen molecule. Iodine cyanide solution is expected to behave similarly.<sup>16-20</sup>

Aqueous iodine cyanide oxidizes potassium iodide to free iodine but the reaction does not proceed to completion as the solution is alkaline owing to hydrolysis of the iodide. However, in the presence of acids, the reaction is quantitative. In aqueous titrations, the acid concentration should be more than 0.04*N*, otherwise the colour change is not sharp. On the other hand, starch becomes ineffective at acid concentrations higher than 4*N*. Nitric acid can be used, but only up to 0.08*M* concentration.



TABLE II.—POTENTIOMETRIC DETERMINATION OF VARIOUS REDUCTANTS WITH IODINE CYANIDE

Reductant	0.1M HCl medium		Acetic acid medium		1:1 Acetic acid-acetic anhydride medium	
	Taken, mg	Found, mg	Taken, mg	Found mg	Taken, mg	Found, mg
Potassium iodide	75.6 63.0 42.0	75.9 62.8 42.2	62.4 41.6 20.8	62.7 41.4 20.7	62.4 41.6 20.8	62.0 41.4 20.9
Sodium thiosulphate	91.5 61.0 30.5	91.7 61.1 30.4	64.8 51.8 32.4	65.0 51.6 32.5	112.0 89.6 44.8	112.5 90.0 44.6
Sodium sulphite	46.5 31.0 15.5	46.4 31.2 15.4	58.4 36.5 21.9	58.2 36.4 22.0	91.0 36.4 27.3	91.3 36.5 27.2
Tin(II) chloride	80.2 53.5 26.7	80.0 53.6 26.6	86.4 57.6 28.8	86.0 57.4 28.9	106.5 71.0 35.5	106.0 71.2 35.6
Arsenic(III) chloride	73.5* 49.0* 24.5*	73.6 48.8 24.6	108.5 77.5 46.5	108.0 77.7 46.7	103.5 88.8 41.4	103.9 88.0 41.2
Antimony(III) chloride	123.0† 82.0† 41.0†	123.0 82.2 41.1	94.8 79.0 47.4	95.2 78.7 47.2	94.8 79.4 47.4	95.0 79.2 47.2
Mercury(II) perchlorate	112.5 75.0 37.5	112.6 75.1 37.4	76.5 61.2 30.6	76.8 61.5 30.4	76.5 61.2 30.6	76.6 61.1 30.7
Iron(II) perchlorate	— — —	— — —	60.0 54.0 30.0	60.2 53.9 30.2	103.6 74.0 29.6	103.4 73.9 29.8
Ammonium thiocyanate	— — —	— — —	51.6 38.7 25.8	51.4 38.8 25.8	69.0 41.4 13.8	69.2 41.5 13.7
Ascorbic acid	66.0 44.0 22.0	65.8 44.2 22.0	— — —	— — —	— — —	— — —
$\beta$ -Naphthol	55.5 37.0 18.5	55.4 36.9 18.6	— — —	— — —	— — —	— — —

\* Arsenic(III) oxide.

† Potassium antimonyl tartrate.

In these redox reactions, iodine(I) is reduced to iodine or iodide, depending on the strength of the reductant. The reactions which entail its reduction to iodide can be followed by direct visual titrations in aqueous medium. In non-aqueous solvents, the formation of the complex tri-iodide ion is possible because of its greater stability in organic solvents than in water.<sup>21</sup> The potential jump at an ICN/KI molar ratio of 1:2 gradually becomes smaller when acetic acid containing increasing amounts of water is used as solvent, owing to the decreasing stability of  $I_3^-$  in the presence of water. Thus the final product of reduction of iodine cyanide is dependent upon the entire system involved.

Sodium sulphite solution becomes yellowish on addition of iodine cyanide and the first potential jump occurs at ICN/SO<sub>3</sub><sup>2-</sup> molar ratio of 1:1. On further addition of the oxidant, the iodide produced is further oxidized to tri-iodide, as is evident from the yellowish brown colour which develops during this part of the titration, and a second jump in potential occurs at a molar ratio of 3:2 for ICN/SO<sub>3</sub><sup>2-</sup>. The

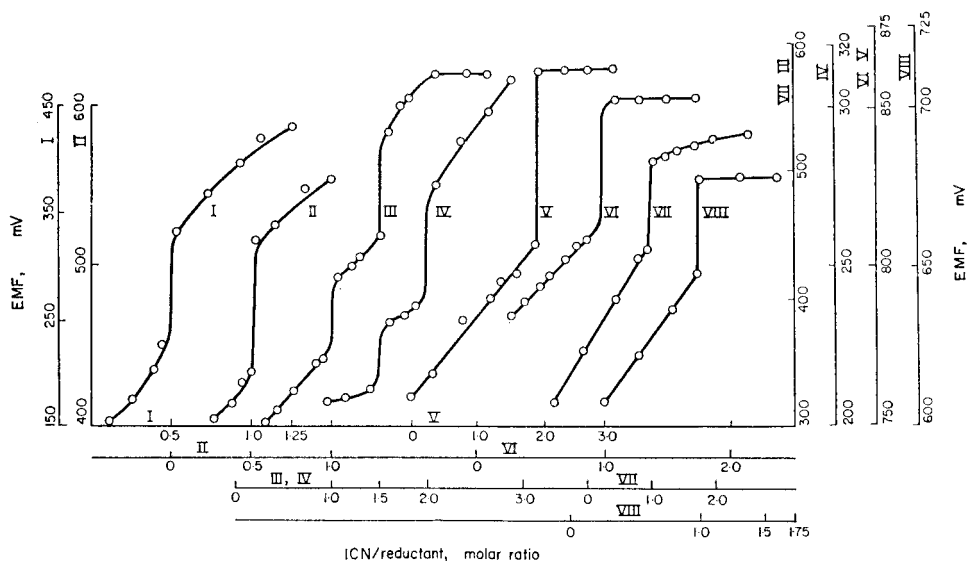
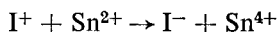


FIG. 1.—Potentiometric titrations of iodine cyanide in glacial acetic acid with I, potassium iodide; II, sodium thiosulphate; III, sodium sulphite; IV, arsenic(III) chloride; V, antimony(III) chloride; VI, ferrous perchlorate; VII, ammonium thiocyanate; VIII tin(II) chloride.

tri-iodide is then converted into iodine, yielding a bright red solution. The rise in potential is slow during this part of the titration and there is no sudden jump in e.m.f. corresponding to an oxidant/reductant molar ratio of 2:1. However, when this ratio is exceeded the curve becomes flat, indicating the presence of excess of iodine cyanide (Figs. 1 and 2).

Similarly iodine cyanide reacts with thiosulphate in 1:2 molar ratio, forming iodide and tetrathionate (Figs. 1 and 3). In non-aqueous media, the solution becomes yellow, then gradually changes through orange to red.

Tin(II) is oxidized to tin(IV) in acetic acid and 1:1 acetic acid-acetic anhydride media in the presence of molar concentrations of anhydrous sodium acetate:



The colour becomes yellow on first addition of iodine cyanide and then brown. The reaction in aqueous medium has been found to be similar. Extraction indicators have worked successfully in titrations with sulphite, thiosulphate and tin(II). However, when tin(II) was titrated with iodine cyanide, with chloroform as indicator, unexpectedly high values were obtained, for reasons unknown.

Arsenic(III) oxide and potassium antimonyl tartrate can be quantitatively titrated with aqueous iodine cyanide in presence of sodium bicarbonate, which destroys the hydriodic acid formed during the course of the titrations, but iodine cyanide does not react with arsenic(III) and antimony(III) chlorides quantitatively in glacial acetic acid and 1:1 acetic acid-acetic anhydride mixture. However, the oxidation is complete in solutions which are  $>1M$  in sodium acetate, probably because the sodium acetate, which is a strong base in these media, reduces the high potentials of the arsenic and antimony couples and thereby renders the titrations possible. The reactions proceed slowly with evolution of considerable heat. Because

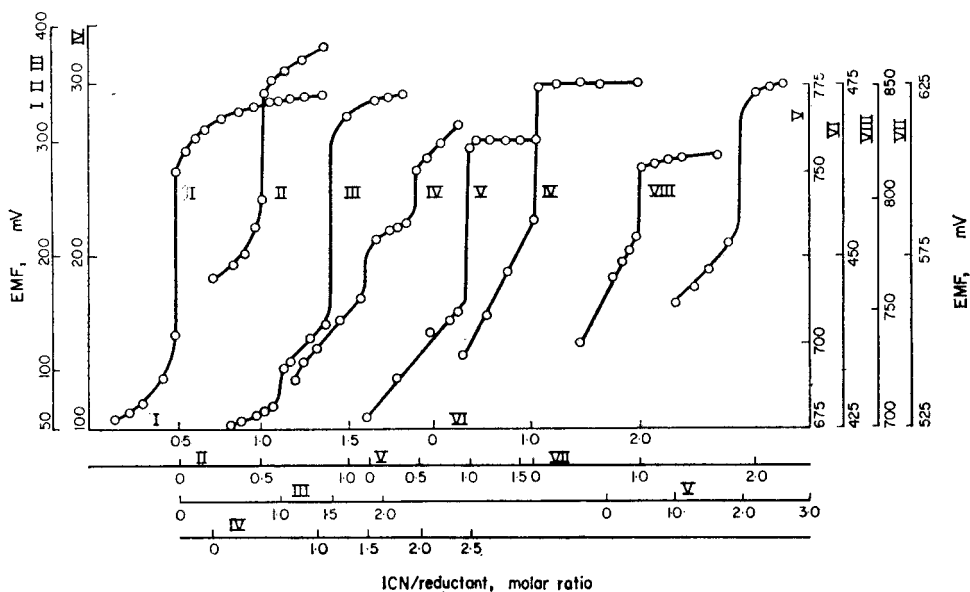


FIG. 2.—Potentiometric titrations of iodine cyanide in acetic acid–acetic anhydride (1:1) mixture with I, potassium iodide; II, sodium thiosulphate, III, sodium sulphite; IV, arsenic(III) chloride; V, ferrous perchlorate; VI, ammonium thiocyanate; VIII, tin(II) chloride, VIII, antimony(III) chloride.

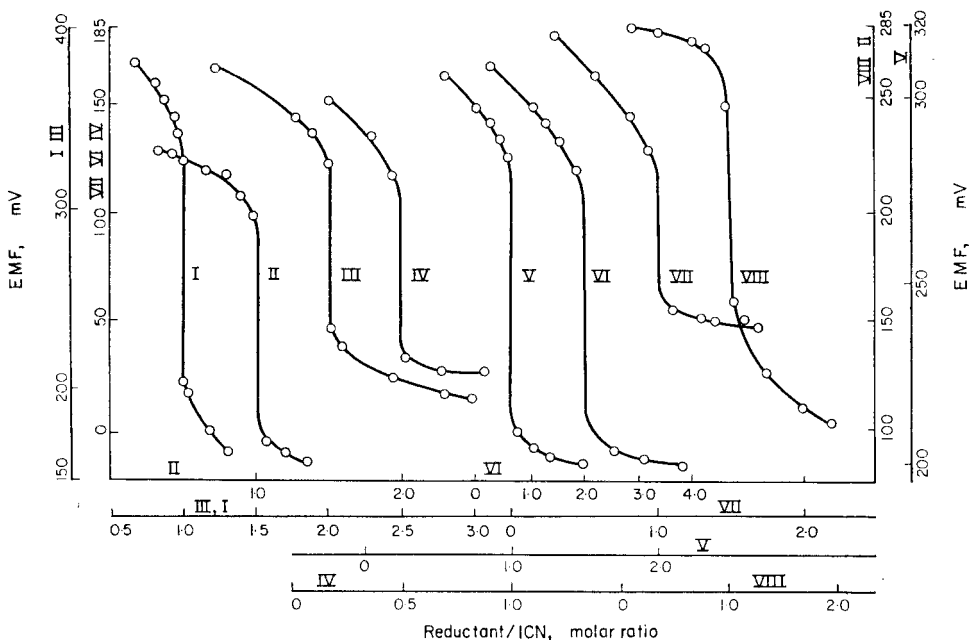


FIG. 3.—Potentiometric titrations of iodine cyanide with I, tin(II) chloride; II, ascorbic acid; III, sodium thiosulphate; IV, arsenious oxide; V, sodium sulphite; VI, mercurous perchlorate; VII, tartar emetic; VIII,  $\beta$ -naphthol in aqueous medium.

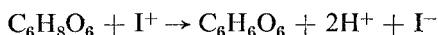
of their high redox potentials, arsenic(III) and antimony(III) reduce iodine cyanide only to elementary iodine, as indicated by the red colour of the solution and a jump in potential at oxidant/reductant molar ratio of 2:1 (Figs. 1 and 2). There is another potential jump in the titration between iodine cyanide and arsenic(III) chloride at ICN/As(III) molar ratio of 3:2 (Figs. 1 and 2), which may be attributed to the formation of tri-iodide:



Iodine cyanide reacts with iron(II) perchlorate in 1:1 molar ratio in non-aqueous media in the presence of anhydrous sodium acetate (Figs. 1 and 2). The reaction is exothermic and the iron(II) solution becomes yellow and then brown on further addition of iodine cyanide, because of the formation of iron(III) acetate. Iodine cyanide is not reduced by iron(II) to iodide even in aqueous medium and therefore visual titration is not possible. Similarly ammonium thiocyanate reacts with iodine cyanide in non-aqueous solvents in 1:1 molar ratio (Figs. 1 and 2), forming thiocyanogen and iodine.

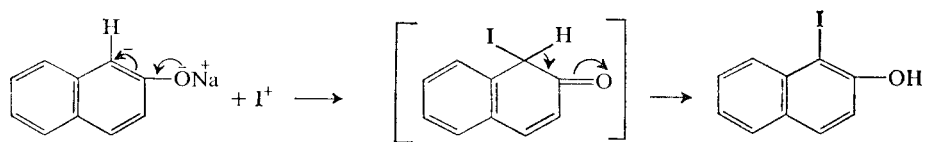
Mercury(I) perchlorate in non-aqueous medium reduces iodine cyanide to iodide and mercury(I) is oxidized to mercury(II). In aqueous medium, the solution should be almost free from mineral acids, otherwise a white precipitate appears on addition of even a drop of iodine cyanide solution. The titrations were, therefore, carried out in presence of sodium bicarbonate. Potassium iodide was added to the iodine cyanide to make the end-point sharp; otherwise a bright yellow colour appeared which changed to yellowish green and rendered the detection of the end-point somewhat difficult.

Iodine cyanide oxidizes ascorbic acid in aqueous medium quantitatively to dehydroascorbic acid:



The titration is not possible in glacial acetic acid or 1:1 acetic acid-acetic anhydride. This is in keeping with the fact that the reducing capacity of ascorbic acid is very much inhibited in organic solvents, compared to its reducing power in aqueous media.

Iodine cyanide reacts with  $\beta$ -naphthol in 1:1 molar ratio, forming  $\alpha$ -iodo- $\beta$ -naphthol:



This titration is not possible in acidic medium because  $\alpha$ -iodo- $\beta$ -naphthol is formed only under alkaline conditions.

It is evident from these studies that redox reactions of iodine cyanide are the reactions of  $\text{I}^+$  and therefore its oxidizing behaviour is similar to that of iodine chloride or bromide. However, oxidation of sodium sulphite with iodine cyanide in non-aqueous solvents is quantitative even in the absence of sodium acetate, whereas iodine chloride has been reported to oxidize sodium sulphite quantitatively only in the presence of excess of sodium acetate.<sup>6</sup> Thus iodine cyanide appears to be a better oxidant than iodine chloride, which in turn is stronger than iodine bromide. It may

also be mentioned that the so-called cyanogen iodide has the iodine atom as the positive end of the dipole of the molecule in acidic medium and the manner in which iodine cyanide ionizes is not a function of its structure alone but also of its environment.

*Acknowledgement*—One of us (R. K. C.) is thankful to the University Grants Commission (India) for the award of a Junior Research Fellowship.

**Zusammenfassung**—Jodcyanid wurde als Oxidationsmittel eingeführt. Es eignet sich zur Bestimmung von Jodid, Sulfit, Thiosulfat, Thiocyanat, Arsen(III), Antimon(III), Zinn(II), Quecksilber(I), Eisen(II), Ascorbinsäure und  $\beta$ -Naphthol in verdünnten wässrigen Mineralsäuren, Eisessig und dem Gemisch Essigsäure-Acetanhydrid 1:1. Der Endpunkt kann visuell und potentiometrisch bestimmt werden.

**Résumé**—On a mis au point le cyanure d'iode en tant qu'oxydant pour le dosage d'iodure, sulfite, hyposulfite, thiocyanate, arsenic(III), antimoine(III), étain(II), mercure(I), fer(II), acide ascorbique et  $\beta$ -naphthol en acides minéraux aqueux dilués, acide acétique glacial et mélange acide acétique-anhydride acétique 1:1, avec méthodes visuelle et potentiométrique de détection de fin de dosage.

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# A GENERAL COMPUTER APPROACH FOR CALCULATING RATE CONSTANTS FROM NEAR-EQUILIBRIUM KINETIC STUDIES

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**Summary**—A general computer approach for estimating rate constants from relaxation times is described. The programme CORNEK is essentially a least-squares refinement programme applied to non-linear systems. It uses directly the differential forms of the first derivatives of mass-balance and rate equations, thus avoiding the time-consuming derivations of near-equilibrium rate equations. The programme has been tested for binary systems such as Cu-histamine, Cu-serine, and the ternary system Cu-histamine-serine.

THE DEVELOPMENT of relaxation techniques has resulted in the elucidation of reaction mechanisms of many fast reactions which were previously inaccessible by using classical techniques.<sup>1</sup> However, at present there is no general method of evaluating rate constants from the expressions relating relaxation time to equilibrium concentrations, equilibrium constants and rate constants. Also, the derivation of such equations from mass balance relationships involves lengthy, though not complicated, algebra.<sup>2</sup> As a result, earlier workers made various simplifying assumptions with or without justification, or tested their kinetic data for only a small number of mechanisms out of a large number of possibilities. The available methods of calculating rate constants are also clumsy when applied to more complicated systems where more than one type of metal ion or ligand exists in the system. In this paper we present a general approach for calculating rate constants from relaxation times. The computer programme CORNEK is essentially a least-squares refinement programme for non-linear systems and is almost completely general. The unique feature of the method discussed here is that in order to make a best fit, the calculated value of the dependent variable, relaxation time, is not required. The programme has been tested for simple and mixed ligand systems.<sup>3,4</sup> It uses directly the differential form of the first derivatives of mass balance and rate equations in order to calculate rate constants from relaxation times, thus avoiding the time-consuming derivations of near-equilibrium rate equations.

## THEORY

The theory of relaxation spectra<sup>1</sup> and the general least-squares<sup>5</sup> approach as applied to parameter estimation have been described in detail elsewhere and therefore only the portions relevant to the present problem will be discussed here. For the sake of clarity the present discussion is in terms of a specific system, a bivalent metal ion with a co-ordination number of four (such as  $\text{Cu}^{2+}$ ) and a bidentate ligand with two ionizing groups (such as protonated glycine). The extension to more general cases will follow essentially the same line and will be apparent towards the end of the discussion. The computer programme CORNEK given in the appendix is, however, a general one and can be used for any system.

For aqueous solutions containing a bivalent metal ion, M, with co-ordination number four and a bidentate ligand,  $H_2A$ , with two dissociable protons, the following equilibria must be considered in order to characterize the distribution of proton or metal complex species (charges on the species have been omitted):



In addition to these expressions, as many more may be written as logically appropriate for describing various reaction paths. For example, we may like to consider the possibility of the monoprotonated form of the ligand reacting with the metal ion. Therefore:



Similarly, any other reaction path or species can be added to this scheme. If the relaxation effect is followed by means of a coloured pH indicator, In, the appropriate equilibrium should be taken into consideration:



The mass balance equations for the system under consideration are:

$$\text{Total metal } (T_M) = [M] + [MA] + [MA_2] \quad (8)$$

$$\text{Total ligand } (T_A) = [A] + [HA] + [H_2A] + [MA] + 2[MA_2] \quad (9)$$

$$\text{Total proton } (T_H) = [H] + [HA] + 2[H_2A] + [HIn] - [OH] \quad (10)$$

$$\text{Total indicator } (T_{In}) = [HIn] + [In] \quad (11)$$

Since the protolytic reactions reach equilibrium much faster than the metal complex reactions under consideration, they can be assumed to be at equilibrium at all times. For species MA,  $MA_2$  we can write the following rate expressions:

$$\begin{aligned} -\delta[MA]/dt = & -k_3[M][A] + \frac{k_3}{K_3}[MA] + k_4[MA][A] - \frac{k_4}{K_4}[MA_2] \\ & -k_5[M][HA] + \frac{k_5}{K_5}[MA][H] + k_6[MA][HA] - \frac{k_6}{K_6}[MA_2][H] \end{aligned} \quad (12)$$

and

$$-\delta[MA_2]/dt = -k_4[MA][A] + \frac{k_4}{K_4}[MA_2] - k_6[MA][HA] + \frac{k_6}{K_6}[MA_2][H] \quad (13)$$

On differentiating (12) and (13), and substituting  $(\delta[A] \cdot [HA]/[A] + \delta[H] \cdot [HA]/[H])$  for  $\delta[HA]$ , and  $(\delta[H] \cdot 2[H_2A]/[H] + \delta[A] \cdot [H_2A]/[A])$  for  $\delta[H_2A]$  and simplifying, the differential forms of the resulting expressions are obtained:

$$\begin{aligned} \frac{-d\delta[MA]}{dt} = & \left( -k_3[M] + k_4[MA] - k_5 \frac{[M][HA]}{[A]} + k_6 \frac{[MA][HA]}{[A]} \right) \delta[A] \\ & + \left( -k_3[A] - k_5[HA] \right) \delta[M] + \left( -k_5 \frac{[M][HA]}{[H]} + \frac{k_5}{K_5} [MA] + k_6 \frac{[MA][HA]}{[H]} \right. \\ & \left. - \frac{k_6}{K_6} [MA_2] \right) \delta[H] + \left( \frac{k_3}{K_3} + \frac{k_5}{K_5} [H] + k_4[A] \right) \delta[MA] \\ & + \left( -\frac{k_4}{K_4} - \frac{k_6}{K_6} [H] \right) \delta[MA_2] \quad (14) \end{aligned}$$

$$\begin{aligned} \frac{-d\delta[MA_2]}{dt} = & \left( k_4[MA] + k_6 \frac{[MA][HA]}{[A]} \right) \delta[A] - \left( k_6 \frac{[MA][HA]}{[H]} \right. \\ & \left. - \frac{k_6}{K_6} [MA_2] \right) \delta[H] - \left( k_4[A] + k_6[HA] \right) \delta[MA] + \left( \frac{k_4}{K_4} + \frac{k_6}{K_6} [H] \right) \delta[MA_2] \quad (15) \end{aligned}$$

Subscripts on rate and equilibrium constants refer to the equation number,  $k_j$ 's are the rate constants for the forward reactions and  $K_j$ 's are the stepwise formation constants; parentheses represent equilibrium concentrations. For a system containing  $n$  complex species,  $n$  such near-equilibrium rate equations are obtained. Similarly, the differential form of the mass balance equations (8–11) is:

$$\delta T_M = 0 = \delta[M] + \delta[MA] + \delta[MA_2] \quad (16)$$

$$\begin{aligned} \delta T_A = 0 = & \left( \frac{2[H_2A] + [HA]}{[H]} \right) \delta[H] + \left( \frac{[H_2A] + [HA] + [A]}{[A]} \right) \delta[A] \\ & + \delta[MA] + 2\delta[MA_2] \quad (17) \end{aligned}$$

$$\begin{aligned} \delta T_H = 0 = & \left( \frac{4[H_2A] + [HA] + [H] + \frac{K_w}{[H]} + [HIn]}{[H]} \right) \delta[H] \\ & + \left( \frac{2[H_2A] + [HA]}{[A]} \right) \delta[A] + \left( \frac{[HIn]}{[In]} \right) \delta[In] \quad (18) \end{aligned}$$

$$\delta T_{In} = 0 = ([HIn]/[In] + 1)\delta[In] + ([HIn]/[H])\delta[H] \quad (19)$$

where  $K_w$  = ionic product of water.

Again substitution for  $\delta[HA]$ ,  $\delta[H_2A]$ ,  $\delta[HIn]$  has been made in terms of  $\delta[H]$ ,  $\delta[A]$ , and  $\delta[In]$ , respectively, as explained earlier. Equations equivalent to (1–19), for a ternary system, are given in Appendix I. On designation of the coefficients of  $\delta[MA]$ ,  $\delta[MA_2]$ ,  $\delta[M]$ ,  $\delta[A]$ ,  $\delta[H]$ , and  $\delta[In]$  as  $a_{i1}$ ,  $a_{i2}$ ,  $a_{i3}$ ,  $a_{i4}$ ,  $a_{i5}$ , and  $a_{i6}$ , respectively,



where  $i = 1, 2, 3, 4, 5$ , and 6 for equations (14–19), respectively, equations (14–19) can be written in the following matrix notation.

$$\mathbf{AX} = \mathbf{Y}$$

$$\begin{array}{c} \left| \begin{array}{cccccc} a_{11} & a_{12} & a_{13} & a_{14} & a_{15} & a_{16} \\ a_{21} & a_{22} & a_{23} & a_{24} & a_{25} & a_{26} \\ a_{31} & a_{32} & a_{33} & a_{34} & a_{35} & a_{36} \\ a_{41} & a_{42} & a_{43} & a_{44} & a_{45} & a_{46} \\ a_{51} & a_{52} & a_{53} & a_{54} & a_{55} & a_{56} \\ a_{61} & a_{62} & a_{63} & a_{64} & a_{65} & a_{66} \end{array} \right| \cdot \left| \begin{array}{c} \delta[\text{MA}] \\ \delta[\text{MA}_2] \\ \delta[\text{M}] \\ \delta[\text{A}] \\ \delta[\text{H}] \\ \delta[\text{In}] \end{array} \right| = \left| \begin{array}{c} -d\delta[\text{MA}]/dt \\ -d\delta[\text{MA}_2]/dt \\ 0 \cdot 0 \\ 0 \cdot 0 \\ 0 \cdot 0 \\ 0 \cdot 0 \end{array} \right| \end{array} \quad (20)$$

By the process of elimination involving elementary row operations, from the matrix equation (20) we can easily obtain:

$$\mathbf{A}'\mathbf{X} = \mathbf{Y}$$

$$\begin{array}{c} \left| \begin{array}{cccccc} a_{11}' & a_{12}' & 0 & 0 & 0 & 0 \\ a_{21}' & a_{22}' & 0 & 0 & 0 & 0 \\ a_{31}' & a_{32}' & a_{33}' & 0 & 0 & 0 \\ a_{41}' & a_{42}' & a_{43}' & a_{44}' & 0 & 0 \\ a_{51}' & a_{52}' & a_{53}' & a_{54}' & a_{55}' & 0 \\ a_{61}' & a_{62}' & a_{63}' & a_{64}' & a_{65}' & a_{66}' \end{array} \right| \cdot \left| \begin{array}{c} \delta[\text{MA}] \\ \delta[\text{MA}_2] \\ \delta[\text{M}] \\ \delta[\text{A}] \\ \delta[\text{H}] \\ \delta[\text{In}] \end{array} \right| = \left| \begin{array}{c} -d\delta[\text{MA}]/dt \\ -d\delta[\text{MA}_2]/dt \\ 0 \cdot 0 \\ 0 \cdot 0 \\ 0 \cdot 0 \\ 0 \cdot 0 \end{array} \right| \end{array} \quad (21)$$

The first two rows now correspond to the near-equilibrium rate equations of Hammes and Steinfield.<sup>2</sup> The corresponding characteristic determinant is:

$$\left| \begin{array}{cc} a_{11}' - \lambda & a_{12}' \\ a_{21}' & a_{22}' - \lambda \end{array} \right| = 0 \quad \text{or} \quad |\mathbf{A}'' - \lambda\mathbf{I}| = 0 \quad (22)$$

where  $\lambda = 1/\tau$ ,  $\tau$  = relaxation time,  $\mathbf{I}$  = the identity matrix, and

$$\mathbf{A}'' = \begin{vmatrix} a_{11}' & a_{12}' \\ a_{21}' & a_{22}' \end{vmatrix}$$

and the characteristic polynomial is:

$$(a_{11}' - \lambda)(a_{22}' - \lambda) - a_{12}' \cdot a_{21}' = 0$$

In general for a square matrix of order  $n$  corresponding to equation (22), the characteristic polynomial is given by:

$$\lambda^n + c_{n-1}\lambda^{n-1} + c_{n-2}\lambda^{n-2} + \cdots + c_1\lambda + (-1)^n |\mathbf{A}''| = 0 \quad (23)$$

where  $c_k$  is the  $k_{th}$  coefficient of the polynomial. The last term is a constant equal to  $(-1)^n$  times the value of the determinant of matrix  $\mathbf{A}''$ .

*Estimation of rate constants by the generalized method of least squares as applied to non-linear systems*

In equation (23)  $c_i$ 's are related to  $a_{ij}$ 's of the secular determinant and are functions

of equilibrium concentrations of all the species, stability constants and the rate constants. In near-equilibrium kinetic studies equilibrium concentrations of various species and the corresponding formation constants are supposed to be obtained from prior knowledge of solution equilibria. A reasonable initial approximation of rate constants to be refined can also be made, and any one of the observed relaxation times can be used in order to calculate the function  $R$  where:

$$R = \lambda^n + c_{n-1}\lambda^{n-1} + c_{n-2}\lambda^{n-2} + \dots + c_1\lambda + (-1)^n \cdot |A''|. \quad (24)$$

The least-squares problem can now be stated mathematically as:

$$S = \sum_{i=1}^{NPT} R_i^2 = \text{minimum (NPT = number of observations)}. \quad (25)$$

The general problem of least-squares adjustment of data has been presented thoroughly by Deming and the reader is referred to Ref. 5 for details of the treatment. The function  $R$  in equation (24), in Deming's notation corresponds to the condition equation:  $F(x, y, a, b, c) = 0$  where  $x, y$  are the independent and dependent variables, respectively, and  $a, b, c$  are the parameters the least-squares estimate of which is needed. The least-squares solution of (25) is:

$$\sum \frac{R_i^{k_1} \cdot R_i^{k_1}}{L_i} \Delta k_1 + \sum \frac{R_i^{k_1} \cdot R_i^{k_2}}{L_i} \Delta k_2 + \dots + \sum \frac{R_i^{k_1} \cdot R_i^{k_n}}{L_i} \Delta k_n = \sum \frac{R_i^{k_1} \cdot R_i}{L_i} \quad (26)$$

$$\sum \frac{R_i^{k_2} \cdot R_i^{k_1}}{L_i} \Delta k_1 + \sum \frac{R_i^{k_2} \cdot R_i^{k_2}}{L_i} \Delta k_2 + \dots + \sum \frac{R_i^{k_2} \cdot R_i^{k_n}}{L_i} \Delta k_n = \sum \frac{R_i^{k_2} \cdot R_i}{L_i} \quad (27)$$

$$\sum \frac{R_i^{k_n} \cdot R_i^{k_1}}{L_i} \Delta k_1 + \sum \frac{R_i^{k_n} \cdot R_i^{k_2}}{L_i} \Delta k_2 + \dots + \sum \frac{R_i^{k_n} \cdot R_i^{k_n}}{L_i} \Delta k_n = \sum \frac{R_i^{k_n} \cdot R_i}{L_i} \quad (28)$$

where  $R_i^{k_j} = \delta R_i / \delta k_j$ , ( $j = 1, 2, \dots, n$ , and  $n =$  number of rate constants to be refined or estimated),  $R_i =$  function  $R$  at  $i$ th observation,  $L_i = (\delta R_i / \delta \lambda_i)^2$ . All summations refer to  $\sum_{i=1}^{NPT}$ . The partial derivatives  $\delta R_i / \delta k_j$ , etc, can be obtained by numerical differentiation using the method of symmetric finite difference. The equations (26)–(28) are known as normal equations, which can be solved for  $\Delta k_1, \Delta k_2, \dots, \Delta k_n$ , etc. There are numerous ways in which these equations can be solved. In the programme CORNEK, the matrix inversion subroutine (MTXIN) has been used for this purpose. The new improved set of the rate constants is thus obtained:

$$k_j^1 = k_j^0 - \Delta k_j, \quad (j = 1, 2, \dots, n). \quad (29)$$

The superscript here refers to iteration number. The procedure is repeated until the function  $S$  converges to a steady value. The iterative adjustments are necessary except for the simple, linear case where the first iteration yields the unique solutions. The simplest iterative procedure<sup>6,7,8</sup> to apply is to take the final estimates in equation (29) as initial estimates and repeat the calculations.

#### THE PROGRAMME CORNEK (CALCULATIONS OF RATE CONSTANTS FROM NEAR EQUILIBRIUM KINETICS)

The programme is in five parts, the main programme and four subroutines.

The main programme deals with the input data, the calculations of derivatives,  $\partial R_i / \partial k_j$ , etc, by numerical differentiation, the setting up of normal equations and

output of results. The statistical parameters such as variance of the function  $R$ , standard deviation in each of the constants estimated, covariance matrix, and correlation matrix are also calculated in the main programme. The subroutine MTORIG simply defines the elements of the coefficient matrix of equation (20). The subroutine MTXOP performs three matrix operations:

1. It operates on the coefficient matrix of equation (20) and reduces it to the coefficient matrix of equation (21).
2. It obtains the values of the determinant of the coefficient matrix of equation (22) by reducing the matrix to a lower, triangular form. The determinant is then given by the product of the elements of the main diagonal:

$$\det \mathbf{A} = |\mathbf{A}| = \prod_{i=1}^n a_{ii}.$$

3. In the subroutine EIGEN it is again called for obtaining the numerical value of the polynomial given by equation (23).

The subroutine MTXIN is a standard matrix inversion subroutine and is used to solve the normal equations.

After the final refinement of rate constants, the subroutine EIGEN calculates the predicted values of the relaxation times for comparison with the experimentally obtained values. The programme EIGEN is also completely general and is based on Muller's<sup>9</sup> method of quadratic interpolation.

The programme has provision for applying relative (% of  $\lambda$  observed) weights to the dependent variable, which is  $\lambda$  in this case. In the absence of the knowledge of weight, unit weights are applied to all observations. The programme can also be used for calculating only the roots (or relaxation times) without refining the constants if so desired. When the shifts in the constants have been calculated, the computer checks their values and reduces any which are excessively large. At no time is a shift allowed to be greater than the corresponding rate constant in that iteration. For the purpose of numerical differentiation to obtain the derivatives in equations (26–28), a small increment ( $\sim 0.1\%$ ) is given to the  $j$ th parameter, the other parameters remaining unchanged, and the value of  $\partial R_i / \partial k_j$  is calculated for all points. The same increment ( $0.1\%$ ) is then given to each of the other parameters in turn and the remaining derivatives are thus obtained.

For each reaction scheme a separate MTORIG subroutine is needed. However, if only new reaction paths are to be considered without changing the number of rate equations, no change is needed in the subroutine, provided in the original derivation of the rate equations these paths have been taken into account. It, therefore, saves considerable time and computations, if all possible reaction paths are taken into account in the derivation of rate equations. The computer can then be asked to ignore any one or more of these paths by simply writing zeros for the corresponding rate constants in the input cards.

The programme calculates variance in the function  $R$  in two different ways:

$$\text{Var}(R) = \sum \frac{R_i \cdot R_i}{L_i} - \sum \frac{R_i \cdot R_i^{k_1}}{L_i} \Delta k_1 \cdots - \sum \frac{R_i \cdot R_i^{k_n}}{L_i} \Delta k_n \quad (30)$$

$$\text{Var}(R) = \sum \frac{R_i \cdot R_i}{L_i} \quad (30')$$

Equation (30) is valid only at the minimum, whereas equation (30') is a general one. Near the minimum the two equations are equivalent. In a good least-squares fit, variance in the function [equation (25)] being minimized continuously decreases and converges to a constant value, shifts in the constants [ $\Delta k_j$  in equations (26–28)], become progressively smaller, the gradient of the residual surface with respect to the parameters being estimated becomes very small, and finally on back-calculation, the calculated values of the dependent variable should be well within the acceptable limits of the technique. However, divergence or inability to converge is sometimes observed. This behaviour is quite often due to an inappropriate reaction mechanism chosen as the model, insufficient accuracy in the calculations of the derivatives, bad initial approximations of the parameters to be refined, and in some cases, depending on the nature of the “residual surface,” inappropriate size of shifts in the constants.

The programme CORNEK contains several print statements converted into comment statements (see listing of the programme). These can readily be used to ascertain that the differences in the quantities [ $E(1), \dots, E(5)$ ], which calculate the derivatives, are significant but as small as possible. The divergence due to bad initial approximations and inappropriate “step-size” can be taken care of by increasing the number of refinement cycles. In most cases, if the model is a correct one, convergence to a stationary minimum is attained in spite of initial wobbling of the function being minimized. However, if the initial approximations of the parameters are too far away from the values at the minimum, convergence in the error function is unlikely, no matter what size of shifts is chosen. The programme has provision for applying fractional shifts if it is felt that in a particular run divergence or wobbling in variance is due to the shifts being too big. At the end of each cycle the computer checks the variance and if it is higher than in the previous cycle, the shifts are reduced in the steps of  $\text{SHIFT} \times [\text{Fractional Shift Factor}]$ . This may be done fifty times in a cycle and if, even then, no step-size gives lower variance the appropriate message is printed out and the process of refinement is terminated. The calculated values of relaxation times are then obtained by using the constants estimated in the last refinement cycle. If reduction in step-size improves variance, the programme continues the refinement with reduced step-size in the usual manner. A good model with reasonable initial guesses rarely requires this treatment. In some runs it may be observed that the value of variance at the final stationary point of convergence is slightly higher than in some earlier cycle. This usually arises from instability in the process of numerical differentiation. However, the corresponding error in the parameters will rarely exceed the estimated standard deviation in the parameters, provided all other requirements of a good fit are satisfied. Our experience with the programme is that in most cases all the conditions of a good fit are met only when the variances in  $R$  calculated by both equations (30) and (30') agree closely (*i.e.* to the first or second decimal place).

### CONCLUSIONS

The least-squares refinement approach provides a powerful and useful tool for calculating the rate constants from relaxation times. In the CORNEK-II version of the present programme, provision is being made to refine the stability constants also. Deming's general treatment does not require that the calculated value of the dependent variable, relaxation time in the present case, should be obtained in order to make the “best fit.” This is very helpful in relaxation studies where experimentally only one or

two relaxation times are observed, whereas the calculations give a spectrum of relaxation times. The programme has been tested to calculate the rate constants for binary systems such as  $\text{Cu}^{2+}$ -serine,  $\text{Cu}^{2+}$ -histamine, as well as for ternary systems involving five relaxations, such as Cu-histamine-serine. In all cases reasonable values of rate constants were obtained and good agreement between the observed and predicted relaxation times was achieved for all observations.

At present the limiting factor in the near-equilibrium kinetic investigations is the accuracy with which relaxation times are measured. It will increase the reliability of the calculated values of rate constants considerably if ten relaxation spectra are taken for each observation so that the variance can be calculated and hence the weight of each observation. The values of the rate constants calculated also depend on the values of formation constants chosen for calculating the equilibrium concentrations of various species. The practice of using the formation constants determined at some ionic strength and temperature other than that maintained in the relaxation studies can also lead to meaningless results. In order to get reliable results from the programme it is essential that the relaxation times cover at least a tenfold variation in the concentrations of reactants and as many observations as possible.

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#### APPENDIX I

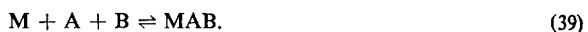
##### *Ternary system Cu(II)-histamine-serine*

M = Copper

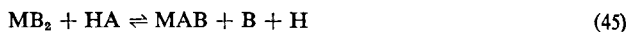
A = Neutral histamine

B = Serine anion

The enthalpy change for the formation of copper chelates under consideration is appreciable ( $\sim 20$  kJ/mole per M—N bond), and therefore, for a  $10^\circ$  temperature-jump relaxations could easily be obtained without using an indicator. The equilibrium expressions characterizing the distribution of proton and metal complex species are:



In addition to equations (31–39), the following likely reaction paths were also considered:



The mass balance equations for the system are:

$$T_M = [M] + [MA] + [MA_2] + [MB] + [MB_2] + [MAB] \quad (47)$$

$$T_A = [A] + [MA] + 2[MA_2] + [H_2A] + [HA] + [MAB] \quad (48)$$

$$T_B = [B] + [MB] + 2[MB_2] + [H_2B] + [HB] + [MAB] \quad (49)$$

$$T_H = 2[H_2A] + [HA] + 2[H_2B] + [HB] + [H] - [OH]. \quad (50)$$

The differential form of the mass balance equations is:

$$\delta T_M = 0 = \delta[M] + \delta[MA] + \delta[MA_2] + \delta[MB] + \delta[MAB] \quad (51)$$

$$\delta T_A = 0 = \left( \frac{[A] + [H_2A] + [HA]}{[A]} \right) \delta[A] + \delta[MA] + 2\delta[MA_2] + \delta[MAB] \\ + \left( \frac{2[H_2A] + [HA]}{[H]} \right) \delta[H] \quad (52)$$

$$\delta T_B = 0 = \left( \frac{[B] + [H_2B] + [HB]}{[B]} \right) \delta[B] + \delta[MB] + 2\delta[MB_2] + \delta[MAB] \\ + \left( \frac{2[H_2B] + [HB]}{[H]} \right) \delta[H] \quad (53)$$

$$\delta T_H = 0 = \left( \frac{2[H_2A] + [HA]}{[A]} \right) \delta[A] + \left( \frac{2[H_2B] + [HB]}{[B]} \right) \delta[B] \\ + \left( \frac{4[H_2A] + [HA] + 4[H_2B] + [H] + K_w/[H]}{[H]} \right) \delta[H]. \quad (54)$$

From equations (31–46) one can obtain five near-equilibrium rate expressions for  $d\delta[MA]/dt$ ,  $d\delta[MA_2]/dt$ ,  $d\delta[MB]/dt$ ,  $d\delta[MB_2]/dt$ , and  $d\delta[MAB]/dt$ . These, with four mass balance equations [differential forms (51)–(54)], give nine equations, which in matrix notation acquire the form of equation (20), *i.e.*:

$$\begin{array}{c|c|c} \begin{array}{c} a_{11} \dots \dots a_{19} \\ \dots \dots \\ \dots \dots \\ a_{91} \dots \dots a_{99} \end{array} & \begin{array}{c} \delta[MA] \\ \delta[MA_2] \\ \delta[MB] \\ \delta[MB_2] \\ \delta[MAB] \\ \delta[M] \\ \delta[A] \\ \delta[B] \\ \delta[H] \end{array} & = - \begin{array}{c} d\delta[MA]/dt \\ d\delta[MA_2]/dt \\ d\delta[MB]/dt \\ d\delta[MB_2]/dt \\ d\delta[MAB]/dt \\ 0 \cdot 0 \\ 0 \cdot 0 \\ 0 \cdot 0 \\ 0 \cdot 0 \end{array} \end{array}$$

## APPENDIX II

### Input data and formats

1. NJ (Number of jobs. For trying more than one [*e.g.* *n*] reaction model, put *n*).  
FORMAT (I2)
2. FSF (If fractional shifts are desired, put the value of "fractional shift factor," *e.g.* for half-shifts write 0.5; otherwise, leave blanks.)  
FORMAT (F10.4)
3. NPT (number of observations); NC (number of constants required to define all the equilibrium expressions, *e.g.* 16 for the ternary system described in Appendix I); NCV (number of constants being refined or estimated); NL (number of types of ligands present in the system, *e.g.* two for a ternary

system and one for a binary system); TNEQ (total number of equations necessary to define the subroutine MTORIG; *i.e.* the number of mass balance equations plus the number of rate equations, *e.g.* nine for the ternary system); NREQ (number of rate equations, equal to the number of complex species); NCD (number of cycles of refinement required, usually 5–10); NDPA (number of dissociable protons on ligand A, *e.g.* two for serine, three for histidine and one for acetic acid); NDPB (number of dissociable protons on ligand B); WTF (weighting factor, unity in the absence of knowledge of weights of the relaxation times; if, on the basis of experimental data, it is concluded that in a particular set of experiments the relaxation times are accurate within  $\pm x\%$ , then the weighting factor is approximately equal to  $x/200$ ).

FORMAT (2 $\times$ , 9 (I2, 4 $\times$ ), F10-5)

4. PH (pH); M (free metal concentration); A (concentration of free ligand A); B (concentration of free ligand B); LAMBDA (inverse of relaxation time).

Number of such cards = NPT

FORMAT (F10-4, 3E10-5, F10-4, E10-5)

5. SC (logarithm of stability constant); RC (rate constants for the forward reaction. In the case of rate constants accurately known, put the exact value. In the case of reaction paths to be ignored put 0.0 and put approximate values of the constants to be refined.); EQEXP (equilibrium expression corresponding to the equilibrium constant on the card, *e.g.*  $M + A = MA$ . This information is only for the purpose of print-out and does not enter into calculations.)

Number of such cards = NC

FORMAT (F10-4, D10-4, 5 $\times$ , 10A4)

6. CV (equation number of the constant to be varied; for example, to refine the forward rate constant for the reaction  $M + A = MA$ , the number needed in this card is 35 on the basis of the reaction scheme given in Appendix I); ICV (increment in the corresponding constant for the purpose of numerical differentiation; this number should usually be less than 1% of the expected value of the corresponding constant.)

Number of such cards = NCV

FORMAT (I3, 7 $\times$ , E10-4)

7. SCHEME (This card is only for the purpose of record. On these cards can be written the left-hand side of rate equations, which in a way records the types of relaxations dealt with, *e.g.*, DDMA/DT, DDMA<sub>2</sub>/DT, *etc.*)

Number of such cards = NREQ

FORMAT (20A4)

8. If NJ is greater than one, repeat steps 2–7 NJ times.

#### Preparation of subroutine 'MTORIG'

The manner in which the present programme is written makes the consistency of notation very important. However, there should be no difficulty if the following procedure is strictly adhered to.

1. Write down the stepwise equilibrium expressions characterizing the formation of proton and metal complex species [*e.g.* equations (1–7)]. Give each equation a number (1, 2, ...). These equations should define all the known and postulated reaction paths. The corresponding equilibrium constant and the forward rate constant will have this number as the subscript. The first  $n$  equations ( $n = \text{NDPA}$ ) should be for the proton-ligand association equilibria, starting with the lowest proton-ligand complex (*e.g.*  $H + A \rightleftharpoons HA$ ). If the system has two types of ligands, then the next  $m$  equations ( $m = \text{NDPB}$ ) should be for the proton association equilibria of the second ligand. The first and second ligands are always referred to as A and B, respectively.

2. On the basis of the reactions written in step 1, derive  $N$  (number of metal complex species) independent near-equilibrium rate equations [*e.g.* equations (14) and (15)].

3. Write mass balance equations and obtain their differential forms [*e.g.* equations (8–11) and (16)–(19)]. This gives all the equations needed for the subroutine MTORIG, which consists of equations that define the elements of matrix A [equation (20)].

The programme requires that the first  $n$  ( $n = \text{NREQ}$ ) column vectors [matrix A, equation (20)] should be the coefficients of differentials of metal complex species ( $\delta[\text{MA}]$ ,  $\delta[\text{MA}_2]$ , *etc.*). In the listing of the programme the subroutine MTORIG gives equations for the copper(II)–histamine system. This subroutine will apply to any system containing a metal ion with co-ordination number of four and a ligand with two dissociable protons. It is assumed that the only metal complex species are MA and MA<sub>2</sub>. These equations can be checked against equations (14–18). Since no indicator was used, equation (19) and the terms  $[\text{HIn}]$ ,  $([\text{HIn}]/[\text{In}])\delta[\text{In}]$  from equation (18) have been deleted.

#### Variables used in the main programme

Variables used for input data have been explained earlier and are not listed here.

RCORIG(I) Reserves the value of RC(I) at the start of each cycle.

LMORIG(I)	Reserves the value of LAMBDA(I).
DLAM(I)	Increment in LAMBDA(I) for the purpose of numerical differentiation.
H(I)	Hydrogen ion concentration.
A1	Elements of the coefficient matrix corresponding to equation (20).
E(I)	Value of the function $R$ (equation 24) with current values of the parameters.
C	Index used to identify the constants to be refined.
ID	Counter for E(I).
E(2), E(3)	Two values of the function $R$ for the purpose of numerical differentiation of the function with respect to constants [RC(C)] to be estimated.
E(4), E(5)	Two values of the function $R$ for the purpose of numerical differentiation with respect to LAMBDA(I).
WT(I)	Weight of the $i$ th observation (= 1 in the absence of knowledge of weights).
DRRC(I,J)	Derivative of the function $R$ at $i$ th observation with respect to $j$ th constant.
DRLAM(I)	Derivative of the function $R$ at $i$ th observation with respect to dependent variable [LAMBDA(I)].
RO(I)	Reserves the value of E(I).
SSQR	Sum-square of the function $R$ over all the observations.
SNUTS	Variance in function $R$ calculated from equation (30).
SNUTI(NCC)	Reserves the value of SNUTS in each cycle for comparison with the last cycle.
NIT	Number of iterations while applying fraction shifts.
DRC(C)	Shift in variable constant $C$ , obtained by solving normal equations.
RCBEK(C)	Reserves the value of $C$ th constant.
B1(I,J)	Left-hand side elements of normal equations. Later on, B1(I,J) represents the elements of the inverse of the coefficient matrix (variance-covariance matrix) of normal equations. Still later (statement 177) it represents the elements of the correlation matrix.
Y(I)	Right-hand side elements of normal equations.
S,SSQR <sub>0</sub>	Variance in function $R$ calculated from equation (29).
STD(I)	Standard deviation in $i$ th constant.
ROOT(N)	Calculated values of LAMBDA(I).



```

C      PROGRAMME CORNEK                                0001
C      C                                                0002
C      C                                                0003
      DOUBLE PRECISION A1(20,20),B1(20,20),D(20,20),Y(20),DRC(10),E(5), 0004
      IRC(20),RCORIG(20),DRRC(20,20),RO(20),SSQRO,S,BR(20,20),WT(20), 0005
      1STD(10), ROOT(10),A11(20,20),DRLAM(20),LMORIG(20),SIGMA(10), 0006
      1L(20),R1,R2,R3,RM,SNUT1(20),RCBEK(20) 0007
      INTEGER CV,C,TNEQ 0008
      DIMENSION H(20),PH(20),A(20),B(20),H2A(20),HA(20),H2B(20), 0009
      1HB(20),LAMBDA(20),SC(20),CV(10),ICV(10),SCLG(20), 0010
      1SCHEME(20,20),REACT(20,20),EQEXP(20,20),DLAM(20), 0011
      1H3A(20),H4A(20),H3B(20),H4B(20) 0012
      REAL M(20),ICV,LAMBDA,IN(20) 0013
      COMMON M,A,B,H,RC,SC,HA,H2A,HB,H2B,A1,IN, 0014
      1H3A,H4A,H3B,H4B,I 0015
      1 FORMAT(I2) 0016
101  FORMAT(2X,9(I2,4X),F10.5) 0017
102  FORMAT(F10.4,3E10.5,F10.4,E10.5) 0018
103  FORMAT( F10.4,D10.4,5X,10A4) 0019
104  FORMAT(20A4) 0020
105  FORMAT(I3,7X,E10.4) 0021
106  FORMAT(I3,2X,D10.4,5X,D20.11,5X,10A4,5X,D10.4) 0022
107  FORMAT(1X,20A4) 0023
108  FORMAT(2X,4D20.10) 0024
109  FORMAT(1H1,4D10.4) 0025
110  FORMAT(1H1,10D10.4,/,10D10.4) 0026
111  FORMAT(///1X,' VARIANCE EXT UTS: 'D20.10,5X,' VARIANCE EXT NUTS: ' 0027
      1D20.10,5X,'NIT =' I3) 0028
112  FORMAT(2X,I3,3X,F6.0,5X,5(D17.10,2X)) 0029
113  FORMAT(2X,E10.4,2X,F10.4,5X,D10.4,5X,10A4,5X,I2) 0030
114  FORMAT(///1X,' ') 0031
115  FORMAT(70X,D10.4) 0032
116  FORMAT(6(2X,E10.4)) 0033
121  FORMAT (1H1, ' VARIANCE-COVARIANCE MATRIX: '/') 0034
124  FORMAT(1H1, ' CORRELATION MATRIX: '/') 0035
125  FORMAT(1H1,'NPT  NC  NCV  NL  TNEQ  NREQ  NCD  NDPA  NDPB' 0036
      1'  WTF') 0037
126  FORMAT(1H0,'THE RELAXATIONS CONSIDERED ARE FOLLOWING:/') 0038
127  FORMAT(2X,'EQUIL.',11X,'LOG(SC)',4X,'RATE CONSTANT',2X,'EQUILIBRIUM 0039
      1'/2X,'CONST(SC) (RC) EXPRESSION'//) 0040
128  FORMAT(1X,' (RC) STD.DEV. EQUILIBRIA 0041
      1  SHIFTS') 0042
129  FORMAT(1X,' ORSD LAMBDA CALCULATED VALUES OF LAMBDA' /) 0043
131  FORMAT(5(2X,D20.10)) 0044
132  FORMAT(/2X,'NO STEP SIZE GAVE LOWER VARIANCE THAN THE LAST CYCLE') 0045
133  FORMAT(F10.4) 0046
      READ(5,1) NJ 0047
      NJD=0 0048
      8 READ(5,133) FSF 0049
      READ(5,101) NPT,NC,NCV,NL,TNEQ,NREQ,NCD,NDPA,NDPB,WTF 0050
      WRITE(6,125) 0051
      WRITE(6,101) NPT,NC,NCV,NL,TNEQ,NREQ,NCD,NDPA,NDPB,WTF 0052
      DC ← I=1,NPT 0053
      4 READ(5,102) PH(I),M(I),A(I),B(I),LAMBDA(I),IN(I) 0054
      DO 5 I=1, NC 0055
      5 READ(5,103) SC(I),RC(I),(EQEXP(I,IC),IC=1,10) 0056
      DO 6 I=1,NCV 0057
      6 READ(5,105) CV(I),ICV(I) 0058
      WRITE(6,126) 0059
      DO 66 I=1,NREQ 0060
      READ(5,104) (SCHEME(I,IC), IC=1,20) 0061

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66 WRITE(6,107) (SCHEME(I,IC),IC=1,20)          0062
WRITE(6,114)                                     0063
NREQP1=NREQ+1                                    0064
DO 12 I=1,NC                                     0065
  SCLG(I)=SC(I)                                   0066
  SC(I)=10.**SC(I)                                 0067
12 RCORIG(I)=RC(I)                               0068
  WRITE(6,127)                                    0069
  DO 7 I=1,NC                                     0070
7 WRITE(6,113) SC(I),SCLG(I),RC(I),(EQEXP(I,IC),IC=1,10),I 0071
  WRITE(6,114)                                    0072
  DO 13 I=1,NPT                                   0073
  LMDRIG(I)=LAMBDA(I)                             0074
  DLAM(I)=00.0001*LAMBDA(I)                       0075
C                                                  0076
C CALCULATES CONCENTRATIONS OF PROTON COMPLEX SPECIES 0077
C                                                  0078
H(I)=10.**(-PH(I))                               0079
HA(I)=SC(1)*H(I)*A(I)                            0080
IF(NDPA.GE.2) H2A(I)=SC(2)*H(I)*HA(I)            0081
IF(NDPA.GE.3) H3A(I)=SC(3)*H(I)*H2A(I)          0082
IF(NDPA.GE.4) H4A(I)=SC(4)*H(I)*H3A(I)          0083
IF(NL.LT.2) GO TO 13                              0084
L1=NDPA+1                                         0085
HB(I)=SC(L1)*H(I)*B(I)                           0086
L2=NDPA+2                                         0087
IF(NDPB.GE.2) H2B(I)=SC(L2)*H(I)*HB(I)          0088
L3=NDPA+3                                         0089
IF(NDPB.GE.3) H3B(I)=SC(L3)*H(I)*H2B(I)        0090
L4=NDPA+4                                         0091
IF(NDPB.GE.4) H4B(I)=SC(L4)*H(I)*H3B(I)        0092
C                                                  0093
13 CONTINUE                                       0094
  NCC=0.0                                         0095
48 CONTINUE                                       0096
  NCCM1=NCC-1                                     0097
  NIT=0                                           0098
31 CONTINUE                                       0099
130 DO 19 J=1,NCV                                 0100
  DO 19 I=1,NPT                                   0101
  ID=1                                            0102
1000 CONTINUE                                     0103
  CALL MDRIG                                     0104
  CALL MTXOP(A1,TNEQ,NREQP1)                     0105
  DO 15 II=1,NREQ                                 0106
15 A1(II,II)=A1(II,II)-LAMBDA(I)                0107
  IF(NREQ.EQ.1) GO TO 150                         0108
  CALL MTXOP(A1,NREQ,2)                           0109
C                                                  0110
C 49 WRITE(6,131) (A1(IV,IVS),IVS=1,NREQ)        0111
150 E(ID)=1.                                       0112
  DO 16 N=1,NREQ                                  0113
16 E(ID)=E(ID)*A1(N,N)                           0114
C                                                  0115
C BEGINS NUMERICAL DIFFERENTIATION                0116
C                                                  0117
RO(I)=E(I)                                        0118
ID=ID+1                                           0119
GO TO (177,177,17,18,61,119), ID                0120
177 C=CV(J)                                       0121
  RC(C)=RC(C)+ICV(J)                              0122

```

```

      GO TO 1000
17  RC(C)=RC(C)-2.*ICV(J)                                0123
      GO TO 1000                                          0124
18  DRRC(I,J)=(E(2)-E(3))/(2.*ICV(J))                    0125
C   WRITE(6,131) E(1),E(2), E(3)                          0126
      RC(C)=RCORIG(C)                                    0127
      IF(J.LT.NCV) GO TO 19                               0128
40  LAMBDA(I)=LAMBDA(I)+DLAM(I)                           0129
      GO TO 1000                                          0130
61  LAMBDA(I)=LAMBDA(I)-2.*DLAM(I)                       0131
      GO TO 1000                                          0132
119 DRLAM(I)=(E(4)-E(5))/(2.*DLAM(I))                    0133
C   WRITE(6,131) E(4),E(5)                                0134
19  LAMBDA(I)=LMORIG(I)                                   0135
C
      SSQRO=0.0                                           0136
      SSQR=0.0                                           0137
      DO 27 I=1,NPT                                       0138
      WT(I)=(1./(LAMBDA(I) *WTF))**2                     0139
      IF(WTF.EQ.1.0) WT(I)=1.0                           0140
27  L(I)=DRLAM(I)**2/WT(I)                                0141
      DO 190 I=1,NPT                                       0142
      SSQR=SSQR+RO(I)*RO(I)                               0143
190 SSQR=SSQR+RO(I)**2/L(I)                               0144
C   DO 62 I=1,NPT                                       0145
C   62 WRITE(6,131) (DRRC(I,J),J=1,NCV),L(I),RO(I),SSQR 0146
      SNUTS=SSQR/(NPT-NCV)                                0147
      SNUT1(MCC)=SNUTS                                    0148
C
C   APPLIES FRACTIONAL SHIFTS IF THE VARIANCE IN THE CURRENT CYCLE
C   IS GREATER THAN THE LAST CYCLE                       0149
C
      IF(NCC.EQ.0) GO TO 34                                0150
      IF(FSF) 662,34,662                                   0151
662 IF(SNUT1(NCC).LT.SNUT1(NCCM1)) GO TO 34              0152
      NIT=NIT+1                                           0153
      DO 33 I=1,NCV                                       0154
      C=CV(I)                                              0155
      DRC(I)=DRC(I)*FSF                                    0156
      RC(C)=RCORIG(C)+DRC(I)                              0157
      RCORIG(C)=RC(C)                                     0158
      IF(NIT.GT.50) RC(C)=RCBEK(C)                       0159
33  CONTINUE                                              0160
      IF(NIT.GT.50) WRITE(6,132)                          0161
      IF(NIT.GT.50) GO TO 98                              0162
      GO TO 31                                             0163
34  CONTINUE                                              0164
C
C   SETS UP NORMAL EQUATIONS                             0165
C
      DO 20 I=1,NCV                                       0166
      DO 20 J=1,NCV                                       0167
      B1(I,J)=0.0                                         0168
      DO 20 KK=1,NPT                                       0169
20  B1(I,J)=B1(I,J)+DRRC(KK,I)*DRRC(KK,J)/L(KK)         0170
      DO 21 I=1,NCV                                       0171
      Y(I)=0                                              0172
      DO 21 KK=1,NPT                                       0173
21  Y(I)=Y(I)+RO(KK)*DRRC(KK,I)/L(KK)                    0174
C   DO 51 I=1,NCV                                       0175
C   51 WRITE(6,116) (B1(I,J),J=1,NCV),Y(I)              0176

```

```

      CALL MTXIN(B1,NCV)                                0184
C
C   CALCULATES SHIFTS                                  0185
C
      DO 22 I=1,NCV                                     0186
      DRC(I)=0.0                                         0187
      DO 22 J=1, NCV                                     0188
22   DRC(I)=DRC(I)+B1(I,J)*Y(J)                         0189
C
      S=SSQRO                                           0190
      DO 122 I=1,NCV                                     0191
122  S=S-Y(I)*DRC(I)                                    0192
      S=S/(NPT-NCV)                                      0193
      WRITE(6,111) S,SNUTS,NIT                          0194
      DO 123 I=1,NCV                                     0195
      SIGMA(I)=B1(I,I)*SNUTS                            0196
123  STD(I)=SIGMA(I)**.5                                0197
      WRITE(6,128)                                       0198
      DO 23 N=1,NCV                                      0199
      C=CV(N)                                            0200
      WRITE(6,106) C,RC(C),STD(N),(E0EXP(C,NI),NI=1,10),DRC(N) 0201
23   CONTINUE                                           0202
      IF(NCC.EQ.NCD) GO TO 98                            0203
      DO 120 I=1,NCV                                     0204
      DO 120 J=1,NCV                                     0205
120  BB(I,J)=B1(I,J)                                    0206
C
C   APPLIES 'UNRESTRICTED SHIFTS' AND NO SHIFT IS ALLOWED TO BE
C   GREATER THAN THE CORRESPONDING RATE CONSTANT
C
      DO 46 I=1,NCV                                     0207
      C=CV(I)                                            0208
      RC(C)=RCORIG(C)                                    0209
      RC(C)=RC(C)-DRC(I)                                0210
      IF(RC(C).LT.0.0) RC(C)=RCORIG(C)-DRC(I)/(DABS(DRC(I)))*.9* 0211
      1RCORIG(C)                                         0212
      RCBEK(C)=RCORIG(C)                                0213
46   RCDRIG(C)=RC(C)                                    0214
47   CONTINUE                                           0215
C
      NCC=NCC+1                                         0216
      GO TO 48                                           0217
C
C   AFTER FINAL CYCLE OF REFINEMENT CALCULATED VALUES OF LAMBDA ARE
C   COMPUTED AND PRINTED
C
98  CONTINUE                                           0218
      WRITE(6,114)                                       0219
      WRITE(6,129)                                       0220
      DO 29 I=1,NPT                                      0221
      CALL MTORIG                                       0222
      CALL MTXOP(A1,TNEQ,NREQP1)                        0223
      CALL EIGEN(A1,NREQ,ROOT)                          0224
29  WRITE(6,112) I,LAMBDA(I),(ROOT(N),N=1,NREQ)      0225
      CONTINUE                                           0226
C
      IF(NCD.EQ.0.0) GO TO 2222                          0227
      WRITE(6,114)                                       0228
      WRITE(6,121)                                       0229
C
C   PRINTS VARIANCE COVARIANCE MATRIX
C
      PRINTS VARIANCE COVARIANCE MATRIX                0230

```

```

C      DO 9 I=1,NCV                                0245
9 WRITE(6,116) (B1(I,J),J=1,NCV)                 0246
C      PRINTS CORRELATION MATRIX                    0247
C      PRINTS CORRELATION MATRIX                    0248
C      PRINTS CORRELATION MATRIX                    0249
C      PRINTS CORRELATION MATRIX                    0250
C      DO 117 I=1,NCV                                0251
DO 117 J=1,NCV                                    0252
117 B1(I,J)=BB(I,J)/(BB(I,I)*BB(J,J))*0.5         0253
WRITE(6,114)                                       0254
WRITE(6,124)                                       0255
DO 118 I=1,NCV                                    0256
118 WRITE(6,116) (B1(I,J),J=1,NCV)                 0257
2222 CONTINUE                                     0258
      NJD=NJD+1                                     0259
      IF(NJD.LT.NJ) GO TO 8                          0260
      STOP                                           0261
      END                                           0262
C      SUBROUTINE MTORIG                             0263
C      DOUBLE PRECISION A1(20,20),RC(20)            0264
C      REAL M(20),IN(20)                             0265
C      DIMENSION A(20),B(20),H(20),SC(20),HB(20),H2B(20),H3B(20),H4B(20), 0266
H1A(20),H2A(20),H3A(20),H4A(20)                   0267
C      COMMON M,A,B,H,RC,SC,HA,H2A,HB,H2B,A1,IN,     0268
H3A,H4A,H3B,H4B,I                                  0269
C      CU-HM SYSTEM 5*5                               0270
C      A1(1,1)=RC(3)/SC(3)+RC(5)/SC(5)*H(I)+RC(4)*A(I)+RC(6)*HA(I) 0271
A1(1,2)=-RC(4)/SC(4)-RC(6)/SC(6)*H(I)             0272
A1(1,3)=-RC(3)*A(I)-RC(5)*HA(I)                   0273
A1(1,4)=-RC(3)*M(I)+RC(4)*SC(3)*M(I)*A(I)-RC(5)*M(I)*HA(I)/A(I)+ 0274
1RC(6)*SC(3)*M(I)*A(I)*HA(I)/A(I)                 0275
A1(1,5)=-RC(5)*M(I)*HA(I)/H(I)+RC(5)/SC(5)*SC(3)*M(I)*A(I)+ 0276
1RC(6)*SC(3)*M(I)*A(I)*HA(I)/H(I)-RC(6)/SC(6)*SC(3)*SC(4)*M(I)*A(I) 0277
1**2.                                               0278
A1(2,1)=-{RC(4)*A(I)+RC(6)*HA(I)}                 0279
A1(2,2)=RC(4)/SC(4)+RC(6)/SC(6)*H(I)              0280
A1(2,3)=0.0                                         0281
A1(2,4)=-{RC(4)*SC(3)*M(I)*A(I)+RC(6)*SC(3)*M(I)*A(I)*HA(I)/A(I)} 0282
A1(2,5)=-{RC(6)*SC(3)*M(I)*A(I)*HA(I)/H(I)-RC(6)/SC(6)*SC(3)*SC(4) 0283
1*M(I)*A(I)**2}                                     0284
A1(3,1)=1.0                                         0285
A1(3,2)=1.0                                         0286
A1(3,3)=1.0                                         0287
A1(3,4)=0.0                                         0288
A1(3,5)=0.0                                         0289
A1(4,1)=1.0                                         0290
A1(4,2)=2.0                                         0291
A1(4,3)=0.0                                         0292
A1(4,4)={H2A(I)+HA(I)+A(I)}/A(I)                  0293
A1(4,5)={2.*H2A(I)+HA(I)}/H(I)                    0294
A1(5,1)=0.0                                         0295
A1(5,2)=0.0                                         0296
A1(5,3)=0.0                                         0297
A1(5,4)={2.*H2A(I)+HA(I)}/A(I)                    0298
A1(5,5)={4.*H2A(I)+HA(I)+H(I)}/H(I)              0299
RETURN                                              0300
END                                                 0301
C      0302
C      0303
C      0304
C      0305

```

```

SUBROUTINE MTXDP(D,IP,IQ)                                0306
DOUBLE PRECISION RR,D(20,20)                            0307
DO 13 N=1,IP                                             0308
IR=IP-N+1                                                0309
IF(IR.LT.IQ) GO TO 13                                    0310
M=IR-1                                                    0311
DO 13 I=1,M                                              0312
RR=D(I,IR)/D(IR,IR)                                     0313
IF(RR)10,13,10                                           0314
10 DO 12 J=1,IR                                          0315
12 D(I,J)=D(I,J)-RR*D(IR,J)                             0316
13 CONTINUE                                              0317
RETURN                                                    0318
END                                                       0319

C                                                         0320
C                                                         0321
SUBROUTINE MTXIN(A760,N760)                              0322
DOUBLE PRECISION A760(20,20)                            0323
DO 764 K760=1,N760                                       0324
CM760=A760(K760,K760)                                    0325
A760(K760,K760)=1.0                                     0326
DO 765 J760=1,N760                                       0327
765 A760(K760,J760)=A760(K760,J760)/CM760              0328
DO 764 I760=1,N760                                       0329
IF(I760-K760)762,764,762                                0330
762 CM760=A760(I760,K760)                               0331
A760(I760,K760)=0.0                                     0332
DO 763 J760=1,N760                                       0333
763 A760(I760,J760)=A760(I760,J760)-CM760*A760(K760,J760) 0334
764 CONTINUE                                              0335
RETURN                                                    0336
END                                                       0337

C                                                         0338
C                                                         0339
SUBROUTINE EIGEN(A2,NR,RRT)                              0340
DOUBLE PRECISION A2(20,20),R(6),RT,HH,G,D,LM,XN,TEMP,RRT(10), 0341
1FPRT,FF(3),A3(20,20)                                    0342
111 FORMAT(50X,E17.10)                                    0343
112 FORMAT(2X,5(D17.10,2X))                              0344
113 FORMAT(2X, 'NONCONVERGENCE FOR THIS POINT')         0345
DO 1 I=1,NR                                              0346
1 RRT(I)=0.0                                             0347
ERR=.01                                                  0348
DRT=.99                                                  0349
570 K=0                                                  0350
581 K=K+1                                                0351
NIT=0                                                    0352
IF(RRT(K).EQ.0.0) GO TO 571                             0353
RT=DRT*RRT(K)                                           0354
M=1                                                      0355
GO TO 580                                                0356
571 RT=-1.0                                              0357
HH= -1.0                                                 0358
M=3                                                      0359
GO TO 580                                                0360
572 FF(1)=FPRT                                           0361
RT=RRT(K)/DRT                                           0362
M=2                                                      0363
GO TO 580                                                0364
573 FF(2)=FPRT                                           0365
HH=RRT(K)-RT                                            0366

```

	RT=RRT(K)	0367
	M=5	0368
	GO TO 580	0369
5573	FF(1)=FPRT	0370
	RT=1.0	0371
	M=4	0372
	GO TO 580	0373
5574	FF(2)=FPRT	0374
	RT=0.0	0375
	M=5	0376
	GO TO 580	0377
5575	FF(3)=FPRT	0378
	LM=-.5	0379
	GO TO 574	0380
5576	FF(1)=FF(2)	0381
	FF(2)=FF(3)	0382
	FF(3)=FPRT	0383
574	DEL=1.+LM	0384
	G=FF(1)*LM**2-FF(2)*DEL**2+FF(3)*(LM+DEL)	0385
	D=G**2-4.*FF(3)*LM*DEL*(FF(1)*LM-FF(2)*DEL+FF(3))	0386
	D=G+G/DABS(G)*DSORT(DABS(D))	0387
	LM=-2.*FF(3)*DEL/D	0388
	HH=LM*HH	0389
	XN=RT+HH	0390
	IF(DABS(HH/XN).LT.ERR) GO TO 575	0391
	RT=XN	0392
	XXX=DABS(HH/XN)	0393
	NIT=NIT+1	0394
	IF(NIT.GT.100) GO TO 591	0395
	M=6	0396
	GO TO 580	0397
575	RRT(K)=XN	0398
	IF(K.LT.NR) GO TO 581	0399
	GO TO 591	0400
580	CONTINUE	0401
	DO 2 I=1,NR	0402
	DO 2 J=1,NR	0403
	2 A3(I,J)=A2(I,J)	0404
	DO 3 I=1,NR	0405
	3 A3(I,I)=A2(I,I)-RT	0406
	CALL MTXOP(A3,NR,2)	0407
	FPRT=1.0	0408
	DO 4 I=1,NR	0409
	4 FPRT=FPRT*A3(I,I)	0410
	J=1	0411
	IF(K.EQ.1) GO TO 590	0412
600	J=J+1	0413
	TEMP=RT-RRT(J-1)	0414
	FPRT=FPRT/TEMP	0415
590	IF(J.NE.K) GO TO 600	0416
	GO TO (572,573,5573,5574,5575,5576), M	0417
591	CONTINUE	0418
	RETURN	0419
	END	0420

*Note added in proof:* For some computers the programme will operate better if the following changes are made.

line (card) 0095; change 0.0 to 1  
line (card) 0155; change 0 to 1  
line (card) 0206; change EQ to GE  
line (card) 0240; change 0.0 to 0.

**Zusammenfassung**—Ein allgemeines Maschinenprogramm zur Ermittlung von Geschwindigkeitskonstanten aus Relaxationszeiten wird beschrieben. Das Programm CORNEK ist im wesentlichen ein auf nichtlineare Systeme angewandtes Verfahren der kleinsten Quadrate. Es verwendet direkt die differentiellen Formen der ersten Ableitungen der Geschwindigkeits- und der Massengleichgewichts-Gleichungen; damit werden die zeitraubenden Ableitungen von gleichgewichtsnahen Geschwindigkeitsgleichungen vermieden. Das Programm wurde an binären Systemen wie Cu-Histamin und Cu-Serin sowie dem ternären System Cu-Histamin-Serin überprüft.

**Résumé**—On décrit un accès général par calculatrice à l'estimation des constantes de vitesse à partir de temps de relaxation. Le programme CORNEK est essentiellement un programme d'étude plus fine par moindres carrés appliqué aux systèmes non linéaires. Il utilise directement les formes différentielles des premières dérivées des équations d'équilibre de masse et de vitesse, évitant ainsi les dérivations des équations de vitesse au voisinage de l'équilibre qui absorbent du temps. Le programme a été essayé pour des systèmes binaires tels que Cu-histamine, Cu-sérine, et le système ternaire Cu-histamine-sérine.

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## ANALYTICA CHIMICA PHILATELICA

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**Summary**—Notable contributors to analytical chemistry who have been honoured by postage stamps, and the significance of their contributions to the development of analytical chemistry, are reviewed.

ON POSTAGE STAMPS there are to be found the likenesses of about a hundred scientists—from Avogadro to Zelinski—who have a place in the history of chemistry. In what follows, the fifteen or so who have made significant contributions to analytical chemistry are identified and their contributions are discussed, together with some irreverent *personalia*.

In 1949 Germany issued a stamp that portrays Theophrastus Bombast von Hohenheim or, as he liked to be called, Paracelsus—a preference not occasioned by modesty. This early sixteenth-century peripatetic physician and iatrochemist, *ca.* 1493–1541, is reputed to have been something less than a man, and intoxicated when he dictated his books. But, sober man or drunk eunuch, he recorded useful findings of the earlier alchemists about separation processes. For example, they knew that when a mixture of gold and silver is treated with nitric acid (*aqua fortis*) the gold remains; Paracelsus goes on to say that, if a copper plate is put into the solution, “the silver falls to the bottom of the vessel like snow”<sup>1</sup>—a nice example of redox potentials at work. Paracelsus was to be dead for 350 years before the thermodynamic basis of these separations was understood. (Incidentally, Sadi Carnot, who began the explanation, and Walther Nernst, who finished it, have both been honoured by postage stamps.)

Paracelsus did much more, by “turning attention away from the transmutation of metals and towards the applications of chemistry in medicine”.<sup>1</sup> This benefited analytical chemistry because his followers were “led to invent methods of purification and tests for purity”.<sup>2</sup>

The influence of Paracelsus as an iatrochemist was not matched for the better part of a century, and then by Joannes Baptista van Helmont, 1577–1644, whom Belgium commemorated philatelically in 1942 (Plate 1). His fame commonly rests on his investigations of what we, following him, call gases; he appropriately coined “gas” from the Greek “chaos”. The concept of indestructibility of matter and the value of quantitative investigations are often associated with Lavoisier but van Helmont had these ideas very clearly, and he died a century—well, 99 years—before Lavoisier was born. Helmont recognized the existence of carbon dioxide (*gas sylvestre*), studied the gases formed in the combustion of organic substances, improved qualitative tests for the examination of mineral waters, and believed that alkali neutralizes all acidity. (He also believed that mice can be formed from a dirty shirt dusted with wheat meal—but is there a quicker way to get mice?)

Ideas about neutralization became more precise with Hermann Boerhaave, 1668–1738, on the 200th anniversary of whose death The Netherlands issued an attractive stamp (Plate 2). This remarkably versatile man had a lasting influence on three separate disciplines—medicine, botany, and chemistry. Of the action of an acid

on an alkali, he said that a "point of saturation" is reached, and if this "be exactly hit, no sign, either of an acid, or an alkali, is discoverable".<sup>3</sup> The substance formed *nec alcali est, nec acidum, sed ex his simul concretis conflatum*. He thought all acids had equal powers of "saturation". Such concepts, with some refining, were fundamental to the development of acid-base titrimetry. And Boerhaave promoted good analytical technique: the "acid is *slowly* poured to an alkali" and "the containing vessel is shook after each addition".<sup>3</sup>

Some of Boerhaave's students were largely, albeit indirectly, responsible for an outstanding contribution to chemistry. In 1724 there appeared a book that was published, Boerhaave said, "under my name, without my participation".<sup>3</sup> This spurious work had been compiled from students' notes of Boerhaave's lectures on chemistry at the University of Leyden. "Many false, ridiculous, and absurd things [were] there attributed to me," yet "I frequently lay under a necessity of seeing the detested piece, even in the hands of my auditors; who, to my face, were daily comparing my words, as I delivered them, with the text".<sup>3</sup> The outcome of Boerhaave's distress and anger was his great *Elementa Chemiae* of 1732: this was translated into English, French, German, and Russian (and was introduced into the hospital schools of Russia, by Imperial edict). It was probably the most influential of the early textbooks of chemistry.

In the eighteenth century there were born three very distinguished chemists who were honoured on their country's stamps on the 200th anniversaries of their births: Carl Wilhelm Scheele (Sweden, 1942), Antoine-Laurent Lavoisier (France, 1943), and Nicolas-Louis Vauquelin (France, 1963).

Scheele was a superb experimentalist who "brought to light more new substances of fundamental importance than any other chemist",<sup>4</sup> and this in a short life, for he died at age 43, two days after his marriage. His achievements include discovering oxygen, independently of Priestley; isolating chlorine; establishing the individuality of manganese and analytically separating iron from it; discovering oxalic acid and using it for precipitating calcium; and decomposing silicates by fusion with alkali carbonates.

Lavoisier's stamp displays the noble head that put chemistry on a quantitative and essentially modern basis before it was severed by the guillotine, in 1794. That singularly unfortunate event made the charming Marie Lavoisier a very wealthy widow, a fact that did not elude that extraordinary physicist-about-Europe, Count Rumford, born Benjamin Thompson in New England—but that story hasn't much analytical chemistry in it.

Vauquelin, 1763–1829 (Plate 3), a peasant's son, was the outstanding analytical chemist of France in the revolutionary period and the inspiring teacher of many who were to enrich chemistry. One young man whom he encouraged was Louis-Jacques Thenard, 1777–1857 (France, 1957), who later collaborated with Joseph-Louis Gay-Lussac (France, 1951) in developing the first practical method for organic elemental analysis and in isolating boron (and who by himself discovered hydrogen peroxide, and thus created the crowning glory of many blondes).

Gay-Lussac, 1778–1850, left his mark on all branches of chemistry and not least on analytical chemistry. The analysis of organic compounds, the precipitating ability of hydrogen sulphide in relation to the acidity of the solution, and researches that made him a founder of quantitative titrimetric analysis: these are among his analytical



PLATE 1.—van Helmont, who represents the transition from alchemist to chemist.



PLATE 2.—Boerhaave, whose fame as a teacher attracted students of all Europe.

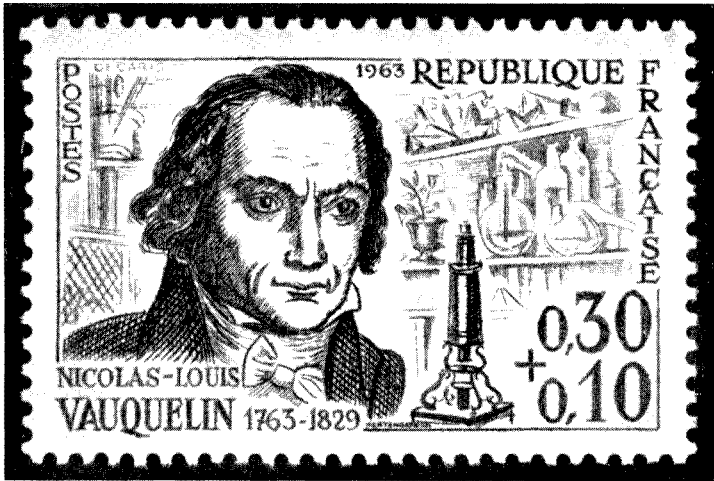


PLATE 3.—Vauquelin, who first isolated chromium and recognized beryllium.



PLATE 4.—von Liebig, who was expelled from school as “hopelessly useless”<sup>7</sup> and later extolled as “the greatest chemist of his age”.<sup>8</sup>

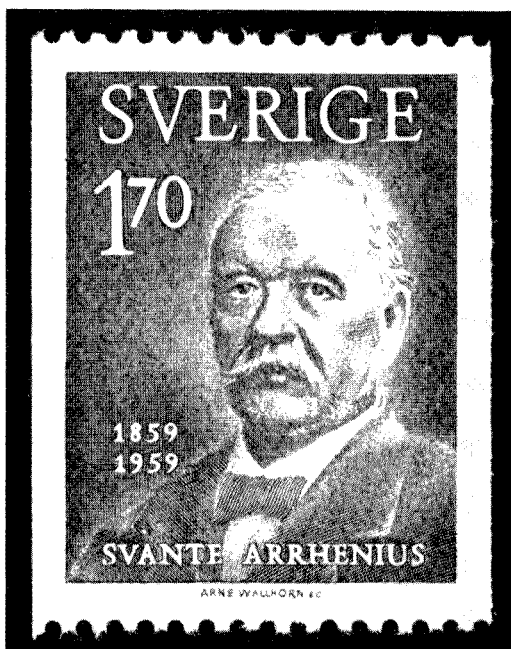


PLATE 5.—Arrhenius, whose professor's reaction to his theory was: "That is very interesting—goodbye".<sup>9</sup>



PLATE 6.—Haber, whose grand gold-from-seawater project floundered on faulty analyses.

contributions. His precipitometric method for the determination of silver with a standard solution of chloride, published in 1832, is still used by Mints throughout the world. "If we consider that Berzelius was the most accomplished analyst the world has yet seen, then surely Gay-Lussac was not far behind him".<sup>5</sup>

His great contemporary, Jöns Jacob Berzelius, 1779–1848 (Sweden, 1939), was a talented teacher, a prolific producer of authoritative articles, an ingenious inventor of analytical apparatus, and a deft discoverer of elements and of accurate methods of analysis. These methods and Berzelius's skill in using them were such that one-third of the 53 atomic weights he reported in 1836 are within 12 parts per thousand of the values accepted today. But this man of so much energy, who for so many years dominated chemistry, eventually ran out of steam. Just one year after his first and only marriage (when he was 56 years old, to a bride of 24) Berzelius wrote: "My health, thank God, is still as good as it used to be, and I pass the time happily, but that internal irrepressible force which drove me in my scientific study has now ceased".<sup>6</sup>

That was in a letter to Justus von Liebig, 1803–1873, who appears on a stamp issued by Germany (Plate 4) on the 150th anniversary of his birth. Liebig studied with both Thenard and Gay-Lussac and later achieved eminence that helped to make Germany the centre of the chemical world. By the time he was 28 years old, he had developed the method for the determination of carbon and hydrogen in organic compounds that, almost unchanged, remained standard for three-quarters of a century (until Pregl's microanalytical techniques). Later, in 1851, Liebig published his method for the determination of cyanide by titration with silver nitrate, the first complexometric titration. This is still described in analytical textbooks and is used in the analysis of electroplating baths.

In the 50 years between the births of Justus Liebig (1803) and Wilhelm Ostwald (1853) several major contributors to analytical chemistry were born, but none of these has yet had philatelic recognition. The only partial exceptions to this that I know are Marcelin Berthelot, 1827–1907 (France, 1927) and Károly Than, 1834–1904 (Hungary, 1954). In 1859 Berthelot developed a sensitive test for ammonia, involving the formation of a blue indophenol (recently adapted to determinations of 5'-nucleotidase in serum), and later did thermochemical studies that contributed to an understanding of neutralization. Than introduced potassium hydrogen iodate (in 1860) and potassium hydrogen carbonate as standards in iodometry and acidimetry, respectively.<sup>5</sup>

In 1969 Sweden issued stamps to commemorate the 60th anniversary of the award of a Nobel Prize in Chemistry to Wilhelm Ostwald, 1853–1932. If any single event marks the transition point of analytical chemistry from an art to a science, it is the publication in 1894 of Ostwald's *Die wissenschaftlichen Grundlagen der analytischen Chemie*. Certainly this revolutionized the study and teaching of analytical chemistry.

Ten years before that book appeared, Ostwald encouraged Svante Arrhenius, 1859–1927 (Plate 5), and began what was to be a very fruitful collaboration. During his research for his doctorate from the University of Uppsala, Arrhenius in his mid-twenties had conceived basic ideas of the ionic theory that was to be so important in analytical and much other chemistry. His bright flashes of insight were very coolly received. A happy exception was afforded by Ostwald, who arranged for Arrhenius to work at the University of Riga. Ostwald and his associates at Riga and later at Leipzig were highly successful in applying the ionic concept to the action of indicators, the dissociation of acids and bases, solubility-product constants, and much else.

Arrhenius's native Sweden honoured him on stamps in 1959 on the 100th anniversary of his birth, and again in 1963 on the 60th anniversary of his Nobel Prize in Chemistry for his ionic theory. Incidentally, Arrhenius considered that Gay-Lussac, who died well before Arrhenius was born, had expressed ideas about the dissociation of salts in solution that were fundamentally correct, although they were not appreciated in 1839. "Gay-Lussac was the first who found what was the truth . . . [he] must have been among the most intelligent men in the world."<sup>9</sup>

Another Nobel Laureate in Chemistry (1920) who worked with Ostwald was Walther Nernst, 1864–1941. When Ostwald moved to the University of Leipzig in 1887, Nernst was his first assistant in physical chemistry. There, when he was 25 years old, he formulated what became known as the Nernst equation, that fundamental relationship for the quantitative interpretation of redox processes. Later, in 1903, Nernst designed the first microbalance based on torsion in a quartz fibre, and then he and a colleague appropriately added a furnace to create the prototype of the thermo-balance. Nernst's portrait on a stamp of the German Democratic Republic (1950) seems to fit what he said about his discovery of the heat theorem that is the basis of the third law of thermodynamics: "this I have just done myself alone".<sup>10</sup>

Nernst was a masterful and masterly theoretician, but he was the loser in a sharp controversy with Fritz Haber, 1868–1934 (Plate 6), about the equilibrium constant for the ammonia synthesis. If the analytical measurements in Haber's laboratory had not been the accurate ones, he might not have received a Nobel Prize (1918), and the First World War might have been shorter. Earlier, before the turn of the century, Haber's work on electrolytic reductions made him the father of controlled-potential electrolyses. But 50 years passed before his child was very active. He was again ahead of his time when he developed the theory of the glass electrode and successfully used it in potentiometric acid-base titrations. Haber wrote: "the glass electrode, in addition to its theoretical interest, is likely to prove of much practical value".<sup>11</sup> That prediction was made in 1909, about 20 years before it began to be fulfilled.

Important contributors to analytical chemistry since the first decade of this century have yet to appear on postage stamps. And great analytical chemists of the nineteenth century are still missing: Bunsen, Dumas, Fresenius, and Mohr, too.

**Zusammenfassung**—Wissenschaftler, die bedeutende Beiträge zur analytischen Chemie geleistet haben und durch Briefmarken geehrt wurden, werden aufgezählt und eine Übersicht über ihren Beitrag zur Entwicklung der analytischen Chemie gegeben.

**Résumé**—On passe en revue ceux ont apporté une contribution notable à la chimie analytique et qui ont été honorés par des timbres postaux, et l'importance de leurs contributions au développement de la chimie analytique.

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## SHORT COMMUNICATIONS

### Potentiometric studies of ternary complex formation

#### Cu(II), Ni, Zn or Cd iminodiacetic acid/amino-acid complexes

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EQUILIBRIUM studies have been reported<sup>1-3</sup> on the mixed ligand complexes of copper(II), nickel, zinc and cadmium with an aminopolycarboxylic acid and a hydroxy-acid or an aliphatic diamine. It has been shown that the metal ions combine first with the aminopolycarboxylic acid in the lower pH region and then these simple 1:1 binary complexes combine with the secondary ligand at higher pH. The resulting 1:1:1 ternary complexes have been found to be more stable than the simple 1:2 binary complexes.

Studies of metal nitrilotriacetates in presence of amino-acids have been made by Israeli *et al.*<sup>4,5</sup> and the stepwise formation of 1:1:1 ternary complexes has been shown. It was therefore considered of interest to carry out equilibrium studies of the metal iminodiacetates in the presence of amino-acids.

### EXPERIMENTAL

Stock solutions of the metal nitrates were prepared and standardized with EDTA as described previously.<sup>2</sup> Glycine was recrystallized several times from doubly distilled water.  $\alpha$ -Alanine, *dl*-aspartic acid and iminodiacetic acid were used as received and their purity was checked by potentiometric titration. All the ligands were further standardized with 0.10M potassium hydroxide free from carbon dioxide. The ionic strength of the reaction mixture was kept approximately constant at 0.10 with potassium nitrate.

### RESULTS AND DISCUSSION

The acid dissociation constants of glycine,  $\alpha$ -alanine and *dl*-aspartic acid were determined by Chaberek and Martell's method,<sup>6</sup> the separate neutralization steps for *dl*-aspartic acid being used (Table I). The formation constants ( $\log K_{MAB}$ ) of the ternary complexes were calculated by the method of Thompson and Loraas.<sup>7</sup>

Curve 1 in Fig. 1 represents the potentiometric titration of iminodiacetic acid (IMDA). It gives a sharp inflexion at  $a = 1$  ( $a =$  moles of base added per mole of ligand) at low pH and a poor inflexion at  $a = 2$  at higher pH, indicating two separate neutralization steps due to the large difference in the dissociation constants of IMDA. Curves 2 and 3, for glycine (Gly) and  $\alpha$ -alanine (Aln) give very poor inflexions, because these form zwitterions. *dl*-Aspartic acid (ASPA) (curve 4) behaves similarly to IMDA, giving a sharp inflexion at low pH and weak one at high pH.

Solutions containing Cu(II), Ni, or Zn and IMDA in equimolar proportions give an inflexion at  $a = 2$  (*e.g.*, curve 5) indicating the formation of 1:1 binary complexes. In all these systems, precipitation starts after  $a = 2$ , with one more inflexion at  $a = 3$ . The colour of the supernatant liquid and the nature of the precipitate probably indicate the formation of the 1:2 M(II)-IMDA complex and precipitation of half of the metal as its hydroxide, which in the case of Cu(II) turns black on standing. For the Cd(II)-IMDA system, a third inflexion is observed at  $a = 1$ , due to the neutralization of the free proton of the carboxylic group of IMDA.

Systems containing equimolar proportions of metal and amino-acid give two inflexions except for Zn-ASPA and Cd-ASPA, which give three. The inflexion at  $a = 1$  (*e.g.*, curves 6 and 7) is due to the formation of the 1:1 metal-amino-acid complex. Beyond this, precipitation starts and an inflexion at  $a = 2$  is obtained, indicating the probable disproportionation of the 1:1 complex into a 1:2 or 1:3 metal-amino-acid complex and the precipitation of metal hydroxide. In the Zn and Cd systems, the inflexions are ill-defined and the titration curves in presence of ASPA are similar to those obtained with IMDA.

When the equimolar systems, Cu(II)-IMDA-Gly, Cu(II)-IMDA-Aln, Ni-IMDA-Gly, Ni-IMDA-Aln, Zn-IMDA-Gly and Zn-IMDA-Aln (*e.g.*, curves 9 and 10) are titrated, two inflexions at  $a = 2$  and  $a = 3$  are observed. First the 1:1 M(II)-IMDA complex is formed, then further addition of alkali neutralizes the proton liberated from the amino-acids and ternary complex formation and an inflexion at  $a = 3$  are observed. These inflexions occur at lower pH than that expected for successive titration of the two ligands<sup>8</sup> (*e.g.*, curves 12 and 13), indicating the formation of a new species,

TABLE I.—IONIZATION CONSTANTS OF SECONDARY LIGANDS [ $25 \pm 1^\circ\text{C}$ ,  $\mu = 0.10$  ( $\text{KNO}_3$ )]

Ligand	$\text{p}K_1$	$\text{p}K_2$
Glycine	—	$9.71 \pm 0.01$
$\alpha$ -Alanine	—	$9.80 \pm 0.03$
<i>dl</i> -Aspartic acid	$3.86 \pm 0.02$	$9.75 \pm 0.04$

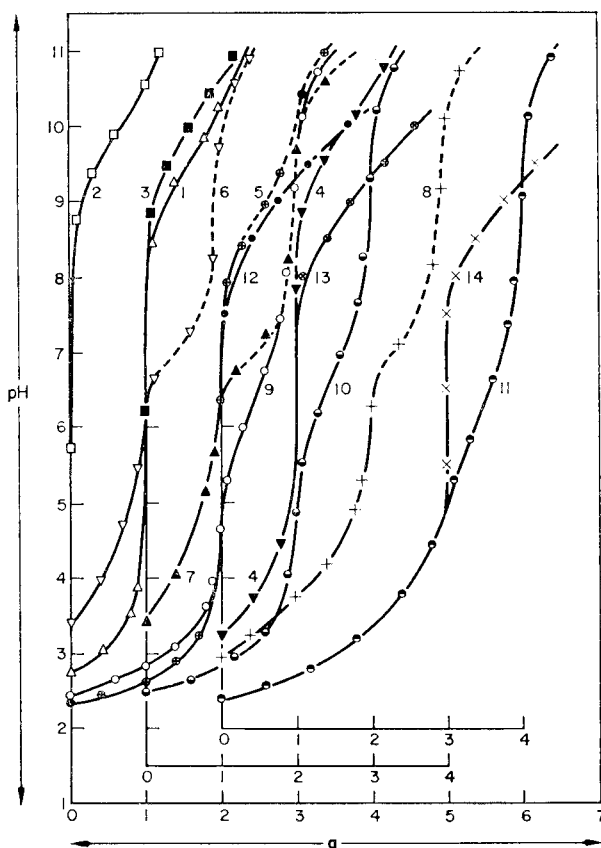


FIG. 1.—Potentiometric titration of mixed chelates of Cu(II) and IMDA. All solutions  $5 \times 10^{-3}M$  in copper nitrate and  $0.10M$  in  $\text{KNO}_3$  at the start of the titration ( $a =$  moles of base added per mole of metal ion).

(1) IMDA; (2) Gly; (3) Aln; (4) ASPA; (5) 1:1 Cu(II)-IMDA; (6) 1:1 Cu(II) Gly; (7) 1:1 Cu(II)-Aln; (8) 1:1 Cu(II)-ASPA; (9) 1:1:1 Cu(II)-IMDA-Gly; (10) 1:1:1 Cu(II)-IMDA-Aln; (11) 1:1:1 Cu(II)-IMDA-ASPA; (12, 13, 14) are the theoretical composite curves for the corresponding mixed systems. Dotted line indicates appearance of a solid phase.

which can only be a 1:1:1 ternary complex. Since IMDA and the amino-acids Gly and Aln can occupy only five co-ordination positions on the metal ion, it may be postulated that the sixth co-ordination position is satisfied by a water molecule, whereas in the case of ASPA as secondary ligand all six co-ordination positions are taken up by the two ligands. No precipitation is observed in the Cu(II) and Ni mixed systems, whereas a solid phase appears to be formed at  $\text{pH} \sim 8.5$  in the mixed systems of Zn, owing to slight disproportionation of the ternary complex.

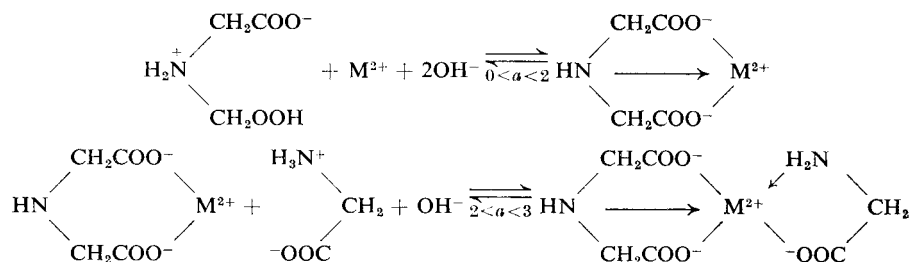
The Cd-IMDA-Gly and Cd-IMDA-Aln systems give a well-defined inflexion at  $a = 1$ , which is due to the neutralization of one of the protons of the carboxylic groups of IMDA. Further addition

of alkali results in formation of the 1:1 Cd-IMDA complex and a poor inflexion at  $a = 2$  is obtained, followed by formation of the ternary complexes, which disproportionate at  $\text{pH} \sim 9$ , giving a white gelatinous precipitate, probably of  $\text{Cd}(\text{OH})_2$ .

The systems, Cu(II)-IMDA-ASPA, Ni-IMDA-ASPA and Zn-IMDA-ASPA (*e.g.* curve 11) give two inflexions, at  $a = 3$  and  $a = 4$ . That at  $a = 3$  can be attributed to the neutralization of the two protons released from IMDA in 1:1 M(II)-IMDA complex formation and of the proton ionized from ASPA at low pH. Formation of the ternary complex is complete at  $a = 4$ . However, with Cd-IMDA-ASPA the first inflexion, at  $a = 2$ , is due to the neutralization of the two protons, one from IMDA and the other from ASPA, which ionize at low pH. Combination of IMDA with the metal ion gives a poor inflexion at  $a = 3$ . Another inflexion at  $a = 4$  is due to the ternary complex formation. Precipitation starts at  $\text{pH} \sim 9$  in the case of Zn-IMDA-ASPA and at  $\text{pH} \sim 10$  in the case of Cd-IMDA-ASPA, which may be due to the formation of metal hydroxide.

Other evidence supporting the formation of ternary complexes is given, for example, by the colour change from the light greenish blue of the 1:1 Cu(II)-IMDA binary complex to blue in the presence of the secondary ligand when the pH is raised.

The sequence of reactions in the glycine system (as an example) may be summarized as follows:



#### FORMATION CONSTANTS AND FREE ENERGIES OF FORMATION OF THE TERNARY COMPLEXES

The results obtained can be compared with those for the addition of a neutral or phenolic bidentate ligand to a M(II)-IMDA complex. A comparison of the results given in Tables II and III clearly indicates that the addition of a neutral bidentate ligand, such as 1,2-propylenediamine (1,2-pn), gives a higher formation constant for the ternary complex than does addition of anionic bidentate (Gly and Aln) or terdentate (ASPA) ligands investigated here. This may be due to coulombic repulsion which occurs between the ligands in the latter systems. On the other hand, the presence of an aromatic ring system in an anionic secondary ligand, *e.g.*, salicylic (SA), sulphosalicylic (SSA) and chromotropic acid (CS) and Tiron, increases the formation constant of the ternary complexes.

TABLE II.—FORMATION CONSTANTS AND FREE ENERGIES OF FORMATION OF MIXED LIGAND IMDA COMPLEXES [ $25 \pm 1^\circ\text{C}$ ,  $\mu = 0.10$  ( $\text{KNO}_3$ )]

System	$\log K_{\text{MAB}}$	$\Delta G^\circ$ , kJ/mole
Cu(II)-IMDA-Gly	$5.87 \pm 0.02$	-33.5
Cu(II)-IMDA-Aln	$5.80 \pm 0.01$	-33.1
Cu(II)-IMDA-ASPA	$6.05 \pm 0.02$	-34.5
Ni(II)-IMDA-Gly	$5.02 \pm 0.01$	-28.7
Ni(II)-IMDA-Aln	$4.68 \pm 0.02$	-26.7
Ni(II)-IMDA-ASPA	$5.70 \pm 0.02$	-32.3
Zn(II)-IMDA-Gly	$4.38 \pm 0.05$	-25.0
Zn(II)-IMDA-Aln	$3.98 \pm 0.05$	-22.7
Zn(II)-IMDA-ASPA	$4.59 \pm 0.02$	-26.2
Cd(II)-IMDA-Gly	$3.79 \pm 0.04$	-21.6
Cd(II)-IMDA-Aln	$3.55 \pm 0.05$	-20.3
Cd(II)-IMDA-ASPA	$3.89 \pm 0.03$	-22.2

TABLE III.—FORMATION CONSTANTS OF THE OTHER IMDA MIXED COMPLEXES  
 [30 ± 1°C,  $\mu = 0.10$  (KNO<sub>3</sub>)] [25 ± 1°C,  $\mu = 0.10$  (KNO<sub>3</sub>)]

System	log $K_{MAB}$	System	log $K_{MAB}$
Cu(II)-IMDA-1,2-pn	8.36 ± 0.04	Cu(II)-IMDA-SA	7.89 ± 0.04
Ni(II)-IMDA-1,2-pn	6.45 ± 0.04	Cu(II)-IMDA-SSA	6.53 ± 0.04
Zn(II)-IMDA-1,2-pn	5.14 ± 0.06	Cu(II)-IMDA-Tiron	10.80 ± 0.06
Cd(II)-IMDA-1,2-pn	4.76 ± 0.09	Cu(II)-IMDA-CS	10.05 ± 0.06

 TABLE IV.—FORMATION CONSTANTS AND FREE ENERGIES  
 OF FORMATION OF MIXED LIGAND NTA COMPLEXES  
 [25 ± 1°C,  $\mu = 0.10$  (KNO<sub>3</sub>)]

System	log $K_{MAB}$	$\Delta G^\circ$ , kJ/mole
Cu(II)-NTA-Gly	5.44*	-31.0
Cu(II)-NTA-Aln	5.36 ± 0.03	-30.6
Cu(II)-NTA-ASP	5.31*	-30.3
Ni(II)-NTA-Gly	4.42*	-25.6
Ni(II)-NTA-Aln	4.24 ± 0.02	-24.2
Ni(II)-NTA-ASP	4.20*	-24.0
Zn(II)-NTA-Gly	3.76 ± 0.04	-21.5
Zn(II)-NTA-Aln	3.36 ± 0.03	-19.2
Zn(II)-NTA-ASP	3.24*	-18.5
Cd(II)-NTA-Gly	3.25 ± 0.05	-18.5
Cd(II)-NTA-Aln	2.80 ± 0.03	-16.0
Cd(II)-NTA-ASP	2.96 ± 0.05	-16.9

\* These values have been taken from the literature.

Ternary complexes with nitrilotriacetic acid (NTA) as the primary ligand and Gly, Aln or ASPA as the secondary ligand are less stable (Table IV) than the IMDA systems. This may be due to steric factors.

The order of complexing power is ASPA > Gly > Aln and Gly > Aln > ASPA for IMDA and NTA respectively as primary ligand. That ASPA is the poorest complexing agent in the NTA systems may be due to decreased basicity of the nitrogen atom caused by the inductive effect of the free carboxylic group, or to steric factors.

A plot of log  $K_{MAB}$  against log  $K_{MB_2}$  shows a linear relationship between the formation constants of the ternary and the 1:2 M(II)-secondary ligand complexes.

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**Summary**—The formation constants, log  $K_{MAB}$ , for the reactions MA + B  $\rightleftharpoons$  MAB [where M = Cu(II), Ni, Zn or Cd, A = terdentate ligand and B = bidentate or terdentate ligand] have been determined. Potentiometric evidence is presented for the stepwise addition of the secondary ligand B to the 1:1 metal iminodiacetate (MA). The formation constants and the free energies of formation ( $\Delta G$ ) have been calculated at 25 ± 1° and  $\mu = 0.10$ . The order in terms of secondary ligands has been found to be ASPA > Gly > Aln and Gly > Aln > ASPA with iminodiacetic and nitrilotriacetic acid as primary ligands respectively (ASPA = aspartic acid, Gly = glycine, Aln = dl-alanine). The plot of log  $K_{MAB}$  against log  $K_{MB_2}$  shows a linear relationship between the formation constants of the ternary and 1:2 M(II)-secondary ligand complexes.

**Zusammenfassung**—Die Bildungskonstanten  $\log K_{MAB}$ , der Reaktionen  $MA + B \rightleftharpoons MAB$  [ $M = Cu(II), Ni, Zn$  oder  $Cd$ ;  $A =$  zweizähliger Ligand;  $B =$  zwei oder dreizähliger Ligand] wurden bestimmt. Aus potentiometrischen Messungen werden Hinweise darauf abgeleitet, daß der Zweitligand Bstufenweise an das 1:1-Metalliminodiacetat (MA) addiert wird. Die Bildungskonstanten und die freien Bildungsenthalpien ( $\Delta G$ ) wurden bei  $25 \pm 1^\circ$  und  $\mu = 0,10$  berechnet. Die Reihenfolge der Zweitliganden ist  $ASPA > Gly > Aln$  mit Iminodiessigsäure als erstem Liganden bzw.  $Gly > Aln > ASPA$  mit Nitrilotriessigsäure ( $ASPA =$  Asparaginsäure,  $Gly =$  Glycin,  $Aln = dl$ -Alanin). Trägt man  $\log K_{MAB}$  gegen  $\log K_{MB_2}$  auf, so erhält man eine lineare Beziehung zwischen den Bildungskonstanten der ternären und der 1:2-Komplexe zweiwertiger Metalle mit den Zweitliganden.

**Résumé**—On a déterminé les constantes de formation,  $\log K_{MAB}$ , pour les réactions  $MA + B \rightleftharpoons MAB$  (où  $M = Cu(II), Ni, Zn$  ou  $Cd$ ,  $A =$  ligand tricoordonné et  $B =$  ligand dicoordonné ou tricoordonné). On présente des preuves potentiométriques pour l'addition par palier du ligand secondaire B à l'iminodiacétate métallique 1:1 (MA). On a calculé les constantes de formation et les énergies libres de formation ( $\Delta G$ ) à  $25^\circ \pm 1^\circ$  et  $\mu = 0,10$ . On a trouvé que l'ordre par rapport aux ligands secondaires est  $ASPA > Gly > Aln$  et  $Gly > Aln > ASPA$  avec respectivement l'acide iminodiacétique et l'acide nitrilotriacétique en tant que ligands primaires ( $ASPA =$  acide aspartique,  $Gly =$  glycine,  $Aln = dl$ -alanine). Le tracé de  $\log K_{MAB}$  en fonction de  $\log K_{MB_2}$  montre une relation linéaire entre les constantes de formation des complexes ternaire et secondaire 1:2 M(II).

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### Determination of iron in biological material by substoichiometric isotopic-dilution analysis

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MOST APPLICATIONS of substoichiometric isotopic-dilution analysis reported in the literature have concerned the determination of microgram or submicrogram amounts of elements, where this analytical technique has often proved to be useful. Another aspect of the technique which has not been paid much attention so far, is the potentiality of performing high precision determinations of elements present in relatively high concentrations. In that case, a very high reproducibility of the substoichiometric isolation may be obtained, and the main limiting factor of the analytical precision will be counting errors, which can be reduced to a low level. In a recent report,<sup>1</sup> the feasibility of substoichiometric isotopic-dilution for major element analysis is clearly demonstrated in the case of iron determination in standard steels.

Iron appears to be well suited for determination by substoichiometric isotopic-dilution because of its tendency to form complexes of high stability with a number of reagents, and because a suitable radioactive tracer (<sup>59</sup>Fe) can be made available at high specific activity. Starý and Růžička<sup>2</sup> reported

a method based on separation of the Fe(III)-EDTA complex from unreacted Fe(III) on a cation-exchange column. In another paper by Starý *et al.*<sup>3</sup> a method based on substoichiometric extraction of Fe(III) cupferronate was proposed. Both these methods were used for submicrogram amounts of iron in synthetic solutions. The EDTA method was also used for the determination of traces of iron in sodium iodide, after introduction of an extraction step with acetylacetone preceding the cation-exchange separation.

In the present work, the EDTA method by Starý and Růžička<sup>2</sup> was adapted for the determination of iron in biological material. After decomposition of the sample with nitric acid/sulphuric acid in the presence of a known amount of <sup>59</sup>Fe tracer, iron(III) is extracted into isopropyl methyl ketone from 3M sodium chloride medium. Iron is back-extracted with dilute nitric acid, and reacted with a substoichiometric amount of EDTA, whereafter the solution is treated in a manner similar to that reported by Starý and Růžička.

Some iron is lost in the preliminary extraction with isopropyl methyl ketone; in most cases 2-4% in the extraction step and 5-10% in the subsequent washing step. The amount of EDTA used in the substoichiometric separation has therefore been fixed at a level corresponding to at most 60% of the estimated iron content of the sample.

## EXPERIMENTAL

### Apparatus

*Counting equipment.* A scintillation counter with a 75 × 75 mm NaI(Tl) crystal.

*Cation-exchange columns.* Columns of 12 mm internal diameter filled with Dowex 50W-X8, 100-200 mesh, Na<sup>+</sup> form, to 50 mm height of resin bed. The column is prepared by treating the resin in the H<sup>+</sup>-form with an excess of 1M sodium hydroxide and washing with water until the eluate is neutral.

### Reagents

The purity of the reagents used was *pro analysi*.

*EDTA solution.* Prepared by dissolving the disodium salt of EDTA in water. The solution was standardized against Fe(III) solutions of known concentration, according to the substoichiometric procedure given below.

*<sup>59</sup>Fe tracer.* A solution of specific activity 3000 mCi/g was diluted with 0.1M hydrochloric acid to a suitable concentration.

### Procedure

About 0.4 g of biological material is weighed into a 100-ml Erlenmeyer flask containing 1 ml of <sup>59</sup>Fe tracer solution. Two ml of concentrated sulphuric acid are added, and decomposition is accomplished by heating on a hot-plate and adding concentrated nitric acid portionwise. The total consumption of nitric acid is about 10 ml. The solution is evaporated to a volume of about 2 ml, cooled, and after addition of 15 ml of 3M sodium chloride, extracted with 15 ml of isopropyl methyl ketone. The organic phase is washed once with 15 ml of 3M sodium chloride. Iron is then back-extracted with 15 ml of 0.01M nitric acid. To the resulting solution is then added a known volume of EDTA solution corresponding stoichiometrically to an amount *y* of iron which is about 60% of the estimated amount of iron in the sample (1 molecule of EDTA corresponds to 1 atom of Fe).

The solution is allowed to stand for 10-15 min at 30-40°, and is then passed through the cation-exchange column (flow-rate about 0.5 ml/min). The column is washed twice with 5 ml of water. The activity of the combined eluates (*A<sub>s</sub>*) is measured with the scintillation counter. After measurement of 1 ml of <sup>59</sup>Fe tracer solution diluted to the same volume (activity *A<sub>r</sub>*), the amount of iron present (*x*) is calculated from the relationship.

$$x = y \cdot \frac{A_r}{A_s}$$

The reagent blank is determined in the same way as described above, and the result is subtracted from *x* to obtain the amount of iron in the sample.

## RESULTS AND DISCUSSION

The method has been tested on two biological standards, namely Bowen's kale<sup>4</sup> and animal blood from IAEA, Vienna. The results of this investigation are given in Table I. For kale, the iron content was also determined by neutron-activation analysis, using the same dissolution procedure as in the isotopic-dilution experiments and subsequently an anion-exchange separation procedure for the isolation of <sup>59</sup>Fe from other activities. The values for kale have been corrected for a loss of 5.5% observed on separate aliquots of the sample by drying for 20 hr at 90°, as recommended by Bowen.<sup>4</sup>

TABLE I.—CONCENTRATION OF IRON IN TWO BIOLOGICAL STANDARDS, DETERMINED BY SUBSTOICHIOMETRIC ISOTOPIC-DILUTION

Standard	Single values, <i>ppm</i>	Mean value, <i>ppm</i>	Relation standard deviation, %
IAEA animal blood	2957, 2945, 2989, 2953, 2964, 2961	2962	0.5
Standard kale, series I	111.2, 115.5, 110.8, 107.1, 118.1, 117.8	113.4	3.6
Standard kale, series II	113.0, 112.3, 110.3, 114.4, 121.1, 119.1	115.0	3.7
Standard kale, neutron-activation analysis	113.0, 121.0, 124.9, 116.9, 109.8	117.1	5.1

As could be expected, a high precision is observed in the analysis of animal blood, which corresponds to determination of about 1 mg of iron. In the case of the kale, where the amount of iron determined is 40–50  $\mu\text{g}$ , a precision of 3–4% is observed. The isotopic-dilution values for kale are in agreement within experimental error with the neutron-activation mean value. Previous results for iron in the kale show a fairly large spread, but point towards a value of about 120 ppm.<sup>5</sup>

The iron "blank" from the chemicals used in the experiments described here was found to be  $7.6 \pm 0.3 \mu\text{g}$ , and refers to chemicals of *pro analysi* grade. The blank level could probably be considerably reduced by using especially purified reagents, but this was not considered necessary when working at the concentration levels studied in this work.

Substoichiometric isotopic-dilution analysis has not been widely used for determination of trace elements in biological material. According to the experience gained in the present work, the technique should be well suited for iron determination in biological samples. The necessary equipment is simple, and results of high precision and accuracy may be obtained.

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**Summary**—Iron is determined in biological material by wet oxidation, in the presence of <sup>59</sup>Fe tracer, extraction of iron(III) chloride into isopropyl methyl ketone, stripping with nitric acid, and substoichiometric separation of the Fe-EDTA complex on a cation-exchanger. The precision is good and the method has been applied to analysis of standard kale and blood.

**Zusammenfassung**—Eisen wird in biologischem Material durch nasse Oxidation, Extraktion von Eisen(III)-Chlorid in Isopropylmethylketon, Rückextraktion mit Salpetersäure und unterstöchiometrische Abtrennung des Fe-EDTA-Komplexes an einem Kationenaustauscher nach Zugabe von <sup>59</sup>Fe als Träger bestimmt. Die Genauigkeit ist gut, das Verfahren wurde auf die Analyse von Standard-Kohl und Blut angewandt.

**Résumé**—On dose le fer dans les substances biologiques par oxydation par voie humide, extraction du chlorure de fer(III) en méthylisopropylcétone, épuration par l'acide nitrique et séparation substoichiométrique du complexe Fe-EDTA sur un échangeur de cations après addition de traceur <sup>59</sup>Fe. La précision est bonne et la méthode a été appliquée à l'analyse de chou et de sang étalons.

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## ANNOTATION

### Dosage du glycérol dans les glycélines techniques—III\* Collaboration internationale au sein de l'I.S.O. et analyse statistique des résultats des essais circulaires effectués

(Reçu le 26 avril 1971. Accepté le 9 juin 1971)

A L'OCCASION de la mise à l'étude, dans le cadre de l'I.S.O., d'une recommandation internationale pour le dosage du glycérol, applicable aux produits à usage industriel, plusieurs experts ont attiré l'attention de notre groupe de travail sur certaines anomalies du mode opératoire<sup>1</sup> actuellement en usage dans les transactions internationales, bien que ce mode opératoire conduise à des résultats corrects.

A la suite d'études expérimentales approfondies, certains de ces experts<sup>2,3</sup> ont été amenés à proposer à la normalisation internationale un mode opératoire modifié permettant de corriger les imperfections mises en évidence.

L'adoption de leurs conclusions se justifie par les résultats d'une étude statistique effectuée à l'occasion d'essais circulaires exécutés à l'échelon international.

#### ESSAIS CIRCULAIRES EFFECTUES

Un programme d'essais circulaires a été décidé, en octobre 1969, afin de comparer le mode opératoire modifié<sup>3</sup> à sa version actuellement en usage.<sup>1</sup>

Rappelons que ces modifications portaient

- (1°) sur le moment choisi pour diluer les préparations: à l'origine des opérations plutôt qu'immédiatement avant le titrage final.
- (2°) sur l'ajout de formiate de sodium comme tampon aussi bien dans l'essai à blanc que dans le dosage avec, comme conséquence, l'adoption d'un pH unique de 7,9 comme point initial et final de tous les titrages potentiométriques, plutôt que l'artifice d'une correction par arrêt de l'essai à blanc à un pH anormal et difficile à justifier étant donné qu'il est différent du pH correspondant, dans ce cas, à la neutralité de la solution.

On attendait de ces modifications les avantages suivants:

- 1—Élimination d'une faible *perte de l'acide formique*, produit par la réaction de base du métapériodate de sodium avec le glycérol.
- 2—Diminution de l'*influence du dioxyde de carbone* apporté, notamment par l'eau de dilution (ajoutée après la neutralisation initiale de la prise dans le mode opératoire incriminé).
- 3—Rétablissement du principe de l'*essai à blanc réel*, indispensable à la correction automatique de l'influence des réactifs et de l'environnement.
- 4—Simplification des paramètres et possibilité d'automatisation de la méthode de dosage.

Quarante-deux opérateurs appartenant à 22 laboratoires distincts et répartis dans cinq pays ont pris part à ces essais circulaires, dont les résultats sont donnés à l'annexe I.

Chacun d'eux a reçu quatre échantillons préparés avec soin, marqués respectivement A, B, C et D ainsi que l'instruction d'en diluer une prise définie et d'utiliser des parties aliquotes de ces dilutions pour les deux termes de la comparaison de façon à éliminer autant que possible toute erreur due au prélèvement des échantillons.

Les échantillons A et B, constitués de glycélines de synthèse à haute teneur en glycérol, avaient été dilués et homogénéisés avant leur répartition en vue de réduire l'influence de l'hygroscopicité de la matière sur les pesées.

L'échantillon C était constitué de glycérol brute naturelle du commerce tandis que l'échantillon D avait été préparé spécialement de façon à présenter une glycéline brute à environ 70% de glycérol

\* Communications I et II—voir références 1 et 3



contenant des impuretés définies, aux teneurs approximatives indiquées ci-après, mélangées à une glycérine pure pour analyse du commerce:

NaCl	6,5%
Na <sub>2</sub> SO <sub>4</sub>	0,3%
NH <sub>4</sub> Cl	0,05%
Triméthylène glycol	1%
Butyrate de Na	0,5%
Acétate de Na	0,2%

Afin d'uniformiser les conditions d'étalonnage de la solution titrée d'hydroxyde de sodium, un lot homogène d'acide sulfamique, étalon primaire pour acidimétrie recommandé par l'IUPAC,<sup>4</sup> avait été divisé et expédié à chacun des laboratoires participants en même temps que les échantillons.

### ANALYSE STATISTIQUE DES RESULTATS

Les 42 opérateurs ont fourni, au total, plus de mille résultats expérimentaux dont l'analyse statistique a été effectuée par les soins de notre secrétariat en suivant les instructions du "Guide pour les essais interlaboratoires" faisant l'objet de la norme française NF × 06.041 de mars 1970. Tous les résultats étaient réunis en huit tableaux, répartis par échantillon et par méthode. Ces tableaux fournissent les trois résultats de chaque opérateur, ainsi que leur moyenne et leur variance éventuellement corrigées comme indiqué ci-après.

L'élimination des résultats aberrants pour la répétabilité (erreurs aléatoires), a été effectué après application du test de Cochran. On a, suivant le cas, supprimé de l'analyse statistique les trois résultats de l'opérateur ou seulement le résultat manifestement aberrant. Dans ce cas, la moyenne arithmétique des deux autres résultats a été insérée à la place du résultat supprimé afin de maintenir l'homogénéité du plan ordinateur.

Ces éliminations nous amènent à émettre des réserves quant à la validité de la comparaison portant sur l'échantillon A (cf.: NF × 06.041/3.1 NOTA). Elles affectent en effet, pour le test de Cochran, 7 opérateurs sur 42, soit plus de 10%, contre respectivement 3, 2 et 1 opérateurs dans les cas des échantillons B, C et D.

On note en outre que, pour l'échantillon A, les résultats obtenus par l'application de la méthode modifiée sont éliminés en plus grand nombre (18) que ceux de la méthode traditionnelle (2), alors que la proportion est égale pour les trois autres échantillons ensemble (3-3).

Il semble que certains opérateurs, peu habitués aux modifications proposées, n'ont atteint le niveau de répétabilité normal qu'après traitement du premier échantillon de la série.

### COMPARAISON DES METHODES

Les données de la comparaison sont condensées au tableau ci-après.

Echantillon	A		B		C		D	
	IUPAC	modifiée	IUPAC	modifiée	IUPAC	modifiée	IUPAC	modifiée
Moyenne	92,35	92,23	90,89	90,90	81,46	81,50	71,33	71,35
Répétabilité $\sigma_r$	0,065	0,071	0,063	0,066	0,089	0,060	0,059	0,069
Reproductibilité $\sigma_R$	0,301	0,262	0,341	0,273	0,276	0,314	0,208	0,227
$t$	3,257		0,165		1,058		0,649	
$F$	1,33		1,56		1,30		1,19	

L'application du test  $t$  de Student<sup>5</sup> montre que les teneurs moyennes obtenues par les deux méthodes ne sont pas significativement différentes pour une probabilité de 1% ( $P = 0,01$ ), sauf dans le cas de l'échantillon A auquel s'appliquent les réserves émises plus haut.

L'application du test  $F$  de Snedecor<sup>6,7</sup> aux écarts-types de reproductibilité montre que ceux-ci ne sont pas significativement différents, pour une probabilité de 1% ( $P = 0,01$ ), sauf dans le cas de l'échantillon B.

### CONCLUSIONS

(1°) Compte tenu des réserves exprimées plus haut pour l'échantillon A, les deux méthodes en comparaison fournissent des valeurs moyennes identiques.

(2°) Les reproductibilités de ces valeurs sont pratiquement identiques, sauf dans un cas sur quatre (échantillon B) où la méthode modifiée est légèrement plus reproductible.

En conséquence, notre groupe de travail a décidé de présenter la méthode modifiée comme projet de recommandation internationale au Comité Technique ISO/TC 47-Chimie.

*Président du groupe de  
travail 2-Glycérine  
I.S.O. Comité technique 47*

R. MORMONT

## ANNEXE

### Liste des laboratoires ayant participé aux essais circulaires

Belgique	OLEOCHIM S.A. Ertvelde Centre de Recherche de la Société SOLVAY ET CIE S.A. Bruxelles Laboratoires VANDERKELEN, Bruxelles
Etats-Unis d'Amérique	ARMOUR-DIAL, Inc. ATLAS Chemical Industries, Inc., Chem. Res. Dept. COLGATE PALMOLIVE Co, R. and D. Dept, Piscataway N.J. DOW Chemical Co, Glycerine Lab. OLIN Corporation, Doe Run. Quality Assurance Lab. SHELL Co, NORCO Plant
France	COLGATE PALMOLIVE FRANCE SOLVAY ET CIE S.A. Tavaux UNION GENERALE DES GLYCERINES, Marseille Laboratoires WOLFF, Paris
Italie	CARLO ERBA, Milano MIRA-LANZA, Lanza di Mesa MIRA-LANZA, Laboratorio Sperimental, Mira MIRA-LANZA, Laboratorio Chimico, Mira MIRA-LANZA, Laboratorio Direzione Centrale MONTECATINI-EDISON, Centro Ricerche di Bollate
République Fédérale Allemande	DALLI-WERKE, Stolberg-Rhld FARBWERKE HOECHST A. G., Frankfurt/M HENKEL & Cie G.m.b.H., Düsseldorf

**Résumé**—42 travailleurs dans 22 laboratoires ont effectué une comparaison inter-laboratoires des méthodes IUPAC et de méthodes modifiées pour le dosage du glycérol. On a utilisé quatre échantillons, et l'on a montré que les méthodes donnent des résultats qui ne diffèrent pas de manière significative dans leurs valeurs moyennes (limites de confiance 99%).

**Summary**—An interlaboratory comparison has been made, by 42 workers in 22 laboratories, of the IUPAC and modified methods for determination of glycerol. Four samples were used, and the methods were shown to give results that did not differ significantly in their mean values (99%) confidence limits.

**Zusammenfassung**—Die IUPAC-Methode und die modifizierte Methode zur Glycerinbestimmung wurden von 42 Experimentatoren in 22 Laboratorien verglichen. Es wurden vier Proben verwendet, und es wurde gezeigt, daß die Ergebnisse sich in ihren Mittelwerten nicht wesentlich unterscheiden (99% Vertrauensgrenze).

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2. R. Mormont et A. C. Gillet, Jr., *XXXVIe Congrès Int. Chim. Ind. Bruxelles*, Sept. 1966 (in *Ind. Chim. Belge*, 1967, 32 S, 735).
3. R. Mormont, A. C. Gillet Jr. et E. Heinerth, *Talanta*, 1969, 16, 701.
4. I.U.P.A.C. *Anal. Chem. Division, Pure and Appl. Chem.*, 1969, 18, 445.
5. G. Charlot, *Les méthodes de la chimie analytique, Analyse quantitative minérale, 5e éd.* p. 211.
6. *Idem, loc. cit.*, p. 209.
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## PUBLICATIONS RECEIVED

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**Electroanalytical Chemistry, Volume 5:** ED. ALLEN J. BARD. Dekker, New York, 1971. Pp. 386. \$28.50, £13.60.

Three topics are covered in this volume, with over half the space devoted to a detailed discussion by Roland Guidelli on Chemical Reactions in Polarography, based on mathematical considerations of the thermodynamics of irreversible processes, of diffusion, and of reaction overpotential. The chapter is well illustrated with examples taken from the literature. The chapter on Hydrated Electrons and Electrochemistry by Geraldine Kenney and David Walker is a most readable and even entertaining survey of this relatively young branch of the science. The authors do not claim to present an exhaustive survey of the literature, but they certainly have written an excellent general review which could be read as well by undergraduates as by research workers. The chapter on Fundamentals of Metal Deposition by J. A. Harrison and H. R. Thirsk reviews the models of the electrocrystallization process at the atomic level—the adatom model, the direct deposition model and the nucleation and growth models. Mechanisms and data for the electrodeposition behaviour of a number of metals are presented and discussed, and a final section deals with the practically very important topic of organic additives in electroplating—a difficult subject to tackle rigorously. This volume maintains the high standard of the series, and is perhaps rather less mathematical than some of the others. The high price will unfortunately deter most private individuals from purchasing.

**Proceedings of the Conference on the Applications of the Mössbauer Effect, Tihany (Hungary) 17th–21st June 1969:** Ed. I. DÉZSI, Akadémiai Kiadó, Budapest, 1971, Pp. 808. £11.00.

This is a record of the most recent international conference on the application of the Mössbauer effect. There are over ninety original papers grouped under several headings. The use of the technique in the study of problems in chemistry, biology and metallurgy is included and there are special sections devoted to relaxation effects, the Goldanskii-Karyagin effect and surface phenomena. In the concluding section there are papers which propose the utilization of the Mössbauer effect in the control of industrial processes such as the preparation of iron oxide electrodes for alkaline batteries and the vulcanization of rubber using tin halide accelerators.

**Biochemistry of Microbial Action:** T. J. FRANKLIN and G. A. SNOW, Chapman and Hall, London, 1971. Pp. xii + 163. £2.25.

This book will prove useful to chemists working in the field of antibiotics and antimicrobial drugs and would make interesting reading for the general scientist.

**Analytical Chemistry of Nitrogen and its Compounds,** in two parts: Eds. C. A. STREULI and P. R. AVERELL, Wiley-Interscience, London, 1970. Pp. XIV + 763. £16.50.

The analytical chemistry of nitrogen and its compounds is comprehensively reviewed by a number of authors. It has the breadth of vision which is common to co-operative works, but also the limitations which many have. There is an unevenness in editing in that some authors list all the methods available in an uncritical manner, whereas others successively translate their practical experience into words. There is also evidence of lack of drive on the part of editors or publishers since most of the articles include references up to only the early 1960's. These defects mar what is basically a valuable work, which is likely to be much consulted by a variety of chemists. Total, inorganic and organic nitrogen in compounds which range from simple salts to proteins and polymers are all covered (although complex nitrides are omitted), and at the very least it should prove a good starting place for those faced with an analytical problem involving nitrogen compounds.

**Low-Frequency Vibrations of Inorganic and Co-ordination Compounds:** JOHN R. FERRARO, Plenum, New York, (Heyden, London) 1971. Pp. 309 + XIV. £8.75.

This is a book for the research worker in inorganic and co-ordination chemistry. It provides practical guidance on the instruments and techniques for obtaining low-frequency infrared spectra and then deals comprehensively with the work carried out up to mid-1969. The arrangement of

the discussion is similar to that used by Nakamoto in his well-known work, which is thus complemented by this book. It is a format which has passed the test of usage, and one can predict that this book will be much used by workers in the field.

**The Interpretation of Vibrational Spectra:** D. STEELE, Chapman and Hall, London, 1971. Pp. 67. £1.25.

This could be retitled "Teach-yourself to interpret infrared spectroscopy". The novel feature is a flow-chart, on the end-covers for convenience of reference, which emphasises the correlation of the several peaks in the spectra arising from the same molecular grouping. There are 26 test spectra to work through and on the reverse side an interpretation is provided. The approach is a good one, and is much better than the traditional one through correlation diagrams. The format also allows the student to become familiar with the characteristic peak shapes and groupings of the most common groups. There is a brief introduction and the inclusion of a few Raman and NMR spectra, all of which require some prior knowledge of spectroscopy. Some may feel that the interpretations provided either go too far or dismiss some of the interpretive difficulties too lightly. However the book does not claim to be anything but an introduction to the subject and as such it could usefully be placed in the hands of students, with the confidence that for an hour or two their interest would be stimulated and that they would have acquired a sound approach to the interpretation of infrared spectra.

**Spectrométrie d'absorption atomique:** MAURICE PINTA. Masson, Paris, 1971. Volume I: Pp. 286 + xx; 110 f. Volume II: Pp. 508 + xxx; 185 f.

The authors and his 17 collaborators have obviously put much effort into these two volumes, which should be welcomed by French-speaking analysts. The first volume is concerned with general problems—theory, apparatus (with a survey of 30 commercial instruments), light sources and flames, interactions, and is concluded by a very useful chapter by the principal author on the experimental approach to optimization of a new procedure. A few pages on terminology and a very comprehensive bibliography including some references from 1970, complete this part. In volume II the detailed information of procedures and methods is arranged according to the type of sample, or perhaps according to the interests of the collaborators. This results in some repetition, but the index allows cross-references to be made readily, and for practising analysts concerned with rocks and soils, minerals, water, plants, biochemistry, petroleum products, metals and alloys, and nuclear energy, to mention some of the chapter headings, this may be the most convenient format. This will certainly be a useful working handbook for the analytical laboratory.

## PAPERS RECEIVED

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- Purity of compounds by extraction-solubility:** R. A. HUMMEL and W. B. CRUMMETT. (16 August 1971)
- 6-Phenyl-2,3-dihydro-*as*-triazine-3-thione and 5,6-diphenyl-2,3-dihydro-*as*-triazine-3-thione as gravimetric reagents for the determination of thallium and palladium:** M. EDRISSI, A. MASSOUMI and I. LALEZARI. (27 August 1971)
- The spectrophotometric determination of 0–50 ng of chromium in 1 ml of human serum:** J. AGTERDENBOS, L. VAN BROEKHOVEN, B. A. H. G. JÜTTE and J. SCHURING. (27 August 1971)
- Potentiometric determination of the active ingredient in sodium pentacyanonitrosylferrate(III):** E. SISKA and E. PUNGOR. (27 August 1971)
- Computer calculation of activation energies of irreversible electrode processes at a dropping mercury electrode:** D. R. CROW and S. L. LING. (26 August 1971)
- Analysis of phase titration of three-component systems containing two mutually immiscible or partially miscible components:** S. K. SURI. (30 August 1971)
- The constitution and stability of acidic periodate solutions:** D. J. B. GALLIFORD, R. H. NUTTALL and J. M. OTTAWAY. (30 August 1971)
- Determination of trace amount of uranium in silicate minerals by the fission-track technique:** HIDEKI MATSUDA, YUTAKA TSUTSUI, SHIGENORI NAKANO and SHUNJI UMEMOTO. (30 August 1971)
- The absorption of carbon dioxide in solutions of monoethanolamine:** D. W. WHYMARK and J. M. OTTAWAY. (30 August 1971)
- Dichloroamine-T as a new oxidimetric titrant in non-aqueous and partially aqueous media—I. Potentiometric determination of some common reductants:** T. J. JACOB and C. G. R. NAIR. (31 August 1971)
- The dependence of the dropping mercury electrode potential at an attained constant polarization rate (current) on the concentration of an electroactive constituent involved in reversible or irreversible electrode reactions:** YECHESKEL ISRAEL. (3 September 1971)
- A fully automated procedure for the determination of sodium hypochlorite and hydrogen peroxide, based on the use of a porous catalytic silver electrode:** B. FLEET, A. Y. W. HO and J. TENYGL. (3 September 1971)
- Controlled potential coulometry: The application of a secondary reaction to the determination of plutonium and uranium at a solid electrode:** J. B. FARDON and I. R. MCGOWAN. (6 September 1971)
- The determination of plutonium and uranium in mixed oxide fuels by sequential redox titration:** P. H. CHADWICK and I. R. MCGOWAN. (6 September 1971)
- Effect of solvent extraction with dithizone on atomic absorption determination of ppm levels of cadmium:** Y. YAMAMOTO, T. KUMAMARU, H. HAYASHI and M. KANKE. (9 September 1971)
- Studies on hydroxyamidines—I. 1,2,3-phenyloxamidine hydrochloride as reagent for vanadium(V):** K. SATYANARAYANA and RAJENDRA KUMAR MISHRA. (15 September 1971)
- Volumetric estimation of micro and semi-micro quantities of L-histidine separately and in the presence of other natural amino acids:** KRISHNA BAHADUR and PADAM SEN. (16 September 1971)
- The analytical chemistry of the barbiturates:** B. MALLICK and W. F. SMYTH. (16 September 1971)
- Salicylaldehyde and  $\beta$ -resorcyraldehyde as indicators for the direct DCTA titration of iron(III):** M. N. DESAI, B. M. DESAI, B. S. PATWARI and M. H. GANDHI. (16 September 1971)
- Rapid mass-spectrometric determination of boron isotopic distribution in boron carbide:** JAMES E. REIN and ROBERT M. ABERNATHEY. (24 August 1971)

## NOTICE

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### IAEA SYMPOSIUM ON NUCLEAR ACTIVATION TECHNIQUES IN THE LIFE SCIENCES

Ljubljana, Yugoslavia, 10-14 April, 1972

The Symposium will be concerned with the applications of nuclear activation techniques in the life sciences and the significance of the results obtained in such applications. It will therefore be concerned both with the techniques themselves and with the interpretation of the data which they yield. A symposium of the same title was held in Amsterdam, Netherlands, in 1967 and this, the second of the series, is intended to cover the advances made in the five year interval.

Topics include sample preparation, activation, data processing, chemical separation (particularly in multicomponent systems), biological analytical reference materials, and studies of cellular and sub-cellular systems in plants and animals.

Further information and forms to accompany abstracts of papers intended for presentation at the Symposium may be obtained from national authorities for atomic energy matters. Abstracts must be submitted through these authorities so as to reach the International Atomic Energy Agency before December 13, 1971.

## SUMMARIES FOR CARD INDEXES

**Effect of precipitate and complex formation on the determination of silver by atomic-absorption spectroscopy:** R. F. LEE and W. F. PICKERING, *Talanta*, 1971, **18**, 1083. (Chemistry Department, University of Newcastle, N.S.W. 2308, Australia.)

**Summary**—In the determination of silver, by atomic-absorption spectroscopy, the presence of small amounts of precipitating agents in the solution to be analysed can result in significant changes in the absorbance at 328.1 nm. The controlling factor is the physical form of the precipitated material. The presence of some complexing agents also causes variable absorption readings, and with ligands such as thiosulphate and cyanide ions the interference can be attributed to secondary reactions associated with the sparingly soluble compounds formed under specific conditions.

**Chromatographic separation of copper with an  $\alpha$ -hydroxyoxime:** JAMES S. FRITZ, DONALD R. BEUERMAN and JOHN J. RICHARD, *Talanta*, 1971, **18**, 1095. (Department of Chemistry and Institute for Atomic Research, Iowa State University, Ames, Iowa, U.S.A.)

**Summary**—Two aliphatic  $\alpha$ -hydroxyoximes have been synthesized and characterized. These reagents are highly selective for the extraction of copper(II) from weakly acidic aqueous solution. A column containing a hydroxyoxime on a solid support effects a quantitative separation of copper(II) from most other metal ions.

**Electronic modulation of microwave-excited electrodeless discharge lamps for use in atomic-fluorescence spectrometry:** R. M. DAGNALL, M. D. SILVESTER and T. S. WEST, *Talanta*, 1971, **18**, 1103. (Department of Chemistry, Imperial College of Science and Technology, London S.W.7, U.K.)

**Summary**—Electronic modulation of electrodeless discharge lamps has been investigated with respect to frequency of operation and modulation waveform. The optimal frequency of operation was found to be *ca.* 20,000 Hz, using a square waveform, and modulation was best achieved by adding the modulation waveform to the reference of the stabilizing element in the microwave power supply. Optimal operating conditions have been established for d.c. and a.c. modes of operation for several sources.

ВЛИЯНИЕ ОБРАЗОВАНИЯ ОСАДКОВ И  
КОМПЛЕКСОВ НА ОПРЕДЕЛЕНИЕ СЕРЕБРА  
МЕТОДОМ АТОМНО-АБСОРБЦИОННОЙ  
СПЕКТРОСКОПИИ:

R. F. LEE and W. F. PICKERING, *Talanta*, 1971, **18**, 1083.

**Резюме**—В определении серебра методом атомно-абсорбционной спектроскопии присутствие незначительных количеств осадителей в анализируемом растворе может вызвать значительные перемены поглощения при 328,1 нм. Это поглощение зависит от физической формы осажденного материала. Изменяющиеся поглощения также вызваны присутствием комплексообразующих агентов, а в случае лигандов как на пример ионов тиосульфата и цианида мешающее действие можно приписать вторичным реакциям, связанным с образованием почти нерастворимых соединений в особенных условиях.

ХРОМАТОГРАФИЧЕСКОЕ ОТДЕЛЕНИЕ МЕДИ  
 $\alpha$ -ОКСИОКСИМОМ:

JAMES S. FRITZ, DONALD R. BEUERMAN and JOHN J. RICHARD, *Talanta*, 1971, **18**, 1095.

**Резюме**—Синтезированы и охарактеризованы два алифатических  $\alpha$ -оксиоксима. Эти реагенты высокоизбирательны для экстракции меди(II) из слабокислых водных растворов. На колонке заполненной оксиоксимом на твердом носителе получается количественное отделение меди(II) от большинства других ионов металлов.

ЭЛЕКТРОННАЯ МОДУЛЯЦИЯ ВОЗБУЖДЕННЫХ  
МИКРОВОЛНАМИ БЕЗЭЛЕКТРОДНЫХ РАЗРЯДНЫХ  
ЛАМП ДЛЯ ИСПОЛЬЗОВАНИЯ В АТОМНО-  
АБСОРБЦИОННОЙ СПЕКТРОМЕТРИИ:

R. M. DAGNALL, M. D. SILVESTER and T. S. WEST, *Talanta*, 1971, **18**, 1103.

**Резюме**—Изучена электронная модуляция безэлектродных разрядных ламп в отношении на частоту операции и форму волны модуляции. Оптимальной частоты операции определена частота около 20,000 гц, пользуясь  $\phi$  квадратной формой волны, а модуляция получена присоединением формы волны модуляции к эталоне стабилизирующего элемента в подаче силы микроволны. Определены оптимальные условия работы для операции ряда источников при постоянном и переменном токах.



**Thermodynamics of the partition of 8-quinolinol between several organic solvents and aqueous buffers:** J. G. MASON and I. LIPSCHITZ, *Talanta*, 1971, **18**, 1111. (Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061, U.S.A.)

**Summary**—The partition coefficients of 8-quinolinol between water and benzene, nitrobenzene, toluene, and chloroform have been determined as a function of temperature and values of  $\Delta H$  and  $\Delta S$  determined for each. Values of the dissociation constant for protonated 8-quinolinol are reported as a function of temperature.

**Spectrochemical determination of rare-earth metals in uranium and its salts:** B. ZMBOVA, M. TRIPKOVIĆ and O. ŠEĆEROV, *Talanta*, 1971, **18**, 1117. (The Boris Kidrich Institute of Nuclear Sciences, Belgrade, Yugoslavia and Institute for Technology of Nuclear and Other Raw Materials, Belgrade, Yugoslavia.)

**Summary**—An emission spectrographic procedure is described for the determination of 0.05–4 ppm of rare-earth metals in uranium metal and its salts. Uranium is expected from the sample with tributyl phosphate, and the impurities are separated by precipitation as hydroxides and oxalates, with yttrium as a carrier. After conversion into the oxides, the rare-earth metals are mixed with graphite and excited in a d.c. arc.

**Adsorption behaviour of a number of metals on weakly basic ion-exchangers in methanol–hydrochloric acid mixtures:** ROKURO KURODA and NOBU-TAKA YOSHIKUNI, *Talanta*, 1971, **18**, 1123. (Laboratory for Analytical Chemistry, Faculty of Engineering, University of Chiba, Yayoi-cho, Chiba, Japan.)

**Summary**—Many metals are not strongly adsorbed on DEAE-cellulose from aqueous hydrochloric acid media. However, some metals can be adsorbed on DEAE-cellulose from methanol–hydrochloric acid media. Distribution coefficients of Zn, Cd, Hg(II) and Bi(III), which show pronounced adsorption, are presented as functions of the methanol and the acid concentrations. Differences in the distribution coefficient between the four metals and a considerable number of other metals are large enough to permit good separations on columns. Among the platinum group metals, Pd(II), Ir(IV) and Pt(IV) are adsorbed from the mixed solvents and may be separated from large quantities of base metals such as Fe(III), Co(II), Ni and Cu(II).

ТЕРМОДИНАМИКА РАСПРЕДЕЛЕНИЯ  
8-ОКСИХИНОЛИНА МЕЖДУ НЕКОТОРЫМИ  
ОРГАНИЧЕСКИМИ РАСТВОРИТЕЛЯМИ И  
ВОДНЫМИ БУФЕРНЫМИ РАСТВОРАМИ:

J. G. MASON and I. LIPSCHITZ, *Talanta*, 1971, **18**, 1111.

**Резюме**—Определены коэффициенты распределения 8-оксихинолина между водой и бензолом, нитробензолом, толуолом и хлороформом в зависимости от температуры; также определены величины  $\Delta H$  и  $\Delta S$  для каждого случая. Приведены величины константы диссоциации протонированного 8-оксихинолина при различных температурах.

СПЕКТРОХИМИЧЕСКОЕ ОПРЕДЕЛЕНИЕ  
РЕДКОЗЕМЕЛЬНЫХ ЭЛЕМЕНТОВ В УРАНЕ И  
ЕГО СОЛЯХ:

V. ZMBOVA, M. TRIPKOVIĆ and O. ŠEĆEROV, *Talanta*, 1971, **18**, 1117.

**Резюме**—Описан метод эмиссионной спектрографии для определения 0,05–4 мкг/г редкоземельных металлов в металлическом уране и его солях. Уран экстрагируют из пробы трибутилфосфатом, а примеси отделяют осаждением в форме гидроокисей или оксалатов, с использованием иттрия в качестве носителя. После превращения в окиси, редкоземельные элементы смешивают с графитом и возбуждают в дуге постоянного тока.

АДСОРБЦИОННЫЕ ХАРАКТЕРИСТИКИ РЯДА  
МЕТАЛЛОВ НА СЛАБООСНОВНЫХ ИОНООБ-  
МЕННИКАХ В СМЕСЯХ МЕТАНОЛА И СОЛЯНОЙ  
КИСЛОТЫ:

ROKURO KURODA and NOBUTAKA YOSHINUKUNI, *Talanta*, 1971, **18**, 1123.

**Резюме**—Ряд металлов адсорбируются только слабо на ДЭАЭ целлюлозе из водных растворов соляной кислоты, но некоторые металлы можно адсорбировать на этом ионообменнике из смесей метанола и соляной кислоты. Приведены коэффициенты распределения сильноадсорбирующихся ионов Zn, Cd, Hg(II) и Bi(III) в зависимости от концентрации метанола и кислоты. Разницы между коэффициентами распределения этих четыре металлов и коэффициентами других металлов довольно выражены чтобы позволять хорошие разделения на колонках. Среди платиновых металлов Pd(II), Ir(IV) и Pt(IV) адсорбируются из смешанных растворителей и отделяются от больших количеств основных металлов, в том числе Fe(III), Co(II), Ni и Cu(II).

**Iodine cyanide as volumetric oxidant:** RAM CHAND PAUL, RAJ KUMAR CHAUHAN, NARESH CHANDER SHARMA and RAM PARKASH, *Talanta*, 1971, **18**, 1129. (Department of Chemistry, Panjab University, Chandigarh, India.)

**Summary**—Iodine cyanide has been developed as an oxidant for the determination of iodide, sulphite, thiosulphate, thiocyanate, arsenic(III), antimony(III), tin(II), mercury(I), iron(II), ascorbic acid and  $\beta$ -naphthol in dilute aqueous mineral acids, glacial acetic acid and 1:1 acetic acid-acetic anhydride mixture, with visual and potentiometric methods of end-point detection.

**A general computer approach for calculating rate constants from near-equilibrium kinetic studies:** V. S. SHARMA and D. L. LEUSSING, *Talanta*, 1971, **18**, 1137. (Department of Chemistry, The Ohio State University, Columbus, Ohio 43210, U.S.A.)

**Summary**—A general computer approach for estimating rate constants from relaxation times is described. The programme CORNEK is essentially a least-squares refinement programme applied to non-linear systems. It uses directly the differential forms of the first derivatives of mass-balance and rate equations, thus avoiding the time-consuming derivations of near-equilibrium rate equations. The programme has been tested for binary systems such as Cu-histamine, Cu-serine, and the ternary system Cu-histamine-serine.

**Analytica chimica philatelica:** R. P. GRAHAM, *Talanta*, 1971, **18**, 1157. (Department of Chemistry, McMaster University, Hamilton, Ontario, Canada.)

**Summary**—Notable contributors to analytical chemistry who have been honoured by postage stamps, and the significance of their contributions to the development of analytical chemistry, are reviewed.

ИОДЦИАН В КАЧЕСТВЕ ТИТРОМЕТРИЧЕСКОГО  
ОКИСЛИТЕЛЯ:

RAM CHAND PAUL, RAJ KUMAR CHAUHAN, NARESH CHANDER SHARMA  
and RAM PARKASH, *Talanta*, 1971, **18**, 1129.

**Резюме**—Иодциан использован в качестве окислителя для определения иодида, сульфита, тиосульфата, тиоцианата, мышьяка(III), сурьмы(III), олова(II), ртути(I), железа(II), аскорбиновой кислоты и  $\beta$ -нафтола в разбавленных водных растворах неорганических кислот, в ледяной уксусной кислоте и в смеси 1:1 уксусной кислоты и ангидрида уксусной кислоты, применением визуальных и потенциометрических методов обнаружения конца титрования.

ОБЩИЙ ПОДХОД ЭЛЕКТРОННОВЫЧИСЛИТЕЛЬНОЙ  
МАШИНЫ ДЛЯ РАССЧЁТА КОНСТАНТ СКОРОСТИ  
РЕАКЦИИ НА ОСНОВЕ ИЗУЧЕНИЯ КИНЕТИКИ  
БЛИЗКО РАВНОВЕСИЮ:

V. S. SHARMA and D. L. LEUSSING, *Talanta*, 1971, **18**, 1137.

**Резюме**—Описан общий подход электронновычислительной машины для расчёта констант скорости реакции на основе времени релаксации. Программа CORNEK в сущности представляет собой программу усовершенствования с помощью наименьших квадратов, примененную на нелинейные системы. Она пользуется непосредственно дифференциальными формами первых производных уравнений баланса массы и скорости реакции, избегая этим образом трудные деривации уравнений скорости реакции близко равновесию. Программа испытана для двойных систем Cu-гистамин и Cu-серин и для треной системы Cu-гистамин-серин.

ANALYTICA CHIMICA PHILATELICA:

R. P. GRANAM, *Talanta*, 1971, **18**, 1157.

**Резюме**—Приведен обзор знаменитых работников в области аналитической химии которые были удостоены почтовой маркии приказан их вклад в развитие аналитической химии.

**Potentiometric studies of ternary complex formation: Cu(II), Ni, Zn or Cd iminodiacetic acid/amino-acid complexes:** GHANSHYAM SHARMA and J. P. TANDON, *Talanta*, 1971, **18**, 1163. (Chemical Laboratories, University of Rajasthan, Jaipur, India.)

**Summary**—The formation constants,  $\log K_{MAB}$ , for the reactions  $MA + B \rightleftharpoons MAB$  [where  $M = \text{Cu(II), Ni, Zn or Cd}$ ,  $A = \text{terdentate ligand}$  and  $B = \text{bidentate or terdentate ligand}$ ] have been determined. Potentiometric evidence is presented for the stepwise addition of the secondary ligand  $B$  to the 1:1 metal iminodiacetate ( $MA$ ). The formation constants and the free energies of formation ( $\Delta G$ ) have been calculated at  $25 \pm 1^\circ$  and  $\mu = 0.10$ . The order in terms of secondary ligands has been found to be  $ASPA > \text{Gly} > \text{Aln}$  and  $\text{Gly} > \text{Aln} > \text{ASPA}$  with iminodiacetic and nitrilotriacetic acid as primary ligands respectively ( $ASPA = \text{aspartic acid}$ ,  $\text{Gly} = \text{glycine}$ ,  $\text{Aln} = \text{dl-alanine}$ ). The plot of  $\log K_{MAB}$  against  $\log K_{MB_2}$  shows a linear relationship between the formation constants of the ternary and 1:2 M(II)-secondary ligand complexes.

**Determination of iron in biological material by substoichiometric isotopic-dilution analysis:** E. GUNDERSEN and E. STEINNES, *Talanta*, 1971, **18**, 1167. (Institutt for Atomenergi, Isotope Laboratories, Kjeller, Norway.)

**Summary**—Iron is determined in biological material by wet oxidation, in the presence of  $^{59}\text{Fe}$  tracer, extraction of iron(III) chloride into isopropyl methyl ketone, stripping with nitric acid, and substoichiometric separation of the Fe-EDTA complex on a cation-exchanger. The precision is good and the method has been applied to analysis of standard kale and blood.

**Dosage du glycérol dans les glycérines techniques—III. Collaboration internationale au sein de l'I.S.O. et analyse statistique des résultats des essais circulaires effectués:** R. MORMONT, *Talanta*, 1971, **18**, 1171. (Président du groupe de travail 2-Glycérine, I.S.O. Comité technique 47.)

**Summary**—An interlaboratory comparison has been made, by 42 workers in 22 laboratories, of the IUPAC and modified methods for determination of glycerol. Four samples were used, and the methods were shown to give results that did not differ significantly in their mean values (99% confidence limits).

ИЗУЧЕНИЕ ПОТЕНЦИОМЕТРИЧЕСКИМ  
МЕТОДОМ ОБРАЗОВАНИЯ ТРОИНЫХ  
КОМПЛЕКСОВ: КОМПЛЕКСЫ  $\text{Cu(II)}$ ,  $\text{Ni}$ ,  $\text{Zn}$  ИЛИ  $\text{Cd}$   
С ИМИНОДИУКСУСНОЙ И АМИНОКИСЛОТАМИ:

GHANSHYAM SHARMA and J. P. TANDON, *Talanta*, 1971, **18**, 1163.

**Резюме**—Определены константы образования  $\lg K_{\text{МАВ}}$  реакций  $\text{МА} + \text{В} \rightleftharpoons \text{МАВ}$  (где  $\text{M} = \text{Cu(II)}$ ,  $\text{Ni}$ ,  $\text{Zn}$ , или  $\text{Cd}$ ,  $\text{A} =$  тридентатный лиганд, а  $\text{B} =$  двудентатный или тридентатный лиганд). Приведены потенциометрические данные которые указывают на ступенчатое присоединение вторичного лиганда  $\text{B}$  к 1:1 иминодиацетату металла ( $\text{МА}$ ). Константы образования и свободные энергии образования ( $\Delta G$ ) рассчитаны при  $25 \pm 1^\circ$  и  $\mu = 0,10$ . Обнаружен порядок вторичных лигандов  $\text{ASPA} > \text{Gly} > \text{Aln}$  и  $\text{Gly} > \text{Aln} > \text{ASPA}$  в случае иминодиуксусной и нитрилотриуксусной кислот в качестве первичных лигандов, соответственно ( $\text{ASPA}$ —аспарагиновая кислота,  $\text{Gly}$ —глицин,  $\text{Aln}$ —д,л-аланин). График  $\lg K_{\text{МАВ}}$  и  $\lg K_{\text{МВ}_2}$  представляет собой прямолинейную зависимость констант образования тройных комплексов и комплексов 1:2  $\text{M(II)}$ -вторичный лиганд.

ОПРЕДЕЛЕНИЕ ЖЕЛЕЗА В БИОЛОГИЧЕСКИХ  
МАТЕРИАЛАХ МЕТОДОМ СУБСТЕХИОМЕТРИЧЕСКОГО  
РАЗБАВЛЕНИЯ ИЗОТОПОВ:

E. GUNDERSEN and E. STEINNES, *Talanta*, 1971, **18**, 1167.

**Резюме**—Железо определяют в биологических материалах мокрым окислением, экстракцией хлорида железа(III) изопропилметилкетонем, отпариванием с азотной кислотой, и субстехиометрическим отделением комплекса  $\text{Fe}$  с ЭДТА на катионообменнике после добавления индикатора  $^{59}\text{Fe}$ . Полученная точность удовлетворительна, а методом можно пользоваться для анализа эталонной кудрявой капусты и крови.

ОПРЕДЕЛЕНИЕ ГЛИЦЕРИНА В ТЕХНИЧЕСКОМ  
ГЛИЦЕРИНЕ—III. МЕЖДУНАРОДНОЕ  
СОТРУДНИЧЕСТВО В РАМКАХ I.S.O. И  
СТАТИСТИЧЕСКИЙ АНАЛИЗ РЕЗУЛЬТАТОВ  
ПОЛУЧЕННЫХ В МЕЖЛАБОРАТОРНЫХ  
ИСПЫТАНИЯХ:

R. MORMONT, *Talanta*, 1971, **18**, 1171.

**Резюме**—Проведено межлабораторное сравнение 42 рабочими в 22 лабораториях метода IUPAC и измененных методов для определения глицерина. Испытание проведено на четыре образца; показано что средние величины полученных результатов не различаются в значительной мере (пределы доверия 99 %).

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- JAMES S.FRITZ, DONALD R.BEUERMAN and JOHN J.RICHARD: Chromatographic separation of copper with an  $\alpha$ -hydroxyoxime . . . . .
- R.M.DAGNALL, M.D.SILVESTER and T.S.WEST: Electronic modulation of microwave-excited electrodeless discharge lamps for use in atomic-fluorescence spectrometry . . . . .
- J.G.MASON and I.LIPSCHITZ: Thermodynamics of the partition of 8-quinolinol between several organic solvents and aqueous buffers . . . . .
- B.ZMBOVA, M.TRIPKOVIĆ and O.ŠEĆEROV: Spectrochemical determination of rare-earth metals in uranium and its salts . . . . .
- ROKURO KURODA and NOBUTAKA YOSHIKUNI: Adsorption behaviour of a number of metals on weakly basic ion-exchangers in methanol-hydrochloric acid mixtures . . . . .
- RAM CHAND PAUL, RAJ KUMAR CHAUHAN, NARESH CHANDER SHARMA and RAM PARKASH: Iodine cyanide as volumetric oxidant . . . . .
- V.S.SHARMA and D.L.LEUSSING: A general computer approach for calculating rate constants from near-equilibrium kinetic studies . . . . .
- R.P.GRAHAM: *Analitica chimica philatelica* . . . . .

### Short Communications

- GHANSHYAM SHARMA and J.P.TANDON: Potentiometric studies of ternary complex formation. Cu(II), Ni, Zn or Cd iminodiacetic acid/amino-acid complexes . . . . .
- E.GUNDERSEN and E.STEINNES: Determination of iron in biological material by substoichiometric isotopic-dilution analysis . . . . .

### Annotation

- R.MORMONT: Dosage du glycérol dans les glycérols techniques—III. Collaboration internationale au sein de l'I.S.O. et analyse statistique des résultats des essais circulaires effectués . . . . .

- Publications Received . . . . .
- Papers Received . . . . .
- Notice . . . . .
- Summaries for Card Indexes . . . . .

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