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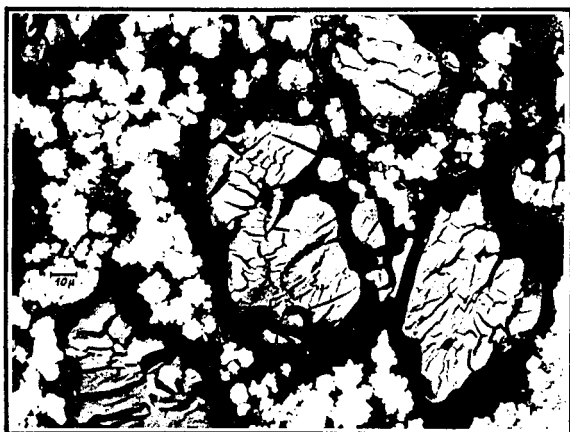
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Microphotograph of a DSK working layer.

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Established as a medium for the rapid publication of papers dealing with all aspects of analytical chemistry, *Talanta* is the natural vehicle for the international communication of progress in this field. As an international journal, its papers are expected to be of a very high standard and to make definite contributions to the subject: they must be new publications. Papers may be written in English, French, or German; all papers have abstracts in these three languages and also in Russian. Special importance is attached to work dealing with the principles of analytical chemistry in which experimental material is critically evaluated, and to similar fundamental studies. Reviews in rapidly expanding fields or of hitherto widely scattered material are considered for publication, but should be critical. Original papers, short communications and reviews are refereed in the normal manner. Preliminary communications are refereed urgently and accorded priority in publication. Correspondence of interest to analytical chemistry is welcomed by the Editor-in-Chief, at whose discretion it is published. A new feature is Annotations, which are critical commentaries on some aspect of analytical chemistry and deal with topics such as sources of error, or the scope and limitations of methods and techniques; these commentaries are refereed.

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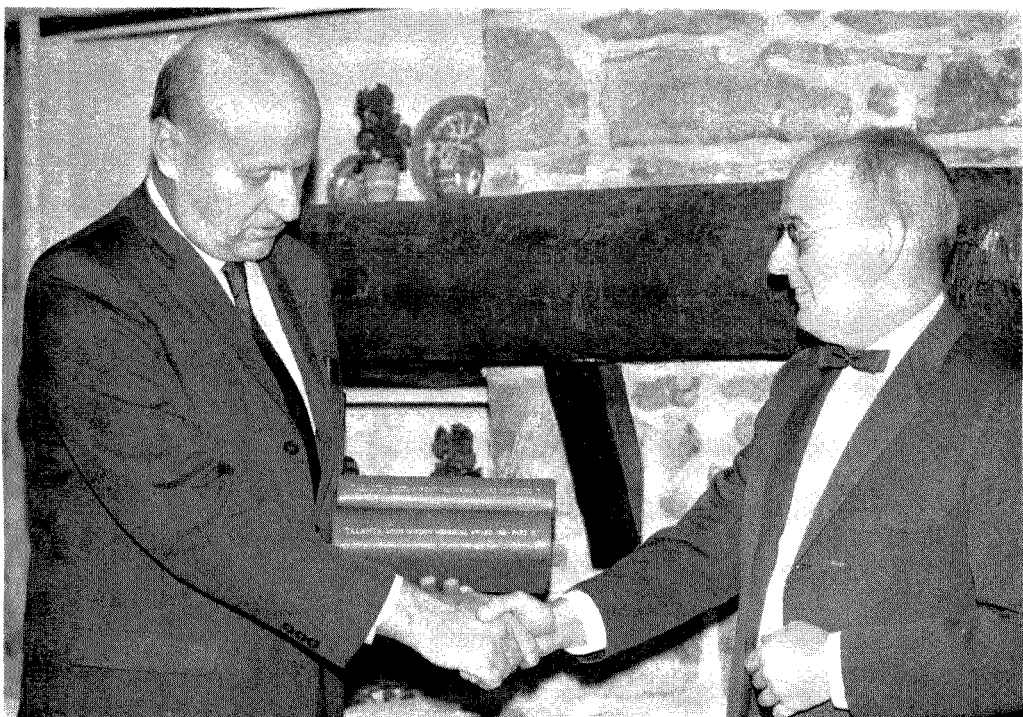
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Louis Gordon Memorial Award 1968

Mr. H. J. FRANCIS, JR. (U.S.A. Regional Editor) presents a specially bound 1968 volume of *Talanta* to Prof. H. FLASCHKA (on left), whose papers with Dr. J. GARRETT on "Substoichiometric Masking" (1968, **15**, 589, 595) were adjudged the best-written, stylistically, of the year. The presentation was made in Pennsylvania on 22nd November 1969.

PROFESSOR L. ERDEY

THIS month marks the 60th birthday of Professor L. ERDEY, Head of the Institute of General and Analytical Chemistry, Technical University of Budapest, and Member of the Hungarian Academy of Sciences. He was born in 1910 in Szeged, studied at the University of Budapest, and graduated in 1932. He obtained his Ph.D. in 1939. He became Professor and Head of his present Institute in 1949. From what was then a small Institute he has built a large teaching and research establishment, with at one time 36 members of staff. With this team he did research on several topics. First he dealt with ascorbinometric titrations, using Variamine Blue indicator. An extensive work on chemiluminescent indicators and titrations was followed by thermoanalytical investigations, works in emission spectroscopy, flame photometry, radiofrequency titrations, catalytic analysis, polarography and related electrochemical techniques, radiochemical and microanalytical methods. He published several hundred papers, and also textbooks on Qualitative and Quantitative Analysis. His main work *Gravimetric Analysis* has been published in Hungarian, English and German. During these creative years he served also as Dean of the Faculty of Chemical Engineering and as Honorary Secretary to the Chemical Sciences Division of the Hungarian Academy. He won the Kossuth prize (the highest award in Hungary for cultural activities) twice. He is the Editor-in-Chief of *Journal of Thermal Analysis* and is on the Editorial Board of several Hungarian Journals of Chemistry. Since its establishment he has served on the advisory board of *Talanta*.

His colleagues, pupils and friends wish him many happy returns and every success in the forthcoming years.

GYULA SVEHLA

NUCLEATION AND CRYSTAL GROWTH OF COPPER(II) 8-HYDROXYQUINOLINATE PRECIPITATED FROM MIXED SOLVENTS

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Summary—The precipitation kinetics of copper(II) 8-hydroxyquinolate, formed in water-acetone mixtures, have been studied in a stop-flow apparatus by spectrophotometric techniques. Three factors are found to be important in improving the physical characteristics of crystals precipitated from mixed solvents. Supersaturation and growth rate can be controlled uniformly by slow rate of change in solvent composition; the presence of acetone significantly reduces the number of effective nuclei; thirdly, large amounts of organic solvent cause a change in the crystal form and its growth mechanism. At room temperature, copper(II) 8-hydroxyquinolate is precipitated as a dihydrate from water-acetone mixtures containing 0–60% acetone, and the crystal growth is limited by a diffusion-controlled process. Anhydrous copper(II) 8-hydroxyquinolate is formed in 70% acetone solutions by a surface-controlled reaction.

EARLIER work reported from this laboratory¹ has demonstrated the possibility of precipitating metal chelates from solutions containing large amounts of organic solvents. The technique involves the addition of about an equal volume of a miscible organic solvent, such as ethanol or acetone, to an aqueous solution of the metal ion. Following the addition of the chelating agent, the solution is warmed to approximately 70°, and the preferential volatilization of the organic solvent is accompanied by the formation of the precipitate.

Particularly striking is the increased size of these crystals as compared to the chemically identical particles obtained by a direct addition procedure. Further, co-precipitation is significantly lowered. These results compare favourably with other, more common methods of precipitation from homogeneous solution.^{2,3} The initial speculation was that these alterations arose solely from the increased solubility of the metal chelates in the mixed solvent media. The gradual and uniform decrease in solubility, caused by the preferential evaporation of the organic solvent component, allowed the crystals to grow under conditions closer to equilibrium, so that the formation of more perfect crystals was favoured.

However, other factors may be more important. It is possible that the presence of the organic solvent may markedly reduce the rate of the chelation reaction and thereby reduce the initial supersaturation. Alternatively, the organic solvent may cause a change in the crystal growth mechanism or may reduce the rate of the slowest step which, again, would permit the development of more perfect crystals. A third possibility is that nucleation processes are altered by the presence of the organic solvent; *e.g.*, the effectiveness of foreign nuclei may be reduced.

The precipitation kinetics of copper(II) 8-hydroxyquinolate were studied under conditions of varying solvent composition and solution supersaturation in order to obtain experimental data which could be used to distinguish between these various

control factors. It had been reported earlier⁴ that the colour and crystal habit of precipitated copper(II) 8-hydroxyquinolate were particularly dependent upon the presence of organic solvents. A much different precipitate was formed from solutions containing over 60% of the organic solvent. Supersaturated solutions of this compound, in solvents varying from 0 to 70% v/v acetone, were formed in the chamber of a 4-jet mixer and passed into a stop-flow observation chamber where they were observed spectrophotometrically. Data, collected at wavelengths at which the predominant interaction with the light-beam was the scattering by solid particles, were treated by fitting various crystal growth equations.

EXPERIMENTAL

Apparatus

Stop-flow apparatus. The all-glass apparatus used for obtaining kinetic data⁵ consisted essentially of four storage cylinders, an efficient 4-jet mixing chamber based on Hartridge and Roughton's device⁶ and a Pyrex precision bore observation tube with an accurate inside diameter of 2 mm. This tube was mounted horizontally and passed directly through the cell compartment of a spectrophotometer. Its position was fixed by an aluminium block which had been adjusted to the dimensions of the cell holder.

Reagents

Water. Distilled water, passed through a "Bantam Demineralizer" containing cation- and anion-exchange resins, was used to prepare all solutions. Monitored water impurities were 0.05 ppm or less.

Acetone. Reagent grade acetone was distilled through a 300-mm Vigreux column. The high- and low-boiling fractions were discarded.

Ammonium acetate buffer solutions. A 2M stock solution was prepared by dissolving 154.2 g of reagent grade ammonium acetate in water, filtering and diluting to 1 litre. All 0.2M solutions used for precipitation reactions were prepared by appropriate dilution of the stock solution.

Copper solutions. A 6.354-g sample of purified electrolytic copper metal (pellets, 99.99% pure) was dissolved in 120 ml of nitric acid (1 + 4). The resulting copper nitrate solution was evaporated almost to dryness, then diluted with water, filtered through a fine porosity Whatman filter paper, and diluted to 1 litre with water.

8-Hydroxyquinoline solutions. Reagent grade 8-hydroxyquinoline was recrystallized from ethanol, and dissolved in appropriate solvents.

Copper 8-hydroxyquinolate solutions. The desired amount of copper standard solution was transferred by pipette into a 500-ml graduated cylinder and the necessary amount of 1M nitric acid added to yield a pH of 2. This solution was then diluted to 500 ml with water and transferred to a 1-litre volumetric flask. The same cylinder was used to measure the desired amount of acetone in which a weighed amount of 8-hydroxyquinoline was dissolved. This solution was then transferred into the rapidly stirred copper solution, and the final volume was adjusted to 1 litre with water.

When aqueous solutions were prepared, the nitric acid was added to the 8-hydroxyquinoline solution in order to dissolve the reagent.

Procedure

Manipulation and testing of the stop-flow apparatus. The reactant solutions were placed in the storage cylinders as follows: 0.2M buffer solution in cylinder 1, copper 8-hydroxyquinolate solution in cylinder 2, a blank solution of buffer and acetone in cylinder 3, and 4M hydrochloric acid cleaning solution in cylinder 4.

The simultaneous outflow of the reactant and buffer solution was maintained for 5 sec by applying a constant nitrogen pressure of 9.6 kN/m². Two sec before the flow was stopped, a sample was collected at the end of the observation tube and used to determine the initial reactant concentration. The stop-cock at the end of the observation tube was closed first to prevent the formation of bubbles in the observation tube. The pressure was then removed as rapidly as possible in order to follow the crystal growth processes at atmospheric pressure. An electric stop-watch was started when the flow was stopped. The recorder was switched on before the flow started.

The efficiency of the mixing chamber was tested with an acid-base reaction and phenolphthalein indicator. Under an applied pressure of 9.6 kN/m² (corresponding to a flow-rate of 10 ml/sec or a flow-speed of 3.2 m/sec) mixing was found to be complete in 3.5 msec.

Preliminary precipitation experiments with copper 8-hydroxyquinolate were carried out with the observation tube vertical, and the absorbance was measured at different heights along the tube. It was found that the final absorbance of a particular run did not depend on the position of measurement, and that it remained constant. This indicated that the growing particles did not migrate or settle, but remained where they formed.

Copper determination. The sample collected after each run was analysed for copper, by a technique described by Reilly⁷ but with several modifications. The 8-hydroxyquinoline interfered in the determination; it was therefore necessary to oxidize it first. After addition of 2 ml of 30% hydrogen peroxide, each sample was heated until a colour change occurred. The temperature was then raised until all of the excess of hydrogen peroxide was removed. The copper was titrated with EDTA at pH 4, with PAN as indicator. The result of this titration determined the value for the initial concentration (C_0) of the run.

THEORETICAL CONSIDERATIONS

Any crystallization process may involve three basic phases: achievement of supersaturation, formation of crystal nuclei, and growth of the nuclei into visible crystals. A comprehensive theoretical treatment, dealing with the overall growth rate of a large number of distinct crystals growing from a supersaturated solution, must be very complex.

The growth process alone may involve such diverse events as diffusion of the solute particles from the bulk of the solution to the crystal surface, adsorption of solute material at the solid-liquid interface, diffusion across the face of the crystal, and dehydration and incorporation of the precipitated material into the crystal lattice. Depending upon experimental conditions, each one of these processes may become the rate-controlling factor. Certainly, the rate laws are not always sufficiently described by one mechanistic step (*e.g.*, within transition regions) and furthermore, complications arising from competing dissolution and agglomeration phenomena may tend to obscure the actual growth laws.

Theoretical treatments which apply to specific growth paths can generally be found. It should be emphasized, however, that extreme care is required in selecting a particular theoretical treatment, for it may involve making unwarranted assumptions about prospective growth paths. The distinction between a diffusion-controlled and a surface-controlled reaction generally serves as a first approach to give some insight into a particular crystal growth system.

The theoretical and practical aspects of diffusion-controlled growth kinetics have been treated by several authors.^{8,9} Careful reconsiderations by Ham¹⁰ confirmed earlier findings that a diffusion-limited process may be approximately described by an expression of the form:

$$C_t = C_0 \exp [-t/\tau]^n \quad (1)$$

Where C_0 = initial concentration of solute at time $t = 0$

C_t = solute concentration at any time t

C_s = equilibrium solubility

n = exponent depending upon the growth mechanism

τ = time constant, depending upon the diffusion coefficient D , the sink radius r_s , the final particle radius $r_{c(\infty)^*}$, and C_0 .

Equation (1) is an approximation,¹⁰ valid for small t when

$$\frac{C_t - C_s}{C_0} > \frac{1}{2}$$

* Shape and size of the actual crystals are approximated by a sphere of equal volume.

It also requires that the dimensions of the precipitate particles remain small compared to their distance of separation, *i.e.*, $r_c/r_s \ll 1$. The latter requirement may be fulfilled for a large number of small particles as well as for a few widely spread large particles.

As long as the particle growth is strictly diffusion-controlled, and the particles are incorporated into the crystal at the point where they are absorbed, the crystal will grow with constant eccentricity. Qualitatively similar rate laws are then predicted for crystals of different shapes, *e.g.*, spheres and spheroids. For this growth mechanism the exponent n of equation (1) will be between 1.0 and 1.5.

There is, however, at least one other, perhaps even more important, possibility by which crystals can grow under diffusion-controlled conditions. In this case, the entire crystal surface is thought to be active in capturing solute material; but the captured particle may be incorporated into the crystal lattice only at certain specific sites. This requires the adsorbed particle to migrate across the face of the crystal, and this process must be sufficiently faster than the diffusion of the solute to the surface layer to maintain the assumed rate-determining mechanism. Under these conditions, the exponent n of equation (1) depends to a larger extent on the shape of growing crystals and varies between 1.0 and 2.0.¹¹

The exponent n would approach a value of 3.0 if a process at the crystal surface should become rate determining. Equation (1) may, therefore, be used to distinguish between diffusion-controlled and surface-controlled precipitation reactions.

Particularly at low supersaturations, crystal growth often proceeds by way of screw dislocations. Burton, Cabrera and Frank¹² have developed rate laws for this type of growth by considering a system of non-dissociated species growing from the vapour phase. Basically the same theory was subsequently applied by Chernov¹³ to crystallization models, involving liquid–solid phase transitions. Recently, this theory was further extended by Reich and Kahlweit¹⁴ to include surface-controlled reactions.

The following simple relationship was derived by Reich and Kahlweit:

$$C_t - C_s = \frac{j}{k_D} + \left(\frac{j}{k_R}\right)^{1/2}. \quad (2)$$

The rate constant k_D of a diffusion-limited process, and k_R , the rate constant of a surface-controlled reaction, may be evaluated if the flux j (in mole.sec⁻¹) of the deposited material can be determined as a function of time. Equation (2) should be most relevant during the latter part of the precipitation process where the supersaturation changes only slowly with respect to time.

For $k_D > k_R$ or for $j \rightarrow 0$, the flux is mainly determined by:

$$j \approx k_R(C_t - C_s)^2. \quad (3)$$

On the other hand, for large flux values:

$$j \approx k_D(C_t - C_s). \quad (4)$$

Equation (2) predicts, therefore, a second-order rate law in the case of a surface-controlled reaction and a first-order rate law for diffusion-limited precipitations.

Similar equations have been developed previously.^{9,16} However, equation (3) differs from Walton's suggestion¹⁷ that the kinetic order should always be equal to the

number of ions required to form a neutral molecule. Equation (3) predicts a second-order rate law for surface-controlled precipitations, regardless of whether the solute species are ions or molecules.

According to Reich and Kahlweit,¹⁵ the flux j may be found from:

$$j = - \frac{dc/dt}{(C_0 - C_t)^{2/3}} \cdot \frac{r_{c(\infty)}}{3\bar{V}(C_0 - C_s)^{1/3}} \quad (5)$$

The molar volume is indicated in equation (5) by \bar{V} . Letting

$$k' = \frac{r_{c(\infty)}}{3\bar{V}} \quad (6)$$

we have:

$$\frac{j}{k'} = \frac{dc/dt}{(C_0 - C_t)^{2/3}} \cdot \frac{1}{(C_0 - C_t)^{1/3}} = Y \quad (7)$$

From equations (3) and (4), we see that, depending upon the rate controlling step,

$$Y \approx \frac{k_D}{k'} (C_t - C_s) \quad (8)$$

or

$$Y \approx \frac{k_R}{k'} (C_t - C_s)^2 \quad (9)$$

Equation (7) is particularly useful for data interpretation of experiments in which the particle sizes have not been determined.

RESULTS AND DISCUSSION

Initial experiments with unsaturated solutions of copper 8-hydroxyquinolate revealed that the absorption spectrum was time-independent and appreciably different from the combined spectra of the reactants. While a possible effect of solvent composition upon the rate of chelation cannot be discounted, the chelation reaction must nevertheless be very fast compared to crystallization rate. From flow experiments it was estimated that the chelation in aqueous solution must be complete in less than 1 msec. For this system, then, chelate formation cannot be effective in controlling the crystal growth process.

Turbidimetrically determined crystallization curves of transmittance *vs.* time are shown in Fig. 1. These curves reveal a steady induction period which is terminated rather abruptly and is followed by a rapid crystal growth, which later on becomes slower and slower as the reaction is approaching equilibrium conditions. Many similarly shaped curves have been reported.

Figure 1 reveals that there exists a definite relationship between the initial concentration (C_0) and the final absorbance (A_e). To find this relationship, final absorbance values were plotted against the initial concentrations (Fig. 2). A straight-line relationship is observed in all cases.

The straight-line equation calculated by least-squares serves to evaluate the concentration terms C_t and C_s ; the solubility (C_s) of copper 8-hydroxyquinolate in a

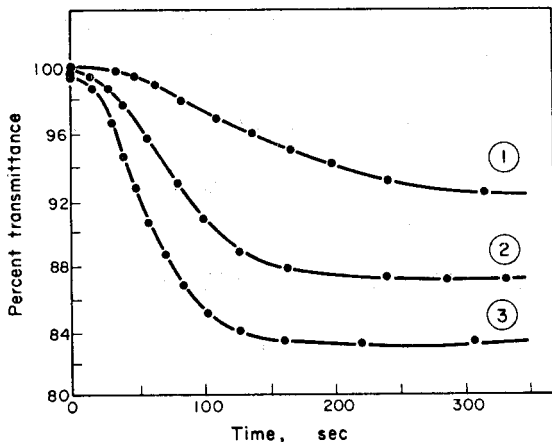


FIG. 1.—Precipitation curves of copper(II) 8-hydroxyquinolate formed in aqueous solution; concentration dependence.

C_0 : ①—0.883; ②—1.090; ③—1.25 (mole/l. $\times 10^4$).

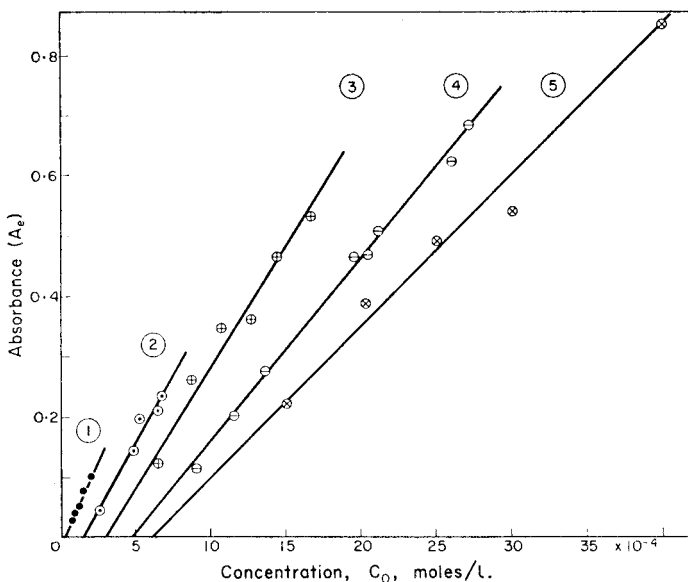


FIG. 2.—Turbidimetric calibration lines for copper(II) 8-hydroxyquinolate precipitated from different solvent media.

Acetone content, % v/v: ① ●—0%; ② ○—20%; ③ ⊕—40%; ④ ⊖—50%; ⑤ ⊗—60%.

given solvent system is obtained from the intercept of the corresponding calibration line with the abscissa.

Combining absorption and scattering laws, Wells¹⁸ derived an expression which is of the same form as Beer's law. A straight-line relationship may, therefore, be expected for cases approaching ideal conditions. It must be pointed out, however, that Wells's expression is at most an approximation since it neglects such important factors as how closely the particles are packed.

The turbidimetric detection method was chosen because ordinary absorption measurements of coloured species in solution were unsuccessful, owing to strong interference from the growing particles. Conductometric measurements, often used for this purpose, were unsuitable, too, since the particles in solution were neutral molecular species.

Figure 3 shows typical experimental data plotted in log-log form according to equation (1). The horizontal lines on each run terminate the region for which this type of data treatment is expected to be best applicable. The lower limit corresponds to the value calculated by setting $C_t = 0.9C_0$, and the upper limit generally indicates the point of the reaction at which $C_t = \frac{1}{2}C_0$. Straight lines are obtained within these limits, which extend over a large portion of the precipitation process. The slope of these lines appears to be independent of the reaction rate. The average slope of all runs considered at a given solvent composition, therefore, may be used to determine the exponent n of equation (1).

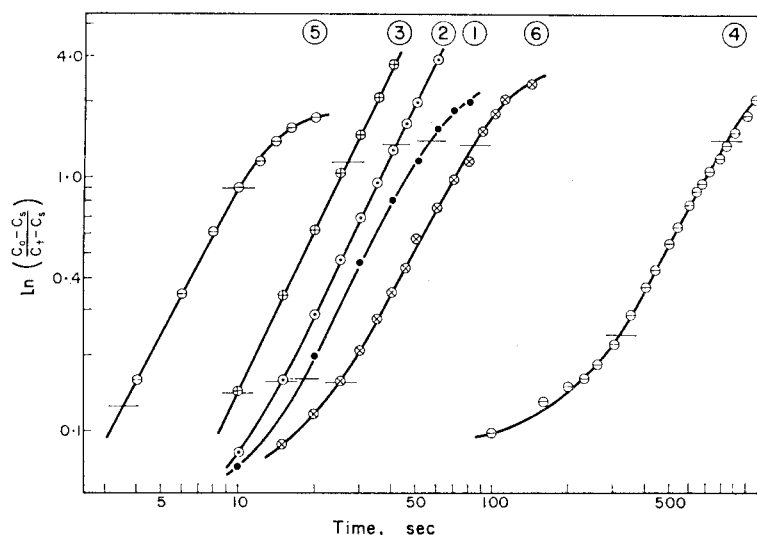


FIG. 3.—Experimental crystal growth data for copper(II) 8-hydroxyquinolate in different solvent media, plotted according to equation (1).

C_0 (mole/l. $\times 10^4$): ①—0.9688; ②—4.456; ③—11.15; ④—9.10; ⑤—31.07; ⑥—15.00.

Table I summarizes the results obtained in the different solvent media. The time constant τ is obtained from the intercept of the precipitation lines with the 1.0 line (ordinate value) of Fig. 3. The minimum and maximum τ value of a given solvent system may serve as a first indication of the range of reaction times studied. It should be noted that the total concentration and the τ value range in run 59 cover approximately two orders of magnitude.

The constancy of the \bar{n} values in Table I is remarkable. There are no significant differences in the average slope values, nor is there an indication of a trend in the values. This suggests clearly that the precipitation mechanism does not change within the entire solvent and concentration range investigated. These data, however do not give a complete answer as to what mechanism is involved in the rate determining

TABLE I

Acetone content, % v/v	Number of runs averaged	Concentration range		Time range		Slope range		Average slope \bar{n}	Standard deviation of \bar{n}
		C_0 min., <i>mole.l.</i> ⁻¹ × 10 ⁴	C_0 max.,	τ min.,	τ max., <i>sec</i>	n_{\min}	n_{\max}		
0	9	0.6545	2.080	7.0	64.0	1.40	2.50	1.89	0.37
20	12	2.349	6.809	10.6	86.0	1.43	2.10	1.87	0.21
40	16	6.412	17.16	11.7	71.0	1.38	2.30	2.02	0.22
50	11	9.10	31.07	9.3	700.0	1.54	2.54	1.95	0.32
60	11	15.00	40.00	6.1	130.0	1.55	2.30	1.88	0.22

step, since the \bar{n} values were found to lie near 2 (*i.e.*, between 1.5 and 3.0). Had these values been consistently less than 2, the growth could be classified as diffusion-controlled. Conversely, values consistently above 2 would clearly indicate surface-control. With the data obtained, it is only clear that the mechanism does not change and that the particles are not incorporated into the crystal at their adsorption sites.

Reich and Kahlweit's treatment was then applied to the same experimental data. ($C_t - C_s$) *vs.* t values of individual runs were plotted and the instantaneous rates (dc/dt) were determined from the slopes. These rates were used as input data in a computer programme used to calculate the necessary parameters to construct the plots shown in Figs. 4*a* and 4*b*.

These two figures illustrate that the plots of j/k' *vs.* supersaturation are linear in all five solvent systems. On the other hand, plots of $(j/k')^{1/2}$ *vs.* supersaturation were curved. Only one run is shown for each solvent system. Actually, 7–10 runs performed under various precipitation conditions were evaluated in this manner for each solvent system, and similar curve shapes were obtained in all cases. Under the conditions investigated, the precipitation of copper 8-hydroxyquinolate appeared to be a diffusion-controlled process.

Figure 4*a* also reveals that the slope of the straight lines obtained varies with changing solvent composition. The slope of these lines, being equal to $k_D/k' = k_D'/r_{o(\infty)}$, is inversely proportional to the final particle size. The general trend observed, therefore, indicates that the final particle size increased with increasing acetone content. Such an effect could be explained in two ways. The increase in particle size could simply result from the larger amount of material which is precipitated from the increasingly concentrated acetone solutions. This possibility was eliminated by the proposed method of plotting the data, which accounted for such an effect. Alternatively, it could be explained by a real decrease in the number of growing particles in solvent media containing more acetone. We believe the latter to be the case. In fact, without counting particles it was qualitatively observed that the number of growing particles per unit volume decreased rapidly with increasing acetone content. For solutions containing 40% or more acetone, it was also found that the number of particles was dependent upon the initial solute concentration C_0 . The number of particles generally increased with increasing supersaturation although C_0 was kept well below the range where homogeneous nucleation could occur. Table II gives a more complete representation of the data and clearly shows the effect of acetone concentration on particle size. It should be emphasized, however, that nucleation, although generally influenced by the supersaturation and by the acetone content, was

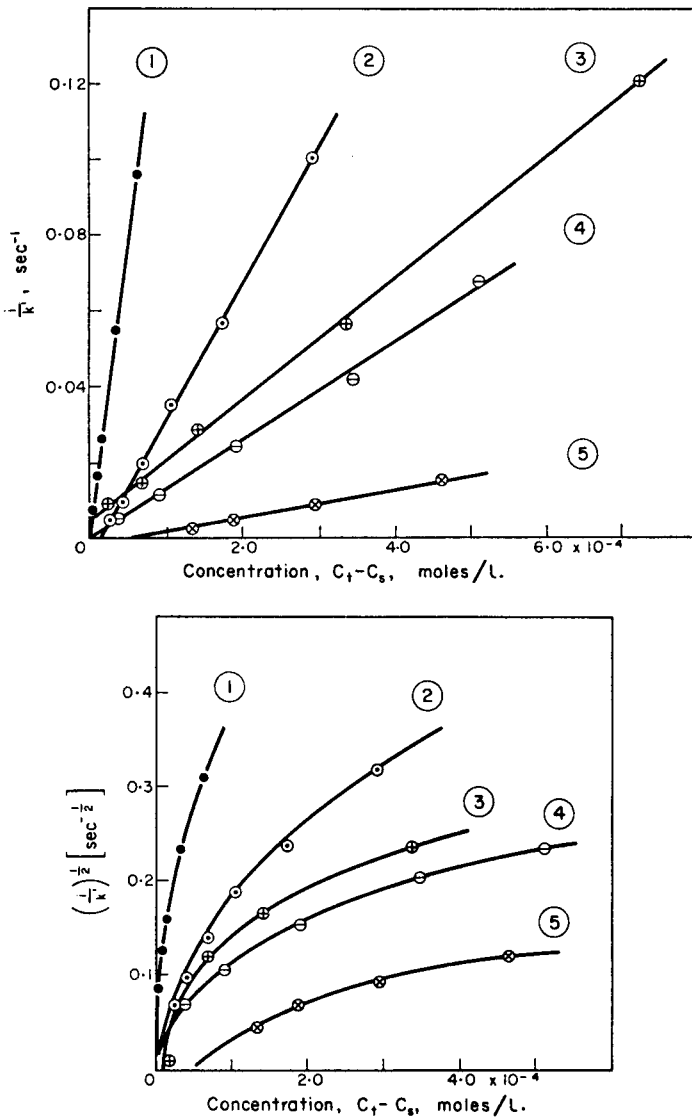


FIG. 4.—Experimental crystal growth data for copper(II) 8-hydroxyquinolate in different solvent media.

(a) First-order rate plots according to equation (8).

(b) Second-order rate plots for the same runs.

C_0 (mole/l. $\times 10^4$): ①—2.080; ②—5.996; ③—14.49; ④—27.10; ⑤—15.00.

a somewhat unpredictable process. Differences in the number of particles did occur even under seemingly identical conditions of successive experiments.

Within this restriction it still appears that the trends in the k_D/k' values are sufficiently uniform to justify interpretation. The 40, 50, and 60% acetone data, despite some scatter, display a clear trend to larger values with increased supersaturation. Since the solutions of higher supersaturations contain more material, one might expect larger particles to be formed. These data indicate exactly the opposite effect.

TABLE II

Acetone content, % v/v	Concentration C_0 mole.l. ⁻¹ × 10 ⁴	Supersaturation $S = \frac{C_0}{C_B}$	$\frac{k_D}{k'} = \frac{k_D \cdot 3V}{r_{c(\infty)}}$	Aver. $\frac{k_D}{k'}$
0	0.6545	2.014	0.146	0.151
	0.7439	2.289	0.148	
	0.9265	2.855	0.163	
	0.9688	2.981	0.112	
	1.670	5.138	0.166	
	2.080	6.400	0.159	
	2.117	6.605	0.161	
20	2.857	2.012	0.0238	0.0323
	2.997	2.110	0.0250	
	4.456	3.138	0.0250	
	5.276	3.715	0.0458	
	5.996	4.222	0.0360	
	6.515	4.588	0.0337	
	6.809	4.793	0.0369	
40	6.412	2.15	0.0018	0.00977
	6.678	2.24	0.0014	
	9.281	3.12	0.0065	
	12.65	4.25	0.0117	
	14.35	4.82	0.0192	
	14.49	4.87	0.0159	
	16.56	5.56	0.0119	
50	9.10	1.88	0.00087	0.00467
	11.51	2.37	0.00203	
	12.70	2.62	0.00178	
	19.60	4.04	0.00156	
	26.40	5.44	0.00173	
	27.10	5.59	0.01262	
	31.07	6.41	0.01210	
60	15.0	2.46	0.00386	0.00555
	20.0	3.28	0.00177	
	25.0	4.10	0.00270	
	25.0	4.10	0.00422	
	30.0	4.92	0.00518	
	40.0	6.56	0.01139	
	40.0	6.56	0.00973	

The larger k_D/k' values require a smaller $r_{c(\infty)}$. The only way in which smaller $r_{c(\infty)}$ values may be obtained with increasing amounts of material is by an even greater increase in the number of growing particles. Since heterogeneous nucleation certainly predominates, the number of foreign particles that may effectively serve as crystal growth sites must increase with increasing supersaturation. This effect has been observed previously for ionic precipitates.^{19,20} The data obtained at 20% acetone concentration may or may not be displaying this trend and the aqueous solutions obviously do not. Therefore, the implication is drawn that the higher acetone concentrations cause the number of effective foreign nuclei to be more supersaturation-dependent.

A comparison of the average k_D/k' values for various solvent compositions shows a pronounced trend toward decreasing values with increasing acetone content. Since this change is much larger than any expected changes in diffusion coefficients, the change must relate to increased particle sizes, which must be caused by a decrease in the number of effective foreign nuclei. There is no rational basis for expecting a

decrease in the total number of foreign nuclei in these solvent systems, which leads to the postulate that the ability of the nuclei to act as effective crystal growth sites must be decreased by the presence of the acetone. The fact that this change is most pronounced with the first addition of acetone (*i.e.*, from 0 to 20%) and decreases until disappearing at about 50% acetone suggests a Langmuir type adsorption of the acetone on the active crystal growth sites. This postulate is also consistent with the supersaturation dependence of particle size since at the high acetone concentrations the more weakly held acetone molecules may be displaced by the precipitating particles at the higher supersaturations.

The practical significance of this effect should not be overlooked. The reduced number of effective nuclei in the mixed solvent media favours the formation of larger crystals, which are more easily separated. In this respect, the technique of precipitation from mixed solvents has a definite advantage over other more common methods of precipitation from homogeneous solution, where it was found that the number of particles produced is often little different from the number obtained by direct mixing of suitable, dilute solutions.²⁰

Precipitation of anhydrous copper(II) 8-hydroxyquinolate

While precipitations from 60% acetone solutions were being performed, it was observed that in some runs, crystals of different appearance and behaviour were formed in addition to the normally occurring crystals. The ordinary crystals were yellow, star-shaped, and did not move in the observation tube. The other crystals were bright green and more compact.

X-Ray powder diffraction data clearly established that the unit cells of the two materials were different. Gravimetric analysis of the two crystal forms confirmed the expected fact that the difference observed arose from a change in the degree of hydration. The yellow form was found to be a dihydrate, while the green crystals were an anhydrous form of copper 8-hydroxyquinolate.

The anhydrous crystal form became predominant in precipitations from 70% acetone. These crystals tended to settle rapidly even at sizes barely visible under strong illumination of the observation tube. The decrease in transmittance due to the presence of these crystals, therefore, never exceeded 2% at a wavelength of 500 nm and was too small to be useful for following the course of reaction. The disappearance of the green chelate complex from solution was therefore used to study the precipitation kinetics, a wavelength of 445 nm being used.

The interpretation of the kinetic data was undertaken as for the dihydrate. No correction was made to take into account any absorption changes due to the presence of precipitate, and runs in which both crystal types occurred were excluded from further considerations. For the runs with 70% acetone solutions, plots identical to those shown in Fig. 3 yielded an average exponent and standard deviation of $\bar{n} = 2.53 \pm 0.16$. This value, being significantly different from \bar{n} for the dihydrate, would indicate that another reaction step, such as a process at the crystal surface, may have become rate-determining.

This first indication was confirmed by applying Reich and Kahlweit's treatment. It can be seen on Fig. 5 that $(j/k')^{1/2}$ vs. $(C_t - C_s)$ now approached a straight line rather than the simple first-order function. The precipitation of anhydrous copper 8-hydroxyquinolate must, therefore, be governed by a surface-controlled reaction.

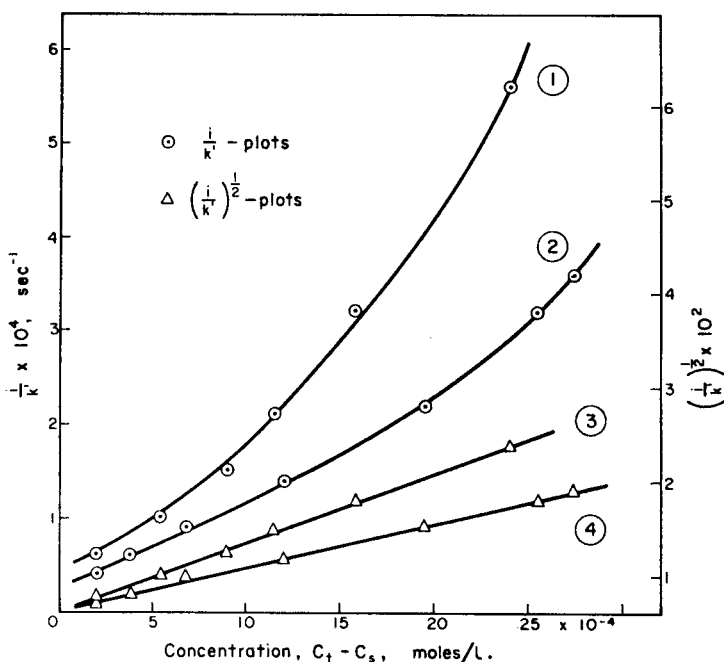


FIG. 5.—Experimental crystal growth data of anhydrous copper(II) 8-hydroxyquinolate precipitated from 70% acetone–water solutions; first- and second-order rate plots according to equations (8) and (9).
 C_0 (mole/l. $\times 10^4$): ① and ③—74.50; ② and ④—38.50.

The difference of three orders of magnitude in the ordinate scales of Figs. 4 and 5, together with determined τ values ranging from 2000 to 10000 sec, indicated that the precipitation of the anhydrous form was a much slower process. As it appears very unlikely that diffusional rates are much affected in going from 60% to 70% acetone solutions, the crystal growth of the anhydrous form cannot be limited by diffusion.

CONCLUSIONS

This study has shown three major factors to be of importance in causing an improvement of the physical characteristics of copper(II) 8-hydroxyquinolate crystals when these are precipitated from mixed solvents. First, the presence of organic solvents such as acetone increases the solubility of this chelate compound sufficiently to permit a controlled precipitation in which the supersaturation and growth rate are conveniently regulated by the evaporation of the organic solvent. Secondly, the number of growing particles is reduced, which leads to the formation of larger, more easily manipulated crystals. The presence of acetone inhibits a considerable number of heterogeneous nuclei from becoming effective growth sites. Thirdly, the actual growth mechanism and crystal composition are altered in the presence of large amounts of acetone. Copper(II) 8-hydroxyquinolate is precipitated at room temperature as a dihydrate in water–acetone mixtures containing from 0 to 60% v/v acetone. Within this range of solvent composition, the precipitation kinetics do not change, and the crystal growth is governed by a diffusion-limited process. Anhydrous copper(II) 8-hydroxyquinolate is produced from 70% acetone solutions.

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Zusammenfassung—Die Fällungskinetik von Kupfer(II)-8-hydroxychinolat, das sich in Aceton-Wasser-Gemischen bildet, wurde in einer stopped-flow-Apparatur spektrophotometrisch untersucht. Drei Faktoren wurden gefunden, die zur Verbesserung der physikalischen Eigenschaften von aus Lösungsmittelgemischen gefällten Kristallen wichtig sind. Übersättigung und Wachstumsgeschwindigkeit können durch langsame Änderung der Lösungsmittelzusammensetzung kontrolliert werden; die Gegenwart von Aceton vermindert die effektive Keimzahl erheblich; große Mengen des organischen Lösungsmittels bewirken einen Wechsel in der Kristallform und dem Wachstumsmechanismus. Bei Zimmertemperatur fällt Kupfer(II)-8-hydroxychinolat als Dihydrat aus Gemischen mit bis zu 60% Aceton; das Kristallwachstum ist diffusionskontrolliert. In 70% Aceton bildet sich wasserfreies Kupfer(II)-8-hydroxychinolat nach einem oberflächenkontrollierten Mechanismus.

Résumé—Les cinétiques de précipitation du 8-hydroxyquinoléinate de cuivre(II), formé en mélanges eau-acétone, ont été étudiées dans un appareil 'stop-flow' par des techniques spectrophotométriques. On a trouvé que trois facteurs sont importants dans l'amélioration des caractéristiques physiques des cristaux précipités à partir de mélanges de solvants. On peut contrôler uniformément la sursaturation et la vitesse de croissance par la vitesse lente de changement dans la composition du solvant; la présence d'acétone réduit notablement le nombre de germes efficaces; troisièmement, de grandes quantités de solvant organique causent un changement dans la forme du cristal et son mécanisme de croissance. A température ordinaire, le 8-hydroxyquinoléinate de cuivre(II) est précipité à l'état de dihydrate à partir de mélanges eau-acétone contenant 0-60% d'acétone et la croissance du cristal est limitée par un processus régi par la diffusion. Le 8-hydroxyquinoléinate de cuivre(II) anhydre est formé en solutions à 70% d'acétone par une réaction régie par la surface.

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SOLVENT EXTRACTION OF Ga(III) AND In(III) FROM AQUEOUS HALIDE MEDIA BY ADOGEN-364

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Summary—Adogen-364 has been used for the extraction of gallium(III) and indium(III) from halogen acid solutions, and the dependence of the extraction on chloride, bromide and iodide ion concentration studied. The separation of Ga(III), In(III) and Al(III) is reported and some conclusions have been drawn about the stoichiometry of the extracted species.

AMINES have found wide application for analytical separations.¹⁻⁴ The extraction of a variety of metal complexes from halogen acids has been reported.⁵⁻⁷ Good *et al.*^{8,9} used long chain alkylamines and quaternary ammonium salts for the extraction of iron(III), cobalt(II), gallium(III) and indium(III) from aqueous chloride solutions. Application of high molecular weight amines for the extraction of some metal iodides including gallium and indium has been reported by Suzuki.¹⁰

The aim of this investigation is to achieve separation of gallium(III), indium(III) and aluminium(III) ions from each other by amine extraction, using Adogen-364 in toluene.

EXPERIMENTAL

Reagents

Adogen-364. Obtained from Archer-Daniels-Midland Co., Minneapolis. It is a water-insoluble trialkyl tertiary amine mixture of C₈ and C₁₀ chains with C₈ predominating: average molecular weight 390; sp. gr. 0.802. Solutions of Adogen-364 were prepared by dilution with toluene.

Gallium and indium solutions. The metal was dissolved in concentrated hydrochloric acid and the solution evaporated almost to dryness to give the chloride. Metal sulphate solutions were prepared by precipitation of gallium and indium hydroxide followed by dissolution in the minimum quantity of concentrated sulphuric acid. Both gallium and indium stock solutions were standardized against EDTA. The metal bromide or iodide was obtained in solution by addition of the corresponding acid to the sulphate solution.

Procedure

The extraction experiments were performed in separating-funnels; 10 ml of the aqueous phase containing gallium and indium at concentration levels of about 10⁻³M at different halogen acid concentrations were shaken for 2 min with an equal volume of Adogen-364 (1% v/v) in toluene. After equilibration the phases were separated and analysed for metal ion concentration.

Each of the separated phases was heated to dryness and the organic residue was destroyed by a mixture of nitric and sulphuric acids. The metal concentration was determined spectrophotometrically with gallion¹¹ for gallium, and Alizarin-S¹² for indium.

RESULTS AND DISCUSSION

Extraction of indium and gallium

Gallium, indium and aluminium were extracted by Adogen-364 from their solutions in halogen acids (HCl, HBr, HI). The results obtained showed that it is possible to separate them.

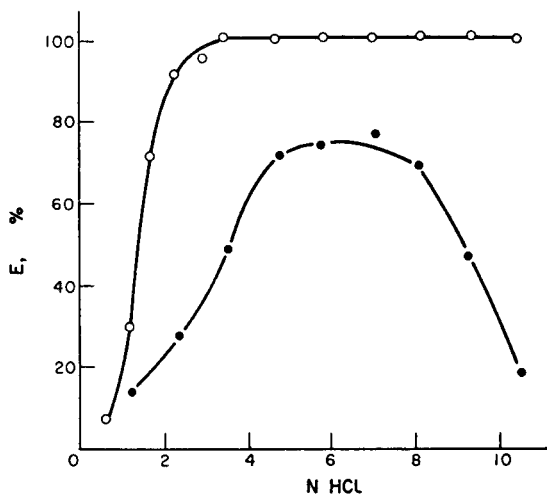


FIG. 1.—Variation of the degree of extraction of Ga(III) and In(III) as function of HCl concentration.

1% solution of Adogen-364 in toluene.

○—Ga(III); ●—In(III)

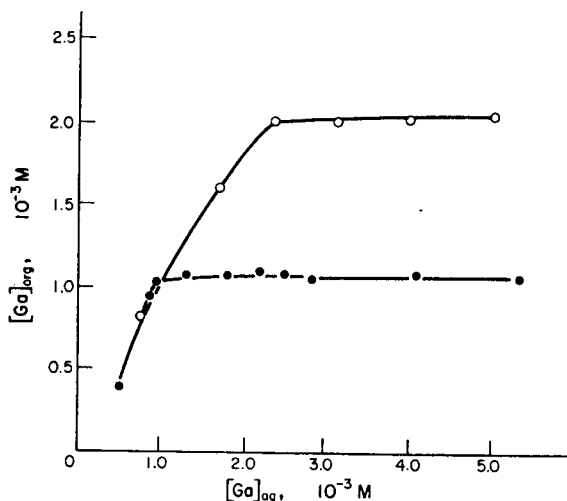


FIG. 2.—Extraction isotherm for Ga(III) and $2.0 \times 10^{-3} M$ Adogen-364 in toluene.

○—From 6M HCl; ●—From 5.5M HBr

The degree of extraction of gallium and indium metal complexes increases with hydrochloric acid concentration as shown in Fig. 1, but the extraction of indium passes through a maximum at higher acid concentration.

The extraction isotherm for the gallium-chloride system (Fig. 2) indicates that the limiting ratio of amine hydrochloride to gallium is 1:1. The data of Woodward¹³ and Kraus¹⁴ indicate that tetrachlorogallate is the predominant species in aqueous hydrochloric acid solutions so that the ion-pair $R_3NH \cdot GaCl_4$ may be the extractable species.

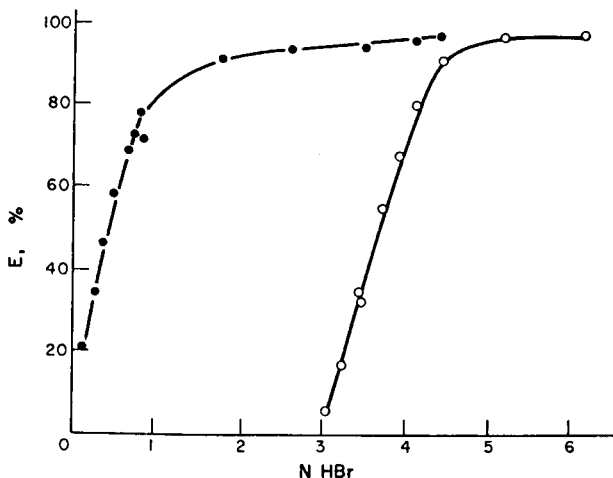


FIG. 3.—Dependence of the degree of extraction of Ga(III) and In(III), on HBr concentration.

1% solution of Adogen-364 in toluene.

○—Ga(III); ●—In(III)

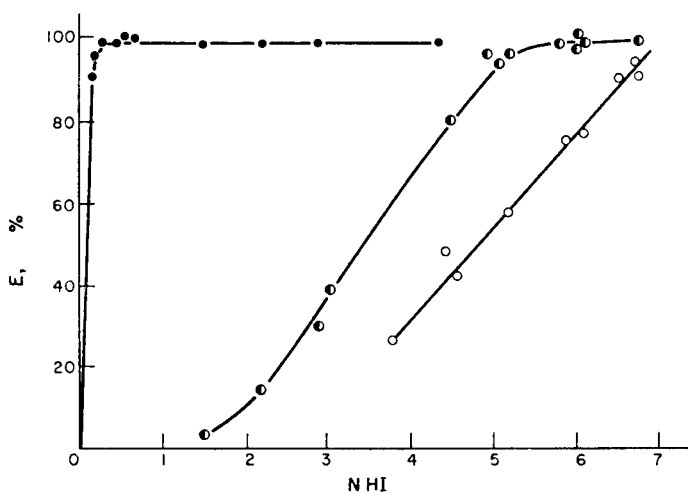


FIG. 4.—Dependence of the degree of extraction of Ga(III) and In(III), on HI concentration.

●—In(III), extraction by 1% amine solution.

●—Ga(III), extraction by 1% amine solution.

○—Ga(III), extraction by 5% amine solution.

The variation of degree of extraction of gallium and indium bromide complexes with the concentration of the acid in the aqueous phase is shown in Fig. 3. The indium bromide complex is extracted at lower acidity than the corresponding gallium complex; 50% extraction is reached for indium at an acidity of 0.5*M*, whereas with gallium 50% extraction is reached only at 3.7*M*. There is no decrease in extractability of indium with increasing concentration of the acid, such as is observed in the chloride system. The extraction isotherm of gallium bromide shows a 2:1 ratio of amine hydrobromide to gallium (Fig. 2), and the ion-pair $(R_3NH)_2 \cdot GaBr_5$ may be extracted. The extraction isotherm of the indium-bromide system indicates that the ratio of

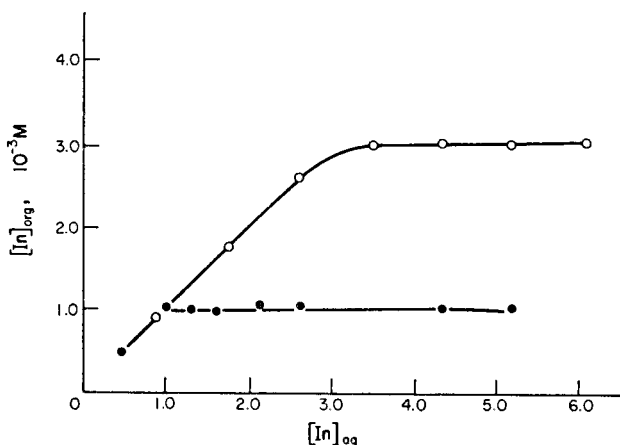


FIG. 5.—Extraction isotherm for In(III) and $3.0 \times 10^{-3} M$ Adogen-364 in toluene.
○—From 2M HI; ●—From 2.5M HBr

TABLE I.—SEPARATION OF INDIUM FROM GALLIUM IN 2M HBr

Ratio of Ga:In	Gallium		Indium	
	Taken, mg	found, mg	Taken, mg	Found, mg
1:1	2.58	2.60	2.90	2.96
1:1	2.58	2.57	2.90	2.90
1:1	2.58	2.58	2.90	—
1:1	2.58	2.57	2.90	2.86
10:1	0.50	0.50	0.05	0.05
10:1	5.00	5.00	0.50	0.50
100:1	10.00	9.92	0.10	0.10
1:10	—	—	0.50	0.53

TABLE II.—SEPARATION OF INDIUM FROM GALLIUM IN 1.5M HI

Ratio of Ga:In	Gallium		Indium	
	Taken, mg	Found, mg	Taken, mg	Found, mg
1:1	2.50	2.47	2.00	1.97
1:10	0.50	0.50	5.00	4.94
1:100	0.05	0.05	5.00	5.00
1:1	2.50	2.43	2.00	1.94
1:100	0.05	0.05	5.00	4.94
1:10	0.50	0.49	5.00	5.00

amine hydrobromide to metal is 3:1 (Fig. 5), and that the ion-association compound $(R_3NH)_3 \cdot InBr_6$ may be extracted.

From hydriodic acid solution, indium is more readily extracted than gallium (Fig. 4). The extraction isotherm of indium iodide was obtained (Fig. 5), indicating an amine hydriodide to metal ratio of 1:1.

From the results obtained, it can be seen that in the case of gallium, with increasing acid concentration, the order of extractability of the various complexes is $Cl^- > Br^- > I^-$, and in the case of indium it is $I^- > Br^- > Cl^-$. These results agree with those obtained by ion-exchange,^{15,16} and solvent extraction methods.¹⁷

TABLE III.—SEPARATION OF GALLIUM FROM ALUMINIUM
IN 6.5*M* HBr

Ratio of Ga:Al	Gallium	
	Taken, <i>mg</i>	Found, <i>mg</i>
1:10	0.50	0.50
1:1	2.50	2.49
1:10	0.50	0.50
1:100	0.50	0.49
1:1	0.50	0.49
1:10	0.50	0.48
1:100	0.50	0.48

TABLE IV.—SEPARATION OF GALLIUM FROM ALUMINIUM
IN 7.0*M* HCl

Ratio of Ga:Al	Gallium	
	Taken, <i>mg</i>	Found, <i>mg</i>
1:1	2.50	2.45
1:10	0.50	0.49
1:100	0.50	0.48
1:1	2.50	2.50
1:10	0.50	0.50
1:100	0.50	0.49

TABLE V.—SEPARATION OF INDIUM FROM ALUMINIUM
IN 5.0*M* HBr

Ratio of In:Al	Indium	
	Taken, <i>mg</i>	Found, <i>mg</i>
1:10	1.00	1.03
1:100	1.00	0.98
1:1	1.00	0.99
1:10	2.00	1.96
1:100	1.00	0.94
1:1	1.00	0.94

Extraction of aluminium by Adogen-364 in all the systems mentioned is negligible over the concentration range studied.

SEPARATION OF GALLIUM, INDIUM AND ALUMINIUM

The extraction results show that it is possible to separate indium and gallium from both 2*M* hydrobromic acid and 1.5*M* hydriodic acid; gallium and aluminium from both 7.0*M* hydrochloric acid and 6.5*M* hydrobromic acid; indium and aluminium from both 5*M* hydrobromic acid and 2*M* hydriodic acid.

The separation of the three elements from each other could be achieved by the extraction of indium from 1.5*M* hydriodic acid followed by the extraction of gallium from 7*M* hydrochloric acid.

Synthetic mixtures of the metal salts were prepared and the suitable acidity of the aqueous phase for the extraction of one component was established by the addition of the corresponding acid. The aqueous phase was shaken twice, each time for 2 min,

TABLE VI.—SEPARATION OF INDIUM FROM ALUMINIUM
IN 2.0M HI

Ratio of In:Al	Indium	
	Taken, mg	Found, mg
1:10	1.00	0.97
1:100	1.00	1.02
1:1	2.02	2.02
1:10	1.00	0.98
1:100	1.00	0.98
1:1	2.00	1.96

with an equal volume of 1% v/v amine solution in toluene. For the separation of gallium from aluminium in hydrobromic acid medium, 5% v/v amine solution in toluene was used. Results of the separations are listed in Tables I–VI. Every element separated was tested spectroscopically for the presence of other cations.

Determination of gallium and indium after separation was carried out spectrophotometrically by means of the reagents mentioned above.

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Zusammenfassung—Adogen-364 ist zur Ausscheidung von Gallium(III) und Indium(III) aus Halogen Säurelösungen benutzt worden und die Abhängigkeit von Chlorid, Bromid und Jodid-Ionen bei der Ausscheidung wurde studiert. Ein Bericht über die Trennung von Ga(III), In(III) und Al(III) wird gegeben und einige Schlüsse wurden über die Stöchiometrie der ausgeschiedenen Arten getroffen.

Résumé—On a utilisé l'Adogen-364 pour l'extraction du gallium(III) et de l'indium(III) à partir de solutions d'hydracides, et l'on a étudié la dépendance de l'extraction par rapport à la concentration en ion chlorure, bromure et iodure. On rapporte la séparation de Ga(III), In(III) et Al(III) et l'on tire quelques conclusions sur la stoechiométrie de l'espèce extraite.

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VERSATILE SPECTROPHOTOMETRIC METHOD FOR THE DETERMINATION OF SILICON*

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Summary—A versatile spectrophotometric method is described for the determination of microgram levels of silicon, as molybdenum blue. It combines the desirable features of existing spectrophotometric methods with three pretreatment procedures, namely (a) the removal of cations with a cation-exchange resin in the H⁺-form, (b) the conversion of all silicon species into the reactive monomer with an alkaline treatment, and (c) the decomposition of silicon fluoride with boric acid in the presence of cation-exchange resin. These pretreatments coupled with the colour development provide five procedures which are applicable to a wide variety of samples including natural and industrial waters and solutions of various nuclear reactor fuels and components. Provisions are included for the selective determination of total silicon.

MICROGRAM amounts of silicon are usually determined by the familiar molybdenum blue colorimetric method. Many variations of this method¹⁻⁶ were investigated in an attempt to establish a reliable, sensitive spectrophotometric method for silicon with sufficient versatility for application to a wide diversity of samples. All the methods investigated, though sufficiently sensitive, had several shortcomings, foremost of which was the low tolerance for diverse ions, especially common anions. To circumvent this major defect, most of the methods were oriented to specific analytical problems and used with close control of sample preparation and with calibration under the same conditions as the samples.

The desirable features of these molybdenum blue procedures have now been combined with three simple pretreatments (see Table I) to provide a truly versatile spectrophotometric method that is free from the limitations mentioned. The pretreatments are (a) conversion of non-reactive silicon species into the reactive monomer with hot sodium hydroxide solution, (b) removal of cations and excess of sodium hydroxide with cation-exchange resin, and (c) complexation of fluoride with boric acid. The basic molybdenum blue method is used alone and in various combinations with these three pretreatments to give five separate procedures. The proposed method has high tolerance for diverse ions and is applicable to a wide variety of samples including natural and industrial waters, and solutions of various nuclear fuels and components. Provisions are made for the selective determination of the sum of the reactive monosilicic and disilicic acids and for the determination of total silicon.

EXPERIMENTAL

Apparatus

Because of the limited but non-negligible solubility of silica in water, especially that which is alkaline, plastic ware was used wherever possible in treatment of samples and to store reagents. Most of the items recommended are commercially available. For filtration, 0.45- μ m membrane

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filters were supported on a 25-mm Millipore filter holder used in conjunction with a Fisher filtrator. The base of the filter holder was extended to a total length of 180 mm with 6-mm tubing to permit direct filtration into a beaker or a 50-ml polyethylene bottle.

Reagents

Silicon-free ammonia solution, ~6M. Expose distilled water to twice its volume of conc. ammonia solution in a sealed polyethylene bag for 12–24 hr, stirring the water constantly by magnetic stirring during the equilibration.

TABLE I.—APPLICABILITY OF THE VARIOUS PROCEDURES

Procedure	Applicability	Diverse ion effect*
I.	Molybdenum blue procedure. Determination of reactive silicon in aqueous solution devoid of fluoride. Samples containing much Cu(II) must be analysed by procedure III. Samples containing Fe are conveniently analysed by procedure III.	The tolerance levels, expressed as diverse ion to silicon molar ratio, are at least 950 for Al; at least 185 for Co, Cr(III, VI), Fe ⁺ , lanthanides [‡] , Mn, Ni, and Zn; 25 for As(V), Hg, Sn(IV), U(VI), and V(V). Copper(II) absorbs at 810 nm, hence its tolerance ratio is only 20. Tin(II) immediately reduces the molybdate and must be absent. The alkaline earths require the use of HNO ₃ instead of H ₂ SO ₄ for pH adjustment. Up to 10 mmole of Cl ⁻ , ClO ₄ ⁻ , NO ₃ ⁻ , and SO ₄ ²⁻ , and 0.005 mmole of phosphate per sample aliquot do not interfere. Citrate, fluoride, oxalate, and tartrate must be absent.
II.	Alkaline pretreatment followed by molybdenum blue procedure. Determination of total silicon in low-salt aqueous solutions devoid of fluoride. Samples containing much Cu(II) must be analysed by procedure IV.	Anions same as procedure I. Cations which form insoluble hydroxides must be absent. Use procedure IV for samples containing cations that form insoluble hydroxides.
III.	Cation-exchange resin treatment followed by molybdenum blue procedure. Determination of the sum of reactive silicon in aqueous metal salt solutions devoid of fluoride.	Anion tolerance same as for procedure I. Metals, except those in the form of anionic complexes, are removed by the cation-exchanger; e.g., 2 mmole of Al, 1.5 mmole of equimolar Fe, Cr, Ni mixture, 0.8 mmole of U, and 0.5 mmole of Bi are removed sufficiently to permit application of the alkaline treatment. The tolerance for metals that form anionic complexes is the same as for procedure I.
IV.	Cation-exchange resin treatment followed by alkaline treatment followed by molybdenum blue procedure. Determination of total soluble silicon in aqueous metal salt solutions devoid of fluoride.	As for procedure III.
V.	Cation-exchange resin-boric acid treatment followed by molybdenum blue procedure. Determination of total silicon in metal salt solutions containing fluoride.	Except for those that exist as stable anionic complexes, cations are removed by the resin. This procedure has been applied successfully to fluoride solutions of "Zircaloy" and to mixtures of Al-U and Zr-U fuel solutions. Niobium at 10 and Sn(IV) and Ti at 25 molar ratio to silicon do not interfere. At least 5 mmole of fluoride can be present in the sample aliquot without adverse effect.

* Based on diverse ion studies at a silicon level of 30 μg (1 μmole). The interference level was established on the basis of a *t*-test at the 95% confidence level.

† Because the molybdenum blue colour is slow to form, the minimum colour development time is 1.5 hr.

‡ Lanthanide oxalates are insoluble, so the sample solution must be centrifuged or filtered.

Ammonium molybdate reagent. Dissolve 50 g of ammonium heptamolybdate tetrahydrate in water, filter the solution through a 0.45- μm membrane filter, then dilute the solution to 500 ml.

Oxalic acid-tartaric acid complexing reagent, 0.75M in each component.

Reducing agent. Dissolve 27 g of sodium hydrogen sulphite, 2 g of sodium hydroxide, and 0.50 g of 1-amino-2-naphthol-4-sulphonic acid in 225 ml of water, filter, and dilute to 250 ml.

Cation-exchanger. Dowex 50W-X8 (or equivalent), 50-100-mesh, in the H^+ -form. The resin must be washed with 6M hydrochloric acid and then with water, then stored without water in a plastic container.

Silicon stock solution, 1.000 mg/ml. Fuse 0.5350 g of pure silica with 2 g of sodium carbonate in a platinum crucible, cool, dissolve the melt and dilute to 250 ml with water containing 0.4% sodium hydroxide. Prepare working standards from the stock solution by dilution with the same sodium hydroxide solution.

Procedures

The basic molybdenum blue method for the determination of silicon is used alone or in various combinations with sodium hydroxide, cation-exchange resin, and boric acid pretreatments to provide five procedures for different types of samples and different determinations (Table I). In all cases, two appropriate standards and a blank are processed simultaneously and the results for the samples are calculated by comparison with the standards.

Procedure I. Place a sample aliquot of 75 ml or less, containing 5–100 μg of reactive silicon, into a 100-ml polyethylene beaker. Adjust the pH to 1.1 ± 0.1 with 6N sulphuric or nitric acid, then add 10 ml of ammonium molybdate reagent. Adjust the pH to 1.3 ± 0.1 with either 6N sulphuric acid or ammonia, and let stand for 10 min. Add 10 ml of the complexing reagent, mix, and after 30 sec but within 1 min of the addition of complexer, add 2 ml of the reducing solution. Wait 20 min for colour development, then dilute the solution to 100 ml with water in a volumetric flask. Measure the absorbance against water at 815 nm (infrared source and detector) or at 795 nm (visible source and detector) in 10- or 50-mm cells.

Procedure II. Place a sample aliquot of 50 ml or less, containing 5–100 μg of silicon, into a 50-ml polyethylene bottle. Add 2 drops of phenolphthalein indicator, then 50% sodium hydroxide solution until the solution turns pink, plus an additional 5 drops. Heat in a boiling water-bath for 20 min and chill to room temperature. Add H^+ -form cation-exchange resin until the solution is neutral, then add approximately 5 ml more. Filter the sample through a 0.45- μm membrane filter and collect the filtrate and water rinses in a 100-ml polyethylene beaker. Continue with the determination as in Procedure I. If much precipitate appears when the sample is made basic, the results will be low and the sample should be analysed by Procedure IV.

Procedure III. Add approximately 10 ml of H^+ -form cation-exchange resin to a 50-ml polyethylene beaker. Transfer a sample aliquot of 25 ml or less, containing 5–100 μg of reactive silicon, onto the resin and mix. Filter the solution through a 0.45- μm membrane filter and collect the filtrate and water rinses in a 100-ml polyethylene beaker. Continue with the determination as in Procedure I.

Procedure IV. Carry the sample through the cation-exchange resin treatment and the alkaline treatment as in Procedures III and II and finish by Procedure I. As there is a filtration before the alkaline treatment, particulate silicon is not determined.

Procedure V. Add approximately 10 ml of H^+ -form cation-exchange resin to a 50-ml polyethylene beaker. Transfer a sample aliquot of 5 ml or less, containing 5–100 μg of silicon, onto the resin and mix. Add 40 ml of saturated boric solution, mix, and let stand for 30 min with intermittent mixing. Filter the sample through a 0.45- μm membrane filter and collect the filtrate and water washes (which must not exceed 70 ml) in a 100-ml polyethylene beaker. Conclude the determination by Procedure I. In fluoride medium, silicon generally exists only as the fluoride-complexed monomer so only total silicon is determinable.

RESULTS AND DISCUSSION

The widely used molybdenum blue procedure for the determination of silicon involves initial formation of the yellow silicomolybdic acid complex, reduction of the yellow complex to the more sensitive molybdenum blue complex, and spectrophotometric measurement of the blue colour. The existing molybdenum blue methods have these three basic steps in common but vary in the specific conditions used to develop and measure the molybdenum blue species. For example, various pH values and molybdenum reagents have been recommended for the formation of the silicomolybdate complex, various organic complexing reagents have been suggested for masking the excess of molybdate and destroying extraneous molybdate complexes,

and many reducing reagents have been used to produce the blue complex. The measurement of the blue complex has been made at several different wavelengths.

The many variations in the colour development phase of the method were studied and evaluated. A discussion of the pertinent variables, pH, reagents, and measurement of the blue complex follows.

Formation of silicomolybdate

The critical variables in the formation of the silicomolybdic acid complex are the chemical state of the silicon, the pH, the quantity and composition of the molybdate reagent, and the presence of anions.

In an aqueous medium, silicon exists as monosilicic acid, disilicic acid, a variety of higher polysilicic acids, and silica. One or any combination of these species may be present, depending on such factors as temperature, pressure, pH, and the presence of various electrolytes.

Monosilicic acid and disilic acid are reported to react quantitatively with ammonium molybdate in 75 sec and 10 min, respectively.⁷ Polysilicic acids and silica react slowly or not at all and must be converted into the reactive monomer if they are to be determined. The conversion can be accomplished by reaction with hydrofluoric acid, by a basic fusion, or by reaction with a hot sodium hydroxide solution. The decomposition in a hot alkaline solution at pH 12–13 is employed in this method. In solutions containing fluoride, the silicon exists predominantly as a fluorosilicate which yields the reactive monomer upon reaction with boric acid, so no conversion is deemed necessary.

The optimum pH for the reaction of monosilicic acid and molybdate has been reported as 1.2–1.3,⁸ 1.6⁹ and 1.6–2.0.¹⁰ Based on a pH study over the range 1.0–2.0, a pH of 1.3 ± 0.1 is recommended, corresponding to formation of α -silicomolybdic acid.¹¹ The simplest method of achieving these conditions is to add the ammonium molybdate solution to a sample acidified to $\text{pH } 1.1 \pm 0.1$. If the pH is too high, colour formation is incomplete.

Previous investigators have recommended different amounts of ammonium molybdate in the form of a water solution or a sulphuric acid solution. All variations gave satisfactory production of the yellow silicomolybdate in low-salt media; however, without exception, the suggested conditions did not provide adequate tolerance for the common anions chloride, nitrate, perchlorate, and sulphate. These ions could be tolerated in quantities only up to about 2 mmole, above which serious negative interference is observed. A much more practical tolerance of about 10 mmole is obtained by using a water solution of molybdate and maintaining the molybdate at 0.85 mmole per test sample. At this molybdate level, phosphomolybdate resists dissociation by oxalic acid and tartaric acid; however, if the amount of oxalic and tartaric acids added is increased to 7.5 mmole of each, satisfactory results are obtained.

Complexation of excess of molybdate and destruction of extraneous molybdate complexes

After the silicomolybdic acid has been formed, an organic complexing reagent is introduced to mask residual molybdate and destroy other molybdate complexes. A 0.75M oxalic acid–0.75M tartaric acid complexing solution is used in this method.

The complexer also slowly breaks up the silicomolybdic acid complex so the interval between the addition of the complexing solution and the addition of the reducing reagent must be kept between 30 and 60 sec. The absorbance of the sample decreases at the rate of 0.005/min. The complexing reagent and the reducing solution may not be added simultaneously because complete dissociation of the phosphomolybdate complex is then not attained.

Reduction of silicomolybdate to molybdenum blue

Chlorostannous acid, iron(II) ammonium sulphate, sodium sulphite, and various mixtures of sodium sulphite, sodium bisulphite, and 1-amino-2-naphthol-4-sulphonic acid have been used to reduce silicomolybdate to the molybdenum blue complex.^{1,2} The last of these, prepared according to Banks and Carlson,⁶ was confirmed to be the most reliable from the standpoint of stability of the reduced species, stability of the reducing solution (shelf life is at least one month), and colour reproducibility. Quantitative colour development is obtained in 20 min and the colour is stable for at least 16 hr.

Under the recommended colour development conditions, the absorbance spectrum of the molybdenum blue complex has a maximum at 815 nm with an infrared source and detector and 795 nm with a visible source and detector. Best results are obtained with the infrared source and detector.

TABLE II.—RESULTS OF THE ANALYSIS OF SILICON STANDARDS AND DIFFERENT TYPES OF SYNTHETIC SAMPLES BY THE VARIOUS PROCEDURES

Procedure	Salt or matrix added	Amount	Recovery*, %
I	None	—	100.0 ± 1.2 (19)
	Various metal salts individually (See Table I)	0.2 mmole	99.9 ± 1.2
II	None	—	98.3 ± 0.4 (4)†
III	None	—	100.8 ± 1.0 (4)
	7:2:1 Fe-Cr-Ni mixture as nitrates	1.5 mmole total	100.6 ± 0.6 (4)
IV	None	—	99.9 ± 1.2 (2)
	Bi(NO ₃) ₃	0.5 mmole	98.0
	Cu(NO ₃) ₂	1.0 mmole	99.5
	Hg(NO ₃) ₂	0.5 mmole	98.0
	7:2:1 Fe-Cr-Ni mixture as nitrates	1.5 mmole total	101.7
V	0.4M SnCl ₄ -2M HCl	1.0 ml	91.0‡
	0.01M KNbO ₃ -4.6M HF	1.0 ml	100.5
	0.08 M SnCl ₄ -4.6M HF	0.25 ml	100.0
		1.0 ml	91.0‡
	0.02M Ti(IV) in HF-HNO ₃	1.0 ml	99.5
	2.0M Al(NO ₃) ₃ -0.014M UO ₂ (NO ₃) ₂ -0.4M ZrF ₄ -3M HF	1.0 ml	99.5 ± 0.9 (5)

* The recoveries are quoted relative to the average silicon recovery in procedure I for pure silicon standards, with the associated standard deviation (number of replicates given in brackets). The silicon level was 30-40 μg throughout.

† The silicon was initially converted into a non-reactive form by evaporation with nitric acid.

‡ In chloride or fluoride media, the anionic Sn(IV) complexes are not completely removed by the resin. Residual Sn(IV) precipitates molybdate.

Use of cation-exchange resin to circumvent diverse ion effects

In an overall silicon method that includes alkaline conversion of inert silicon into reactive silicon, colour development and measurement, metal ions affect the determination in many ways. They may precipitate as the hydroxide, molybdate, oxalate, or other salts during colour development. They may prevent complete conversion of inert silicon species into the determinable monosilicate by precipitating at high pH and occluding silicon. They may, like copper, absorb at the working wavelength. Finally they may consume reductant. Cation-exchange resin in the H^+ -form can be used effectively to avoid most, if not all, of these undesirable side-effects. The cation-exchange resin is also used to neutralize the sodium hydroxide introduced in the alkaline conversion treatment. This practice keeps the introduction of anions to a minimum. In many laboratories, including this one, highly radioactive samples must often be analysed. Use of the resin enables sufficient reduction of the activity level to permit removal of the sample from the shielding facility.

Effects of diverse ions; method reliability

The effects of diverse ions on the various procedures and the applicability of the various schemes to different types of samples have been studied. Table I summarizes the effects of diverse ions and Table II lists the results for silicon standards processed by the various schemes. Some of the standards were mixed with metal salts or acid-metal salt matrices known to be troublesome. It can readily be seen that the three pretreatments have little effect on the recovery of silicon and that each procedure produces highly satisfactory results within its limitations.

Based on results collected over a 2-month period, the attainable precision at the 30–40- μg silicon level is 1.25% relative standard deviation.

Zusammenfassung—Ein vielseitiges spektrophotometrisches Verfahren zur Bestimmung von Silicium im Mikrogrammbereich als Molybdänblau wird beschrieben. Es verbindet die Vorteile bekannter spektrophotometrischer Verfahren mit drei Vorschriften zur Vorbehandlung: (a) der Entfernung von Kationen mit einem Kationenaustauschharz in der H^+ -Form; (b) der Überführung aller Siliciumspezies durch Alkalibehandlung in das reaktionsfähige Monomere; (c) die Zersetzung von Siliciumfluorid mit Borsäure in Gegenwart von Kationenaustauschharz. Diese Vorstufen ergeben zusammen mit der Farbentwicklung fünf Verfahren, die auf viele verschiedenartige Proben anwendbar sind, darunter natürliche und industrielle Wässer und Lösungen verschiedener Kernreaktorbrennstoffe und -bestandteile. Die selektive Bestimmung von Gesamtsilicium ist berücksichtigt.

Résumé—On décrit une méthode spectrophotométrique polyvalente pour le dosage du silicium à des teneurs de l'ordre du microgramme, en tant que bleu de molybdène. Elle combine les caractères désirables de méthodes spectrophotométriques existantes avec trois techniques de prétraitement, nommément (a) l'élimination des cations avec une résine échangeuse de cations sous la forme H^+ , (b) la conversion de toutes les espèces du silicium en le monomère réactif par un traitement alcalin, et (c) la décomposition du fluorure de silicium par l'acide borique en la présence d'une résine échangeuse de cations. Ces prétraitements associés avec le développement de la coloration fournissent cinq techniques qui sont applicables à une large variété d'échantillons comprenant l'eau naturelle et industrielle et des solutions de divers combustibles et constituants de réacteurs nucléaires. On inclut des dispositions particulières pour la détermination sélective du silicium total.

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END-POINT EVALUATION IN INSTRUMENTAL TITRIMETRY—I

LINEAR EXTRAPOLATION OF HYPERBOLIC TITRATION CURVES

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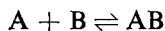
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Summary—A method is described for the estimation of a systematic titration error which is introduced by linear extrapolation of hyperbolic titration curves in amperometric, photometric, and other instrumental titrations. It is assumed that the titration is based upon a single-step ion-association reaction $mA + nB \rightleftharpoons A_mB_n$ and that the measured physical property falls within known minimum and maximum values. The procedure is suitable for end-point determination, even when the titration curves have extensive curvature, and for predicting the choice of optimum experimental conditions for a given titration.

IN MANY instrumental titrations, such as conductometric, amperometric, spectrophotometric, thermometric, and other titrations, the measured physical property represents a summation of partial contributions which are directly proportional to molar concentrations of the individual species involved in the equilibrium. The appropriate proportionality constants can be defined according to the method under consideration (see *e.g.*, ref. 1). Usually, their values depend upon the experimental conditions employed and may even be zero. In all these titrations hyperbolic titration curves are obtained with linear segments on both sides of a more or less pronounced bend in the vicinity of the equivalence point. The linear segments of the curve are extrapolated and the point of intersection is taken to be both the end-point and the equivalence point.

Such graphical end-point extrapolation presents no problem if the curvature around the equivalence point is insignificant and the linear segments are long enough. In practice, however, titration curves with extensive curvatures are fairly common. Tyrrell,² for example, presented a family of thermometric titration curves discussing the necessary criteria to obtain a sharp end-point. Usually, (Figs. 1 and 2) the extrapolated end-point deviates considerably from the true equivalence point. Thus, systematic titration errors may occur, their magnitude depending upon the concentration of the substance to be determined and upon the completeness of the reaction.

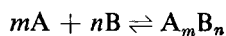
Most of the discussion of the problems of end-point extrapolation has been limited to the simple ion-combination reaction



Langer and Stevenson³ advocated two procedures for the end-point evaluation, using

chords of the hyperbola. The first is based on the fact that if one asymptote to the titration curve is known, the second can easily be constructed by means of the theorem saying that on any chord the parts between the hyperbola and the two asymptotes are of equal length. The second procedure is based on the theorem that the bisector of any pair of parallel chords of the hyperbola goes through the intersection point of the asymptotes. Thus, the end-point of a hyperbolic titration curve is found as the point of intersection of the bisectors of two different pairs of parallel chords. Grunwald⁴ has used a method of end-point calculation based on the curvature of the titration curve. If the mathematical expression of the titration curve is known, the equivalence point can be calculated as an intersection point of two secants. One of them is drawn across the curvature before the equivalence point, the second is given by a pair of points beyond the equivalence point. Again, one point is chosen, the other is calculated. This procedure may be easily applied only if the equilibrium is of a simple type. An easy but approximate way of systematic error estimation in photometric titrations based on the formation of a simple complex AB is given in the monograph by Ringbom,⁵ and the expression derived by him is discussed below [cf. equation (10)]. The problem of the end-point evaluation when one of the asymptotes is known has been solved by Khadeev.⁶ The estimation of the amperometric titration error has been studied by Gordienko and co-workers⁷ for cases where one of the equilibrium species is not involved in the electrode reaction. Klas^{8,9} has examined the titration curve and the end-point evaluation in radiometric precipitation titrations in which one of the ions forming the precipitate is labelled. He has also treated the problem of the systematic errors¹⁰ in these titrations.

Less attention has been paid to the titration curves for a general case of reaction



despite the known fact that the linear extrapolation of such a curve is subject to greater systematic errors. Brinkman has given expressions for the estimation of this error, but we have been unable to discover a full explanation of their derivation or value.¹¹ A rigorous investigation of the conditions required for the existence of extrema on titration curves and their locations was undertaken by Goldman and Meites.¹ They considered the general ion-combination reaction in which the product did not make any contribution to the physical property measured. The practical application of their expressions involves a detailed knowledge of the equilibrium itself and of the individual proportionality constants. A general equation of the amperometric precipitation curve for the above-mentioned equilibrium was also derived by Mar'yanov,¹² who also discussed the conditions for the existence of an extremum. Klas¹³ evaluated a correction of the consumption of titrant in relation to the solubility of a precipitate A_mB_n in a radiometric titration.

The present paper deals with the problem of systematic errors arising in linear extrapolations of titration curves with considerable curvature. It is supposed that the titration is based on a one-step reaction and that the measured property is directly proportional to the concentration of the product A_mB_n and reaches a limiting constant value beyond the equivalence point, so that the position of the horizontal asymptote parallel to the abscissa is known. These conditions are often encountered in practice and the treatment permits easy end-point evaluation, even if the titration curve has pronounced curvature.

Derivations of equations

Consider the case of a titrimetric determination of a substance A with a standard solution of substance B in which the product A_mB_n is formed, essentially in one step. It is supposed that equilibrium is attained after each addition of the titrant, and is characterized by a formation constant

$$K_{mn} = \frac{[A_mB_n]}{[A]^m[B]^n} \quad (1)$$

which is usually the conditional (effective) stability constant.

The equations for the analytical concentrations of the constituents A and B are

$$c_A = [A] + m[A_mB_n] \quad (2)$$

$$c_B = [B] + n[A_mB_n] = ac_A \quad (3)$$

the parameter a (equivalent fraction) representing the ratio of the added titrant to the total amount of the substance A being titrated. To obtain the equation expressing the dependence of the measured equilibrium concentration of the product A_mB_n , terms from equations (2) and (3) are substituted into (1):

$$K_{mn} = \frac{[A_mB_n]}{(c_A - m[A_mB_n])^m (ac_A - n[A_mB_n])^n} \quad (4)$$

This rearranges to give

$$F(a, [A_mB_n]) = K_{mn}(c_A - m[A_mB_n])^m (ac_A - n[A_mB_n])^n - [A_mB_n] = 0 \quad (5)$$

The derivative of this function forms the basis of a general equation of the tangent to the curve $[A_mB_n] = f(a)$ with the variables X and Y

$$\begin{aligned} X\{nc_A K_{mn}(c_A - m[A_mB_n])^m (ac_A - n[A_mB_n])^{(n-1)}\} - Y\{K_{mn}(c_A - m[A_mB_n])^{(m-1)} \\ \times (ac_A - n[A_mB_n])^{(n-1)}[m^2(ac_A - n[A_mB_n]) + n^2(c_A - m[A_mB_n]) + 1\} \\ + mK_{mn}c_A(ac_A - n[A_mB_n])^n (c_A - m[A_mB_n])^{(m-1)} - (m + n - 1)[A_mB_n] = 0. \end{aligned} \quad (6)$$

Of more interest is an expression for the intersection of a given extrapolation tangent with the abscissa, $Y = c_A/m$. This straight line corresponds to the limiting value for the measured physical quantity, if the substance A is quantitatively converted into the complex A_mB_n . Substitution for Y and for the parameter a from equation (4), gives

$$X = \frac{n}{m} + \frac{c_A + m(m + n - 1)[A_mB_n]}{mnc_A[A_mB_n]} \sqrt[n]{\frac{[A_mB_n]}{K_{mn}(c_A - m[A_mB_n])^m}} \quad (7)$$

It is convenient to introduce a new variable, *i.e.*, the distribution coefficient $\delta_{mn} = m[A_mB_n]/c_A$, which represents the relative amount of the substance A bound into the complex, or the relative part of the maximum change in the physical quantity to be measured during the titration. Then equation (7) may be rewritten

$$X = \frac{n}{m} + \frac{1 + (m + n - 1)\delta_{mn}}{n\delta_{mn}} \left(\frac{\delta_{mn}}{m(1 - \delta_{mn})^m} \right)^{1/n} (K_{mn}c_A^{(m+n-1)})^{-1/n} \quad (8)$$

or

$$X = \frac{n}{m} + f_{mn}(K_{mn}c_A^{(m+n-1)})^{-1/n} = \frac{n}{m} + \Delta a \quad (9)$$

Thus, the deviation from the equivalence point $X = n/m$ is obtained as a product of the function f_{mn} and a constant which involves the value of the stability constant K_{mn} and the analytical concentration of the substance A to be titrated.

Systematic error in linear extrapolations of hyperbolic titration curves

To show the significance of the deviations which are inherent in the common procedure of extending the linear segments of the titration curve plot, values of c_A and K_{mn} were chosen so that the curvatures of the theoretical curves Figs. 1 and 2 were pronounced. The titration curve in Fig. 1 is calculated for the formation of AB, ($m = n = 1$) and it is seen that the linear branch extends as far as $\delta_{11} = 0.4$. If this segment is used to extrapolate the end-point, a deviation $(\Delta a)_{0.2} = 0.15$ results. When the tangent is drawn from a point in the middle of the maximum attainable change, the deviation $(\Delta a)_{0.5} = 0.30$ is obtained which, in its turn, represents a positive 30% systematic error.

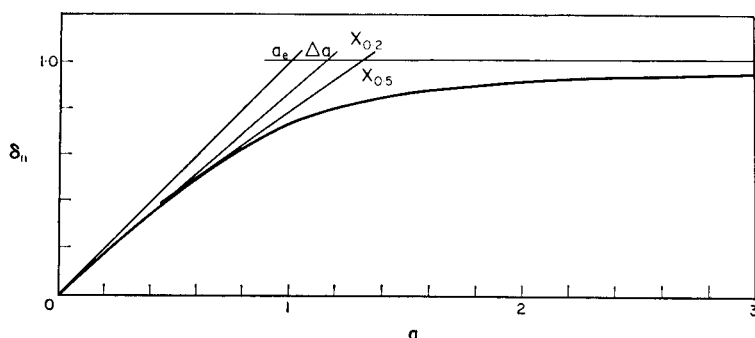


FIG. 1.—Dependence of distribution factor upon the equivalent fraction for the formation of complex AB; $K_{11}c_A = 10$.

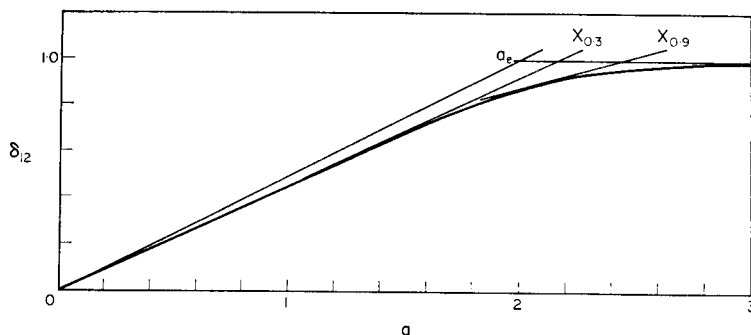


FIG. 2.—Dependence of the distribution factor upon the equivalent fraction for the formation of complex AB_2 ; $c_A\sqrt{K_{12}} = 10$.

Figure 2 shows the shape of the curve calculated for the formation of the AB_2 , ($m = 1, n = 2$). It is linear up to $\delta_{12} = 0.6$. The extrapolation of the tangent at $\delta_{12} = 0.3$ intersects the horizontally extrapolated straight line at the point where the deviation from the equivalence point is $(\Delta a)_{0.3} = 0.175$. If the part about $\delta_{12} = 0.9$

is used for extrapolation, a serious deviation results $[(\Delta a)_{0.9} = 0.47]$. Thus, the extent of the systematic deviation increases, as the point used to draw the extrapolation tangent approaches the equivalence point. The general equation (8) allows the theoretical evaluation of the systematic error, if the type of the titration product and the values of the parameters δ_{mn} , K_{mn} and c_A are known.

The expressions $\log f_{mn}$ for individual types of titration products are summarized in Table I. To evaluate the extent of the end-point deviation for the more important types of titration products, the numerical values of the correction function f_{mn} given in Table II might be found useful.

TABLE I.—EXPRESSIONS OF THE CORRECTION FACTOR FOR THE MORE IMPORTANT TYPES OF TITRATION PRODUCTS

Type	$\log f_{mn}$
AB	$\log(1 + \delta_{11}) - \log(1 - \delta_{11})$
AB ₂	$\log(1 + 2\delta_{12}) - \frac{1}{2} \log(1 - \delta_{12}) - \frac{1}{2} \log \delta_{12} - \log 2$
AB ₄	$\log(1 + 4\delta_{14}) - \frac{1}{4} \log(1 - \delta_{14}) - \frac{3}{4} \log \delta_{14} - \log 4$
AB ₆	$\log(1 + 6\delta_{16}) - \frac{1}{6} \log(1 - \delta_{16}) - \frac{5}{6} \log \delta_{16} - \log 6$
A ₂ B	$\log(1 + 2\delta_{21}) - 2 \log(1 - \delta_{21}) - \log 2$

TABLE II.—VALUES OF THE CORRECTION FACTOR f_{mn} FOR VARIOUS TYPES OF TITRATION PRODUCTS

δ_{mn}	Type				
	AB f_{11}	AB ₂ f_{12}	AB ₄ f_{14}	AB ₆ f_{16}	A ₂ B f_{21}
0.05	1.105	2.524	2.875	2.653	0.609
0.10	1.222	2.000	2.021	1.849	0.741
0.20	1.500	1.750	1.591	1.455	1.094
0.30	1.857	1.746	1.483	1.351	1.633
0.40	2.333	1.837	1.468	1.324	2.500
0.50	3.000	2.000	1.500	1.333	4.000
0.60	4.000	2.245	1.568	1.367	6.875
0.70	5.667	2.619	1.677	1.426	13.33
0.80	9.000	3.250	1.856	1.523	32.50
0.90	19.00	4.667	2.213	1.709	140.0
0.95	39.00	6.653	2.640	1.922	580.0

In Fig. 3 there is a quite interesting dependence of the correction function values upon the position of the tangential point for individual types of the titration product $A_m B_n$. Apparently, the greater the ratio B:A, the greater the range of the linear part of the titration curve. The extrapolation tangents merge with the linear segment of the titration curve and the systematic error due to the extrapolated end-point remains constant up to the value of δ_{mn} , where the bend of the curve begins to occur. In the range of δ_{mn} from 0.2 to 0.4 the values of the function f_{mn} are fairly close within the range 1.1 to 1.80. Thus, in many cases an average value of f_{mn} may be used irrespective of the type of the complex.

Even in the case when the initial part of the curve (δ_{mn} approaching zero) is used to extrapolate the end-point, the evaluated consumption of the titrant does not correspond to the theoretical value. With the complex AB, for example, it is higher

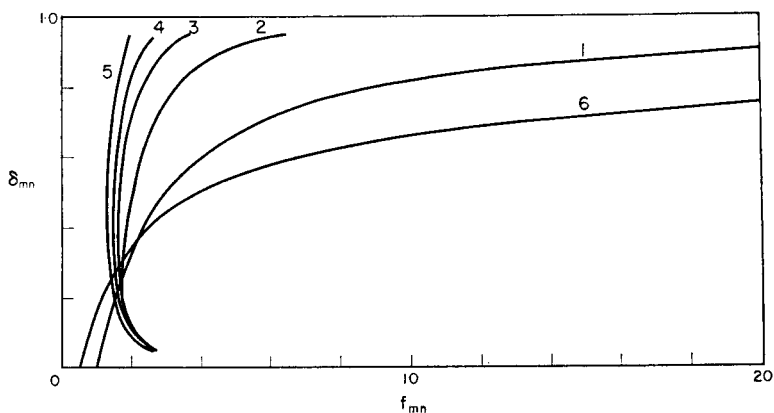


FIG. 3.—Dependence of correction factor f_{mn} upon the values of distribution factors for various types of titration products: (1) AB; (2) AB₂; (3) AB₃; (4) AB₄; (5) AB₆; (6) A₂B.

by the value $1/(K_{11}c_A)$. This systematic error becomes negligible only with low values of the term $(K_{mn}c_A^{(m+n-1)})^{-1/n}$, and depends thus upon the stability of the titration product.

The relative error, which is due to linear extrapolation of the end-point, can be readily expressed from equation (9)

$$\text{Error, \%} = \Delta a \frac{m}{n} 100 \quad (10)$$

If equation (10) is evaluated for the case of the complex AB, the solution obtained resembles the expression which was derived by Ringbom [cf. equation (34) in his monograph⁵] by another approach.

Equation (10) can also be taken as a relationship between a permissible relative error in the titration of the substance A, the stability constant and the position of the extrapolation straight line on the titration curve being given by the value of the correction term f_{mn}

$$\log \Delta a \frac{m}{n} = \log \frac{m}{n} + \log f_{mn} - \frac{m+n-1}{n} \log c_A - \frac{1}{n} \log K_{mn}. \quad (11)$$

The numerical values for the last two terms in equation (11) are given in Table III on the suppositions that the part of the curve at $\delta_{mn} = 0.2$ is taken for the end-point extrapolation and that an accuracy of 0.1% is required. If the concentration of the substance to be titrated is known (e.g., $10^{-4}M$), the minimum value of $\log K_{mn}$ necessary to achieve the required level of accuracy can be obtained.

End-point evaluation by the method of fan-traced tangents

To apply the proposed procedure for end-point evaluation, the stoichiometry of the titration product and the position of the horizontal asymptote corresponding to the maximum attainable value of the measured physical quantity must be known. As shown in Fig. 4, the tangents are laid off from the points chosen on a plot of the experimental titration curve, for instance at δ_{mn} equal to 0.2, 0.4, 0.6 and 0.8.

TABLE III.—PERMISSIBLE VALUES OF SOME PARAMETERS FOR A SUPPOSED 0.1% RELATIVE ERROR AND USING THE TANGENTIAL POINT AT $\delta_{mn} = 0.2$

Type	AB	AB ₂	AB ₃	AB ₄	AB ₅	AB ₆	A ₂ B
$\log K_{mn}$	6.8	14.1	21.7	29.6	37.6	45.7	10.7
$\frac{m+n-1}{n} \log c_A + \frac{1}{n} \log K_{mn}$	2.82	3.06	3.25	3.40	3.52	3.63	2.66

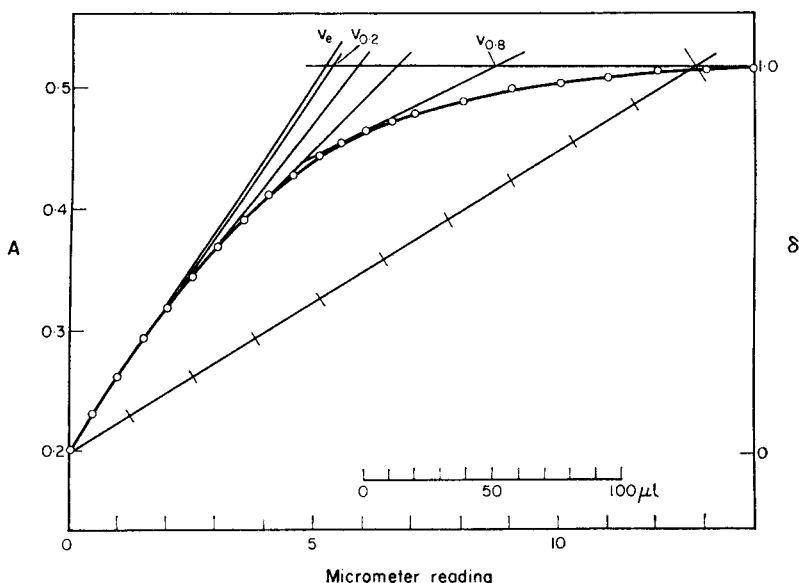


FIG. 4.—End-point evaluation by the method of fan-traced tangents.

The relative values of the distribution coefficient, δ , are evaluated either arithmetically or geometrically. A convenient method is to circumscribe a circle of convenient radius (e.g., 100 mm) from the beginning of the curve. A line is drawn from the centre of this circle to the intersection point with the horizontal asymptote and this serves as a scale to draw a system of lines parallel to the abscissa, which cut the ordinate at suitable values of δ .

General methods for tangent construction to plane curves are known, but they are rather complicated. Any simple method may be used and if the titration curve is fairly symmetrical in the vicinity of the tangential point, the secant cutting equal parts of the curve on both sides of the point is suitable for orientation of the tangent. If the tangent is led through a longer linear segment of the titration curve, the tangential point is identified with the middle of this section.

Further, the intersects of the individual tangents with the upper asymptote are evaluated. Since the consumption of the titrant is directly proportional to the values of a , equation (9) can be used to evaluate the distance between the two intersection points:

$$v_o - v_a = k(f_o - f_a). \quad (12)$$

The values of the correction factors are read from Table II. The systematic deviation

is calculated by multiplying the constant k by the relevant correction factor, e.g.,

$$\Delta v_c = k f_c. \quad (13)$$

The proposed procedure would be applicable even in case of an unknown composition of the titration product. Since the ratio of the differences in subsequently evaluated volumes is equal to the ratio of differences in corresponding correction factors, we obtain, for instance,

$$\frac{v_3 - v_1}{v_2 - v_1} = \frac{f_3 - f_1}{f_2 - f_1}. \quad (14)$$

Then the stoichiometry of the titration product could be solved by comparing the tabulated values. However, this approach can hardly yield unambiguous information since the volume differences are to a great extent influenced by inaccurate construction of the tangents.

EXPERIMENTAL

An aliquot of an ethanolic solution containing 57.8 μg of commercial diphenylthiocarbazone (dithizone) was transferred to the titration cuvette (length 30 mm) and 1 ml of hexamethylenetetramine buffer solution of pH 5.0 was added. The solution was diluted with a further amount of ethanol and water in order to produce 20 ml of 50% (by volume) alcoholic solution. For the photometric microtitration¹⁴ 0.001M lead nitrate was dispensed with a syringe microburette.

As may be seen in Fig. 4, the bend of the experimental titration curve obtained is so great that the end-point evaluation seems to be quite difficult. Following the proposed procedure, a series of tangents was drawn and the following volumes (expressed as micrometer readings) were found: $v_{0.2} = 5.30$; $v_{0.4} = 5.78$; $v_{0.6} = 6.64$; $v_{0.8} = 8.65$.

Lead ion forms a chelate $\text{Pb}(\text{HDz})_2$ with dithizone, and since a dithizone solution is titrated with a lead salt (titrant B), the titration product is of the type A_3B . For the evaluation of the constant k the two extreme volume readings may be used. Thus, we obtain

$$k = \frac{8.65 - 5.30}{32.50 - 1.094} = 0.1067$$

From equation (13) the correction values are found and used to express the end-point consumption v_e

$$\begin{aligned} (\text{for } \delta_{0.2}) \quad v_e &= 5.30 - 0.1067 \times 1.094 = 5.30 - 0.12 = 5.18 \\ (\text{for } \delta_{0.8}) \quad v_e &= 8.65 - 0.1067 \times 35.5 = 8.65 - 3.47 = 5.18 \end{aligned}$$

The agreement obtained is fairly good.

Zusammenfassung—Es wird zur Ermittlung eines systematischen Titrationsfehlers ein Verfahren angegeben, das sich durch lineare Extrapolation hyperbolischer Titrationskurven bei amperometrischen, photometrischen und anderen instrumentellen Titrationen ergibt. Es wird angenommen, daß die Titration auf einer einstufigen Ionenassoziation $m\text{A} + n\text{B} \rightleftharpoons \text{A}_m\text{B}_n$ beruht und die gemessene physikalische Eigenschaft zwischen bekannten unteren und oberen Grenzwerten liegt. Das Verfahren eignet sich zur Endpunktsbestimmung, auch wenn die Titrationskurven stark gekrümmt sind, und zur Voraussage der besten experimentellen Bedingungen für eine gegebene Titration.

Résumé—On décrit une méthode pour l'estimation d'une erreur de titrage systématique qui est introduite par extrapolation linéaire de courbes de titrage hyperboliques dans les titrages ampérométriques, photométriques et autres titrages instrumentaux. Il est admis que le titrage est basé sur une réaction d'association ionique en un seul stade, $m\text{A} + n\text{B} \rightleftharpoons \text{A}_m\text{B}_n$ et que la propriété physique mesurée se situe entre des valeurs minimale et maximale connues. La technique convient pour la détermination de la fin de réaction, même quand les courbes de titrage ont une courbure accentuée, et pour prédire le choix des conditions expérimentales optimales pour un titrage donné.

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SHORT COMMUNICATIONS

α -(Phenylazo)-4-nitrobenzyl cyanide, a new acid-base indicator

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THERE are few acid-base indicators applicable in strongly alkaline medium. In an earlier paper¹ was recommended the use of the 4-nitro- and 2,4-dinitrophenylhydrazones of *p*-nitroacetophenone as new acid-base indicators for the titration of weak acids. In this paper a further new indicator is described, α -(phenylazo)-4-nitrobenzyl cyanide. This compound can be prepared from benzyl cyanide by means of nitration and coupling with diazotized aniline. Indicator constants in mixtures of organic solvent and water have been determined on the basis of absorption spectra, according to the method used for the determination of the dissociation constants of Methyl Red in a mixture of alcohol and water² and according to our earlier method.

EXPERIMENTAL

Preparation of α -(phenylazo)-4-nitrobenzyl cyanide

4-Nitrobenzyl cyanide. To 2.9 g of benzyl cyanide add 2.5 ml of 94–98% nitric acid dropwise with stirring, at below 30°, then stir for 30 min more. Pour the mixture into 50 ml of water and neutralize with alkali. Filter off the separated product and recrystallize it from alcohol. Yield 1.4 g, m.p. 116° (literature value 116–7°).

α -(Phenylazo)-4-nitrobenzyl cyanide. Dissolve 0.93 g of aniline in a mixture of 25 ml of 1M hydrochloric acid and 5 ml of water and add 0.69 g of sodium nitrite. Filter the diazonium salt solution and add it to 1.62 g of nitrobenzyl cyanide dissolved in 110 ml of ethanol, then neutralize the solution with 1M sodium hydroxide. Filter off the separated product and dry it at 100°. Yield 0.6 g, m.p. 201°. The substance is used as a 0.1% solution in 96% ethanol.

Determination of the dissociation constant

To a glycol and sodium hydroxide buffer solution of known pH add enough organic solvent to give the required amount in a volume of 10 ml, and then 10 drops of 0.1% solution of indicator. Record the absorption spectrum. From the absorption spectra for various solvent media and pH values the dissociation constants of the indicator can be calculated according to our earlier work.³

Titration of weak acids

Dissolve about 1 mequiv of the weak acid in 50 ml of ethanol or acetone, or aqueous ethanol or acetone, add 10 drops of indicator solution and titrate with 0.1M aqueous sodium hydroxide (magnetic stirring).

DISCUSSION

Indicator constants

Figures 1 and 2 show the absorption spectra of the indicator dissolved in water and 75% ethanol and the method of calculation of the pK values therefrom. Table I lists the dissociation constants, absorption maxima and isosbestic points of the indicator.

Functioning of the indicator

p-Nitrobenzyl cyanide is also an acid-base indicator. This behaviour is due to the presence of the cyanide group. In consequence of the strongly electron-attracting cyanide group, an active methylene group comes into being, which easily dissociates a proton to form a nitronic acid. A more advantageous indicator property is gained, if *p*-nitrobenzyl cyanide is coupled with diazotized aniline. The acid colour of α -(phenylazo)-4-nitrobenzyl cyanide is yellow, the alkaline colour violet. The violet

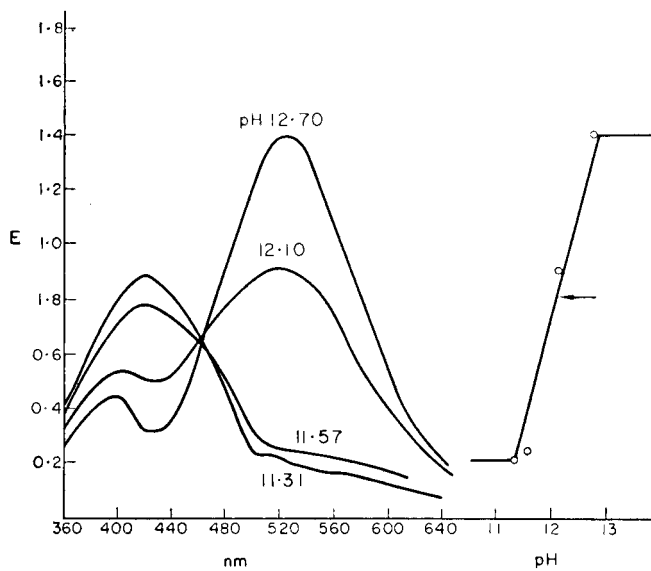


FIG. 1.—Absorption spectra of indicator in aqueous solution at various pH values, and plot of absorbance (E) at 520 nm vs. pH.

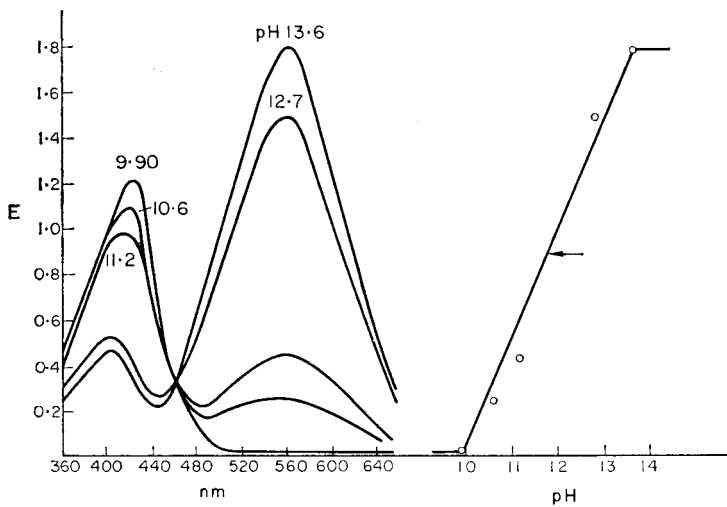
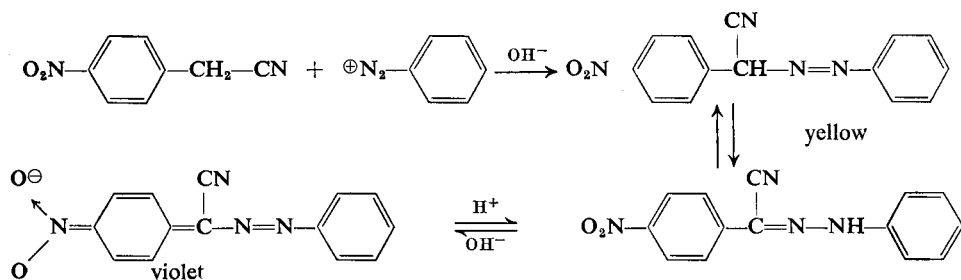


FIG. 2.—Absorption spectra of ethanolic indicator solution at various pH values, and plot of absorbance (E) at 560 nm vs. pH.

TABLE I.—INDICATOR CONSTANTS IN MIXTURES OF ORGANIC SOLVENT AND WATER

Solvent	λ_{\max} , nm	Isosbestic point, nm	Apparent pK
water	520	460	12.10
25% ethanol	540	460	11.10
50% ethanol	560	460	11.35
75% ethanol	560	460	11.75
25% acetone	540	460	11.20
50% acetone	560	464	10.80
75% acetone	560	465	10.30

colour in alkaline medium is due to the nitronic acid structure:



The indicator constants of α -(phenylazo)-4-nitrobenzyl cyanide are markedly altered when the indicator is dissolved in an organic solvent. The absorption maximum of the indicator shifts 40 nm to longer wavelengths in acetone or in ethanol. This change may be explained by the fact that the indicator is less soluble and dissociated in water than in organic solvents.

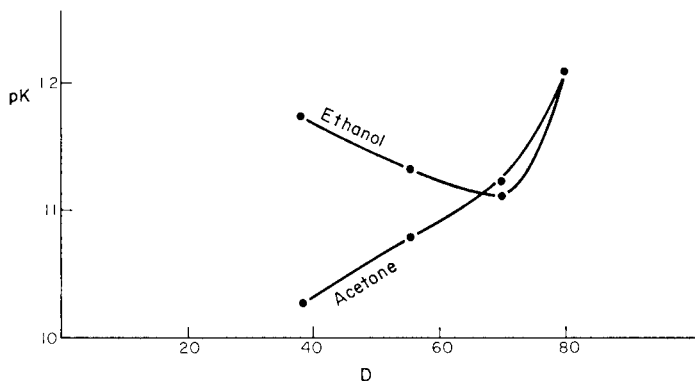


FIG. 3.—Variation of pK with dielectric constant of solvent medium.

When a weak acid carries no charge or is negatively charged, the value of pK increases in ethanolic or acetone medium.⁴ The case is reversed with a positively charged weak acid. In other words, in ethanol or in acetone, weak acids carrying no charge or a negative charge become still weaker, while positively charged weak acids become stronger. The weak acids in Table II and α -(phenylazo)-4-nitrobenzyl cyanide indicator belong to the first group. In Fig. 3 the pK values of the indicator are plotted as a function of the dielectric constant of the solvent. This figure shows that in acetone the pK value of α -(phenylazo)-4-nitrobenzyl cyanide decreases with decrease of the dielectric constant

of the medium, and in ethanol the value first decreases then increases slightly, but the pK value is always smaller in ethanol than in water. This property of α -(phenylazo)-4-nitrobenzyl cyanide is irregular and opposite to that of carboxylic acids. According to our earlier investigations¹ the pK value of phthalein indicators in acetone and ethanolic medium increases to a high degree, whereas that of nitronic acids is almost unchanged by variation of the dielectric constant of the medium. Though this irregular behaviour of α -(phenylazo)-4-nitrobenzyl cyanide is disadvantageous in titration of weak acids, nevertheless it becomes possible to titrate weak acids, using this indicator over a wide pK interval. The relatively strong trichloroacetic acid can also be titrated, with this indicator being used in acetone medium, as in this medium the pK value of weak carboxylic acids increases, while that of the indicator decreases. The weaker acids are to be titrated in ethanol or aqueous ethanol, where the pK values of the acids and the indicator are only slightly changed.

Results

Table II shows results obtained with the indicator used in titrations with 0.1M sodium hydroxide, in aqueous ethanol and acetone media. All three protons of citric acid can be titrated.

TABLE II.—TITRATION OF WEAK ACIDS (100% PURE)

Acid	Medium	Colour change	Error in titration, %
Tartaric	ethanol	yellow \rightarrow violet-red	+0.6
Trichloroacetic	acetone	yellow \rightarrow violet	-0.2
Citric	20% ethanol	yellow \rightarrow pink	0
Salicylic	acetone	yellow \rightarrow violet	-0.8
Monochloroacetic	acetone	yellow \rightarrow violet	+0.6
Nicotinic	20% ethanol	yellow \rightarrow pink	-0.5
Anthranilic	ethanol	yellow \rightarrow violet-red	0
4,6-Dinitro- <i>o</i> -cresol	ethanol	yellow \rightarrow pink	+0.6

When 1 mequiv of sodium tartrate was dissolved in a mixture of 20 ml of water and 30 ml of ethanol and 10 drops of 0.1% indicator solution were added, the addition of 0.06 ml of 0.1M sodium hydroxide produced the transition colour. This 0.06 ml is the indicator error, and should be deducted from the result of the titration.

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Summary—A new acid-base indicator, α -(phenylazo)-4-nitrobenzyl cyanide, is proposed. The indicator changes colour from yellow to violet in the presence of alkali owing to the formation of a nitronic acid structure. This indicator is applicable for the titration of weak acids in acetone and ethanol media or in a mixture of these organic solvents and water, with 0.1M aqueous sodium hydroxide as titrant. The absorption spectra have been recorded for the indicator in 25%, 50% and 75% aqueous ethanol and acetone. By means of the spectra the dissociation constants in these media have been determined. The pK value of α -(phenylazo)-4-nitrobenzyl cyanide is 12.10 in water, and is decreased considerably in acetone but only slightly in ethanol. This behaviour is similar to that of positively charged weak acids and irregular for a weak acid carrying no charge or a negative charge.

Zusammenfassung—Ein neuer Säure-Base-Indikator, α -(Phenylazo)-4-nitrobenzylcyanid, wird vorgeschlagen. Der Indikator ändert seine Farbe in Gegenwart von Alkali von Gelb nach Violett, wobei sich eine Nitronsäuregruppierung bildet. Er ist zur Titration schwacher Säuren in Aceton- und Äthanolmedien oder einem Gemisch dieser organischen Lösungsmittel mit Wasser geeignet, wobei 0,1M wäßriges Natriumhydroxid als Titrant dient. Die Absorptionsspektren des Indikators wurden in 25%, 50% und 75% wäßrigem Äthanol und Aceton registriert. Mit Hilfe der Spektren wurden die Dissoziationskonstanten

in diesen Medien bestimmt. Der pK -Wert von α -(Phenylazo)-4-nitrobenzylcyanid beträgt 12,10 in Wasser und sinkt in Aceton beträchtlich, in Äthanol nur schwach. Dieses Verhalten entspricht dem von positiv geladenen schwachen Säuren; für eine schwache Säure ohne Ladung oder mit negativer Ladung ist es ungewöhnlich.

Résumé—On propose un nouvel indicateur acide-base, l' α -(phénylazo) 4-nitrobenzyl cyanure. La coloration de l'indicateur passe du jaune au violet en la présence d'alcali par suite de la formation d'une structure acide nitronique. Cet indicateur est applicable au titrage d'acides faibles en milieux acétone et éthanol ou dans un mélange de ces solvants organiques et d'eau, avec comme agent de dosage la soude aqueuse 0,1*M*. On a enregistré les spectres d'absorption de l'indicateur en éthanol et acétone aqueux à 25%, 50% et 75%. Au moyen des spectres, on a déterminé les constantes de dissociation dans ces milieux. La valeur du pK de l' α -(phénylazo) 4-nitrobenzyl cyanure est de 12,10 dans l'eau et décroît considérablement en acétone mais seulement légèrement en éthanol. Ce comportement est semblable à celui d'acides faibles chargés positivement et irrégulier pour un acide faible ne portant pas de charge ou portant une charge négative.

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Gas-chromatographic determination of ultramicro amounts of selenium in pure sulphuric acid

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SPECTROPHOTOMETRIC,^{1,2} fluorimetric^{3,4} and catalytic⁵ methods for the determination of selenium are based on the formation of selenenols which are quantitatively made from selenium(IV) and aromatic *o*-diamines such as 3,3'-diaminobenzidine or 2,3-diaminophthalene. Tanaka and Kawashima⁶ have presented a critical study of some 4-substituted *o*-phenylenediamines as spectrophotometric reagents for selenium. Nakashima and Tōei⁷ have recently proposed a very sensitive gas-chromatographic procedure for selenium by electron-capture detection of 5-chloropiaselenol. The present paper describes the gas chromatographic determination of selenium in pure sulphuric acid.

Lovelock⁸ has shown that the nitro group in an organic substance is more sensitive than the chlorine group to electron-capture detection. Hence 4-nitro-*o*-phenylenediamine is used as reagent in the gas chromatographic determination of selenium. As the oxidation number of selenium in pure sulphuric acid is not four but zero because of the reducibility by trace amounts of sulphurous acid, a bromine-bromide redox buffer is used for the conversion of elemental selenium into selenous acid.

EXPERIMENTAL

Reagents

4-Nitro-*o*-phenylenediamine hydrochloride solution. A 1% acidic solution is stable at room temperature for at least a week.

Stock selenium solution, 1 mg/ml. Selenium dioxide (351.3 mg) dissolved in 250 ml of distilled water. Diluted to provide working solutions.

Stock bromine-bromide redox buffer solution (0.1*M* bromine—0.2*M* bromide). Bromine water (saturated, 45.7 g) and potassium bromide (2.38 g), diluted to 100 ml with distilled water. Diluted to provide working solutions.

Selenium-free concentrated sulphuric acid. Dilute 100 ml of concentrated sulphuric acid with an equal volume of water, add 20 ml of 48% hydrobromic acid and heat strongly till dense white fumes appear.

Apparatus

A Shimadzu Model GC-3AE gas chromatograph (Kyoto, Japan) equipped with an electron-capture detector was used. The glass column (1 m long, 4 mm bore) was packed with 15% SE-30 on 60-80 mesh Chromosorb W. The column and detector temperature was maintained at 200°. The nitrogen flow-rate was 44 ml/min.

Procedure

Put 1 ml (1.8 g) of sulphuric acid into a 100-ml beaker containing 10 ml of water and 3 ml of $10^{-3}M$ bromine-bromide redox buffer, and heat the solution in a hot water-bath for 20 min. Cool the solution and transfer it to a 100-ml separatory funnel, using 10 ml of distilled water for rinsing. Add 2 ml of 1% 4-nitro-*o*-phenylenediamine solution and let stand for 2 hr. Extract the 5-nitropiaselenol into 1 ml of toluene by shaking for 5 min. Inject 5 μ l of the extract into the gas chromatograph column and measure the height of the peak with 3.7-min retention time (Fig. 1).

Prepare a calibration curve by adding known amounts of selenous acid to selenium-free sulphuric acid, or from guaranteed purity sulphuric acid without using the oxidation procedure.

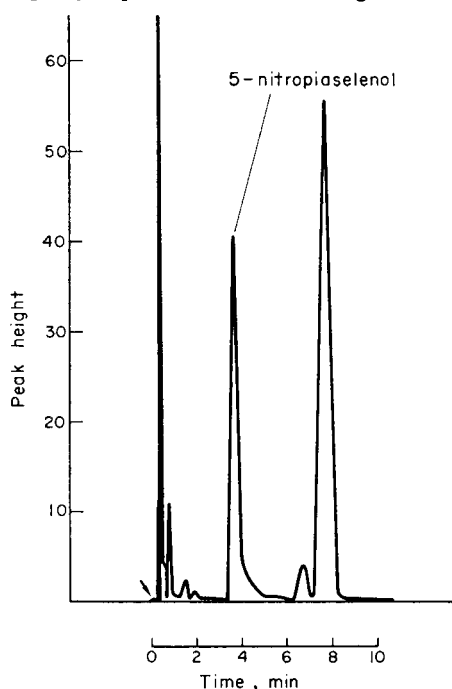


FIG. 1.—Gas chromatogram of 5-nitropiaselenol.
Column 15% SE30/Chromosorb W in 1 m \times 4 mm glass column.
Carrier gas nitrogen, flow-rate 44 ml/min. Sample 5 μ l (0.12 μ g Se/ml).

RESULTS AND DISCUSSION

It was found that selenium(IV) reacts quantitatively with the reagent to form 5-nitropiaselenol, if there is a 50000-fold molar excess of reagent; 2 ml of the reagent solution were therefore used. It was shown earlier⁶ that 4-nitro-*o*-phenylenediamine does not react quantitatively with selenium(IV) at pH above 2. The reaction time at room temperature was measured at pH 0 and 1 and it was found that the reaction was complete in 1 hr. As expected, heating hastened the reaction and 5 min at 100° are sufficient for complete reaction. It was found that with 1 ml of toluene the volume of aqueous phase could be varied from 20 to 50 ml without effect on the efficiency of extraction.

As selenium in sulphuric acid is present as selenium(0) because of reduction by sulphurous acid, the selenium must be oxidized to selenous acid. The bromine-bromide redox buffer used has a standard potential of +1.09 V, and selenous acid is stable between +0.74 and +1.15 V at pH 0. Oxidation was shown to be complete by recovery experiments with 0.053 μg of amorphous selenium treated with 2 ml of $10^{-3}M$ bromine-bromide solution in a hot water-bath (about 90°) for 20 min. The recovery of the selenium was between 96 and 106%.

The minimum molar excess of buffer needed was found to be 1500-fold relative to selenium, but at room temperature must not exceed 7500-fold, or turbidity appears and affects the extraction; 7 ml of $10^{-3}M$ redox buffer is the maximum permissible.

The oxidation is complete in 10 min at the temperature of a hot water-bath ($\sim 90^\circ$) and in 20 min at room temperature.

The determination of selenic acid by this method was not successful, because selenium(VI) was not reduced to selenous acid by the redox buffer and selenium(VI) did not react with 4-nitro-*o*-phenylenediamine. Selenium in commercial pure sulphuric acid was determined and the result checked for accuracy by spiking the sample with 0.030 μg of selenium(IV). The results are shown in Table I.

TABLE I.—SELENIUM CONTENT OF SULPHURIC ACID

Supply company	Se, $10^{-6}\%$	
	Analytical grade reagent	Extra pure reagent
A	1.8	9.4
B	1.9	2.5
C	5.3	2.4
D	5.0	1.3
E	2.6	3.2

As the sensitivity of an electron-capture detector tends to vary during operation, the gas chromatograms should be run successively and an unknown content of selenium should be determined along with standard samples which contain similar amounts of selenium. The proposed procedure should find wide application where ultramicro amounts of selenium are to be determined. Its outstanding features are that it is simple, highly sensitive and rapid, and no special skill is necessary.

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Summary—Ultramicro amounts of selenium in pure sulphuric acid are converted into selenous acid with a bromine-bromide redox buffer solution. The selenous acid reacts quantitatively with 4-nitro-*o*-phenylenediamine to form 5-nitropiaselenol which can be extracted into toluene. The extract is very sensitive to electron-capture detection in gas chromatography, and the sensitivity is higher than that of 5-chloro- or 4,5-dichloro-piaselenol. The calibration curve (peak heights) is linear up to 0.15 μg of selenium in 1 ml of toluene. Pure sulphuric acid, commercially available, contains $10^{-6} \sim 10^{-5}\%$ selenium.

Zusammenfassung—Ultramikromengen Selen in reiner Schwefelsäure werden mit einer Brom-Bromid-Redoxpufferlösung in selenige Säure übergeführt. Die selenige Säure reagiert mit 4-Nitro-*o*-phenylen-diamin quantitativ zu 5-Nitropiaselenol, das in Toluol extrahiert werden kann. Der Extrakt ist durch Gaschromatographie mit Elektroneneinfangdetektor sehr empfindlich nachzuweisen; die Empfindlichkeit ist höher als bei 5-Chlor- oder 4,5-Dichlorpiaselenol. Die Eichkurve (in Peakhöhen) ist linear bis 0,15 μg Selen in 1 ml Toluol. Handelsübliche reine Schwefelsäure enthält 10^{-6} bis $10^{-5}\%$

Résumé—On convertit des ultra-microquantités de sélénium dans l'acide sulfurique pur en acide sélénieux par une solution tampon redox brome-bromure. L'acide sélénieux réagit quantitativement avec la 4-nitro *o*-phénylènediamine pour former le 5-nitropiasélénol qui peut être extrait en toluène. L'extrait est très sensible à la détection par capture d'électrons en chromatographie en phase galeuse, et la sensibilité est plus élevée que celle du 5-chloroou du 4,5-dichloropiasélénol. La courbe d'étalonnage (hauteurs de pic) est linéaire jusqu'à 0,15 μg de sélénium dans 1 ml de toluène. L'acide sulfurique pur, commercialement accessible, contient $10^{-6} \sim 10^{-5}\%$ de sélénium.

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Stability constants of lanthanide complexes with salicylhydroxamic acid

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SALICYLHYDROXAMIC ACID (SHA) forms lanthanide complexes which may be of analytical value. The present paper describes the determination of their stability constants in 3:1 v/v acetone–water medium. They have limited solubility in water but are soluble in the mixed solvent medium.

EXPERIMENTAL

Reagents

Lanthanide perchlorates. The corresponding oxides (99%, Johnson Matthey) were digested in perchloric acid and the excess of perchloric acid was removed by evaporation. The solutions were diluted to the desired concentration and were standardized by conventional methods.

Salicylhydroxamic acid. Prepared by the method of Ray and Bhaduri.¹

The other chemicals used were of reagent grade.

Procedures

The general procedure consists of the titration with standard sodium hydroxide solution of 50 ml of acetone–water mixture (3:1 v/v) having metal ion concentration $\sim 2 \times 10^{-3}M$, reagent concentration $\sim 1 \times 10^{-2}M$, and sodium perchlorate in sufficient amount to maintain an ionic strength of 0.1. After each addition of a definite amount of alkali and stirring, the pH values were recorded with a Cambridge pH-meter with glass and calomel electrodes. Stirring was effected with a magnetic stirrer. The pH-meter was calibrated with aqueous buffers (pH 4.00 and 9.18) before and after titration. All titrations were carried out at $25 \pm 0.5^\circ$. The acid dissociation constant of the ligand was determined by the same procedure but with the omission of the metal ion.

Calculations

Standard procedures were followed and the formation constants of the first two stages of reaction, K_1 and K_2 , were evaluated graphically by using the equation

$$\frac{\bar{n}}{(1 - \bar{n})[R^-]} = \frac{(2 - \bar{n})[R^-]}{(1 - \bar{n})} \cdot K_1 K_2 + K_1$$

and the last two stages, K_2 and K_3 , were evaluated by using the equation

$$\frac{(1 - \bar{n})}{(2 - \bar{n})[R^-]} = \frac{(3 - \bar{n})[R^-]}{(2 - \bar{n})} \cdot K_2 K_3 + K_2$$

where \bar{n} is the average ligand number, R^- is the ligand and $K_n = [LnR_n]/[LnR_{n-1}][R^-]$, Ln denoting a lanthanide(III) ion.

The significance of pH in acetone-water mixtures in which formation constants of rare earth complexes have been previously evaluated has been discussed.²

DISCUSSION

The value of the acid dissociation constant of the reagent and formation constants of rare earth-salicylhydroxamic acid complexes are given in Table I.

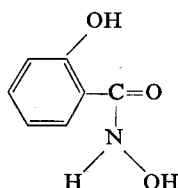
TABLE I.—FORMATION CONSTANTS OF RARE EARTH-SALICYLHYDROXAMIC ACID COMPLEXES

Metal ion	Log K_1	Log K_2	Log K_3	Log β_3
La ³⁺	6.30	5.96	4.90	17.16
Pr ³⁺	6.94	6.50	4.98	18.42
Nd ³⁺	7.03	6.64	5.10	18.77
Sm ³⁺	7.20	6.77	5.01	18.98
Eu ³⁺	7.40	6.84	5.04	19.28
Gd ³⁺	7.35	6.80	4.60	18.75
Dy ³⁺	7.72	7.00	5.06	19.78
Er ³⁺	7.82	7.03	5.10	19.93
Yb ³⁺	8.13	7.25	*	
Y ³⁺	7.24	6.50	*	

Temperature 25 + 0.5°C; ionic strength 0.1, pK_a, 8.86.

* Precipitation occurs.

Salicylhydroxamic acid (I) can behave as a monobasic and dibasic acid:



Consequently, the complexes of praseodymium, neodymium and samarium have been prepared and analysed. The composition is MR_3 as shown by the typical analysis: found, Sm_2O_3 , 28.8%; C, 41.6%; H, 3.0%; N, 7.9%; calculated, Sm_2O_3 , 29.07%; C, 41.05%; H, 3.01%; N, 7.82%.

However, for a dibasic acid where $pK_2 \gg pK_1$ the highest complex species is formed well before the second stage of ionization of the acid begins, and the formation function may be derived by assuming the ligand to be monobasic. In fact, the maximum \bar{n} values reached in our present experiments are ~ 2.5 which also supports our assumption of 1:3 complex formation.

The formation constants increase fairly regularly with decrease in ionic radius, with the gadolinium complex being less stable than predicted from simple ionic considerations.

In general $\log K_1 > \log K_2 > \log K_3$ for a given metal ion. However, the differences in the values between the three constants are not much, indicating that there is almost equal tendency for the formation of neutral complex species LnR_3 as for LnR^{2+} .

The overall stability constants, β_3 , of rare earth salicylhydroxamates are comparable with those of complexes of oxygen-donating ligands such as benzoylacetone and benzoylphenylhydroxylamine complexes, measured in the same solvent mixture. The dissociation constants (pK_a) of salicylhydroxamic acid, benzoylacetone³ and benzoylphenylhydroxylamine³ are 8.86, 9.58 and 10.26 respectively. It is expected that the rare earth complexes derived from salicylhydroxamic acid would be weaker than complexes derived from the other two. In fact, the average values of $\log \beta_3$ of rare earth benzoylacetones and benzoylphenylhydroxylamines are ~ 20 and 21 respectively, which are greater than

those of the salicylhydroxamic acid complexes, ~ 19 . It was not possible to determine $\log K_3$ for ytterbium and yttrium because of precipitation of their complexes even when their \bar{n} values reached ~ 2 .

From the stability constants it can be deduced that if the physical characteristics of the precipitate are satisfactory, salicylhydroxamic acid might be as successful as benzoyl phenylhydroxylamine⁴ for the gravimetric determination of the lanthanides.

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Summary—The stability constants of La, Pr, Nd, Sm, Eu, Gd, Dy, Er, Yb and Y complexes of salicylhydroxamic acid have been determined potentiometrically in 3:1 v/v acetone-water medium at $25 \pm 0.5^\circ$ and at an ionic strength of 0.1 with respect to sodium perchlorate. The stability constants are comparable with those of other lanthanide complexes with oxygen-donating ligands such as benzoylacetone and benzoylphenylhydroxylamine.

Zusammenfassung—Die Stabilitätskonstanten der Komplexe von La, Pr, Nd, Sm, Eu, Gd, Dy, Er, Yb und Y mit Salicylhydroxamsäure wurden potentiometrisch in 3:1 (v/v) Aceton-Wasser-Medium bei $25 \pm 0,5^\circ$ und einer Ionenstärke von 0,1 an Natriumperchlorat ermittelt. Die Stabilitätskonstanten sind vergleichbar mit denen anderer Komplexe von Lanthaniden mit über Sauerstoff koordinierenden Liganden wie Benzoylacetone und Benzoylphenylhydroxylamin.

Résumé—On a déterminé potentiométriquement les constantes de stabilité des complexes de La, Pr, Nd, Sm, Eu, Gd, Dy, Er, Yb et Y avec l'acide salicylhydroxamique en milieu acétone-eau 3:1 (v/v) à $25 \pm 0,5^\circ$ et pour une force ionique de 0,1 en ce qui concerne le perchlorate de sodium. Les constantes de stabilité sont comparables à celles d'autres complexes de lanthanides avec des ligands donateurs d'oxygène tels que la benzoylacetone et la benzoylphénylhydroxylamine.

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Complexometric determination of molybdenum(VI)

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OF THE methods proposed for the complexometric determination of molybdenum, only those based on the formation of the stable Mo(V)-EDTA complex have been of practical value. This intensely yellow complex, with composition $(\text{MoO}_2)_2\text{Y}^{2-}$ (where H_4Y is EDTA) is formed by reduction of molybdate in strongly acidic medium with hydrazine sulphate in the presence of EDTA. The excess of EDTA is then (after adjustment to the proper pH) titrated with a suitable cation and corresponding indicator, for example with copper sulphate and PAN¹⁻³ or calcein,⁴ lead and Xylenol Orange,⁵ iron(III) and sulphosalicylic acid,⁶ or zinc and alizarin complexone⁷ or Eriochrome Black T.⁸

Yaguchi and Kajiwara⁹ studied the reaction of molybdenum with hydroxylamine hydrochloride and found that a 1:1 complex is formed, but wrongly assumed that on addition of EDTA a Mo(V)-complex is formed. Lassner and Schedle¹⁰ in a critical paper stated that when molybdate solution is boiled with hydroxylamine (HyOH) hydrochloride no reduction takes place and that a 1:1:1 ternary complex Mo(VI)-HyOH-EDTA is formed. This ternary complex is more stable than the simple Mo(VI)-EDTA complex. Molybdenum cannot be displaced from it by copper at pH 4.5 and is only slowly displaced by bismuth at pH 2.

A complexometric method based on the formation of this 1:1:1 complex should be superior to all previous ones, because twice as much EDTA is required per mole of molybdenum. However, the authors¹⁰ mentioned as disadvantages the poor selectivity, the need to use an empirical factor, and the unsuitability of the method in the presence of tungsten.

Recently, Lassner *et al.*¹¹ mentioned that similar complexes are formed by DCTA and NTA, but made no attempt to exploit them for determination of molybdenum. We can expect that use of DCTA would be superior to use of EDTA because DCTA forms more stable complexes, and displacement reactions (which might interfere in back-titrations) proceed slowly or not at all.

We have found that a very stable Mo-HyOH-DCTA complex is formed on prolonged boiling of molybdenum solutions with hydroxylamine. The excess of DCTA can easily be titrated with zinc chloride at pH 5 (hexamine buffer) or even with thorium nitrate at pH 3-4, Xylenol Orange being used as indicator in both cases. The displacement of molybdenum with zinc proceeds so slowly, that at the end-point the red colour of the zinc-Xylenol Orange lasts for at least 3 min. In addition we have found that phosphate, up to a 1:1 concentration ratio relative to molybdenum, does not interfere and that the displacement is then even slower than in its absence. Larger amounts of phosphate (*e.g.*, 10:1 ratio) obscure the end-point. We have also found very simple conditions for reliable determination of molybdenum in the presence of large amounts of tungstate.

A similar reaction with TTHA (triethylenetetraminehexa-acetic acid) leads to the formation of a 2:1 complex. Back-titration with zinc gives a less sharp end-point, however, making this reaction inconvenient for analytical purposes. DTPA, which forms a 1:1:1 complex in acidic medium, is also unsuitable.

EXPERIMENTAL

Reagents

Ammonium molybdate, 0.05M. Standardized gravimetrically with 8-hydroxyquinoline.

Other reagents include 0.05M solutions of zinc chloride, thorium nitrate, EDTA and DCTA; 10% hexamine solution and 0.5% Xylenol Orange solution. Solid hydroxylamine hydrochloride is used (a solution is unsuitable).

Determination of molybdenum

Procedure. To the nearly natural solution of molybdenum (containing 5-40 mg of Mo) add

TABLE I.—DETERMINATION OF MOLYBDENUM

Mo taken, mg	0.05M DCTA added, ml	Back-titration		Mo found, mg	Error, mg
		0.05M Zn, ml	0.05M Th, ml		
2.06	2.87	2.58	—	1.3 ₆	-0.6 ₇
2.06	4.79	4.40	—	1.8 ₇	-0.1 ₈
4.12	1.91	1.05	—	4.1 ₃	+0.0 ₁
4.12	2.87	—	1.82	4.0 ₈	-0.0 ₄
4.12*	4.79	3.95	—	4.0 ₈	-0.0 ₈
20.61	9.80	3.95	—	20.6 ₃	+0.0 ₂
20.61†	6.70	‡	—	—	—
41.21	11.76	3.17	—	41.2 ₁	0
41.21	11.76	—	3.22	40.9 ₇	-0.2 ₄
61.82	23.93	—	10.77	63.1 ₃	+1.3 ₁
61.82	23.93	10.55	—	64.1 ₈	+2.3 ₈
82.42	23.93	6.40	—	84.0 ₉	+1.6 ₇

* Added 50 mg Na₂HPO₄.

† Added 500 mg Na₂HPO₄.

‡ Bad end-point.

1–2 g of hydroxylamine hydrochloride, dilute to 150–200 ml and heat to boiling. The solution becomes yellow or slightly blue-green, depending on the molybdenum concentration. Add excess of DCTA and boil the solution (pH 4.5) for a further 15 min. The solution turns yellow or yellow-green. Cool, add hexamine solution to adjust the pH to 5–5.5, add a few drops of Xylenol Orange and titrate with 0.05M zinc to a red-violet colour which lasts at least 3 min.

Results. Good results were obtained for 5–40 mg of molybdenum (Table I). For smaller amounts than 5 mg the results are low, for higher amounts than 40 mg the results are high. The back-titration can also be carried out with thorium nitrate at pH 3–4. At pH <3 a slightly red colour appears before the end-point and makes the end-point more difficult to discern.

Determination of molybdenum in the presence of tungsten

We have found that this method can also be used in the presence of tungsten, provided that sufficient hydroxylamine hydrochloride (10 g) is used for formation of the Mo–HyOH–DCTA complex. The procedure is the same as described above. Table II shows the influence of hydroxylamine

TABLE II.—EFFECT OF HYDROXYLAMINE HYDROCHLORIDE ON THE DETERMINATION OF MO IN THE PRESENCE OF W

HyOH added, g	Mo taken, mg	W added, mg	0.05M DCTA, ml	Back-titration 0.05M Zn, ml	Mo found, mg	Error, mg
1	12.36	184	4.79	4.75	0.1 ₉	–12.1 ₇
2	12.36	184	4.79	3.50	6.1 ₉	–6.1 ₇
3	12.36	184	4.79	2.80	9.5 ₅	–2.7 ₉
4	12.36	184	4.79	2.30	11.9 ₄	–0.4 ₂
5	12.36	184	4.79	2.25	12.1 ₉	–0.1 ₇
5	12.36	276	4.79	3.60	5.7 ₁	–6.6 ₅
7	12.36	276	4.79	2.33	11.8 ₀	–0.5 ₄
10	12.36	276	4.79	2.20	12.4 ₂	+0.0 ₅
10	12.36	368	4.79	2.30	11.9 ₄	–0.4 ₂

hydrochloride, Table III summarizes results for molybdenum determination in the presence of up to 276 mg of tungsten. It can be seen that EDTA is a less satisfactory reagent.

Boiling solutions containing only molybdenum, tungsten and hydroxylamine are highly coloured (yellow to intense yellow-green). After addition of DCTA the resulting colour is green or blue-green depending on the amount of tungsten present. For this reason the amount of tungsten is limited to

TABLE III.—DETERMINATION OF MO IN THE PRESENCE OF W

Mo taken, mg	W taken, mg	0.05M DCTA, ml	0.05M EDTA, ml	Back-titrn.		Mo found, mg	Error, mg
				Zn, ml	Th, ml		
4.12	9.2	4.79	—	3.95	—	4.0 ₃	–0.0 ₉
4.12	27.5	4.79	—	3.95	—	4.0 ₃	+0.0 ₉
4.12	92.0	4.79	—	3.93	—	4.1 ₃	+0.0 ₁
4.12	230.0	2.87	—	2.03	—	4.0 ₃	–0.0 ₉
4.12	276.0	4.79	—	4.00	—	3.7 ₉	–0.3 ₃
12.36	92.0	—	9.71	6.80	—	13.9 ₆ *	+1.6 ₀
12.36	9.2	—	4.86	—	2.64	10.6 ₄	–1.7 ₂
4.12	276.0	—	4.86	3.85	—	4.8 ₄ *†	+0.7 ₂
20.61	46.0	—	9.71	4.90	—	23.0 ₇ *	+1.4 ₆
20.61	46.0	9.57	—	5.25	—	20.7 ₂	+0.1 ₁
41.21	92.0	16.27	—	7.70	—	41.2 ₅ ‡	+0.0 ₄
8.24	276.0	4.79	—	—	3.17	7.7 ₇	–0.4 ₇
20.61	9.2	9.57	—	—	5.22	20.8 ₆	+0.2 ₅
41.21	184.0	14.35	—	—	5.82	40.9 ₂	–0.2 ₉

* Fast displacement.

† Unsharp end-point.

‡ Average of three determinations.

300 mg/500 ml. Dilution to 500 ml is without effect on the Mo determination. Back-titration with thorium nitrate is less reliable at higher concentrations of tungsten and is recommended only for smaller amounts of tungsten. Generally the solutions have to be boiled at pH 4.5–5. At lower pH the formation of the Mo–HyOH–DCTA complex is not quantitative, probably on account of formation of Mo–W polycations (see ref. 10).

That a very large excess of hydroxylamine is needed may be due to catalysis by molybdenum(VI) of the decomposition of hydroxylamine,¹² besides the decomposition occurring on boiling.

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Summary—In acidic medium molybdenum(VI) forms a stable complex on boiling with excess of DCTA and hydroxylamine hydrochloride. Molybdenum can then be determined by back-titration of the excess of DCTA either with zinc chloride at pH 5–5.5 or with thorium nitrate at pH 3–4.5, Xylenol Orange being used as indicator in both cases. A simple method for the determination of molybdenum in the presence of moderate amounts of tungsten is also described.

Zusammenfassung—In saurem Medium bildet Molybdän(VI) beim Kochen mit überschüssiger DCTA und Hydroxylaminhydrochlorid einen stabilen Komplex. Molybdän kann dann durch Rücktitration der überschüssigen DCTA mit Zinkchlorid bei pH 5–5,5 oder mit Thoriumnitrat bei pH 3–4,5 bestimmt werden, wobei beidesmal Xylenolorange als Indikator dient. Ein einfaches Verfahren zur Bestimmung von Molybdän in Gegenwart mäßiger Mengen Wolfram wird ebenfalls angegeben.

Résumé—En milieu acide, le molybdène(VI) forme un complexe stable par ébullition avec un excès de DCTA et de chlorhydrate d'hydroxylamine. On peut alors doser le molybdène par titrage en retour de l'excès de DCTA soit avec le chlorure de zinc à pH 5–5,5, soit avec le nitrate de thorium à pH 3–4,5, l'Orangé Xylénol étant utilisé comme indicateur dans les deux cas. On décrit aussi une méthode simple pour le dosage du molybdène en la présence de quantités peu élevées de tungstène.

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The dissociation constants of alizarin fluorine blue

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SINCE the introduction of the method by Belcher, Leonard and West in 1958,¹ the formation of a blue complex between alizarin fluorine blue (3-aminomethylalizarin-*N,N*-diacetic acid), cerium(III)

or lanthanum(III), and fluoride has become accepted as a valuable spectrophotometric procedure for the determination of fluoride. Earlier work had shown its suitability as an indicator in EDTA titrations,² and it has been proposed for the spectrophotometric determination of uranyl ion.³ For satisfactory prediction of optimum conditions in its use, the acid dissociation constants of alizarin fluorine blue have been determined by potentiometric titration (glass electrode). The importance of adequate data on the equilibrium constants of organic reagents has been emphasized by Ringbom, who has also mentioned the present scarcity of such information for reagents now in use.⁴

EXPERIMENTAL

Reagents

Alizarin fluorine blue. Thin-layer chromatography showed traces of alizarin, which were removed as far as possible by dissolving 1 g of alizarin fluorine blue in the minimum quantity of 0.5M sodium hydroxide (10–15 ml), diluting to 100 ml, adjusting the pH to 6.5–7.0 (the solution went deep wine-red) with hydrochloric acid and extracting with five 20-ml portions of methylene dichloride. The aqueous phase was then cooled in an ice-bath, and hydrochloric acid added dropwise until a heavy orange precipitate formed. After 2 hr the alizarin fluorine blue was filtered off, washed with ice-cold water, and dried in a vacuum desiccator at 50° over phosphorus pentoxide.

Alizarin fluorine blue disodium salt. Purified alizarin fluorine blue was weighed and suspended in water, under a nitrogen atmosphere, and the volume of sodium hydroxide required for half-neutralization was added from a micrometer syringe. The mixture was shaken till homogeneous, then water was removed by evaporation under vacuum. The damp solid remaining was dried at 50° over phosphorus pentoxide. The sodium content was checked by emission spectroscopy.

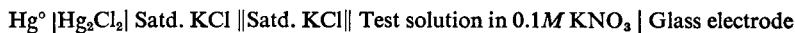
Potassium hydroxide solution. Analytical grade potassium hydroxide pellets in excess of the required weight were quickly washed with demineralized water, dried, and dissolved in demineralized water boiled free from air, about half the final volume being used. The solution was passed through a freshly regenerated column of IRA 400 ion-exchange resin (hydroxide form) into a polythene vessel, and washed through with demineralized water until the desired total volume was obtained. The solution was standardized potentiometrically with potassium hydrogen phthalate, and stored under nitrogen free from carbon dioxide.

Hydrochloric acid. Prepared by dilution of analytical grade acid and standardized potentiometrically with sodium carbonate.

Other reagents were analytical grade.

Apparatus

An Electronic Instruments Ltd. Model 39A Vibron vibrating capacitor pH meter, fitted with an E.I.L. type GHS 23 general purpose glass electrode, and a saturated calomel reference electrode. The cell used was



Procedure

The test solution was maintained at $25 \pm 0.1^{\circ}$ in a double-walled vessel, by circulating water from a thermostat, and stirred by a small glass paddle. To minimize electrical interference the titration vessel and stirrer motor were surrounded by earthed brass gauze screens, and the metal of the apparatus stand was earthed. Samples of test substance were weighed individually on a microbalance and titrated (micrometer syringe burette) at ionic strength 0.1 (potassium nitrate).

RESULTS AND DISCUSSION

Bjerrum defined the degree of formation \bar{n} of proton complexes, where \bar{n} gives the average number of protons attached. In dealing with dissociation of acids, it is more convenient to use a quantity $R = n - \bar{n}$, where n is the total number of dissociable protons; R then represents the average number of protons dissociated and it can be shown⁵ that

$$R = \frac{aC_a + [\text{H}^+] - [\text{OH}^-]}{C_a}$$

where C_a is the analytical concentration of the acid and a = eqivs. of base per mol.

Then, by applying the conditions of mass balance and electroneutrality to the solution, it eventually follows that

$$\sum_{i=0}^n (R - i)\lambda_i [\text{H}^+]^{n-i} = 0$$

where λ_i is the overall proton dissociation constant for the i th dissociation, defined by

$$\lambda_i = k_1 k_2 \dots k_i$$

This equation gives the relation between $[H^+]$ and the degree of neutralization for any polyprotic acid.

Alizarin fluorine blue has four ionizable protons, and so the equation contains four unknowns. However, since k_1 and k_2 are well separated from k_3 and k_4 the simplifying assumption can be made that alizarin fluorine blue behaves as a mixture of two dibasic acids, and values of k_1 and k_2 , and k_3 and k_4 , can be obtained by considering separately the appropriate regions of the titration curve.

For a dibasic acid the general equation becomes

$$R[H^+]^2 + (R - 1)k_1[H^+] + (R - 2)k_1k_2 = 0$$

or

$$\frac{(R - 1)}{Rk_2[H^+]} + \frac{1}{k_1k_2} = \frac{(2 - R)}{R[H^+]^2}$$

Values of k_1 and k_2 can be obtained from the slope and intercept of the resulting linear plot. For accurate calculation, pairs of values were chosen from the titration curve, and the k values obtained by solving the resulting equations simultaneously.

The nitrogen atom of the iminodiacetic acid group can be protonated, but the protonation constant was not determined. If it is sufficiently different from k_1 , the result for the latter will not be affected.

The main problem was the low solubility (approx. $5 \times 10^{-4}M$) of alizarin fluorine blue in water, and its slowness to dissolve. Mixed solvents do not improve the solubility sufficiently to justify their use with subsequent extrapolation to obtain a value for the dissociation constants in water. Since alizarin fluorine blue is readily soluble in alkali, the determination was carried out in two stages. Constants k_1 and k_2 were determined by dissolving the weighed sample in a known amount of potassium hydroxide solution and back-titrating with hydrochloric acid. To determine k_3 and k_4 the disodium salt of alizarin fluorine blue was titrated with potassium hydroxide. The higher solubility of the salt enabled a higher concentration to be used, with consequent improvement in the precision. The mean values and standard deviations of the constants found are $k_1 = 1.28 \pm 0.30 \times 10^{-5}$; $k_2 = 2.82 \pm 0.24 \times 10^{-8}$; $k_3 = 3.72 \pm 0.19 \times 10^{-11}$; $k_4 = 6.39 \pm 0.12 \times 10^{-12}$. A distribution diagram, showing the proportion of alizarin fluorine blue present in each ionized form at different

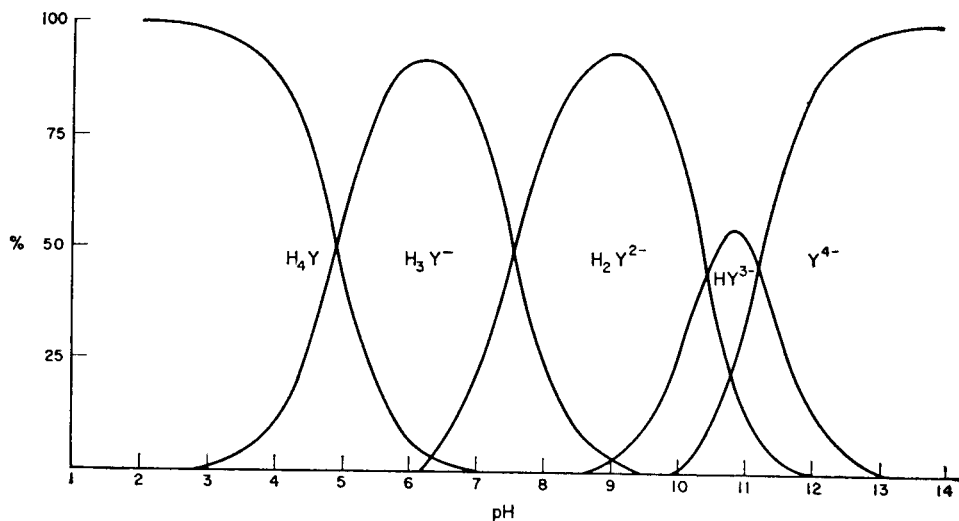
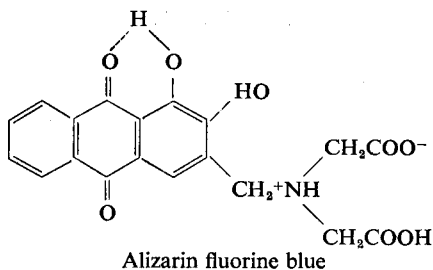


FIG. 1

pH values, is given in Fig. 1, where H_4Y represents the undissociated alizarin fluorine blue molecule.



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Summary—Dissociation constants for the analytical reagent alizarin fluorine blue (3-aminomethylalizarin-*N,N*-diacetic acid) have been determined by potentiometric titration at ionic strength 0.1, and are $k_1 = 1.28 \pm 0.30 \times 10^{-5}$; $k_2 = 2.82 \pm 0.24 \times 10^{-8}$; $k_3 = 3.72 \pm 0.19 \times 10^{-11}$; $k_4 = 6.39 \pm 0.12 \times 10^{-12}$.

Zusammenfassung—Die Dissoziationskonstanten des analytischen Reagens Alizarinfluorinblau (3-Aminomethylalizarin-*N,N*-diessigsäure) wurden durch potentiometrische Titration bei der Ionenstärke 0,1 ermittelt. Sie betragen $k_1 = 1,28 \pm 0,30 \cdot 10^{-5}$; $k_2 = 2,82 \pm 0,24 \cdot 10^{-8}$; $k_3 = 3,72 \pm 0,19 \cdot 10^{-11}$; $k_4 = 6,39 \pm 0,12 \cdot 10^{-12}$.

Résumé—On a déterminé les constantes de dissociation pour le réactif analytique alizarine fluorine bleue (acide 3-aminométhylalizarine *N,N*-diacétique) par titrage potentiométrique à la force ionique 0,1, et elles sont $k_1 = 1,28 \pm 0,30 \times 10^{-5}$; $k_2 = 2,82 \pm 0,24 \times 10^{-8}$; $k_3 = 3,72 \pm 0,19 \times 10^{-11}$; $k_4 = 6,39 \pm 0,12 \times 10^{-12}$.

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Complexometric titration of total iron with *o*-mercaptobenzoic acid as indicator

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VARIOUS methods have been reported in the literature for the EDTA titration of iron(III) and iron(II). For the use of EDTA to determine total iron in a system containing both iron(III) and iron(II), the iron(II) has to be oxidized. Iron(III) can be titrated with EDTA, with ammonium thiocyanate,¹ salicylic acid,² sulphosalicylic acid,³ Tiron^{4,5} etc as indicator. These direct complexometric titrations have, however, poor end-points. Further, the formation of the iron(III) EDTA complex is slow at room temperature and a higher temperature (up to 60°) is advisable, but the increased risk of hydrolysis necessitates the use of a pH in the region of 1.

o-Mercaptobenzoic acid (MBA) is proposed in the present investigation as an indicator for the determination of iron. Arutyunov and Bakalyan⁶ have reported the estimation of iron in food products by titration of the red precipitate formed between iron and MBA. However, the titration

is very slow, the end-point is not sharp, and the titration has to be carried out with a precipitate present. The precipitation can be avoided by the use of a pyridine-sulphuric acid buffer system. MBA forms a soluble deep blue complex with iron(II) in this medium (pH 6.4-7.4) and this can be titrated against EDTA, giving a very sharp colour change from blue to light yellow at room temperature (25-30°).

Iron(III) can also be determined conveniently because it is reduced by MBA to iron(II). Iron(III) forms a transient blue colour which soon disappears and then with excess of the reagent the deep blue iron(II) complex is formed. The reduction can be hastened by addition of ascorbic acid or hydroquinone before the reagent. The blue iron(II) complex is susceptible to oxidation but this can be prevented by addition of ascorbic acid or hydroquinone. Further, iron can be determined even in the presence of a large excess of copper if the latter is masked with sodium thiosulphate or ascorbic acid.

EXPERIMENTAL

Reagents

All solutions were prepared from analytical grade materials.

Iron(II), 0.01M. Prepared by dissolving the requisite amount of $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ in a litre of water containing 5 ml of concentrated sulphuric acid, and standardized against potassium dichromate, *N*-phenylanthranilic acid⁷ being used as indicator.

Iron(III), 0.01M. Prepared by dissolving the requisite amount of $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ in a litre of water containing 5 ml of concentrated sulphuric acid, and standardized by the tin(II) chloride method.⁷

o-Mercaptobenzoic acid. A 1% w/v solution in redistilled ethanol; stored in the refrigerator.

Pyridine, redistilled.

EDTA, 0.01M. Standardized against calcium, with Murexide⁸ as indicator.

Determination of iron

To 5 ml of solution containing up to 5 mg of iron, add 15-20 mg of ascorbic acid or hydroquinone, let stand for 2 min, then add pyridine to adjust the pH to 6.4-7.4, followed by 3-4 ml of indicator solution, and titrate immediately with EDTA till the colour changes from blue to light yellow.

Determination of iron in presence of copper

To 5 ml of solution containing up to 5 mg of iron and 12 mg of copper add 15-20 mg of ascorbic acid, 2 ml of pyridine, 6-7 ml of 10% sodium thiosulphate solution and 3-5 ml of indicator solution and titrate immediately with EDTA till the colour changes from red to light yellow. If more copper is present, add the amount of sodium thiosulphate solution calculated to mask the copper completely; 5 ml of 10% sodium thiosulphate solution masks 0.25 mmole of copper (15.9 mg).

RESULTS

Typical titration results are shown in Tables I-IV.

TABLE I.—TITRATION OF IRON(II)

Fe(II) taken, mg	Fe(II) found, mg	Error, mg	Fe(II) taken, mg	Fe(II) found, mg	Error, mg
0.558	0.558	—	2.233	2.241	+0.008
1.168	1.160	-0.008	2.792	2.800	+0.008
1.675	1.680	+0.005	5.584	5.579	-0.005

TABLE II.—TITRATION OF IRON(III)

Fe(III) taken, mg	Fe(III) found, mg	Error, mg	Fe(III) taken, mg	Fe(III) found, mg	Error mg
0.558	0.558	—	2.233	2.241	+0.008
1.168	1.168	—	2.792	2.800	+0.008
1.675	1.670	-0.005	5.584	5.580	-0.004

TABLE III.—TITRATION OF TOTAL IRON

Fe(II) taken, mg	Fe(III) taken, mg	Total Fe, mg	Total Fe, found, mg	Error, mg
0.558	2.792	3.350	3.345	-0.005
1.168	2.332	2.400	3.995	-0.005
2.792	1.675	4.467	4.459	-0.008
5.584	0.558	6.142	6.138	-0.004

TABLE IV.—TITRATION OF IRON IN THE PRESENCE OF COPPER, WITH SODIUM THIOSULPHATE AS MASKING AGENT

Taken, mg		Fe found, mg	Error, mg
Fe	Cu		
0.558	6.354	0.558	—
2.792	6.354	2.800	+0.008
0.558	12.71	0.556	-0.002
2.792	12.71	2.785	-0.007

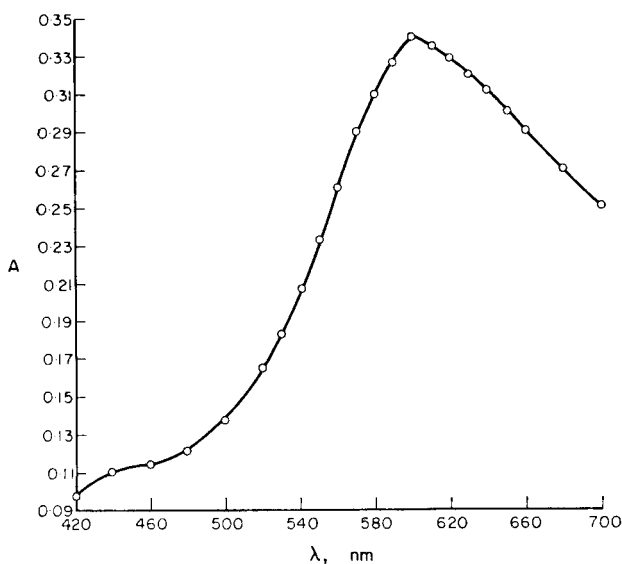


FIG. 1.—Absorption spectrum of the iron(II) complex with MBA at pH 6.4. 1 ml of 0.0025M iron(II) + 2 ml of pyridine + 1 ml of 1% MBA, diluted to 10 ml.

The absorption spectrum of the complex is shown in Fig. 1. Continuous variation⁹ and mole ratio¹⁰ plots showed that a 1:2 Fe-MBA complex is formed. The complex has maximum absorption over the pH range 6.4-7.4.

The stability constant, calculated by Harvey and Manning's method,¹¹ was found to be $\log K = 7.7$ at 25°, at ionic strength 0.1.

Effect of diverse ions

Co(II), Ni, Mn(II) and Cu(II) interfere seriously in the titration and also form coloured complexes. Cu(II) can, however, be masked with sodium thiosulphate. There was no interference by

anions such as chloride, fluoride, tartrate, phosphate, oxalate, citrate and acetate in amounts up to 250 mg.

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Summary—The soluble deep blue complex of iron(II) with *o*-mercaptobenzoic acid in aqueous pyridine medium (pH 6.4–7.4) can be titrated with EDTA at room temperature with a sharp colour change from blue to light yellow. *o*-Mercaptobenzoic acid forms a 2:1 complex with iron(II), maximum absorption at 600 nm. Its stability constant was found to be $\log K = 7.7$. With iron(III), a transient blue colour is first formed which soon becomes colourless and then on the addition of excess of reagent, the deep blue complex is formed on reduction of the iron(III). Iron can be titrated in the presence of copper, if the latter is masked with sodium thiosulphate. Cobalt and nickel interfere. Common anions such as chloride, tartrate, phosphate, oxalate, citrate and acetate have no interference.

Zusammenfassung—Der lösliche tiefblaue Komplex von Eisen(II) mit *o*-Mercaptobenzoessäure in wäßrigem Pyridinmedium (pH 6,4–7,4) kann bei Raumtemperatur mit EDTA bis zu einem scharfen Farbumschlag von blau nach lichtgelb titriert werden. *o*-Mercaptobenzoessäure bildet mit Eisen(II) einen 2:1-Komplex mit Absorptionsmaximum bei 600 nm. Für seine Stabilitätskonstante wurde $\log K = 7,7$ gefunden. Mit Eisen(III) erscheint vorübergehend eine blaue Färbung, dann wird die Lösung farblos und bei Zugabe von überschüssigem Reagens bildet sich der tiefblaue Komplex nach Reduktion des Eisen(III). Eisen kann in Gegenwart von Kupfer titriert werden, wenn dieses mit Natriumthiosulfat maskiert wird. Kobalt und Nickel stören, häufiger vorkommende Anionen wie Chlorid, Tartrat, Phosphat, Oxalat, Citrat und Acetat stören nicht.

Résumé—On peut titrer le complexe soluble bleu foncé du fer(II) avec l'acide *o*-mercaptobenzoïque en milieu pyridine aqueuse (pH 6,4–7,4) au moyen d'EDTA à température ordinaire, avec un changement de coloration net du bleu au jaune clair. L'acide *o*-mercaptobenzoïque forme un complexe 2:1 avec le fer(II), maximum d'absorption à 600 nm. On a trouvé que sa constante de stabilité est $\log K = 7,7$. Avec le fer(III) il se forme d'abord une coloration bleue fugace qui bientôt disparaît puis, par addition d'un excès de réactif, il se forme le complexe bleu foncé par réduction du fer(III). On peut doser le fer en la présence de cuivre, si ce dernier est dissimulé au moyen de thio-sulfate de sodium. Le cobalt et le nickel gênent. Les anions communs tels que chlorure, tartrate, phosphate, oxalate, citrate et acétate ne gênent pas.

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Hydrolysis of substituted 8-acetoxyquinolines

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In this study, the hydrolysis of 2-methyl-8-acetoxyquinoline, an ester of analytical interest for the precipitation of metal ions from homogeneous solution (PFHS),¹ and of 5-chloro-8-acetoxyquinoline are compared and contrasted with the hydrolysis of the parent ester 8-acetoxyquinoline, in the presence and absence of metal ions.

EXPERIMENTAL

Reagents

8-Acetoxyquinoline. PFHS grade, stored over phosphorus pentoxide.

2-Methyl-8-acetoxyquinoline. Synthesized by the method of Büchi *et al.*² from 2-methyl-8-hydroxyquinoline, and stored over phosphorus pentoxide.

5-Chloro-8-acetoxyquinoline. Prepared by refluxing 10 g of 5-chloro-8-hydroxyquinoline, 10 ml of pyridine and 50 ml of acetic anhydride for 7 hr; the excess of reagents was then removed by heating under reduced pressure on a steam-bath, and the residue distilled (162–164°, 8 mbar). The product was recrystallized from benzene-petroleum ether to yield white platelets m.p. 82–84°.

Metal ion solutions. Prepared from the perchlorate salts. The copper(II) solution was standardized iodometrically.

The water used was distilled and demineralized.

Procedure

pK_a Values. About 60 mg of ester were weighed into the titration vessel, then dissolved in 1.0 ml of absolute ethanol, and diluted with 100.0 ml of 0.05M perchloric acid which was 0.10M in sodium perchlorate, and then titrated potentiometrically at 25.0 ± 0.1°, under nitrogen, with a standard carbonate-free solution of sodium hydroxide. The pK_a values were calculated in the manner of Takamoto *et al.*³ Calculations showed that the hydrolysis that occurred during a potentiometric titration was negligible.

Hydrolyses of esters. Solutions made by adding 1.0 ml of a freshly prepared ethanolic solution of ester to 99 ml of perchloric acid (for pH values <3) or of a buffer solution (acetate for pH 3–6, phosphate for pH 6–7, borate for pH > 8) were adjusted to an ionic strength of 0.1, where necessary, with sodium perchlorate. The solutions, usually 2 × 10⁻⁵M in ester, were kept at 25.0 ± 0.1°, and samples withdrawn at appropriate intervals for measurement of absorbance (with 8-acetoxyquinoline, at 251.5 nm for pH <5 and at 240 nm for pH >5; with the 2-methyl ester, generally at 255 nm; with the 5-chloro ester, at 257 nm for pH <3.9 and at 235 nm for pH >3.9).

Values of log (A_∞ - A_t), where A_∞ and A_t are the absorbances at the completion of the hydrolysis and at time *t*, when plotted against *t* yielded straight lines extending over several half-lives, indicating that the reactions were first-order with respect to ester.

Some rate constants for the 2-methyl ester, for the same conditions of temperature and ionic strength but with the ester at higher concentration (0.01–0.02M), were determined by a bromometric method⁴ for the determination of 2-methyl-8-hydroxyquinoline. These constants were consistent with those determined spectrophotometrically.

RESULTS AND DISCUSSION

For the hydrolysis of 8-acetoxyquinoline, Wasmuth and Freiser⁵ showed that the variation of the observed first-order rate constant with pH could be accounted for by assuming it to be a consequence of several hydrolysis reactions: that of the protonated ester catalysed by H⁺, that of the free ester catalysed by H⁺, a hydrolysis of the free ester without catalysis by H⁺ or OH⁻ (but possibly involving intramolecular catalysis by the quinoline nitrogen), and hydrolysis of the free ester catalysed by OH⁻. This leads to the following expression for the observed rate constant:

$$k_{\text{obs}} = \frac{[\text{H}^+]}{K_a + [\text{H}^+]} \{k_1[\text{H}^+]\} + \frac{K_a}{K_a + [\text{H}^+]} \{k_2[\text{H}^+] + k_3 + k_4[\text{OH}^-]\}$$

in which *k*₁, *k*₂, *k*₃ and *k*₄ are the rate constants for the four hydrolysis reactions in the order mentioned above, and *K*_a is the acid dissociation constant of the protonated ester.

The results we obtained for the hydrolysis of both 2-methyl-8-acetoxyquinoline and 5-chloro-8-acetoxyquinoline can be described by this equation as shown in Fig. 1, the curves of which were plotted from the data of Table I. The curve for 8-acetoxyquinoline is based on the work of Barca and

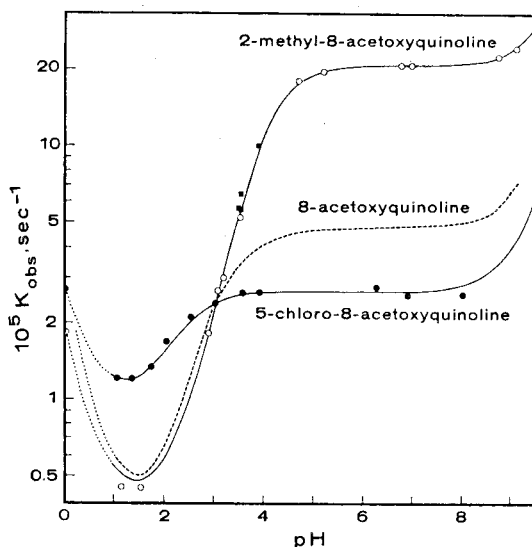


FIG. 1.—Variation, with pH, of observed first-order rate constants for hydrolysis of 8-acetoxyquinolines. (The curves below pH 1 are dotted because the ionic strength is greater than 0.1.) The points plotted as squares are for the hydrolysis of 2-methyl-8-acetoxyquinoline in the presence of 0.01–0.06M copper(II).

Freiser;⁶ for this ester we obtained similar hydrolysis data over a narrower pH range. The similarities in the pH–rate constant relationships of the three esters suggests that they have the same hydrolysis mechanism.

The hypothesis^{5,6} that the pH-independent hydrolysis of the neutral ester is due to intramolecular nucleophilic catalysis by the nitrogen atom is supported by our finding that k_3 for 2-methyl-8-acetoxyquinoline is higher, and for 5-chloro-8-acetoxyquinoline is lower, than that for 8-acetoxyquinoline: this accords with the order of basicity of the nitrogen atom in the three esters.

Freiser *et al.*⁶ observed that the hydrolysis of 8-acetoxyquinoline is catalysed by several metal ions, the effect (with bivalent ions) on k_{obs} being given by $\frac{K_a k_m [M^{2+}][OH^-]}{K_a + [H^+]}$ as an additional factor in the equation cited earlier.

We confirmed catalysis of the hydrolysis of 8-acetoxyquinoline by both copper(II) and nickel ions, with very good agreement: k_m for Cu^{2+} , $8.5 \times 10^7 l^2 \cdot mole^{-2} \cdot sec^{-1}$ (compared with 9.1×10^7);⁶ k_m for Ni^{2+} , $\sim 1.6 \times 10^4 l^2 \cdot mole^{-2} \cdot sec^{-1}$ (compared with $\sim 1.5 \times 10^4$).⁶ In contrast, though, we detected no catalysis of the hydrolysis of 2-methyl-8-acetoxyquinoline by either copper(II) (0.01–0.06M, at pH 3.5–3.9) or nickel (0.01M, at pH 6.1–6.5). With 5-chloro-8-acetoxyquinoline, catalysis by copper(II) was observed, k_m being $\sim 10^8 l^2 \cdot mole^{-2} \cdot sec^{-1}$ (from experiments at pH 2.5–3.5 with $[Cu^{2+}] = 0.01M$).

Our observation that the hydrolysis of 2-methyl-8-acetoxyquinoline appears uncatalysed by metal ions, whereas the hydrolysis of both the parent ester and the 5-chloro derivative is catalysed, supports the view⁶ that the catalysis involves co-ordination of the metal ion to both the nitrogen and

TABLE I.—RATE CONSTANTS FOR HYDROLYSIS OF 8-ACETOXYQUINOLINES AND pK_a VALUES (25.0°C; ionic strength = 0.1)

Rate constant	2-methyl-8-acetoxyquinoline	5-chloro-8-acetoxyquinoline	8-acetoxyquinoline ⁶
$k_1, l \cdot mole^{-1} \cdot sec^{-1} \times 10^5$	1.5	1.8	2.55
$k_2, l \cdot mole^{-1} \cdot sec^{-1} \times 10^3$	36	2.1	3.7
$k_3, sec^{-1} \times 10^5$	20.7	2.68	4.7
$k_4, l \cdot mole^{-1} \cdot sec^{-1}$	1.8	0.8	1.14
pK_a of the conjugate acid:	3.99 ± 0.03	$2.33 \pm 0.02^*$	3.08 ± 0.01

* A spectrophotometric determination, at 245.5 nm, yielded the value 2.31 ± 0.04 .

the carbonyl oxygen of the ester, to form a 7-membered ring. Models show that such co-ordination is prevented by a methyl group in the 2-position but is unhindered in the other two compounds. If chelation involved the ether oxygen, the 2-methyl group would exert no appreciable steric effect.

The fact that the hydrolysis of 2-methyl-8-acetoxyquinoline is much less affected by metal ions gives an advantage to this ester, in comparison to 8-acetoxyquinoline, as a reagent for the homogeneous precipitation of metal ions. With the parent ester, the rate of hydrolysis depends, *inter alia*, on the nature and concentration of the metal ion being precipitated, and may be several times the rate in the absence of the latter; with the 2-methyl compound, prediction of the rate of hydrolysis, and hence control of the precipitation, is more readily achieved.

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Summary—In the absence of metal ions, the hydrolysis of 2-methyl-8-acetoxyquinoline and of 5-chloro-8-acetoxyquinoline follow the same reaction paths as those of the parent ester 8-acetoxyquinoline, including an intramolecular catalysis by the quinoline nitrogen. Unlike the hydrolysis of the other esters, that of the 2-methyl compound appears not to be catalysed by metal ions, and this is consistent with the view that catalysis by a metal ion involves the formation of a 7-membered chelate structure.

Zusammenfassung—In Abwesenheit von Metallionen verläuft die Hydrolyse von 2-Methyl-8-acetoxychinolin und von 5-Chlor-8-acetoxychinolin ebenso wie die des zugrundeliegenden Esters 8-Acetoxychinolin über eine intramolekulare Katalyse durch den Chinolinstickstoff. Anders als die Hydrolyse der übrigen Ester wird die des 2-Methylderivats offenbar nicht durch Metallionen katalysiert. Dies stimmt mit der Auffassung überein, daß die Metallionenkatalyse die Bildung einer 7-gliedrigen Chelatstruktur einschließt.

Résumé—En l'absence d'ions métalliques, l'hydrolyse de la 2-méthyl-8-acétoxyquinoléine et de la 5-chloro 8-acétoxyquinoléine suit le même processus réactionnel que l'ester apparenté 8-acétoxyquinoléine, incluant une catalyse intramoléculaire par l'azote quinoléique. A l'opposé de l'hydrolyse des autres esters, celle du composé 2-méthylé apparaît ne pas être catalysée par les ions métalliques, et ceci est en accord avec la conception que la catalyse par un ion métallique implique la formation d'une structure chélatée heptagonale.

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Acid dissociation and metal chelate formation equilibria of some halogenated diphenylthiocarbazonates

(Received 12 May 1969. Accepted 2 July 1969)

IN THE COURSE of an investigation of the effect of ligand substitution on the rate of formation of zinc, nickel and cobalt dithizonates^{1,2} it was found that both electron-releasing and -withdrawing substituents resulted in ligands which reacted more rapidly with the metal ions than did the parent

compounds. This substituent effect is markedly different from that generally observed in equilibrium parameters such as the pK_a of the ligand or the formation constant of the chelate. Change of charge density at the site of chelation is generally reflected in a corresponding change of pK_a and $\log K_f$ in a given series. This study of the pK_a values for the ligands and of $\log K_f$ values for the Co(II), Ni and Zn chelates was undertaken to learn whether the unusual kinetic behaviour would be observed in the acid dissociation and/or the metal chelate formation equilibria.

EXPERIMENTAL

Materials

The di-*p*-fluoro, di-*p*-chloro-, di-*p*-bromo-, di-*p*-iodo-, and di-*m*-trifluoromethyl-phenylthiocarbazonates were synthesized³⁻⁵ by coupling two molecules of the diazonium compound with sodionitromethane in an alkaline ethanolic medium, giving the nitroformazyl compound which was then reduced by ethanolic ammonium sulphide solution to give the thiocarbazide product. The latter, in turn, was oxidized to the corresponding diphenylthiocarbazonate. These synthesized dithizonates as well as diphenylthiocarbazonate were purified by precipitation with absolute ethanol from solutions of freshly distilled chloroform that had been treated with hydroxylamine hydrochloride.^{6,7}

The melting points were found to be: di-*p*-fluoro 149–50° (lit.⁸ 146–8°), di-*p*-chloro 72–3° (lit.⁹ 173–4°), di-*p*-bromo 150–1° (lit.⁹ 151–2°), di-*p*-iodo 159–60° (lit.⁹ 160–1°) and di-*m*-trifluoromethyl 130–1° (lit.⁹ 128–9°).

The absorption spectra in the region 320–760 nm as well as the peak ratios of these compounds in chloroform solutions were compared with those previously reported (Table I).

TABLE I.—ABSORPTIVITY DATA FOR DITHIZONES IN CHCl₃ AT 25°C

Diarylthiocarbazonate	λ_1 min, nm	λ_1 max, nm	λ_2 min, nm	λ_2 max, nm	λ_3 min, nm	ϵ_1 max/ ϵ_2 max
Diphenyl (C ₁₂ H ₁₂ N ₄ S)	700 <i>a</i>	605 605	507 505	443 445	364 —	2.4 2.5
Di- <i>p</i> -fluorophenyl (C ₁₂ H ₁₀ F ₂ N ₄ S)	707 <i>a</i>	606 607	507 507	447 447	365 —	2.5 2.5
Di- <i>p</i> -chlorophenyl (C ₁₂ H ₁₀ Cl ₂ N ₄ S)	717 <i>a</i>	622 621	515 515	458 458	373 —	2.5 2.6
Di- <i>p</i> -bromophenyl (C ₁₂ H ₁₀ Br ₂ N ₄ S)	718 <i>a</i>	626 626	522 522	458 458	373 —	2.5 2.5
Di- <i>p</i> -iodophenyl (C ₁₂ H ₁₀ I ₂ N ₄ S)	718 <i>a</i>	635 635	530 530	466 464	384 —	2.6 2.6
Di- <i>m</i> -trifluoro- methylphenyl (C ₁₅ H ₁₀ F ₆ N ₄ S)	718 <i>a</i>	610 610	508 510	443 445	357 —	1.4 1.4

a Reported values.⁸

Buffer solutions were prepared from reagent grade chemicals and demineralized water. At pH values below 7 they were freed from heavy metal ions by extraction with dithizone solution in carbon tetrachloride,¹⁰ and were made up to 0.30M ionic strength by adjustment with sodium perchlorate solution.

The aqueous solutions of zinc, cobalt(II) and nickel perchlorates were standardized by titration with EDTA solution.¹¹ 1,4-Dioxan was purified by refluxing with metallic sodium¹² and redistilled daily. A 50% v/v aqueous dioxan solution was the medium for all absorbance measurements made in the determination of equilibrium constants. The stabilities of the dioxan solutions of the halogen substituted dithizonates toward oxidation were found to decrease in the order F > Cl > Br > I, a behaviour similar to that found for their chloroform solutions.¹ To prevent the oxidation of the solutions of these dithizonates the freshly distilled dioxan was vigorously shaken with a few crystals of hydroxylamine hydrochloride for about 10 min, followed by filtration before use.

Apparatus

A Cary 14 spectrophotometer was employed for all the spectrophotometric measurements made in this study.

A Beckman Research pH meter with a glass-calomel electrode pair was used for pH measurements. Standardization against Beckman buffers of pH 4.00 and 6.86 was carried out before each set of measurements. For measurements in 50% v/v aqueous dioxan solutions appropriate corrections

were made for converting the pH meter readings into the corresponding hydrogen ion concentrations.

An ultrasonic disintegrator Model T-40Cl (Ultrasonic Industries, Inc., Albertson, L.I., N.Y.) was very useful for ensuring quick and complete dissolution of the ligands in dioxan.

Determination of acid dissociation constants

In each experiment, a series of 10–12 or more different solutions was prepared, each containing a mixture of buffer solution of 0.30M ionic strength, demineralized water and dioxan. That volume of ligand solution which on dilution would give an ionic strength of 0.10M and a final composition of 50% v/v aqueous dioxan, was added by pipette to each mixture just before the absorbance at the appropriate wavelength was recorded (Table II). Although in previous studies¹⁴ a small change of absorbance

TABLE II.—ABSORPTIVITY DATA FOR DITHIZONES IN DIOXAN (A) AND IN 50% v/v AQUEOUS DIOXAN MEDIUM (B) IN THE REGION 320–760 nm AT 25°C

Diarylthiocarbazone		λ_1 min, nm	λ_1 max, nm	λ_2 min, nm	λ_2 max, nm	λ_3 min, nm	ϵ_1 max/ ϵ_2 max
Diphenyl	(A)	710	618	512	447	363	1.5
	(B)	700	598	505	435	360	
Di- <i>p</i> -F-phenyl	(A)	710	615	516	450	367	1.5
	(B)	700	596	506	424	350	
Di- <i>p</i> -Cl-phenyl	(A)	720	627	523	458	370	1.5
	(B)	700	596	506	424	350	
Di- <i>p</i> -Br-phenyl	(A)	723	632	525	456	370	1.4
	(B)	706	616	516	448	362	
Di- <i>p</i> -I-phenyl	(A)	726	638	530	465	380	1.6
	(B)	720	625	526	458	376	
Di- <i>m</i> -CF ₃ -phenyl	(A)	725	620	510	440	358	0.95
	(B)	715	600	510	420	348	

with time had been observed, arising from slight oxidative decomposition of the ligand, it was found in this study that solutions prepared with the freshly distilled and hydroxylamine-treated dioxan were entirely stable for a number of hours.

A plot of the absorbance values of the series of solutions against pH gave the characteristic sigmoid-shaped curves with inflection points corresponding to the pK_a values of the ligands. A more reliable graphical method from which the acid dissociation constants were calculated (Table III) is the one based on the equation,¹⁴

$$pH = pK_a + \log \frac{l\epsilon_{HL}T_L - A}{A - l\epsilon_L T_L} \quad (1)$$

or
$$pH = pK_a + \log f(A) \quad (2)$$

and
$$pH = pK_a \text{ at } \log f(A) = 0$$

TABLE III.—ACID DISSOCIATION CONSTANTS OF DITHIZONES AND FORMATION CONSTANTS OF THEIR 1:1 METAL CHELATES IN 50% v/v AQUEOUS DIOXAN SOLUTIONS OF 0.10M IONIC STRENGTH AT 25°C

Diarylthiocarbazone	$pK_a(\lambda^*)$	Log $K_{f1}(\lambda^*)$		
		Co(II)	Ni(II)	Zn(II)
Diphenyl	5.77(600)	6.43(520)	5.69(600)	6.16(500)
From Ref. 14	5.80		5.83	6.18
Di- <i>p</i> -F-phenyl	4.99(596)	5.94(440)	5.14(480)	5.75(500)
Di- <i>p</i> -Cl-phenyl	4.63(610)	5.63(440)	4.90(610)	5.37(510)
Di- <i>p</i> -Br-phenyl	4.40(616)	5.39(520)	4.72(430)	5.35(510)
Di- <i>p</i> -I-phenyl	4.03(625)	4.84(440)	4.66(625)	5.02(510)
Di- <i>m</i> -CF ₃ -phenyl	2.57(600)	3.48(580)	3.33(490)	3.83(495)
Di- <i>o</i> -CH ₃ -phenyl ¹⁴	6.23		5.90	4.50
Di- <i>p</i> -CH ₃ -phenyl ¹⁴	6.40		6.60	6.45

* Wavelength used for absorbance measurements, nm.

where ϵ_{HL} and ϵ_L are the molar absorptivities of the neutral and anionic forms of the ligand, A the absorbance, all at the same pH value, l is the path-length, and T_L is the total ligand concentration (in mole. l^{-1}). A plot of pH *vs.* $\log f(A)$ gave a straight line of unit slope with an intercept [at $\log f(A) = 0$] equal to the pK_a of the acid.

Determination of formation constants of 1:1 metal complexes

The solutions were prepared as for the pK_a determination except that each mixture contained a definite amount of the metal ion added as standard perchlorate solution. Just before the absorbance was recorded an aliquot of the ligand solution was added to the mixture to give a solution of 0.10M ionic strength in 50% v/v aqueous dioxan medium, with a metal-ligand concentration ratio (T_M/T_L) of 100 or more in order to prevent the formation of the 1:2 chelate complex. In the case of nickel, chelate precipitation could be avoided only when T_M was under $5 \times 10^{-4}M$.

Absorbance measurements at the wavelength maximum of the metal complex were made at various time intervals. Extrapolation of absorbance to zero time was necessary since in the presence of metal ions, a slow change due to ligand oxidation was observed.

The variation of absorbance with pH provided the basis of the graphical method for the calculation of the formation constant.¹⁴

$$K_{f1} = \frac{[H^+]}{K_a T_M} \frac{(A - \epsilon_{HL} T_L l)}{(\epsilon_{ML} T_L l - A)} \quad (3)$$

$$\log K_{f1} = pK_a - \log T_M - pH + \log \frac{(A - \epsilon_{HL} T_L l)}{(\epsilon_{ML} T_L l - A)} \quad (4)$$

where K_{f1} is the formation constant of the 1:1 complex and A is the extrapolated absorbance. The value of $\log K_{f1}$ for each metal complex was determined from a plot of $\log f(A)$ *vs.* pH; this gave a straight line of unit slope with an intercept [at $\log f(A) = 0$] equal to $\log T_M K_a K_{f1}$. The precision of $\log pK_a$ and $\log K_{f1}$ was ± 0.05 .

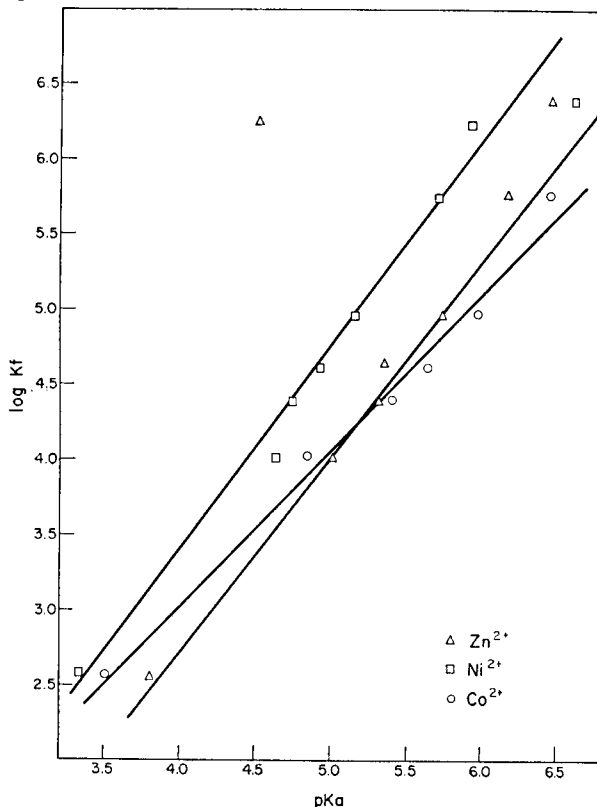


FIG. 1.—Variation of dithizonate chelate stabilities with reagent basicity ($\log K_{f1}$ *vs.* pK_a) in 50% v/v aqueous dioxan at 25°C.

DISCUSSION

The effect of the substituents on the acid dissociation constants of the ligands is in reasonable accord with what could be expected from their electronic influence. There is a roughly linear correlation of the pK_a values of the ligands with the value of the Hammett σ constants of the substituents. Furthermore, as can be seen from Fig. 1, the variation of chelate stability with ligand basicity is in complete accord with the conventional $pK_a - \log K_f$ relationships. The explanation for the unusual kinetics of chelate formation with these substituted dithizones must be sought elsewhere.

Although of the reagents studied the *m*-trifluoromethyl analogue forms the weakest chelates, it is important to note that its complexes have proton displacement constants ($K_{T_1}K_a$) that are the highest in the series so that its chelates will form in significantly more acidic media than will those of dithizone. This property, plus a greater stability of the compound towards oxidative degradation, should make it quite a useful analytical reagent.

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Summary—The acid dissociation constants (K_a) of di-*p*-fluoro-, di-*p*-chloro-, di-*p*-bromo-, di-*p*-iodo- and di-*m*-trifluoromethyl-phenylthiocarbazonen and the equilibrium formation constants (K_{f_1}) of their 1:1 complexes with Co(II), Ni and Zn have been determined at 25° in 50% v/v aqueous dioxan at 0.10 *M* ionic strength. Each of the electron-withdrawing substituents gives a reduction in pK_a roughly proportional to its Hammett σ value, and $\log K_{f_1}$ increases linearly with pK_a .

Zusammenfassung—Die Säuredissoziationskonstanten (K_a) der Di-*p*-fluoro-, Di-*p*-chloro-, Di-*p*-bromo-, Di-*p*-jodo- und Di-*m*-trifluoromethyl-phenylthiocarbazonen und die Bildungskonstanten (K_{f_1}) ihrer 1:1-Komplexe mit Co(II), Ni und Zn wurden bei 25° in 50% (V/V) wäßrigem Dioxan bei der Ionenstärke 0,1*M* bestimmt. Jeder der elektronenabziehenden Substituenten vermindert pK_a um einen Wert, der etwa seinem σ -Wert nach Hammett proportional ist; $\log K_{f_1}$ steigt linear mit pK_a .

Résumé—On a déterminé, à 25° en dioxane aqueux à 50% v/v et avec une force ionique 0,10*M*, les constantes de dissociation acide (K_a) des di-*p*-fluoro-, di-*p*-chloro-, di-*p*-bromo-, di-*p*-iodo- et di-*m*-trifluorométhylphénylthiocarbazonen et les constantes de formation d'équilibre (K_{f_1}) de leurs complexes 1:1 avec Co(II), Ni et Zn. Chacun des substituants attracteur d'électrons donne une réduction du pK_a approximativement proportionnelle à sa valeur σ de Hammett, et $\log K_{f_1}$ croît linéairement avec pK_a .

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NOTICES

IUPAC INTERNATIONAL CONGRESS ON ANALYTICAL CHEMISTRY KYOTO, JAPAN, 3-7 APRIL 1972

To celebrate its 20th Jubilee, The Japan Society for Analytical Chemistry is planning to hold an International Conference on Analytical Chemistry in 1972. The Congress will cover most areas of analytical chemistry, with special emphasis on trace analysis and the use of non-aqueous solvents. Further information can be obtained from the Organizing Committee, International Congress on Analytical Chemistry, Kyoto International Conference Hall, Takaraike, Sakyo-ku, Kyoto, Japan.

6TH INTERNATIONAL SYMPOSIUM ON MICROTECHNIQUES

This Symposium, under the auspices of IUPAC, is being organized by The Austrian Society for Microchemistry and Analytical Chemistry, and will be held in Graz, Austria, 7-11 September 1970. Further information may be obtained from Prof. Dr. G. Kainz, c/o Intercongress Reisedienst und Betreuung Ges. m. b. H., Stadiongasse 6-8, A-1010 Vienna, Austria.

2ND JOINT MEETING OF THE SOCIETY FOR ANALYTICAL CHEMISTRY WITH THE ANALYTICAL CHEMISTRY SECTION OF THE KONINKLIJKE NEDERLANDSE CHEMISCHE VERENIGING, APRIL, 1970

A joint Meeting on "Accurate Methods of Analysis for Major Constituents", is to be held at Imperial College of Science and Technology, London, 3-4 April 1970.

The scientific programme will consist of invited and submitted papers. It is hoped that the subject matter of the papers presented will complement that of the first Joint Meeting held at Enschede in April, 1968, on Limits of Detection in Analysis and will reflect modern developments in the determination of macro constituents. Those wishing to submit papers (in English) are invited to send as soon as possible an abstract (of about 200 words) to one of the Joint Secretaries of the Scientific Committee. (Dr. F. J. Bryant, Analytical Sciences Division, Building 551, A.E.R.E., Harwell, Didcot, Berks, England, or Dr. H. L. Kies, Gebouw Voor Analytische Scheikunde, Jaffalaan 9, Delft, Holland.) The closing date for submitted papers was 17 November 1969.

3RD CONFERENCE ON ANALYTICAL CHEMISTRY, HUNGARY BUDAPEST, 24-29 AUGUST 1970

This conference is organized by the Analytical Chemistry Section of the Hungarian Chemical Society under the sponsorship of IUPAC and the Hungarian Academy of Sciences. The topics are Separation methods in analytical chemistry, Organic analysis, and Thermal analysis. Further details may be obtained from the Hungarian Chemical Society, Budapest V, Szabadság tér 17, Hungary.

TRADE MARKS

Our attention has been drawn to the trade mark status of the word "Nimonic", a trade mark of Henry Wiggin & Co. Ltd, referring to their nickel-chromium high-temperature alloys. The term should not be used as a generic term for such alloys (see *Talanta*, 1969, **16**, 438).

Authors are asked to be particularly careful to indicate when trade marks are being used, by putting them in inverted commas and giving them a capital initial letter.

PAPERS RECEIVED

- Two new spectrophotometric reagents for copper: LAWRENCE STOOKEY. (10 November 1969)
- Extraction of vanadium(V)-*N*-benzoyl-*N*-phenylhydroxylamine complexes from sulphuric acid media containing chloride or fluoride ions: ELSIE M. DONALDSON. (17 November 1969)
- Complexation of nickel by *o*-(2-thiazoylazo)-4-chlorophenol: F. KAI and H. IZUMI. (19 November 1969)
- Studies on nucleation from solution of some analytically important metal chelates: J. A. VELAZQUEZ and O. E. HILEMAN, JR. (20 November 1969)
- Determination of vanadium in refractory metals, steel, cast iron, alloys and silicates by extraction of its NBPFA complex from sulphuric-hydrofluoric acid media: ELSIE M. DONALDSON. (21 November 1969)
- On the extraction of acids and neptunium from aqueous alcohol and acetone solutions: A. ALIAN, R. SHABANA and A. HAGGAG. (26 November 1969)
- Arsenazo III and its analogues—VII. The colour reactions of rare earths with a new reagent—carboxinitrazo: S. B. SAVVIN and T. V. PETROVA. (28 November 1969)
- Colour changes of chemical indicators—III. Colour specification and its accuracy: STANISLAV KOTRLÝ and KAREL VYTRÁS. (3 December 1969)
- Determination of some methylcarbamate insecticides by a.c. polarography and cyclic voltammetry: M. D. BOOTH and B. FLEET. (3 December 1969)
- Determination of carbon monoxide in metal carbonyl complexes—II. Development of a volumetric finish: A. D. CAMPBELL and P. E. NELSON. (4 December 1969)
- Relative sensitivity of rare earth elements in spark-source mass spectrometry: ELEN ROALDSET. (8 December 1969)
- Direct titrimetric microdetermination of thallium(I), indium and gallium—I. Microdetermination of indium-thallium(I) and indium-gallium without separation: O. C. SAXENA. (9 December 1969)
- Extractions with long-chain amines—I. Extraction of some metal Xylenol Orange complexes into methyltrioctylammonium chloride (Aliquat 336-S): RUDOLF PŘIBIL and VLADIMÍR VESELÝ. (9 December 1969)
- Mass spectrometric analysis of carbon monoxide-nitrogen mixtures: J. R. MAJER. (12 December 1969)
- Organic solvent effect on phosphomolybdic acid and its analytical application: TAITIRO FUJINAGA, MUTSUO KOYAMA and TOSHITAKA HORI. (12 December 1969)
- Dosage protométrique des hydrogènes mobiles à l'aide de l'amidure de sodium: MARCEL MIOCQUE, JEAN-MICHEL VIERFOND and ANNICK REYNET. (12 December 1969)
- Indirect determination of fluorides by the EDTA titration of samarium: H. F. COMBS and E. L. GROVE. (17 December 1969)
- Hydrocarbures et pollution atmosphérique: DENISE HALOT. (18 December 1969)

SUMMARIES FOR CARD INDEXES

Nucleation and crystal growth of copper(II) 8-hydroxyquinolate precipitated from mixed solvents: TONY RIHS, MARLAND C. THURSTON and LESTER C. HOWICK, *Talanta*, 1970, **17**, 123. (Department of Chemistry, University of Arkansas, Fayetteville, Arkansas 72701, U.S.A.)

Summary—The precipitation kinetics of copper(II) 8-hydroxyquinolate, formed in water–acetone mixtures, have been studied in a stop–flow apparatus by spectrophotometric techniques. Three factors are found to be important in improving the physical characteristics of crystals precipitated from mixed solvents. Supersaturation and growth rate can be controlled uniformly by slow rate of change in solvent composition; the presence of acetone significantly reduces the number of effective nuclei; thirdly, large amounts of organic solvent cause a change in the crystal form and its growth mechanism. At room temperature, copper(II) 8-hydroxyquinolate is precipitated as a dihydrate from water–acetone mixtures containing 0–60% acetone, and the crystal growth is limited by a diffusion-controlled process. Anhydrous copper(II) 8-hydroxyquinolate is formed in 70% acetone solutions by a surface-controlled reaction.

Solvent extraction of Ga(III) and In(III) from aqueous halide media by Adogen-364: SH. A. SHERIF, A. S. ABDEL-GAWAD and A. M. EL-WAKIL, *Talanta*, 1970, **17**, 137. (National Research Centre, Dokki, Cairo, U.A.R.)

Summary—Adogen-364 has been used for the extraction of gallium(III) and indium(III) from halogen acid solutions, and the dependence of the extraction on chloride, bromide and iodide ion concentration studied. The separation of Ga(III), In(III) and Al(III) is reported and some conclusions have been drawn about the stoichiometry of the extracted species.

Versatile spectrophotometric method for the determination of silicon: FRANKLIN A. DUCE and STANLEY S. YAMAMURA, *Talanta*, 1970, **17**, 143. (Idaho Nuclear Corporation, Idaho Falls, Idaho 83401, U.S.A.)

Summary—A versatile spectrophotometric method is described for the determination of microgram levels of silicon, as molybdenum blue. It combines the desirable features of existing spectrophotometric methods with three pretreatment procedures, namely (a) the removal of cations with a cation-exchange resin in the H⁺-form, (b) the conversion of all silicon species into the reactive monomer with an alkaline treatment, and (c) the decomposition of silicon fluoride with boric acid in the presence of cation-exchange resin. These pretreatments coupled with the colour development provide five procedures which are applicable to a wide variety of samples including natural and industrial water and solutions of various nuclear reactor fuels and components. Provisions are included for the selective determination of total silicon.

НУКЛЕАЦИЯ И РОСТ КРИСТАЛЛОВ
8-ОКСИХИНОЛИНАТА МЕДИ(II) ОСАЖДЕННЫХ
ИЗ СМЕШАННЫХ РАСТВОРИТЕЛЕЙ:

TONY RINS, MARLAND C. THURSTON and LESTER C. HOWICK, *Talanta*, 1970, 17, 123.

Резюме—Кинетика осаждения 8-оксихинолината меди(II) в смесях воды и ацетона изучена спектрофотометрическим методом в приборе для останки потока. Установлены три важных фактора для улучшения физических характеристик кристаллов осажденных из смешанных растворителей. Пересыщение и скорость роста поддерживается константным применением медленного изменения состава растворителя; присутствие ацетона в значительной мере снижает число эффективных ядер; в-третьих, большие количества органического растворителя вызывают изменение формы кристалла и его механизма роста. При комнатной температуре 8-хинолилат меди(II) осаждается в форме дигидрата из смесей воды и ацетона содержащих 0–60 % ацетона, а рост кристаллов ограничен регулируемым диффузией процессом. Безводный 8-хинолилат меди(II) образуется в 70 % тном ацетоне контролируемой поверхностью реакцией.

ИЗВЛЕЧЕНИЕ Ga(III) И In(III) ИЗ ВОДНЫХ
ГАЛОИДНЫХ РАСТВОРОВ С АДОГЕНОМ-364:

SH. A. SHERIF, A. S. ABDEL-GAWAD and A. M. EL-WAKIL, *Talanta*, 1970, 17, 137.

Резюме—Адоген-364 использован для извлечения галлия(III) и индия(III) из растворов галоидных кислот и изучена зависимость экстракции от концентрации хлорид-, бромид- и иодионов. Приведены результаты разделения Ga(III), In(III) и Al(III) и сделаны выводы о стехиометрии извлеченных ионов.

МНОГОСТОРОННИЙ СПЕКТРОФОТОМЕТРИЧЕСКИЙ
МЕТОД ОПРЕДЕЛЕНИЯ КРЕМНИЯ:

FRANKLIN A. DUCE and STANLEY S. YAMAMURA, *Talanta*, 1970, 17, 143.

Резюме—Описан многосторонний спектрофотометрический метод определения микрограммовых количеств кремния в форме молибденового голубого. Метод объединяет желательные характеристики имеющихся спектрофотометрических методов, именно (а) уклонение катионов с катионообменником в H^+ форме, (б) превращение всех кремниевых соединений в реактивный мономер обработкой с щелочью и (в) разложение фторида кремния с боровой кислотой в присутствии катионообменника. Эти предварительные обработки вместе с проявлением окраски представляют собой пять процедур, применимых на ряд разнообразных образцов, включающих природные и промышленные воды и растворы различных топлив ядерных реакторов и их компонентов. Селективное определение общего кремния также принято во внимание.

End-point evaluation in instrumental titrimetry—I. Linear extrapolation of hyperbolic titration curves: J. VŘEŠŤÁL and S. KOTRLÝ,® *Talanta*, 1970, 17, 151. (Department of Analytical Chemistry, College of Chemical Technology, Pardubice, Slov. povstání 565, Czechoslovakia.)

Summary—A method is described for the estimation of a systematic titration error which is introduced by linear extrapolation of hyperbolic titration curves in amperometric, photometric, and other instrumental titrations. It is assumed that the titration is based upon a single-step ion-association reaction $mA + nB \rightleftharpoons A_m B_n$ and that the measured physical property falls within known minimum and maximum values. The procedure is suitable for end-point determination, even when the titration curves have extensive curvature, and for predicting the choice of optimum experimental conditions for a given titration.

α -(Phenylazo)-4-nitrobenzyl cyanide, a new acid-base indicator: LÁSZLÓ LÉGRÁDI, *Talanta*, 1970, 17, 161. (Nitrokémia Works, Füzögyártelep, Hungary.)

Summary—A new acid-base indicator, α -(phenylazo)-4-nitrobenzyl cyanide, is proposed. The indicator changes colour from yellow to violet in the presence of alkali owing to the formation of a nitronic acid structure. This indicator is applicable for the titration of weak acids in acetone and ethanol media or in a mixture of these organic solvents and water, with 0.1 M aqueous sodium hydroxide as titrant. The absorption spectra have been recorded for the indicator in 25%, 50% and 75% aqueous ethanol and acetone. By means of the spectra the dissociation constants in these media have been determined. The pK value of α -(phenylazo)-4-nitrobenzyl cyanide is 12.10 in water, and is decreased considerably in acetone but only slightly in ethanol. This behaviour is similar to that of positively charged weak acids and irregular for a weak acid carrying no charge or a negative charge.

Gas-chromatographic determination of ultramicro amounts of selenium in pure sulphuric acid: YASUAKI SHIMOISHI and KYŌJI TŌEI, *Talanta*, 1970, 17, 165. (Department of Chemistry, Faculty of Science, Okayama University, Okayama, Japan.)

Summary—Ultramicro amounts of selenium in pure sulphuric acid are converted into selenous acid with a bromine-bromide redox buffer solution. The selenous acid reacts quantitatively with 4-nitro-*o*-phenylenediamine to form 5-nitropiaselenol which can be extracted into toluene. The extract is very sensitive to electron-capture detection in gas chromatography, and the sensitivity is higher than that of 5-chloro- or 4,5-dichloro-piaselenol. The calibration curve (peak heights) is linear up to 0.15 μ g of selenium in 1 ml of toluene. Pure sulphuric acid, commercially available, contains $10^{-6} \sim 10^{-5}\%$ selenium.

ОПРЕДЕЛЕНИЕ КОНЦА ТИТРОВАНИЯ В
ИНСТРУМЕНТАЛЬНОЙ ТИТРИМЕТРИИ—I. ЛИНЕЙ-
НАЯ ЭКСТРАПОЛЯЦИЯ ГИПЕРБОЛИЧЕСКИХ
ТИТРАЦИОННЫХ КРИВЫХ:

J. VŘEŠŤÁL and S. KOTRLÝ, *Talanta*, 1970, 17, 151.

Резюме—Описан метод определения систематической ошибки титрации, которая введена линейной экстраполяцией гиперболических титрационных кривых в амперометрической, фотометрической и других инструментальных титрациях. Принято, что титрация основана на ионоассоциационной, протекающей в одном шаге реакции



и что измеренная физическая характеристика находится в диапазоне ограниченном знакомыми минимальными и максимальными величинами. Методом можно пользоваться для определения конца титрования, даже в случае сильно закрученных титрационных кривых и для предварительного отбора оптимальных опытных условий для данной титрации.

α -(ФЕНИЛАЗО)-4-НИТРОБЕНЗИЛЦИАНИД—НОВЫЙ
КИСЛОТНОЩЕЛОЧНЫЙ ИНДИКАТОР:

LÁSZLÓ LÉGRÁDI, *Talanta*, 1970, 17, 161.

Резюме— α -(фенилазо)-4-нитробензилцианид предложен в качестве нового кислотно-щелочного индикатора. Индикатор изменяет цвет из желтого в фиолетовый в присутствии щелочи, вследствие образования структуры на основе нитроновой кислоты. Этим индикатором может пользоваться для титрования слабых кислот в ацетоновых и спиртовых средах или в смесях этих органических растворителей и воды, с 0,1M водным раствором гидроокиси натрия в качестве титрованного раствора. Получены спектры светопоглощения индикатора в 25 %, 50 % и 75 % водном растворе спирта и ацетона. На основе этих спектров вычислены константы диссоциации в этих средах. pK α -(фенилазо)-4-нитробензилцианида составляет 12,10 в воде, а снижается значительно в ацетоне, но только в небольшой мере в спирте. Это поведение похоже поведению положительно заряженных слабых кислот, а неправильно в случае слабой кислоты без заряда или отрицательно заряженной слабой кислоты.

ОПРЕДЕЛЕНИЕ УЛЬТРАМИКРОКОЛИЧЕСТВ
СЕЛЕНА В ЧИСТОЙ СЕРНОЙ КИСЛОТЕ МЕТОДОМ
ГАЗОВОЙ ХРОМАТОГРАФИИ:

YASUAKI SHIMOIZUMI and KYOJI Tobe, *Talanta*, 1970, 17, 165.

Резюме—Ультрамикроколичества селена в чистой серной кислоте превращаются в селенистую кислоту с использованием окислительно-восстановительного буферного раствора брома-бромиды. Селенистая кислота реагирует количественно с 4-нитро-*o*-фенилендиамином с образованием 5-нитропиаселенола, который экстрагируют толуолом. Экстракт весьма чувствительный на электроннозахватывающий детектор газового хроматографа, и его чувствительность больше чем 5-хлор- или 4,5-дихлорпиаселенола. Калибрационная кривая (высота пиков) линейная до 0,15 мкг селена в 1 мл толуола. Чистая серная кислота (коммерческая) содержит 10^{-6} до 10^{-5} % селена.

Stability constants of lanthanide complexes with salicylhydroxamic acid: T. SESHADRI, *Talanta*, 1970, 17, 168. (Regional Research Laboratory, Jorhat-6, Assam, India.)

Summary—The stability constants of La, Pr, Nd, Sm, Eu, Gd, Dy, Er, Yb and Y complexes of salicylhydroxamic acid have been determined potentiometrically in 3:1 v/v acetone–water medium at $25 \pm 0.5^\circ$ and at an ionic strength of 0.1 with respect to sodium perchlorate. The stability constants are comparable with those of other lanthanide complexes with oxygen-donating ligands such as benzoylacetone and benzoylphenylhydroxylamine.

Complexometric determination of molybdenum(VI): RUDOLF PŘIBIL and VLADIMÍR VESELÝ, *Talanta*, 1970, 17, 170. (Laboratory of Analytical Chemistry, J. Heyrovský Polarographic Institute, Czechoslovak Academy of Sciences, Prague 1, Jilská 16, Czechoslovakia.)

Summary—In acidic medium molybdenum(VI) forms a stable complex on boiling with excess of DCTA and hydroxylamine hydrochloride. Molybdenum can then be determined by back-titration of the excess of DCTA either with zinc chloride at pH 5–5.5 or with thorium nitrate at pH 3–4.5, Xylenol Orange being used as indicator in both cases. A simple method for the determination of molybdenum in the presence of moderate amounts of tungsten is also described.

The dissociation constants of alizarin fluorine blue: C. K. LAIRD and M. A. LEONARD, *Talanta*, 1970, 17, 173. (Department of Inorganic and Analytical Chemistry, Queen's University, Belfast, N. Ireland).

Summary—Dissociation constants for the analytical reagent alizarin fluorine blue (3-aminomethylalizarin-*N,N*-diacetic acid) have been determined by potentiometric titration at ionic strength 0.1, and are $k_1 = 1.28 \pm 0.30 \times 10^{-5}$; $k_2 = 2.82 \pm 0.24 \times 10^{-8}$; $k_3 = 3.72 \pm 0.19 \times 10^{-11}$; $k_4 = 6.39 \pm 0.12 \times 10^{-12}$.

КОНСТАНТЫ УСТОЙЧИВОСТИ КОМПЛЕКСОВ
ЛАНТАНИДОВ С САЛИЦИЛГИДРОКСАМОВОЙ
КИСЛОТОЙ:

T. SESHADRI, *Talanta*, 1970, 17, 168.

Резюме—Константы устойчивости комплексов La, Pr, Nd, Sm, Eu, Gd, Dy, Er, Yb и Y с салицилгидроксиамовой кислотой определены потенциометрическим методом в растворе ацетон—вода 3:1 (по объему), при $25 \pm 0,5^\circ$ и ионной силы 0,1 в отношении на перхлорат натрия. Константы устойчивости сравниваемы с константами других комплексов лантанидов с кислород-подавающими лигандами, как на пример бензоилацетоном и бензоилфенилгидроксиламинном.

КОМПЛЕКСОНОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ
МОЛИБДЕНА (VI):

RUDOLF PŘIBIL and VLADIMÍR VESELÝ, *Talanta*, 1970, 17, 170.

Резюме—В кислых средах молибден(VI) образует устойчивый комплекс при кипячении с избытком ДЦТА и хлористоводородным гидроксиламинном. Молибден определяют оттитровыванием избытка ДЦТА с хлоридом цинка при pH 5–5,5 или с нитратом тория при pH 3–4,5, пользуясь ксиленилоранжевым в качестве индикатора в обоих случаях. Также описан несложный метод определения молибдена в присутствии умеренных количеств вольфрама.

КОНСТАНТЫ ДИССОЦИАЦИИ АЛИЗАРИНФТОРОВОГО ГОЛУБОГО:

C. K. LAIRD and M. A. LEONARD, *Talanta*, 1970, 17, 173.

Резюме—Определены константы диссоциации аналитического реагента ализаринфторового голубого (3-аминометилализарин-*N,N*-диуксусной кислоты) методом потенциометрической титрации при ионной силе 0,1; они составляют $K_1 = 1,28 \pm 0,30 \times 10^{-8}$; $K_2 = 2,82 \pm 0,24 \times 10^{-8}$; $K_3 = 3,72 \pm 0,19 \times 10^{-11}$ и $K_4 = 6,39 \pm 0,12 \times 10^{-12}$,

Complexometric titration of total iron with *o*-mercaptobenzoic acid as indicator: L. M. BHANDARI, M. M. L. KHOSLA and S. P. RAO, *Talanta*, 1970, 17, 176. (Defence Laboratory, Jodhpur, India.)

Summary—The soluble deep blue complex of iron(II) with *o*-mercaptobenzoic acid in aqueous pyridine medium (pH 6.4–7.4) can be titrated with EDTA at room temperature with a sharp colour change from blue to light yellow. *o*-Mercaptobenzoic acid forms a 2:1 complex with iron(II), giving maximum absorption at 600 nm. Its stability constant was found to be $\log K = 7.7$. With iron(III), a transient blue colour is first formed which soon becomes colourless and then on the addition of excess of reagent, the deep blue complex is formed on reduction of the iron(III). Iron can be titrated in the presence of copper, if the latter is masked with sodium thiosulphate. Cobalt and nickel interfere. Common anions such as chloride, tartrate, phosphate, oxalate, citrate and acetate give no interference.

Hydrolysis of substituted 8-acetoxyquinolines: E. J. BILLO, R. P. GRAHAM[®] and P. G. CALWAY, *Talanta*, 1970, 17, 180. (Burke Chemical Laboratories, McMaster University, Hamilton, Ontario, Canada.)

Summary—In the absence of metal ions, the hydrolysis of 2-methyl-8-acetoxyquinoline and of 5-chloro-8-acetoxyquinoline follow the same reaction paths as those of the parent ester 8-acetoxyquinoline, including an intramolecular catalysis by the quinoline nitrogen. Unlike the hydrolysis of the other esters, that of the 2-methyl compound appears not to be catalysed by metal ions, and this is consistent with the view that catalysis by a metal ion involves the formation of a 7-membered chelate structure.

Acid dissociation and metal chelate formation equilibria of some halogenated diphenylthiocarbazonates: ABDUL R. AL-SALIHY and HENRY FREISER, *Talanta*, 1970, 17, 182. (Department of Chemistry, University of Arizona, Tucson, Arizona 85721.)

Summary—The acid dissociation constants (K_a) of di-*p*-fluoro-, di-*p*-chloro-, di-*p*-bromo-, di-*p*-iodo- and di-*m*-trifluoromethylphenylthiocarbazonates and the equilibrium formation constants (K_{f1}) of their 1:1 complexes with Co(II), Ni and Zn have been determined at 25° in 50% v/v aqueous dioxan at 0.10 *M* ionic strength. Each of the electron-withdrawing substituents gives a reduction in pK_a roughly proportional to its Hammett σ value, and $\log K_{f1}$ increases linearly with pK_a .

КОМПЛЕКСОНОМЕТРИЧЕСКОЕ ТИТРОВАНИЕ
ОБЩЕГО ЖЕЛЕЗА С ИСПОЛЬЗОВАНИЕМ
О-МЕРКАПТОБЕНЗОЙНОЙ КИСЛОТЫ В
КАЧЕСТВЕ ИНДИКАТОРА:

L. M. BHANDARI, M. M. L. KHOSLA and S. P. RAO, *Talanta*, 1970, 17, 176.

Резюме—Темносиний растворимый комплекс железа(II) с о-меркаптобензойной кислотой в водном растворе пиридина (рН 6,4–7,4) можно титровать с ЭДТА при комнатной температуре с получением резкой перемены цвета из синего в слабо-желтый. о-Меркаптобензойная кислота образует комплекс 2:1 с железом(II) с максимальным светопоглощением при 600 нм. Определена его константа устойчивости $\lg K = 7,7$. Железо(III) в первых образует преходящую синюю окраску, раствор затем обесцвечивается, а добавлением избытка реагента образуется темносиний комплекс после восстановления железа(III). Железо можно титровать в присутствии меди если последний ион маскирован тиосульфатом натрия. Кобальт и никель мешают определению. Обыкновенные анионы хлорид, цитрат, тартарат, фосфат, оксалат и ацетат не мешают определению.

ГИДРОЛИЗ ЗАМЕЩЕННЫХ 8-АЦЕТОКСИХИНОЛИ-
НОВ:

E. J. VILLO, R. P. GRANAM® and P. G. CALWAY, *Talanta*, 1970, 17, 180.

Резюме—В отсутствии ионов металлов гидролиз 2-метил-8-ацетоксихинолина и 5-хлор-8-ацетоксихинолина следит смер реакции родственного эфира 8-ацетоксихинолина, включая интрамолекулярный катализ азотом хинолина. В отличие от гидролиза других эфиров гидролиз 2-метилсоединения по-видимому не катализируется ионами металлов; этот факт в согласности с взглядом что катализ ионом металла включает в себя образование 7-членной хелатной структуры.

КИСЛОТНАЯ ДИССОЦИАЦИЯ И РАВНОВЕСИЯ
ОБРАЗОВАНИЯ ХЕЛАТОВ МЕТАЛЛОВ НЕКОТОРЫХ
ГАЛОИД-ЗАМЕЩЕННЫХ ДИФЕНИЛТИОКАРБАЗО-
НОВ:

ABDUL AL-SALINY and HENRY FREISER, *Talanta*, 1970, 17, 182.

Резюме—Определены константы кислотной диссоциации (K_a) ди-п-фтор-, ди-п-хлор-, ди-п-бром-, ди-п-иод- и ди-м-трифтомметилфенилтиокарбазонов и равновесные константы образования (K_{r_1})/их 1:1 комплексов с Co(II), Ni и Zn при 25° в 50 % водном растворе диоксана (по объему) и ионной силы 0,10 М. Каждый из электронноудаляющих заместителей снижает pK_a грубо пропорционально значению σ Хамметта; $\log K_{r_1}$ увеличивается линейно с pK_a .

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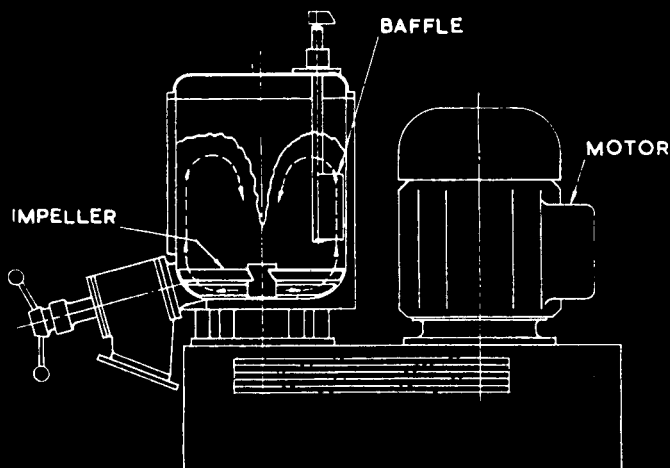
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