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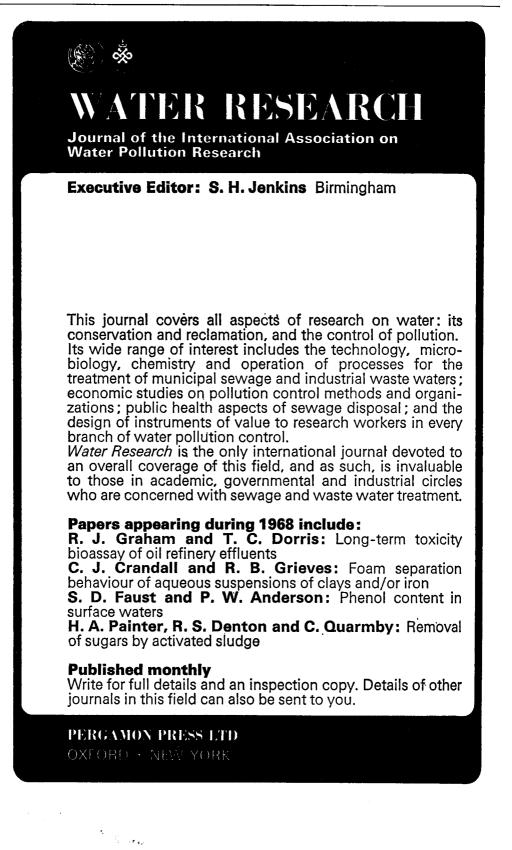
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EDITORIAL

WE WOULD draw your attention to the report, appearing on p. 559 of this issue, of the work of the Analytical Chemistry Division of the International Union of Pure and Applied Chemistry. It is important that the work of the Division should be widely publicized, because it is essential that the vast amount of research done on analysis should be collected, collated, evaluated and as far as possible systematized. Only in this way can international agreement be reached on standard methods, standard nomenclature *etc*. There must therefore be adequate communication between the army of research workers and the general and intelligence staff at headquarters. The purpose of publishing this report is to make the general strategy widely known, and to encourage feedback of information from the field of operations. The Analytical Chemistry Division is *our* Division and needs and deserves our support.

INORGANIC ANALYSIS IN ORGANIC SOLVENTS-III

ADSORPTION CHARACTERISTICS OF METAL CHELATE COMPOUNDS ON ALUMINAS AND SILICA GELS

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(Received 10 September 1968. Accepted 30 September 1968)

Summary—The general adsorption characteristics of 8-quinolinol, actioporphyrin, β -diketone and 8-quinolinethiol chelates of metals are described. These, with adsorption isotherm studies, indicate that the mechanism is of a chemisorption type with, in the case of oxo-chelating agents, high heats of adsorption. It appears that hydrogen-bonding to Brønsted sites on the adsorbents is an essential feature of the process and that multilayers of adsorbate are readily formed. This observation is supported by rate studies which show that the adsorption is a two-stage process with a break at a point corresponding to monolayer coverage. Both stages are diffusion controlled with relatively low probability. Infrared and X-ray diffraction studies, although of limited value, support these conclusions. The requirements of more generally applicable chelating agents and adsorbents for analytical purposes are discussed and predicted.

ADSORPTION chromatographic separations of molecular chelates from organic solutions are attractive for the isolation of metals before their determination for a variety of reasons: several investigations¹⁻⁷ have been made, the most extensive^{1,7} showing considerable promise. However, applications of the technique are markedly limited and only chromium⁸ and copper⁹ have been determined by methods based on this technique; the high degree of precision and accuracy attained in these two determinations justifies investigations designed to extend the method to other elements.

Qualitative observations

The adsorption, especially of 8-quinolinol chelates, has certain clear characteristics.

(a) The adsorbent must possess surface hydroxy groups for adsorption to occur; thus, silica gel, chromatographic alumina (*i.e.*, aluminium hydroxide/alumina) boric acid, sodium dihydrogen phosphate and similar compounds are active, whereas calcium carbonate, titanium dioxide, fused alumina, *etc.*, are poor adsorbents. Aluminas of widely varying Brockmann¹⁰ activity display virtually identical properties towards the chelates, and even variations in the spread of adsorbed bands caused by different degrees of strong heating before chromatography can be explained in terms of change of numbers of active adsorption sites rather than change of their degrees of activity. Attempts to change the activity of the adsorbent during elution (*e.g.*, by saturating the organic solvent with water) cause little change in the process, and application of higher temperatures (*e.g.*, by using *o*-dichlorobenzene as eluting solvent at up to 160°) has no appreciable effect. (b) The solvent, especially with respect to its dielectric constant, has some effect in that increased spreading of adsorbed bands can generally be achieved by increasing the dielectric constant of the solvent, e.g., from 2.3 for dioxan or benzene to 35 for nitrobenzene. In addition, some decomposition occurs with dimethylformamide (37) and formamide (109). However, in no case can an adsorbed chelate be eluted quantitatively in reasonable times or with practicable volumes of solvent.

(c) The chelating agent is of paramount importance and its choice forms the major part of this investigation. However, it is worth noting at this point that aetioporphyrin chelates of copper(II), nickel(II) and vanadium(IV) can be adsorbed on silica gel from benzene-ligroin solutions (1:20) and then quantitatively separated by elution with a 1:4 mixture of the solvents. β -Diketone chelates behave in a manner essentially similar to 8-quinolinol compounds, the strength of adsorption being slightly more strong and irreversible. Substitution of halogen in the 5-, 6-, 7- or 5,7-positions of the quinoline has little effect except for slight broadening of the bands, and this can be ascribed merely to changes of solubility of the substituted chelates in the selected solvents. In view of the difficulty of preparing porphyrin chelates for analytical purposes, the anomalous spectrophotometric behaviour of the diketone chelates in solution, and the excellent spectrophotometric and precipitation properties of the simpler 8-quinolinol chelates, the last-named were prefetred for further analytical investigation.

(d) The irreversibility of adsorption of all 8-quinolinol chelates from organic solvents is a most striking feature. Even chromium⁸ can only be recovered quantitatively if relatively high flow-rates (>1 ml/min on 5-mm diameter and 50-mm length columns of 100-200 mesh aluminas) of 1:1 chloroform-benzene solutions (dielectric constant, 3.5) of its 8-quinolinol or 2-methyl-8-quinolinol chelate are maintained; if lower flow-rates or solvents of lower dielectric constant are employed, at least some of the compound is irreversibly retained on the column. Analogous copper chelates^{9,11} are eluted only when an approximately 0.5% solution of the parent chelating agent in the selected solvent is used: otherwise the copper compounds are as irreversibly retained as all others. At the same time, the chelating agents themselves show little retention on any of the adsorbents.

Adsorption isotherms

As might be expected, adsorption of the chelates on various adsorbents fits fairly closely to the Freundlich isotherm. Results for copper(II)-2-methyl-8-quinolinol chelate (in the absence of reagent) are shown in Fig. 1: evidently the extent of adsorption increases with increasing Brønsted-site (OH) surface population, and the similarity of slopes indicates that the same mechanism operates on all the adsorbents examined. From this work it became apparent that equilibrium is reached, if at all, extremely slowly, and its true value may not be reached even after 24 hr. Moreover, it appeared that the quantities of chelate adsorbed were far in excess of the surface areas available for monolayer adsorption. The isotherms were not sensitive to small $(\pm 0.2^{\circ})$ changes of temperature.

Adsorption isotherms (Figs. 2(a)-(d) respectively) were prepared for copper(II), nickel(II), chromium(III) and iron(III) 2-methyl-8-quinolinol chelates on silica gel and alumina at 25° from benzene solution; measurements of concentration were made spectrophotometrically after equilibration for exactly 6 hr—an arbitrarily

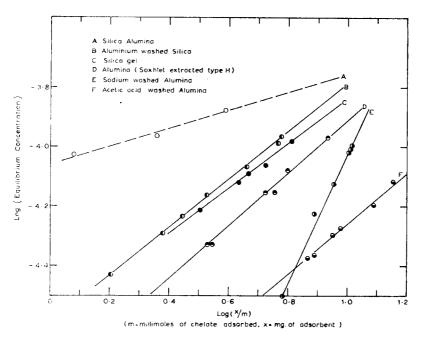


FIG. 1.—Adsorption isotherms of the copper(II) 2-methyl-8-quinolinol chelate on various adsorbents.

chosen but satisfactory period for comparison purposes. Under these conditions, the isotherms of uranium(VI) and cerium(IV) chelates could not be obtained, since the degree of adsorption was so high that no significant equilibrium concentration remained in solution: 50μ mole of the uranium chelate were completely adsorbed on 0.1 g of alumina from 10 ml of solution.

It would be expected that the plateaux of the isotherms (type L3)¹² for the iron, nickel and chromium compounds would correspond to a definite stage in the adsorption process. Table 1 gives the apparent surface areas of the alumina and silica gel based on adsorption of p-nitrophenol¹³ and the assumption that monolayer coverage is obtained at the inflexion at the plateaux (or, in the case of copper, when the rate of change of equilibrium concentration with respect to quantity absorbed clearly becomes constant). The agreement between the p-nitrophenol results and those from the chelates is, for this type of experiment, remarkably good, and bearing in mind that this type of measurement gives an estimate of the number of available active sites rather than a true surface area, then the hypothesis that monolayer coverage is attained on the plateaux and that multilayer adsorption occurs at higher equilibrium concentrations receives substantial support. It is interesting to note that owing to insufficient sensitivity X-ray diffractometry does not reveal any adsorbed species at the monolayer stage, but multilayers provide powder photographs showing that a species apparently identical with the crystalline chelate is present.

The isotherms for copper do not display a clear-cut plateau but evidence of co-operative adsorption is shown by their convex shape at lower equilibrium concentrations (type S).¹² This may be explained by formation of the chelate dihydrate, which would remove adsorbed water and expose further active sites at the adsorbent

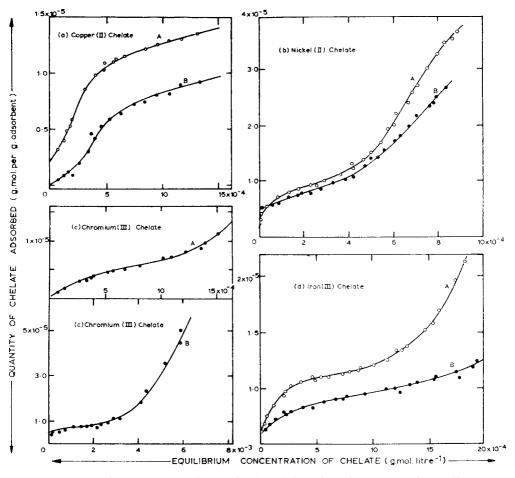


FIG. 2.—Adsorption of 2-methyl-8-quinolinol chelates from benzene at 25°C on (A) silica gel and (B) alumina.

TABLE I.—APPARENT SPECIFIC SURFACE AREAS OF ADSORBENTS BASED ON ASSUMED MONOLAYER COVERAGE BY *p*-NITROPHENOL AND BY 2-METHYL-8-QUINOLINOL CHELATES

		Speci	fic surface area	$, m^{2}/g$
	Estimated projected	Silica	a gel	Alumina
Solute (adsorbate)	adsorbate area, A^2	From isotherms	From kinetics	From isotherms
p-Nitrophenol	15	(1) 10.8		9.0
		(2) 3.6		
Copper(II) chelate	150	(1) 13.3	<u> </u>	9.4
11		(2) —	3.6	
Nickel(II) chelate	135	(1) 9.0	8.8	7.3
Iron(III) chelate	130	(1) 10.2	6.5	7.1
Chromium(III) chelate	130	(1) 6.6	9.0	6.3
		(2) —	2.7	
Mean		(1) 11 ± 1		

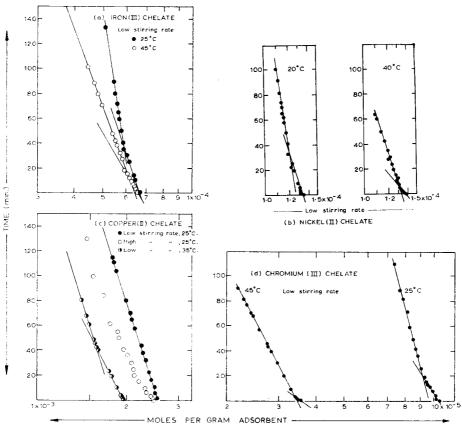


FIG. 3.—Kinetics of adsorption of 2-methyl-8-quinolinol chelates on silica gel (0.04 g, 170-200 BSS mesh, 75-90 µm diameter) from benzene solutions (12.5 ml).

surface. Slight colour changes, viz., a brown adsorbed phase from the yellow anhydrous solution, support this suggestion. The chromium chelate does not, apparently, cover as fully as other species although the discrepancy is reproducible: it may be that the assumed projected surface area of the chelate is in error or that only the most active adsorption sites are effective in the case of this chelate. The latter is a reasonable hypothesis in view of the inner orbital character of chromium compounds and the known chromatographic behaviour of its chelates.

The Brunauer, Emmett and Teller isotherm¹⁴ for the nickel chelate did predict agreement between Brunauer's point B and the calculated monolayer attainment. However, in view of the doubt in applying such an isotherm and argument to solution adsorption, the result may have been fortuitous.

Adsorption rate studies

Typical absorbance-time relationships for benzene solutions are shown in Figs. 3(a)-(d). It is evident that, except for certain conditions of copper and chromium adsorption, the rate plots show two distinct branches and the results cannot be interpreted in terms of a single rate process of any order. However, the processes are

both of first order, the activation energies are similar and typical of physically controlled processes, and the rates are markedly dependent on stirring speeds (see Fig. 4 and, in Fig. 3, the effect of excessively vigorous stirring on the adsorption of the copper chelate, where the irreproducibility seems to stem from an abrading action in the suspension). The break-points on the curves correspond reasonably closely to monolayer coverage.

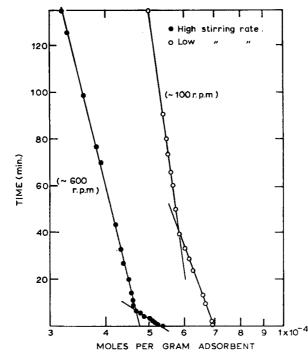


FIG. 4.—Effect of stirring rate on kinetics of adsorption of chromium(III) 2-methyl-8quinolinol chelate.

Most equations used to describe the kinetics of adsorption processes relate to gas-solid interactions,¹⁵ and studies on solution-solid adsorption kinetics^{16,17} use parameters dependent ultimately on equilibrium conditions. Chelate adsorption from solution is slow and true equilibrium is apparently not reached.

However, it can be shown that for a first-order process¹⁸

$$k = \frac{2 \cdot 303}{t} \log \frac{N_0}{N_0 - N_t}$$

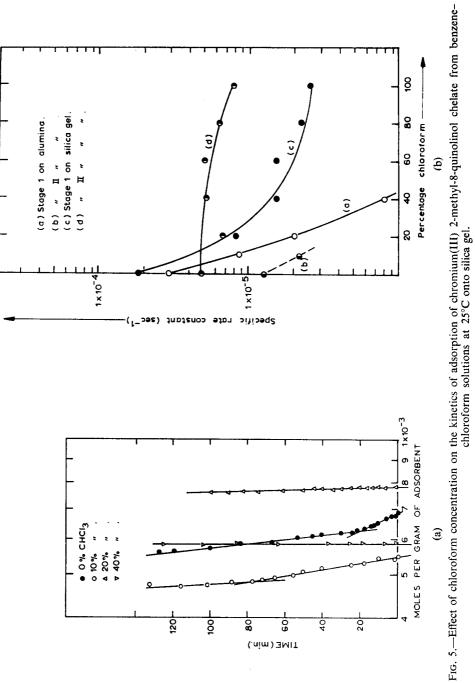
where N_0 is the initial number of moles of chelate per unit weight (g) of adsorbent and N_t the number of moles adsorbed per g of adsorbent at time t. Hence the rate constants can be evaluated from the slopes of $\log d_t vs. t$ plots, where d_t is the absorbance of the solution at time t, and "activation energies" can be calculated by applying the Arrhenius equation to these rates. Details are given in Table II.

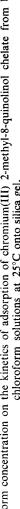
It is interesting to note that rates of adsorption of the 2-methyl-8-quinolinol chelate of chromium decrease as the proportion of chloroform is increased in a mixed chloroform-benzene solvent (Fig. 5(a) and (b), Table II): in fact, with alumina as

		t			Rat	Rate constants, 10 ⁻⁵ sec ⁻¹	$10^{-5} sec^{-1}$			Activation	
Chelate	chci, %	Stage	10°C	20°C	25°C	30°C	35°C	40°C	45°C	energy, kcal. mole ⁻¹	e.u.
Copper(II) ^a	0	1	3.4	11	6.8		10·5 4·96	13-4 6-20		8-5	- 51
Nickel(II) ^b	0	7 1	11	6.8 2.4	[]	10-2 3-6		15-3 5-5	11	7·3 8·3	55 53
Iron(III) [»]	0	7 7		5·1 1·6	5·6 2·5	8-8 2-7	10-0 2-6	12-9 4-5	15-0 5-9	8·1 9·8	53 49
Chromium(III) ^a	0 8	- 19 -		5.5 2.0	9.4 4:2	13.7 5.8	14·7 7·2	18·1 9·3	22·6 11·8	7.7 9.2	53 49
	9	- 7	1 1	1.5	8 	Ō	On alumina ^e at 20°C	20°C			
	64 g	- 7 -		0.65 1.9 0.66		CHCI, %		k (stage 1) 10^{-5} sec ⁻¹	}		
	8 8	- 0		0.46 0.46		00		3·46 1·14			
	100	0 - 0		1.60 0-39 1-27		88	8	0-50 0-13			

Inorganic analysis in organic solvents-III

479





adsorbent the second stage disappears at a chloroform proportion of about 20%, while with silica gel the relative rates are reversed at about the same concentration. Nevertheless, it appears that the first minor additions of chloroform have proportionately major effects presumably due to marked preferential adsorption of the chloroform on the most active sites. Moreover, at lower temperatures (< 25°) the second stage is not evident in the copper chelate adsorption.

From the theory of rate processes, "entropies" of activation can be calculated: they are invariably large (\sim 50 cal.mole⁻¹.deg⁻¹, Table II) and negative, in accord with a low probability and correspondingly low rates for a given activation energy. This treatment does not take into account geometric factors, but the low probability can be qualitatively explained in terms of stringent requirements for the orientation and juxtaposition of the solute before adsorption: chemisorption, inclusive of displacement of adsorbed solvent molecules, is not significant as a rate-controlling process. It is generally assumed that activation energies in adsorption processes are dependent on surface coverage, *i.e.*, either different sites have different activation energies (and presumably the more active are covered first) or the probability of adsorption decreases as the sites are covered. However, in the present work it is evident from the results that adsorption rates are independent of surface activity and coverage until a complete change in character occurs at a stage corresponding to attainment of approximately monolayer coverage.

On the assumption that the process is solely diffusion controlled, the mass transfer coefficient, α , can be evaluated from the expression: flux, $f_{x,t} = -A\alpha C$. Hence, since -dC/dt = kC and $\alpha = 2D/d$, the diffusion coefficient of the solute becomes D = Vkd/2A, where V is the volume of the solution, C the concentration, A the surface area of the adsorbent and d the diameter of its particles which are assumed to be approximately spherical; k is the rate constant. Substitution of typical experimental quantities in this expression gives values of $D \sim 10^{-8} \text{ mm}^2 \text{.sec}^{-1}$. Even allowing for the necessary approximations these values are excessively low for such a system, so simple diffusion control is unlikely: these observations, coupled with the low probabilities of the adsorption, suggest that molecular orientation, perhaps coupled with diffusion, ¹⁹ controls the process.

Miscellaneous investigations

Heats of preferential adsorptions of the chelates have already been discussed at some length.⁹ In summary, it appears that there is a critical value of approximately 6 kcal.mole⁻¹ above which adsorption is irreversible; below that value elution can be achieved, either by using chelating agent solutions for elution in the case of copper(II), or by changing the agent.

Infrared studies are not conclusive: alumina itself shows broad bands which mask the significant bands of adsorbed species but undoubtedly the surface hydroxyl groups of silica gel disappear during adsorption of the chelates [evidenced²⁰ by the disappearance of the 3740 cm^{-1} (s) band]. The chelates do not decompose in any drastic manner on either adsorbing surface.

Experiments on adsorbents previously coated with a monolayer of chelate showed that spreading of the bands of chelates could be achieved much more readily, in accord with the lower (\sim 3-7 kcal.mole⁻¹) heats of preferential adsorption. However, elution was far from quantitative and attempts to isolate mixed chelates of copper by

using eluting solutions of highly substituted 8-quinolinols in benzene-chloroform were not successful.

Conclusions

From the evidence, it is clear that adsorption of the chelates proceeds in two stages: the first caused by hydrogen-bonding to surface hydroxyl groups and the second an incipient crystallization.¹⁵ The surface bonding is strong, heats of preferential adsorption being as high as 30 kcal.mole⁻¹, and the adsorption process is diffusion controlled.

	Reagent		8-Qu	inolinethiol			2-Methyl-8- quinolinethiol
	Adsorbent	Silica gel		Alumi	na		Alumina
		CHCl ₃ C ₆ H ₆		Ligroin– C ₆ H ₆ —	CHCl3-	−C ₆ H ₆	C. H. Jianaia
Metal	Solvent	1:19	C_6H_6	1:1	1:19	1:4	C ₆ H ₆ –ligroin 1:19
Copper(II)		0.4	0.4	0.3	0.6	0.7	~0.5
Nickel(II)		0.7	0.6	0.5	0.8	0.9	~ 0.7
(ron(III)		0.75	0.7	0.2	~ 1.0	~ 1.0	~ 0.8
Chromium(III)		0.2	0.1	<0.1	03	0.4	~ 0.2

TABLE III.— R_f Values of 8-quinolinethiol chelates

Under these circumstances it is unreasonable to postulate²¹ π -bonding to the organic part of the chelate and the only reasonable sites for the hydrogen bonding appear to be hetero atoms of the chelating agent residues which surround the metal atom, and of these it is known²² that oxygen would form far stronger bonds than nitrogen. In that case the hydrogen bond would be weaker if, instead of the O-H-O bridge, a bond of type (a) O-H-N, (b) O-H-S or (c) S-H-O were formed, where the first-named atom is that at the adsorbent surface. Type (a) is demonstrated by the aetioporphyrin chelates, which, although successfully and successively eluted, are not of sufficiently wide analytical application. For type (b) 8-quinolinethiol was chosen as chelating agent: its chelates retain many of the analytical advantages of its oxy-analogues and although it is susceptible to air oxidation it can be kept as its sodium salt and used in gravimetric and spectrophotometric determinations^{23,24} of several metals; more important, its chelates are at least slightly soluble in several organic solvents, including benzene, chloroform, ligroin and n-butanol, without decomposition. By the techniques described before, the 8-quinolinethiol chelates of copper(II), nickel(II) and chromium(III) were successfully separated with a column loading of 100 μ g of mixed chelates per g of adsorbent (type H alumina). Some tailing and perhaps decomposition occurs with the iron(III) compound. Typical R_t values are given in Table III, although for each a range from < 0.1 to > 0.9 can be achieved by slightly changing the dielectric constant of the solvent. The elution of copper(II) is not assisted by use of reagent solutions. Heats of preferential adsorption¹¹ are low for these chelates and correspond with their R_f values. The simple 8-quinolinethiol chelates have certain disadvantages, notably their low solubility, and preliminary experiments with 2-methyl-8-quinolinethiol showed greater potential in flexibility, quantitative recovery and extension to other metals.

Separation of the same metals, as their 2-methyl-8-quinolinol chelates, can be

achieved on zinc sulphide or arsenic(III) sulphide, provided that these adsorbents are freshly precipitated and air-dried, thus demonstrating the use of hydrogen-bonding of type (c). Despite some ligand exchange with zinc on its sulphide, distinct elutions from both adsorbents can readily be demonstrated. Fuller details of this and the work with substituted 8-quinolinethiols will be reported in a later communication.

At this stage, the structure of the single and multilayer deposits can only be conjectured. However, any epitaxy or effect transmitted into the thicker layers from the monolayer can only be of very short order, otherwise X-ray diffractometry would show divergence from the normal d-spacings of the chelates. It is known²⁵ that intramolecular hydrogen-bonding can occur with the 8-quinolinol chelate of vanadium(V), viz., Ox₂·VOOH, presumably without substantial distortion of the molecule: in the case of intermolecular bonding of the chelates to the adsorbent hydroxyl groups the distortional effect may also be minimal, thus allowing the formation of almost or completely normal multilayers by π or van der Waals bonding. Whether the "incipient crystallization" is due to minor solid state energetic changes at the adsorbent surface compared with the normal crystalline form or whether precipitation of a supersaturated solution of the chelates is encouraged on the surface is again debatable; indeed the "normal" solutions of the chelates may really be supersaturated, since it is difficult to find a clear demarkation or saturation point at concentrations as high as 4% w/v especially when these solutions are allowed to evaporate in air. It will be important to decide on the type of process, since one of the reasons for the success of the chromium⁸ and copper⁹ determinations is the high loading capacity of alumina, which allows retention of large excesses of interfering chelates: if other chelating agents, allowing further separations but involving weaker hydrogen bonding, are chosen the loading of the columns may be too small to allow practicable analyses to be carried out if multilayer adsorption does not occur.

The case of elution of the copper chelates of 8-quinolinols with reagent solutions is particularly interesting and characteristic, and it may well be connected with the polar positions of the potentially octahedrally co-ordinated copper.²⁶ It is known¹¹ that copper does, under suitable conditions, form triligand chelates with 8-quinolinols although the third is but weakly held. However, its bonding may be comparable with that of one planar 8-quinolinol residue already in competition with hydrogenbonding. In that case it is possible to envisage the copper's moving along the alumina surface by a ligand-exchange, secondary-complex or cascade process. The eluate apparently contains only the diligand species and free reagent, as might be expected from this hypothesis, and use of other substituted 8-quinolinols in the eluting solution did not lead to any detectable mixed chelates, though markedly reducing the efficiency of the elution process.

EXPERIMENTAL

Reagents

 β -Diketone,²⁷ 8-quinolinol⁸ and 8-quinolinethiol²⁴ chelates were prepared by standard methods. Commercial reagents were used except in the following cases: 5-halogeno-, 5,7-dihalogeno- and 5,7-dinitro-8-quinolinols,²⁸⁻³⁰ 6-chloro-2-methyl-8-quinolinol,³¹ 8-quinolinethiol.³² Small quantities of 2-methyl-8-quinolinethiol were prepared as follows: 0-1 mole of 2-methylquinoline was heated with excess of chlorosulphonic acid at 120° until dissolution was complete; after cooling the mixture was poured onto crushed ice (2 kg) and the mixed sulphonyl chlorides extracted with 100 ml of ether; the solvent was subsequently removed *in vacuo*, which also served to dry the residue. The product was reduced in ethereal solution with a 70% excess of lithium aluminium hydride. In the resulting mixture of thiols only the 8-derivative is an effective chelating agent, so the mixture was used as reagent for preparing the chelate by the method²⁸ used for 8-quinolinethiol. Solvents were of analytical reagent grade or specially purified.³³ The authors gratefully acknowledge the gift of small quantities of 8-quinolinethiol from Dr. Dalziel and of certain actioporphrin chelates from the B.P. Research Centre, Sunbury, who also supplied the aluminium-washed silica gel of exclusively Brønsted type.

Chromatography

The chromatographic studies were carried out by methods described previously.⁸ Commercial chromatographic alumina (Peter Spence type "H", 100–200 mesh) and silica gel (Hopkin and Williams "MFC") and specially prepared silica gels were employed in these and the isotherm studies.

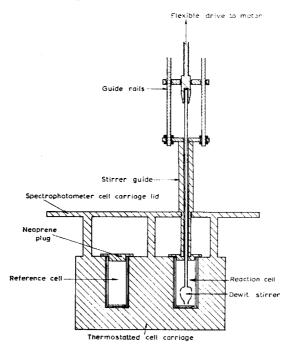


FIG. 6.--Rate measurement apparatus.

Acid-washed alumina. Prepared from type "H" by stirring with acetic acid (1 + 1) for 30 min, filtering, extracting in a Soxhlet apparatus with demineralized water for 2 hr, then activating under standard conditions.

Sodium-washed alumina. Obtained by stirring type "H" in 5% w/v aqueous sodium hydroxide for 30 min, filtering, drying, sieving and activating under standard conditions.

Silica-alumina. The commercial catalyst (55% alumina) ground to 100–200 mesh and activated.

Adsorption isotherms

Adsorbent (0.01 g) was equilibrated by rotation in a glass-stoppered vial on a "Rolamix" machine with 10 ml of originally $\sim 10^{-8}M$ solutions of the chelates in the appropriate solvent. Consistent agitation was achieved and reasonable constancy of temperature ($25 \pm 2^{\circ}$) was maintained in a temperature-stabilized room. Isotherms were obtained by spectrophotometric analysis after the arbitrarily chosen 6 hr of equilibration.

Adsorption rate studies

The assembly used is shown in Fig. 6 and was based on the Unicam SP600 spectrophotometer: about 0.04 g, accurately weighed, of 170-200 BS mesh (75-90 μ m particle size) adsorbent was kept in suspension in 12.5 ml of solution within a controlled-temperature 40-mm cell (1) fitted with a neoprene lid, by means of a small de Witt stirrer (2) rotated at constant speed (usually 100 rpm for "low" stirring rates and 600 for "high") via a retractable flexible drive (3) from a small electric motor. Temperature control was to better than $\pm 0.1^{\circ}$ and the speeds and mesh sizes were chosen from preliminary experiments, bearing in mind the need for reasonably large adsorbent surface areas coupled with sufficient speed of settling to avoid error in the rate measurements. The stirrer was withdrawn during absorbance measurements; where high concentrations of solute were involved, absorbances were measured at wavelengths where molar absorptivities were of suitable values. For the activation energy evaluations measurements were made at 5 intervals in the range 20-45°.

Infrared spectra

These were obtained on a Perkin-Elmer 621 instrument either by the potassium bromide pressed disc technique or by soaking previously prepared self-supporting discs of adsorbent in the chelate solution, washing in benzene and then drying at 50°.

X-Ray diffraction

Silica gel (400 mesh) was equilibrated with the chelate solution in benzene and was then examined by the powder-photograph technique and results were compared with those for the pure chelate. The adsorbent was completely amorphous and no characteristic pattern could be obtained with it or with "monolayer"-covered samples.

> Zusammenfassung-Das allgemeine Adsorptionsverhalten der Metallchelate von 8-Hydroxychinolin, Ätioporphyrin, β -Diketonen und 8-Mercaptochinolin wird beschrieben. Dies zeigt im Zusammenhang mit Untersuchungen von Adsorptionsisothermen, daß der Mechanismus zum Chemisorptionstyp gehört. Dabei treten im Falle über Sauerstoff koordinierender Chelatbildner hohe Adsorptionswärmen auf. Es scheint, daß Wasserstoffbrücken zu Brønstedzentren an den Adsorbentien für den Prozeß wesentlich sind und daß leich mehrere Adsorptionsschichten aufgebaut werden. Diese Beobachtung wird gestützt durch kinetische Untersuchungen, die zeigen, daß die Adsorption in zwei Stufen abläuft, wobei nach Bildung einer Monoschicht eine Änderung sichtbar wird. Beide Stufen sind diffusionskontrolliert und haben relativ geringe Wahrscheinlichkeit. Infrarot- und Röntgenbeugungsuntersuchungen stützen diese Folgerungen, obgleich sie nur von begrenztem Wert sind. Anforderungen an allgemeiner verwendbare Chelatbildner und Adsotbentien für analytische Zwecke werden vorausgesagt und diskutiert.

> Résumé-On décrit les caractéristiques générales d'adsorption des chélates de métaux avec la 8-bydroxyquinoléine, l'étioporphyrine, la β -dicétone et le 8-quinoléinethiol. Celles-ci, avec des études d'isotherme d'adsorption, montrent que le mécanisme est d'un type chimisorption avec, dans le cas d'agents oxo-chélatants, des chaleurs élevées d'adsorption. Il apparaît que l'enchaînement par liaison hydrogène sur des positions de Brønsted des adsorbants est un caractère essentiel du processus et qu'il se forme aisément de multicouches de produit adsorbé. Cette observation est appuyée par des études de vitesse qui montrent que l'adsorption est un processus en deux étapes avec une rupture en un point correspondant au recouvrement par une seule couche. Les deux étapes sont contrôlées par diffusion avec une probabilité relativement faible. Des études d'infra-rouge et de diffraction de rayons X, quoique de valeur limitée, étayent ces conclusions. On laisse prévoir les conditions nécessaires pour les agents chélatants le plus généralement applicables et les adsorbants pour des buts analytiques et en discute.

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AN INVESTIGATION INTO THE USE OF PLATINUM WARE FOR SILICATE ANALYSIS*

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Summary—The amount of platinum dissolved from platinum apparatus used for dissolving silicate materials to obtain solutions for analysis has been determined. The study included apparatus made from an alloy containing 95% platinum and 5% gold. The affinity of iron and platinum was investigated, together with the problem of removing iron from platinum after the latter has been contaminated during fusions. The behaviour of platinum in aclassical scheme for the analysis of silicate materials was investigated and the distribution of the platinum in various precipitates established. Platinum has been found to interfere in commonly used methods for the determination of silica, aluminium, iron, titanium, calcium and magnesium.

It is well known that platinum interferes in conventional methods for analysis of silicates, though very few exact details are available. The opening-out of silicate materials usually involves the use of platinum apparatus, and platinum may be dissolved in variable amounts which are assumed to be small and are often ignored in the analytical procedures. Hillebrand *et al.*¹ recommend the removal of platinum by precipitation with hydrogen sulphide after the fusion, as its distribution in subsequent stages is unpredictable, but this considerably prolongs the analysis. Groves² recognizes that platinum passes into the filtrate from an R_2O_3 precipitation with ammonia, and states that it accompanies the calcium oxalate precipitate. Bennett and Hawley³ state that platinum is dissolved during alkaline fusions in platinum crucibles, but they make no allowance for its presence in subsequent procedures.

It is well known that iron, particularly iron(II), has a strong affinity for platinum when the two substances are heated together; this effect is particularly pronounced when materials containing iron are fused with alkaline fluxes. Iron that adheres to the platinum crucible must be removed after the sample has been dissolved, or low iron results will be obtained; some platinum is simultaneously removed. Iron must be removed from platinum ware before an analysis is started.

We have been unable to find any detailed information on the behaviour of platinum crucibles during various types of fusions, and on the subsequent behaviour of platinum during analyses. This report describes the work done to obtain a clearer understanding of this problem, which is of great importance in silicate analysis work.

The iron absorbed by the platinum during fusions with alkaline fluxes is very difficult to remove, and no effective method has been found. The best method is repeated ignitions alternated with potassium pyrosulphate fusions, though, after seven such treatments, significant amounts of iron may still be removed with each fusion. It is recommended that separate crucibles should be reserved for iron determinations, and that an acidic flux should be used for the fusion.

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Crucibles made from a 5% gold-95% platinum alloy are superior to pure platinum crucibles in that they are at least as good in their resistance to attack and iron absorption, and have the added advantage of not deforming easily with handling.

When platinum apparatus is used for an analysis involving fusion, account must be taken of the platinum introduced into the solution and its possible interference in the methods used. The amount dissolved varies according to experimental conditions and the crucibles and samples used.

EXPERIMENTAL

Determination of platinum

The first essential was a fairly sensitive method for the determination of platinum with as few interferences as possible. The tin(II) chloride method is well known; its sensitivity has been increased by extraction of the platinum complex into organic solvents,^{4,5} but this procedure was not found to be reproducible and did not give the sensitivity claimed. Measurement in aqueous solution was found to be entirely satisfactory. The tolerance for titanium, calcium and magnesium has been reported to be well within the limits required; nickel and chromium give high results, but moderate amounts of copper and cobalt can be tolerated.⁴ We found that 0·1 mg of platinum could be measured in the presence of 500 mg of iron or 1000 mg of aluminium; up to 1·5 g of sulphate and nitrate have no effect, and sodium chloride can be tolerated up to the saturation level. However, if ammonia has been added to the sample at any stage of the analysis, the portion used for the platinum determination must be boiled with sulphuric acid for 30 min before colour development.

Fluxes used

Five types of flux are used at the National Institute for Metallurgy (N.I.M.) and are described here. Other fluxes which have been investigated and found to be inferior are sodium fluoride, sodium hydrogen fluoride, lithium tetraborate, boric acid, and sodium tetraborate. Many nonrefractory silicates are dissolved in hydrofluoric acid and the fluorides decomposed with sulphuric acid, particularly for the determination of the alkali metals; attack on the platinum is insignificant, however, so the technique is not considered in this report.

Sodium carbonate fusion. The sample is mixed with 8 times its weight of flux in a platinum crucible covered with a lid, and fused, slowly at first, then for 30 min, with occasional swirling,¹ at the full heat of a Méker burner. The fusion is applicable to most non-refractory silicate materials.

Sodium carbonate sinter. Sample (1 g) is mixed with sodium carbonate (2 g) in a platinum dish and heated over a Méker burner at full heat for 10 min, then placed in a muffle furnace at 1200° for 5 min.⁷ Refractory silicates such as sillimanite are not completely dissolved.

Sodium carbonate and sodium borate fusion. The fusion mixture is composed of equal amounts of sodium carbonate and anhydrous sodium borate.¹ The fusion conditions are the same as for sodium carbonate. The fusion is applicable to refractory silicates and zirconium ores.

Sodium peroxide and sodium hydroxide sinter. A mixture of 2 g of sodium peroxide and 1.5 g of sodium hydroxide is mixed with 0.5 g of sample (3 and 2 g respectively for a 1-g sample) and sintered at 440° for 30–60 min in a muffle furnace. The technique is applicable to refractory silicates, and is particularly suited to samples containing iron(II). Zirconium ores are not dissolved. Silica remains soluble when the cooled fused mass is leached in water and the solution is poured into hydrochloric acid.

Potassium hydrogen fluoride fusion. A mixture of 2 g of flux with 0.5 g of sample is heated gently in a crucible until all moisture has been evolved, then at the full heat of a Méker burner until the sample has dissolved. The fusion should not take more than 1 min from the time that the full heat is applied. The fluorides are decomposed by heating with 3.5 ml of conc. sulphuric acid for 10 min after the initial effervescence has ceased. Silicon is volatilized as the tetrafluoride during the fusion. The fusion is applicable to all the silicate materials that have been investigated.

¹¹Lithium fluoride and boric acid fusion. A mixture of 3 g of lithium fluoride and 2 g of boric acid is placed in the crucible, and 0.5 g of sample placed on top.⁸ The mixture is heated for 15 min at the full heat of a Méker burner. Then 10 ml of conc. sulphuric acid are added, and the crucible is heated gently until effervescence has ceased. The temperature is increased until copious fumes of sulphur trioxide are evolved and is then maintained for 2–3 min. Silicon, boron, and fluorine are volatilized. Refractory materials are not completely dissolved.

Lithium metaborate fusion. A sample weighing 0.2 g is mixed with 1 g of lithium metaborate (anhydrous) and placed in a muffle furnace at 950° for 10–15 min.⁹ The fused mass is cooled, and leached with dilute nitric acid. If platinum-gold alloy crucibles are used, the mass comes away from the crucible on cooling and can be taken out, leaving the crucible free for use again without leaching. The fusion is uncertain for refractory materials, and does not dissolve zirconium ores.

Behaviour of platinum crucibles during fusions

Although a number of factors can be shown to affect the dissolution of platinum, there are also some that we have been unable to explain and still do not fully understand. The amount of platinum dissolved by the fluxes used is shown in Table I; the sodium carbonate fusion and the sodium hydroxide-sodium peroxide sinter have been selected for more detailed study, and are not included in the Table.

The sample used contained about 8% of iron(II) oxide and 7% of iron(III) oxide. Dilute hydrochloric acid was used for leaching and the platinum was determined in the solution. After ignition, 5 g of potassium pyrosulphate were fused in the crucible, and platinum and iron were determined after leaching in dilute hydrochloric acid. The crucibles were cleaned by repeated potassium pyrosulphate fusions until the iron dissolved by each fusion was less than 15 μ g. It is, of course, possible that iron was still present but insoluble in molten potassium pyrosulphate, though there is no experimental evidence to substantiate this.

Effect of iron(II) and (III)

It is well known that platinum and iron have a strong affinity, and that if an iron compound is heated with platinum, some iron is absorbed by the platinum and is difficult to remove, *e.g.*, the rapid deterioration of platinum crucibles if they are frequently placed on steel hot-plates. When silicate rocks are fused with acidic fluxes, such as potassium hydrogen fluoride or pyrosulphate, there is no tendency for iron to be absorbed by the platinum; in fact, the reverse occurs, and any iron already absorbed by the platinum is partially removed. Also, the amount of platinum dissolved is about 0.5 mg for 5 g of flux. With alkaline fluxes, such as sodium carbonate, the amount of platinum dissolved is about 0.5 mg for 5 g of flux. With alkaline fluxes, such as sodium carbonate, the amount of platinum dissolved can be substantial and appears to be related both to the amount and the oxidation state of the iron. The results in Table II were obtained by mixing 0.03 g of iron(II) or iron(III) (as the sulphate), with 0.5 g silica and 4 g of sodium carbonate and fusing as described above. The cooled melts were leached with dilute hydrochloric acid, and the crucibles were then ignited

	No. of	Pt in leach	Crucible cleane	d with $K_2S_2O_7$
Flux	detns.	solution,	Pt dissolved, mg	Fe removed, mg
Sodium carbonate and sodium tetraborate	3	1·1 ± 0·8	0·67 ± 0·13	0.2 ± 0.1
Sodium carbonate sinter	6	6.8 ± 0.9	0.62 ± 0.60	0.008 ± 0.002
Lithium metaborate	4	0.012 ± 0.004	0.66 ± 0.15	0.047 ± 0.036
Lithium fluoride and boric acid	8	6.1 ± 4.0	not d	letermined
Potassium hydrogen fluoride	4	0.15 ± 0.03	0.60 ± 0.12	0.07 ± 0.07
Hydrofluoric acid and sulphuric acid	4	<0.02	not de	termined

TABLE I.—Amount of platinum dissolved during fusion with fluxes in platinum crucibles and the amount of iron absorbed by the crucible

TABLE II.—BEHAVIOUR OF IRON AND PLATINUM DURING SODIUM CARBONATE FUSIONS

		F-(II)	Pt in leach		ution from , fusion
Crucible*	Fe(III) g	Fe(II) g	solution <i>mg</i>	Pt mg	Fe mg
11	0.03		1.92	0.54	0.17
22	0.03		5.04	1.58	0.19
45	0.03		2.90	0.80	0.01
11		0.03	0.08	0.66	2.08
22		0.03	0.30	2.08	12.24
45		0.03	0.16	0.77	4.08
11			0.61		
22			0.41		
45			0.34		

* Dates of manufacture: 11-1963; 22-1963; 45-before 1960.

for 30 min at the full heat of a Méker burner. The crucibles, after the fusions with iron(II), had brown strains inside, but none occurred with iron(III). The stains were assumed to be due to oxidation of iron(II) absorbed by the platinum. Then 5 g of potassium pyrosulphate were fused in each of the crucibles for 10 min, and the cooled melts were leached with dilute hydrochloric acid. Iron and platinum were determined in the solution. For comparison, the fusion was repeated with only sodium carbonate and silica, and the platinum was determinec. As shown in Table II, more platinum was dissolved in the presence of iron(III) than of iron(II), though considerably more iron(II) appears to have been absorbed by the crucible. It is possible, however, that iron(II) is more easily removed by molten potassium pyrosulphate than iron(III) is, and the latter remains on the platinum. The greater amount of platinum dissolved when no iron is present is probably due to the higher flux: sample ratio; an average of 8 mg of platinum was dissolved by fusing 4 g of sodium carbonate in the absence of any sample. The importance of removing iron from crucibles after they have been used with alkaline fluxes is amply illustrated. The absorption of iron(II) by the crucible can be avoided by using an oxidizing flux.

The removal of iron from platinum ware

The importance of the removal of iron from platinum apparatus cannot be overstressed, especially if iron is to be determined. No really efficient method has been found for the removal of iron from platinum, but of several substances investigated, molten potassium pyrosulphate is the most effective, though the crucibles used had to be ignited in air before the iron would dissolve in the flux. Tables III and IV show the amount of iron absorbed by platinum and the ineffectiveness of hydrochloric acid and potassium pyrosulphate for the removal of the iron. The sample used was a silicate rock containing approximately 8% of iron(II) oxide and 7% of iron(III) oxide. The cooled melts were dissolved in dilute hydrochloric acid, and the platinum was determined in the leach solution. The crucibles were then ignited for 30 min before each potassium pyrosulphate fusion or hydrochloric acid leach. Platinum and iron were determined on the resulting solutions.

The oldest crucibles, 45 and 79, appeared to absorb least iron and yield least platinum. They had become hardened from prolonged use and, on microscopic examination, their interior surfaces were seen to be pitted and very rough. It is interesting that these are the only crucibles that do not contain rhodium (see Table V). Crucible 22, which absorbed most iron and yielded most platinum, had the highest rhodium content. After being used to obtain the results in Table IV, the shiny interior surface of crucible 29 became etched and dull; a coarse crystal structure was visible to the naked eye. Crucibles 11, 22, and 87 had a similar crystal structure. The structure of crucible 79 was finer but still visible to the naked eye. Crucibles 45 and 47 had a very fine structure visible only under a microscope. It appears that platinum displays its most favourable properties when it has a fine crystal structure.

The exteriors of the crucibles were then examined by X-ray fluorescence. The results are shown in Table V.

No standards were used, so the results are purely comparative and no absolute values can be given. Iridium may be present in some crucibles, but the results were uncertain. The copper and nickel content could not be reduced by boiling the crucibles in nitric acid so the contamination was probably not on the surface. The manufacturers confirmed that small additions of iridium and rhodium are made to platinum to reduce crystal growth. It has been suggested that the crystal structure observed in some crucibles is caused by mistreatment, but this was discounted when the structure was observed in new crucibles, e.g., 29. The manufacturers agree that the use made of crucible 29 should not have caused deterioration of the platinum.

			For ea	ch fusion	0.5 g of	sample wa	as taken				
	Year of		Sample leach	1st HCl	cleaning	2nd HCl	cleaning	3rd HCl	cleaning	K ₂ S ₂ O	7 fusion
Crucible	manufacture	Flux	Pt, mg	Pt, mg	Fe, mg	Pt, mg	Fe, mg	Pt, mg	Fe, mg	Pt, mg	Fe, mg
11	1963	Na ₂ CO ₃	3.40	0.070	2.57	<0.03	1.29	<0.03	1.43	0.060	2.86
22	1963	Na ₂ CO ₃	3.20	0.020	2.74	<0.03	2.23	<0.03	2.11	1.15	6.07
45	pre 1960	Na ₂ CO ₃	3.32	<0.03	0.009	<0.03	0.004	<0.03	0.006	0.38	0.070
47	1964	Na ₂ CO ₃	4.80	<0.03	0.036	<0.03	0.020	<0.03	0.044	0.18	0.056
79	pre 1960	Na ₂ CO ₃	1.74	<0.03	0.86	<0.03	0.62	<0.03	0.34	0.31	0.49
87	1963	Na ₂ CO ₃	3.00	0.060	2.37	<0.03	1.94	<0.03	2.06	0.86	7.91

TABLE III.—REMOVAL OF IRON FROM PLATINUM CRUCIBLES WITH HYDROCHLORIC ACID AND POTASSIUM PYROSULPHATE For each finite 0.5 a of compute were taken

An investigation into the use of platinum ware for silicate analysis

	Date of		Leach solu- tion	1st f	usion	2nd	fusion	3rd f	usion
Crucible	manufacture	Flux		Pt, mg	Fe, mg	Pt, mg	Fe, mg	Pt, mg	Fe, mg
11	1963	Na ₂ CO ₃	8.25	0.91	7.97	1.20	2.69	0.71	0.97
22	1963	Na_2CO_3	5.60	2.27	16.33	3.20	7.69	0.75	0.91
45	pre 1960	Na_2CO_3	3.16	0.42	0.011	0.34	0.017	0.30	0.003
47	1964	$Na_2O_2 + NaOH$	0.42	0.32	0.066	0.33	0.064	0.37	0.020
79	pre 1960	$Na_2O_2 + NaOH$	1.06	0.37	0.097	0.40	0.12	0.37	0.11
87	1963	$Na_2O_2 + NaOH$	1.32	0.45	0.31	0.85	0.33	0.36	0.18
29*	Jan. 1966	Na ₂ CO ₃	2.64	0.69	7.40	0•48	2.12	0.86	1.94
	Date of		4t fus		5th fusion	f	6th usion		'th sion
Crucible	manufacture	Flux	Fe,	mg	Fe, mg	r F	e, mg	Fe	, mg
11	1963	Na_2CO_3	0.2	27	0.44	(0•30	0	16

TABLE IV.-REMOVAL OF IRON FROM PLATINUM CRUCIBLES BY POTASSIUM PYROSULPHATE FUSION

* New and unused

1963

1964

1963

pre 1960

pre 1960

Jan. 1966

Na₂CO₃

Na₂CO₃

Na₂CO₃

 $Na_2O_2 + NaOH$

 $Na_2O_2 + NaOH$

 $Na_2O_2 + NaOH$

22

45

47

79

87

29*

TABLE V.—QUALITATIVE X-RAY FLUORESCENCE ANALYSIS OF PLATINUM CRUCIBLES FOR IMPURITIES

0.29

0.020

0.18

0.31

1.07

0.31

0.040

0.025

0.19

1.06

0.12

0.010

0.070

0.060

0.34

Crucible	Fe	Ni	Cu	Rh	Remarks
11	В	В	В	С	
22	С	В	В	D	
29	В	В	В	В	Ir also detected
45	в	В	D	Α	
47	В	в	D	С	
79	D	В	D	Α	Pd and Zn also detected
87	в	В	D	С	
Not det	ected				C—About five times B
Just det	ectable	:			D—About ten times B

Table VI shows the results of further similar work with a pyroxenite containing 8.5% of iron(II) oxide and 0.75% of iron(III) oxide. The results are similar and again seem to indicate that attack on platinum is higher for the newer crucibles than the old. This does not necessarily imply that the newer crucibles are of inferior manufacture, but it may indicate that the properties of the platinum improve with long use. The amount of iron removed by the molten potassium pyrosulphate is unexpectedly low. This emphasizes the difficulty of predicting what results will be obtained with any particular combination of flux and sample. Although experimental conditions were reproduced as closely as possible in Tables III, IV, and VI, large variations in the amounts of platinum dissolved and iron absorbed do occur, and no explanation can be given for this behaviour.

The ineffectiveness of hydrochloric acid and potassium pyrosulphate in the cleaning of crucibles creates great difficulties in the determination of iron in silicate materials. Once a platinum crucible has been contaminated with iron, it is very difficult to ensure that the iron has been effectively removed even after 7 cleanings with potassium pyrosulphate. Also, if an alkaline flux is used to decompose

0.16

0.020

0.080

0.020

0.28

	Data of	Pt removed	$K_2S_2O_7$	fusion	N 7 (
Crucible	Date of manufacture	during fusion, <i>mg</i>	Pt, mg	Fe, mg	No. of detns.
1	new 1967	5.3 ± 1.9	0.65 ± 0.01	0.02 + 0.00	2
20	1966	7.7 ± 4.2	0.69 ± 0.06	0.10 ± 0.01	5
29	1966	6.0 ± 4.0	0.76 + 0.05	0.05 ± 0.02	5
33	1963	1.8 ± 0.5	0.64 + 0.06	0.05 ± 0.02	5
45	pre 1960	1.6 ± 0.6	0.81 + 0.04	0.05 + 0.05	5
52	new 1967	7.4 ± 2.5	0.64 + 0.02	0.01 + 0.00	2
88	1963	6.0 + 3.0	0.93 ± 0.10	0.52 ± 0.04	5
89	1963	1.6 ± 0.7	0.70 ± 0.11	0.03 ± 0.01	5

TABLE VI.—PLATINUM ATTACKED BY SODIUM CARBONATE FUSIONS, AND IRON REMOVED BY POTASSIUM PYROSULPHATE Conditions: 0.5 g sample; 4 g of sodium carbonate; 5 g of potassium pyrosulphate

TABLE VII.—DISSOLUTION OF OXIDIZED PLATINUM IN HYDROCHLORIC ACID AND POTASSIUM PYROSULPHATE BEFORE AND AFTER IGNITION

	Hot conc.	Hot conc. HCl rinse		nd K ₂ S ₂ O ion
Crucible	Pt, mg	Fe, mg	Pt, mg	Fe, mg
21	0.16	0.15	0.75	0.02
31	0.18	0.21	0.74	0.03
34	0.16	0.17	0.69	0.10
35	0.10	0.15	0.66	0.03
Ignited (21	0.12	0.28	0.38	0.09
before 31	0.13	0.19	0.59	0.01
HCI 34	0.06	0.24	0.68	0.10
rinse (35	0.08	0.17	0.76	0.01

the sample, the analyst can never know how much iron has been absorbed by the crucible. Probably the best way of ensuring accurate iron determinations is to use acid fluxes (*e.g.*, potassium hydrogen fluoride) to decompose the sample in crucibles used only for this work and never used for alkaline fusions.

Electrolytic treatment of platinum

It is well substantiated that the life of platinum electrodes is considerably lengthened if they are previously used as the anode to electrolyse a sodium hydroxide solution. The reason is not fully understood, but is is believed that the surface of the platinum is in some way rendered passive. It was thought possible that the same treatment might improve the quality of crucibles, but experiment proved it did not.

Oxidation of platinum by sodium peroxide

After sintering of samples with sodium peroxide and sodium hydroxide and leaching, the crucibles had a black stain, which disappeared if they were either ignited to red heat for a few seconds or rinsed with hot conc. hydrochloric acid. To ascertain the nature of the strain, pyroxenite samples were sintered and then leached with water.

The stains were removed by leaching with hot hydrochloric acid, then fusing 5 g of potassium pyrosulphate in the crucible, cooling and leaching; platinum and iron were determined in both solutions. From the results (Table VII) it appears that the stain may be an oxide of platinum that is soluble in hydrochloric acid and is partly reduced to the metallic state on heating. This may explain the attack on platinum during alkaline fusions when oxidizing agents are present.

Behaviour of platinum-gold alloy crucibles

Crucibles made from an alloy consisting of 5% gold and 95% platinum have recently become popular for silicate analysis, particularly when spectrographic and X-ray fluorescence techniques are

			D 4	K.2S2	O7 fusion
Crucible	Sample	Flux	Pt in leach solution, <i>mg</i>	Pt removed, mg	Fe removed, <i>mg</i>
101	0.5	Na ₂ CO ₃	7.20	0.54	0.05
101			8.20	0.74	0.02
102			4.70	0.34	0.53
102			5.72	0.54	0.34
101	0.5	$Na_2O_2 + NaOH$	0.88	0.29	0.06
101			0.32	0.48	0.01
102			0.66	0.33	0.08
102			0.34	0.34	0.17
101	0.2	KHF,	0.26	0.28	0.05
101		-	0.26	0.70	0.04
102			0.26	0.51	0.50
102			0.26	0.40	0.05
101	0.2	LiBO ₂	0.02	0.68	0.07
102		-	0.02	0.72	0.11

TABLE VIII.—ATTACK ON CRUCIBLE, AND IRON ABSORBED DURING FUSIONS IN PLATINUM-GOLD ALLOY CRUCIBLES

used. The main reason is that fluxes such as lithium metaborate and tetraborate do not "wet" the surface of the alloy, and melts can be poured out and the crucible left completely clean. If the melts are cooled in the crucible, the solid mixture comes away from the walls and can be tipped out, leaving the crucible ready for the next fusion. The alloy is much harder than pure platinum, and does not deform easily on handling, so should last longer.

Table VIII shows the results obtained with the pyroxenite (method as for Table VI). The crucibles showed no loss in weight on ignition at 1100° for 30 min. The dissolution of platinum and absorption of iron were no worse than when pure platinum crucibles were used.

Behaviour of platinum during silicate analysis

In every analysis that uses platinum crucibles, variable amounts of platinum will be dissolved and be present in solution during the subsequent analytical procedures. It is thus of the utmost importance to the analyst to know how platinum affects the course of an analysis. The behaviour of platinum in the various steps in the conventional method of analysis of silicate rocks was therefore studied.

Methods of analysis

Typical or simulated rock samples were fused with either sodium carbonate or a mixture of sodium peroxide and sodium hydroxide. The cooled melts were leached with dilute hydrochloric acid, and the solution was analysed for platinum. The sample solution was evaporated to dryness in a porcelain dish, and the silica rendered insoluble by baking. The residue was redissolved in hydrochloric acid, and the silica was filtered off, ignited in a platinum crucible, and volatilized as silicon tetrafluoride. The residue was fused with potassium pyrosulphate, then dissolved in dilute hydrochloric acid, and the platinum in the solution was determined. The solution was then combined with the original filtrate, and neutralized (Methyl Red) with ammonia. Then the solution was boiled and filtered, and the precipitate washed with dilute ammonium chloride solution. The amount of platinum in the filtrate and the precipitate was determined.

Aluminium was determined (a) by weighing the ignited ammonia precipitate and deducting iron, titanium, etc., and (b) by complexing the aluminium, iron, and titanium with EDTA, decomposing the aluminium complex with fluoride and titrating the liberated EDTA with zinc chloride solution, with dithizone as indicator.¹⁰

Iron was determined (a) titrimetrically with dichromate [sodium diphenylaminesulphonate indicator, tin(II) chloride reduction] and (b) spectrophotometrically with 1,10-phenanthroline. The hydrogen peroxide method (10% sulphuric acid medium) was used for titanium. The effect of platinum on all five methods was investigated.

Pt dissolved during fusion of the sample, mg	Pt in filtrate after separation of silica mg	Pt in residue from volatilizion of SiO ₂ mg
6.2	6.2	0.30
6.7	6.6	0.34
6-2	6.2	0.21

TABLE IX.—PLATINUM PRECIPITATED DURING SEPARATION OF SILICA

Calcium was precipitated with ammonium oxalate in the presence of 5 g of ammonium chloride in boiling solution neutral to Methyl Red, with 1 hr digestion before filtration. Magnesium was precipitated as magnesium ammonium phosphate and ignited to magnesium pyrophosphate. The amount of platinum in both precipitates was studied.

Results

Silica. Table IX shows that all the platinum appeared to be in the filtrate after these paration of the silica. About 0.3 mg of platinum was dissolved from the crucible during the potassium pyrosulphate fusion of the residue after volatilizion of the silica.

Iron, aluminium and titanium. Platinum forms very stable ammine complexes that are not easily decomposed and do not react with tin(II) chloride in the spectrophotometric determination of the platinum. Thus the filtrate and precipitate from the "ammonia precipitation" could not be analysed directly for platinum. The difficulty was overcome for the precipitate by igniting it in a zirconium crucible, fusing the oxides with sodium peroxide and leaching with dilute hydrochloric acid, and for the filtrate by evaporating it to dryness with nitric acid to remove ammonium salts, then either boiling for 30 min or fuming strongly for 5 hr with conc. sulphuric acid.

Table X shows that relatively little platinum is precipitated with aluminium hydroxide, the amount increasing with increasing amounts of iron, but not reproducibly, so no precise prediction can be made as to the amount of platinum expected ineither the filtrate or the precipitate. In most experiments recovery of platinum was not complete, probably because small amounts of the ammines remained undecomposed by the sulphuric acid treatment.

The indirect determination of aluminium by weighing the mixed oxides and subtracting the weights of other substances present is obviously affected by the amount of platinum present and is not satisfactory.

Platinum interferes in the EDTA procedure¹⁰ by causing (a) results to be low (Table XI) and (b)

		Pt found, mg	
Fe ₃ O ₃ added, <i>8</i>	Al ₃ O ₃ added, g	Filtrate	Precipitate
0.14	0	4.95	1.12
0.14	0	5.65	0.20
0.09	0	5.72	0.42
0.06	0	5.95	0.14
0.03	0	6.00	0.12
0.14	0.32	6.00	0.11
0.14	0.21	5.97	0.10
0.14	0.11	6.10	0.09
0.12	0.32	6.10	0.08
0.09	0.32	6.10	0.02
0.075	0.20	6.20	<0.05
0.075	0.20	6.15	<0.05
0.075	0.20	6.22	<0.05
0.075	0.20	6.10	0.20
0.075	0.20	5.95	0.22
0.075	0.32	6.00	0.02
0.075	0.32	6.05	0.07
0.00	0.20	6.12	0.02

TABLE X.—PRECIPITATION OF PLATINUM BY IRON AND ALUMINIUM HYDROXIDES Solutions contained 6.2 mg of platinum. Iron(III) and aluminium were added as chlorides.

Pt added mg	Relative error %	Pt added mg	Relative error %
1.2	-0.5, -0.9, -0.7	5.0	-1.1, -1.4, -2.2
2.5	-0·9, -0·6, -1.6	6.2	-1.2, -0.9, -2.2
3.7	-0.9, -1.1, -1.4	7.4	-0.7, -3.2, -2.8

TABLE XI.--INTERFERENCE OF PLATINUM IN ALUMINIUM DETERMINATION IN THE PRESENCE OF IRON ed 5 m

TABLE XII.—EFFECT OF PLATINUM ON THE DETERMINATION OF IRON WITH 1,10-PHENANTHROLINE OR BY DICHROMATE TITRATION

	1,10-Phenar	nthroline	Dichromate		
Pt added <i>mg</i>	Fe taken mg	Fe found mg	Fe taken mg	Fe found mg	
0	0.100	0.101, 0.099	40.0	40.0, 40.0	
1.22		0.102, 0.099		40.9, 40.9	
1.83		0.100, 0.099		40.9, 40.8	
4.90		0.099, 0.099		40.6, 41.5	
9.80		0.101, 0.107		41.8, 41.9	

TABLE XIII.—PLATINUM PRECIPITATED	WITH
MAGNESIUM AMMONIUM PHOSPHATE	
Solutions contained 6.2 mg of plating	um

Machal	Pt recovered, mg		
MgO added, $-\frac{g}{g}$	Filtrate	Precipitate	
0.3	4.02	1.96	
0.3	4.27	1.83	
0.3	4.05	2.01	
0.3	3.50	2.42	
0.3	3.88	2.08	
0.2	3.13	2.82	
0.1	2.80	3.18	
0.02	2.88	2.86	
0.02	4·75	1.24	

the indicator to be decomposed. No explanation is offered for (a) other than the possibility of a 1:1 ternary aluminium-platinum complex (possibly with EDTA) sufficiently stable (thermodynamically or kinetically) not to react with fluoride; (b) is thought to be due to platinum catalysis of the oxidation of dithizone by iron(III).

Table XII shows that up to 10 mg of platinum does not interfere in the 1,10-phenanthroline method for iron, but there is considerable interference in the volumetric method, possibly because platinum(IV) forms a complex with tin(II)¹¹ and this would be titrated along with the iron.

Attempts to eliminate platinum interference, by adding ammonia to form the ammine complex and then redissolving the precipitate with hydrochloric acid, reducing, and titrating, reduced the error by about half. The error could be further reduced, though not eliminated, by filtering off and washing the precipitate before redissolving it in hydrochloric acid, mainly because part of the platinum passes into the filtrate. It has been shown that platinum does not interfere in the silver reductor method if the first sharp end-point is used.12

Platinum (up to 10 mg) does not interfere in the hydrogen peroxide method for titanium.

The calcium oxalate precipitate retains less than 0.01 mg of platinum (from 8 mg). Magnesium ammonium phosphate coprecipitates appreciable amounts of platinum, even when only 20 mg of magnesium oxide are present, Table XIII. The amounts precipitated are erratic and show little apparent relationship to the amount of magnesium present.

CONCLUSIONS

When a sample is fused with a flux in a platinum crucible or dish, platinum will be dissolved. The amount depends on several factors, the most important of which is the type of flux used. Alkaline fluxes dissolve more platinum than acidic fluxes do; the greatest attack is by sodium carbonate, and the amount dissolved can be as high as 10 mg if the sample contains appreciable amounts of iron. If the sample contains iron(II) considerable amounts of iron may be absorbed by the platinum. A preferable method of dissolving silicate materials is a sinter, at 440°, with a mixture of sodium peroxide and hydroxide. Refractory materials are completely dissolved, a clear solution is normally obtained, platinum attack is reduced, and iron(II) is oxidized so that less iron is absorbed by the platinum. With potassium hydrogen fluoride and pyrosulphate fusions, platinum attack usually amounts to 0.5 mg and iron is not absorbed by the platinum, so that these fusions are recommended where iron is to be determined. With lithium metaborate fusions, the amount of platinum dissolved is ~ 0.01 mg.

Zusammenfassung—Es wurde die Platinmenge bestimmt, die sich aus Platingerät beim Aufschluß von Silikatmineralien zur Herstellung von Analysenlösungen auflöst. Auch Geräte aus einer Legierung von 95% Platin und 5% Gold wurden untersucht. Die Affinität von Eisen und Platin wurde erforscht sowie das Problem, wie man Eisen aus Platin entfernt, wenn es bei einer Schmelze damit verunreinigt wurde. Das Verhalten von Platin in einer Silikatanalyse nach klassischem Schema wurde untersucht und die Verteilung von Platin auf die verschiedenen Niederschläge ermittelt. Es wurde gefunden, daß Platin bei allgemein verwendeten Methoden zur Bestimmung von Kieselsäure, Aluminium, Eisen, Titan, Calcium und Magnesium stört.

Résumé—On a déterminé la quantité de platine dissoute d'un appareil en platine utilisé pour la dissolution de produits au silicate pour obtenir des solutions pour l'analyse. L'étude inclut un appareil fait d'un alliage contenant 95% de platine et 5% d'or. On a étudié l'affinité du fer et du platine, en même temps que le problème de l'élimination du fer du platine après que ce dernier ait été contaminé durant les fusions. On a étudié le comportement du platine dans un schéma classique pour l'analyse de produits au silicate et établi la répartition du platine dans divers précipités. On a trouvé que le platine gêne dans les méthodes communément employées pour le dosage de la silice, de l'aluminium, du fer, du titane, du calcium et du magnésium.

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SOME VICINAL DIOXIMES AS GRAVIMETRIC REAGENTS

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Summary—A series of 3,3-substituted indane-1,2-dionedioximes has been synthesized and their reactions with transition metals have been investigated. From the results obtained it is suggested that the selectivity of such dioximes, as gravimetric reagents, is not a function of the dioxime grouping but is due to metal-metal bonding in the complex.

AMONG the factors which influence the choice of an organic chelating reagent as a selective precipitant for one metal ion species in a mixture are the relative stabilities and solubilities of the chelates formed. The stability of the chelates depends essentially on the strength of the ligand-metal bonds, which in turn is determined by the relative electron densities at the bonding atoms, the polarizability of these atoms, and the distances apart of the centres of electron density. For any two metals forming complexes with a particular chelating ligand, the differences in the stabilities of the complexes are thus attributable to (a) the differences in the electronegativities of the two metals, and (b) the sizes and distribution of the electronic orbitals of the two metal ions.

The palladium chelates of reagents such as dimethylglyoxime and 4-alkylcyclohexane-1,2-dionedioximes are stable at lower pH values than are the corresponding nickel compounds. Since the electronegativity of palladium is only slightly different from that of nickel, we may consider that the stability increase is caused by the larger size of the palladium ion and its greater polarizability. In the chelate the metal atom has four equidistant nitrogen atoms as nearest neighbours, and because the nitrogenmetal orbital overlap is greater in the palladium chelates the bond formed is potentially stronger.

In an attempt to make a vicinal dioxime that would be more selective than dimethylglyoxime or the 4-alkyl-cyclohexane-1,2-dionedioximes for palladium, we have synthesized and studied¹ the compound indane-1,2-dionedioxime. Because the nitrogen atoms of the two oximino groups are attached to carbon atoms of a 5membered alicyclic ring and these carbon atoms effectively exhibit distorted sp^2 hybridization there is an increased N-N separation and hence an increased N-metal separation, in comparison with dimethylglyoxime and its analogues. The nickel chelate should be relatively more affected than the palladium chelate, and this is indeed the case,¹ a higher pH being needed for precipitation of the nickel chelate than for the dimethylglyoxime and 4-methylcyclohexane-1,2-dionedioxime complexes.

The effect of substituents in the 3-position of indane-1,2-dionedioxime have now been investigated. Preliminary results with one such reagent have been reported.²

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EXPERIMENTAL

Reagents

The following members of the monoxime series 3-R'-3R''-indane-1-one-2-oxime were prepared by slight modifications of existing methods.³⁻⁵

R' = H—; $R'' = CH_3$ —; 3-methylindane-1-one-2-oxime³ $R' = R'' = CH_3$ —; 3,3-dimethylindane-1-one-2-oxime³ R' = H—; $R'' = C_6H_5$ —; 3-phenylindane-1-one-2-oxime⁴ $R' = CH_3$ —; $R'' = C_6H_5$ —; 3-methyl-3-phenylindane-1-one-2-oxime⁵ $R' = R'' = C_6H_5$ —; 3,3-diphenylindane-1-one-2-oxime³

All the compounds were prepared via the appropriately substituted indane-1-one, which was converted into the 2-oxime with amyl nitrite and sodium methoxide.

Although for ease of filtration of the metal-dioxime complexes it is advantageous to form the oximes *in situ*, for investigations of their reactions it is necessary to use solutions of the dioximes, so that any precipitates formed can be attributed to the correct reagent. The dioximes were prepared by heating a mixture of the monoxime with hydroxylamine hydrochloride, ethanol and 10% w/v sodium hydroxide solution.

The dioximes were recrystallized from ethanol, and for those with melting points close to those of the monoximes, identity was checked by taking the melting points of mixtures with the appropriate monoxime.

Reactions of the monoximes and dioximes with metal ions

The reactions with metal ions were investigated by adding aqueous ethanolic solutions of the compounds to aqueous solutions of the appropriate salts of the metal ions, and adjusting the pH of each solution to 2.0, 7.0 or 9.0 with ethanolic solutions of hydrochloric acid or ammonia. (The ratio of ethanol/water was empirically determined to be such as to prevent precipitation of either the metal salt or the oxime.) The solutions were left either for 1 hr at room temperature or for 30 min at $80 \pm 1^{\circ}$.

The ions used were Co(III), Cu(II), Au(III), Ir(II), Fe(II), Fe(III), Mn(II), Ni(II), Os(IV), Pd(II), Pt(IV), Rh(II), Ru(IV). These were selected from the larger number used to test the reaction of indane-1-one-2-oxime and indane-1,2-dionedioxime.¹ Results are given in Table I.

DISCUSSION

As expected, palladium(II) gave precipitates with all the dioximes at all the pH values used. The increasing hydrophobic effect of the heavier hydrocarbon substituents was manifested by the insolubility of their nickel, copper(II) and gold(III) complexes.

It is noteworthy that copper(II) does not give precipitates with the monoximes, although they contain the same —CO—C=N—OH— grouping as α -benzoinoxime. It is considered that this is due to the difference in the dispositions of the orbitals in the two types of compounds. The benzoinoxime has a much less rigid structure than have the indane monoximes.

Platinum(II) did not give the expected precipitates with the dioximes. However, on formation of platinum(II) from platinum(IV) in situ by reduction with hydroxylamine, precipitates were obtained with all the dioximes at pH 7.0 and 9.0 and with the phenyl-substituted dioximes at pH 2.0. This was attributed to a kinetic effect. The solvent sheath of platinum(II) in aqueous solution is probably so kinetically stable ["inert," probably owing to the polarizability of platinum(II)] that it does not allow the entry of the nitrogen co-ordination system of the oxime. During reduction from platinum(IV) to platinum(II) with its attendant change from 6- to 4-co-ordination and the formation of a transition complex with the reductant, the oxime nitrogen atom may enter into the co-ordination sphere of the platinum(II) and result in precipitation of the indane complex.

			TABLE I		
Oxime Metal		Monoxime		Dioxime	
Oxine Metal	рН	Observation	pН	Observation	
1	Pd(II) Au(III) Ru(IV)	7, 9 7, 9 2, 7, 9	yellow ppte <i>i</i> , <i>a</i> brown ppte <i>ii</i> , <i>b</i> purple colour, <i>b</i>	7, 9 2, 7	yellow ppte <i>i</i> , <i>c</i> yellow ppte <i>i</i> , <i>c</i>
	Co(II) Cu(II) Fe(II)			9 9 9	red brown ppte i light brown ppte i red brown colour
2	Pd(II)	2 7 9	yellow ppte <i>ii, a</i> yellow ppte <i>i, c</i> yellow ppte <i>i, a, d</i>	2, 7, 9	yellow ppte i
	Au(III) Rh(II)	9 7 9	yellow ppte <i>ii</i> yellow ppte <i>ii</i> , <i>b</i> yellow ppte <i>ii</i>	2, 7	yellow ppte <i>ii</i> , b
	Ru(IV)	2 7, 9	purple colour b brown colour b	• • •	
	Cu(II) Ni(II) Os(IV)			2,7,9 9 7,9	brown ppte <i>ii</i> yellow ppte <i>i</i> , <i>a</i> brown colour <i>b</i>
3	Pd(II) Au(III) Os(IV) Fe(II)	2, 7. 9 2 7, 9 7, 9	yellow ppte <i>ii</i> , <i>a</i> yellow ppte <i>ii</i> , <i>a</i> brown colour <i>b</i> yellow colour <i>b</i>	2, 7, 9 2 7, 9	yellow ppte <i>i</i> yellow ppte <i>ii</i> brown colour <i>b</i>
	Cu(II) Ni(II) Co(II)	., .	jenen ooreat e	7,9 9 9	light brown ppte light brown ppte light brown ppte
4	Pd(II)	2 7, 9	yellow ppte <i>i</i> , <i>a</i> , <i>d</i> yellow ppte <i>i</i>	2, 7, 9	yellow ppte i
	Cu(II) Au(III) Co(II) Ni(II)			2, 7, 9 2 9 9	brown ppte <i>i</i> , <i>a</i> yellow ppte <i>ii</i> , <i>b</i> brown ppte <i>ii</i> yellow ppte <i>i</i> , <i>c</i>
	Os(IV) Ru(IV)	7, 9 9	brown colour <i>b</i> purple colour <i>b</i>	7,9	brown colour b
Pt(II) Rh(II	Pd(II)	2 7, 9	yellow ppte <i>i</i> , <i>a</i> , <i>d</i> yellow ppte	2, 7, 9	yellow ppte <i>i</i>
	Pt(II) Rh(III) Pr(IV)	2 2 9	yellow ppte <i>i</i> , <i>b</i> yellow ppte <i>i</i> , <i>b</i> yellow ppte <i>ii</i> , <i>b</i>	2	yellow ppte <i>ii</i> , b
	Au(III) Cu(II)	2, 7, 9	yellow colour b	2,7 2,7,9	yellow ppte <i>i</i> , <i>b</i> brown ppte <i>i</i>
	Ni(II) Co(II)			2, 7, 9 2 7, 9	orange ppte <i>ii</i> pale brown <i>ii</i> yellow ppte <i>ii</i> , b
	Os(IV) Fe(II)			7,9 7,9 7,9	brown ppte <i>ii</i> , <i>b</i> purple ppte <i>ii</i> , <i>b</i>

TABLE I

Legend:

Substances: 1. 3-Methylindane-

2. 3-3-Dimethylindane-

3. 3-Phenylindane-

4. 3-Methyl-3-phenylindane-

5. 3,3-Diphenylindane-

Amount of precipitate: i copious amount

ii faint precipitate

All precipitates produced at room temperature and not affected by heating in suspension except those marked:

1-one-2-oxime

a—dissolves on heating

b-produced on heating

c—coagulates on heating

d—reprecipitates on cooling.

Although gold(III) has the same *d*-electron configuration as platinum(II) a similar kinetic effect does not occur with gold.

Consideration of the electronic orbitals theoretically available for bonding, and of models of the oximes of the ionic species Ni(II), Cu(II), Pd(II), Pt(II), Au(III), shows no obvious reasons why the electronic overlaps and hence the stabilities of complexes formed with the dioximes should not be Ni < Cu < Pd > Pt = Au. The electronegativities on the Allred-Rochow scale⁶ and the probable polarizabilities of these ionic species would tend to indicate that the stabilities of the copper(II) complexes should be enhanced relative to those of nickel and that on these considerations alone, these dioximes should be better reagents for copper than for nickel. The relative thermodynamic stabilities of nickel and copper dimethylglyoximates⁷ confirm this, but other factors also play a part. In nickel dimethylglyoximate the metal d_{z^2} orbitals are used to give Ni-Ni bonds and an insoluble polymeric form arises.⁸ The monomer, in which the d_{2} orbital is used to co-ordinate solvent molecules, is a highly soluble yellow complex.9 Only on polymerization is the familar insoluble red complex formed. Copper dimethylglyoximate is simply a hydrated dimer, the d_{z^2} orbital of each copper ion being co-ordinated with one of the hydrogen-bonded oxygen atoms in the adjacent molecule in the dimer, and the sixth co-ordination sites being occupied by water molecules. These and the water associated with the oxime bridge by hydrogen-bonding or by dipole-dipole interaction cause the copper dimer to be so solvated as to be soluble in water.

If, because of steric hindrance, the copper complexes could be caused to bond in a somewhat different manner, or be made so hydrophobic as to be insoluble then these compounds could be ideal gravimetric reagents for copper.

In the metal complexes of the 3,3-disubstituted indane dioximes, the substituents are in a plane normal to that containing the rest of the metal complex. Models indicate that if the complex units are stacked as in the palladium dimethylglyoximate complex,⁹ then in a 3-substituted indane oxime the oxime bridges are somewhat shielded from solvent approach by the alkyl or aryl groups above and below it in the polymer. With the diphenyl complex this is so marked that it is thought possible that almost no solvation of the oxime-hydrogen-bond bridges would occur, and that if the metal complexes were stable, they would be so insoluble that this reagent should be capable of precipitating μ g-amounts of the metals.

From a consideration of molecular models, it would appear to be impossible to pack the copper 3,3-diphenylindane-1,2-dionedioximate units to form dimers similar to those of copper dimethylglyoximate but they can be packed like palladium dimethylglyoximate to give a polymer. From the results obtained with the monophenyl and the diphenyl oximes, we consider it probable that this packing is used. Attempts to verify this by X-ray analysis have not yet proved successful.

Determination of palladium

Those of the oxime series which had potential uses as gravimetric reagents for palladium were further investigated. Solubility of the reagent was accounted a prime consideration, and since it is generally better¹ to prepare the dioxime *in situ*— by oximation of the monoxime at a pH at which excess of dioxime is hydrolysed to the monoxime—the solubility of only the monoxime was determined (Table II), though

the extent of co-precipitation was compared for both classical and homogeneous solution (PFHS) precipitation methods.

Oxime	Solubility, <i>mg</i> /100 g of solution
Indane-1-one-2-oxime	4 9 ± 1
3-Methylindane-1-one-2-oxime	48 ± 1
3,3-Dimethylindane-1-one-2-oxime	45 ± 1
3-Phenylindane-1-one-2-oxime	48 ± 1
3-Methyl-3-phenylindane-1-one-2-oxime	54 ± 1
3,3-Diphenylindane-1-one-2-oxime	58 ± 1

TABLE II---SOLUBILITIES OF THE MONOXIMES

Direct precipitation

Palladium chloride solution (2.5 mg of palladium) was heated to 60°, and brought to pH 2 (hydrochloric acid). A 20% excess of 0.5% w/v dioxime solution in ethanol was added, the suspension was digested for 2 hr, then the precipitate was filtered off, washed free from chloride and reagent, and dried at $105-110^{\circ}$.

Precipitation from homogeneous solution

A 20% excess of 0.5 w/v monoxime solution in ethanol was added to a palladium solution, the pH adjusted to 2.0, and the mixture stirred until any precipitate had redissolved. An ethanolic 5% w/v solution of hydroxylamine hydrochloride (100% excess) was added and the mixture heated at 60-65° for 3 hr. The precipitate was then treated as before.

Results

Recoveries (%) were

	Monomethyl	Dimethyl	Monophenyl	Diphenyl
Direct	98.4 ± 0.3	99·8 ± 0·3	104 ± 1.5	110 ± 2
PFHS	99.8 ± 0.1	99·2 ± 0·2	99·4 ± 0·3	100.2 ± 0.5

The direct method always gave slow filtration and precipitates difficult to wash free from reagent. Analysis of the monophenyl and diphenyl complexes prepared by the direct method showed that co-precipitation of the reagent had occurred.

The diphenyldioxime appeared to be potentially a very sensitive reagent for trace amounts of palladium. Investigation showed that the optimum pH range for precipitation was 1-4, that up to 200% excess of reagent caused no co-precipitation in PFHS, and that as little as 100 μ g of palladium could be determined with an error of about 4%.

Application

Palladium generally occurs with the other noble metals and copper and nickel, both in nature and in alloys used for catalytic purposes, jewellery, or for metallurgical applications.

Since many of these metals give precipitates with either the monoxime or the dioxime, a prior separation is necessary. The most convenient is reverse-phase chromatography on tri-n-butyl phosphate supported on cellulose, with 6M hydro-chloric acid as eluent.¹⁰ Palladium and platinum are not separated, however, and the area of the thin layer containing these elements is removed, wet-oxidized to remove organic matter, and then treated with the monoxime at pH 2.0 and 70° for 30 min. The mixture is filtered hot, and the residue (platinum) washed with hot aqueous

ethanol. The filtrate, which contains the palladium, is then treated as described. Up to a 20-fold amount of platinum can be tolerated.

Conclusion

The results so far indicate that it is necessary to re-assess the selectivity of the vicinal dioxime group, hitherto considered to be highly selective, only palladium(II), nickel(II) and platinum(II) yielding insoluble products. The selectivity however is not a function of the group itself, but of metal-metal bonding. A search for a more selective functional group, based on a knowledge of the disposition of the d orbitals and the possibility of π -bonding between the ligands and the central metal atom, is necessary. Some of the compounds investigated, even though not as "selective" as dimethylglyoxime, are potentially useful as reagents for the determination of palladium.

> Zusammenfassung—Eine Reihe von 3,3-substituierten Indan-1,2-diondioximen wurde synthetisiert und ihre Reaktionen mit Übergangsmetallen untersucht. An Hand der erhaltenen Ergebnisse wird die Vermutung geäußert, daß die Selektivität solcher Dioxime als gravimetrischer Reagentien nicht an der Dioximgruppierung liegt, sondern an Metall-Metall-Bindungen im Komplex.

> Résumé-On a synthétisé une série d'indane 1,2-dionedioximes 3,3-substituées et étudié leurs réactions avec les métaux de transition. Des résultats obtenus, on suggère que la sélectivité de telles dioximes, en tant que réactifs gravimétriques, n'est pas fonction du groupement dioxime mais est due à l'enchaînement métal-métal dans le complexe.

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SEPARATION OF METAL IONS ON TIN(IV) TUNGSTATE AND SELENITE PAPERS

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Summary-Papers impregnated with the inorganic ion-exchangers tin(IV) tungstate and selenite have been shown to be useful for ionexchange chromatography of several metal ion mixtures, and suitable solvent systems have been developed and evaluated.

SYNTHETIC inorganic ion-exchangers sometimes show high selectivities for metal ions.¹ This outstanding property can be utilized in chromatography by impregnating papers with these materials. For this purpose the inorganic material has definite advantages over organic resins: its synthesis and impregnation on paper is easier; it does not shrink significantly in contact with aqueous solvents or exchanging ions; the amount of the ion-exchanger on the paper can be varied and papers with different ion-exchange capacities can be easily prepared; it is more selective and many difficult separations can be made easily. When used in conjunction with mixed solvent systems the inorganic ion-exchange papers become even more effective for the separation of cations. Tin(IV) tungstate, a cation-exchanger, was synthesized in these laboratories² and the chromatographic behaviour of 46 cations in 45 solvent systems on tin(IV) tungstate papers was reported earlier.³ In the present communication results are presented for 15 more solvents for the paper chromatography of 47 cations on these papers. Tin(IV) selenite papers have also been prepared and their behaviour towards 47 cations in 40 solvent systems has been studied. As a result a number of interesting separations have been developed.

EXPERIMENTAL

Preparation of ion-exchange papers

Tin(IV) tungstate. Whatman No. 1 paper strips, 140 × 30 mm, prepared as reported earlier.³ Tin(IV) selenite. Paper strips dipped in 8.2% w/v tin(IV) chloride solution for 5 sec, blotted, dried at room temperature, dipped in 6.7% w/v selenium dioxide solution for 5 sec, drained, dried at room temperature, washed with distilled water, and again dried at room temperature. It is necessary to wash the papers as soon as they are dry after the selenium dioxide impregnation.

Procedure

Thin glass capillaries were used to spot the test solutions. The papers were conditioned for 10 min in 200×50 mm glass jars containing the solvent and then developed until the solvent had ascended 110 mm, unless otherwise stated. Test solutions and detection reagents were prepared as before.³ The solvent systems used were as follows.

Systems used for tungstate papers

- 1. Acetonylacetone + acetone + 50% hydrochloric acid (7:3:1)
- Butanol + acetonylacetone + acetic acid + 50% hydrochloric acid (3:3:3:1)
 Ethyl methyl ketone + butanol + 50% hydrochloric acid (6:3:1)
 Butanol + dioxan + 10M hydrochloric acid (6:2:2)

- 5. Ethyl methyl ketone + acetone + 1M hydrochloric acid (7:3:3)
- 6. Isopropanol + acetylacetone + 50% hydrochloric acid (6:3:1)

- 7. Dioxan + satd. soln. of sodium fluoride + 1M hydrochloric acid (3:1:6)
- 8. 2M Perchloric acid + chloroform + acetone (a, 1:2:5) (b, 1:1:3) (c, 2:1:5)
- 9. 0.5M Perchloric acid
- 10. Isopropanol + acetylacetone + 50% perchloric acid (6:3:1)
- Ethyl malonate + isobutyl methyl ketone + 50% nitric acid (6:3:1)
 Butanol + dioxan + isopropyl ethyl ether + 50% hydrochloric acid (3:3:3:1)
- 13. Methylamine + acetone + 50% hydrochloric acid (7:2:1)

Systems used for selenite papers

- 1. Methanol + 10M hydrochloric acid + formic acid (6:2:2)
- 0.1M sulphuric acid
- 3. 2M Nitric acid + 10% formic acid (1:1)
- 0.1M Perchloric acid
- 5. 0.1M Ammonium chloride
- 1.0M Perchloric acid
- 7. Methanol + 10M hydrochloric acid + acetic acid (a, 6:1:4), (b, 4:1:6), (c, 10:1:1)
- 8. 1% EDTA solution
- 9. 0.1M Nitric acid
- 10. 0.1M Hydrochloric acid
- 11. 0.1M Boric acid + 0.1M sodium hydroxide (pH 10)
- 12. 0.1M Citric acid + 0.1M trisodium phosphate (pH 7)
- 13. 1% Selenium dioxide solution in 0.1M nitric acid
- 14. 2M Nitric acid + 1% potassium nitrate solution (1:1)
 15. 2M Nitric acid + 10% potassium nitrate solution (1:1)
 16. 2M Nitric acid + 10% tartaric acid solution (1:1)
- 17. 4M Nitric acid + acetone + n-propanol (a, 1:1:1), (b, 2:1:1), (c, 1:2:1), (d, 1:1:2), (e, 1:4:1), (f, 1:1:4), (g, 4:3:3)
- 18. 0.05M Ammonium acetate
- 19. 0.2M Boric acid + 0.2M sodium chloride + 0.05M borax (25:25:12, pH 8.5)
- 20. 0.05M Potassium hydrogen phthalate (pH 4.2 and 6.2)
- 21. 0.1M Ammonium chloride + 0.1M hydrochloric acid (1:1)
- 22. Methanol + acetone + 10M hydrochloric acid (1:1:1)
- 23. 1% Citric acid solution
- 24. 0.1M Hydrochloric acid + 0.1M ammonium tartrate (1:1)
- 25. 1% Sodium potassium tartrate solution
- 26. 30% Formic acid
- 27. 6M Hydrochloric acid + 1% EDTA solution (2:8)
- 28. n-Butanol + 10M hydrochloric acid + 26M formic acid (7:1:3)
- 29. 1.0M Acetic acid
- 30. 2M Nitric acid + satd. soln. of potassium nitrate (1:1)
- 31. 0.5M Hydrochloric acid

RESULTS

The results for the most useful systems are summarized in Tables I and II. $R_{\rm T}$. and $R_{\rm T}$ refer to the leading and tailing edges of the spots. These solvents were chosen because some interesting separations can be achieved with them.

Separation of cations

These ion-exchangers proved to be so selective that in many cases one cation could be separated from almost all the others tested. Tables III and IV give the results, the interfering ions and the time of development being specified for each solvent. The $R_{\rm L}$ and $R_{\rm T}$ values are given in parentheses. Numerous separations can be worked out from the data in Tables I and II; many of these were tested experimentally and found feasible; in some cases there was less spreading of the spots when mixtures of cations were chromatographed.

Some useful separations obtainable on selenite papers with solvent systems not listed in Table II are summarized in Table V.

						Solve	ent syst	tem				
Cations		1		2		3		4		5		6
_	$R_{\rm L}$	RT	R _L	R _T	$R_{\rm L}$	R _T	R _L	R _T	RL	R_{T}	R _L	RŢ
Be ²⁺	0.20	0.00	0.23	0.04	0.20	0.00	0.52	0.26	0.40	0.00	0.38	0.00
Mg ²⁺	0.06	0.00	0.10	0.00	0.00	0.00	0.20	0.00	0.13	0.00	0.08	0.00
Al ³⁺	0 06	0.00	0.00	0.00	0.00	0.00	0.50	0.00	0.42	0·10	0.46	0.00
K+	0.07	0.00	0.16	0.08	0.00	0.00	0.07	0.00	0 ·20	0.10	0.00	0.00
Ca ²⁺	0.02	0.00	0.10	0.00	0.00	0.00	0.08	0.00	0.30	0·10	0.00	0.00
Ti ⁴⁺	0.06	0.00	0.00	0.00	0.07	0.00	0.37	0.00	0.07	0.00	1.00	0.00
V4+	0.24	0.01	0.13	0.00	0.10	0.00	0.40	0·22	0.40	0.00	0.42	0.18
Cr ³⁺	0.07	0.00	0.00	0.00	0.00	0.00	0.20	0.00	0.31	0.00	0.08	0.00
Mn ²⁺	0.35	0.21	0.15	0.04	0.00	0.00	0.36	0.21	0.43	0·18	0.10	0.00
Fe ²⁺	0.85	0.55	0.56	0.00	0.00	0.00	1.00	0.85	0.67	0.00	1.00	0.00
Fe ³⁺	0.94	0.63	0.57	0.00	0.00	0.00	1.00	0.87	0.67	0.00	1.00	0.00
C0 ²⁺	0.20	0.32	0.20	0.06	0.00	0.00	0.75	0.54	0.41	0.21	0.22	0.05
Ni ²⁺	0.00	0.00	0.00	0.00	0.00	0.00	0.20	0.00	0.47	0.21	0.09	0.00
Cu ²⁺	0.52	0.45	0.40	0.28	0.45	0.30	0.76	0.60	0.53	0.31	0.20	0.33
Zn²⊦	0.83	0.51	0.61	0.52	0.70	0.62	0.92	0.80	0.94	0.87	0.68	0.60
Ga ³⁺	1.00	0.84	0.67	0.54	0.60	0.50	1.00	0.90	0.00	0.00	1.00	0.88
As ³⁺	0.50	0.15	0.34	0.00	0.35	0.00	0.66	0.00	0.24	0.00	0.31	0.00
Se ⁴⁺	1.00	0.55	0.00	0.00	0.00	0.00	0.16	0.00	0.06	0.00	0.00	0.00
Rb+	0.06	0.00	0.12	0.04	0.00	0.00	0.07	0.00	0.17	0.07	0.00	0.00
Sr ²⁺	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.18	0.07	0.00	
Y ³⁺	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.18	0.00		0.00
Zr ⁴⁺	0.10	0.00	0.62	0.55	0.00	0.00	0.10	0.00	0.00		0.00	0.00
Nb ⁵⁺	0.56	0.00	0.02	0.35	0.00		0.66		0.00	0.00	0.85	0.00
Mo ⁶⁺	0.50	0.00	0.50	0.33	0.43 0.60	0.00		0.00	0.05	0.00	0.53	0.00
Ru ³⁺	0.07	0.00	0.30			0.00	0.97	0.83	0.05	0.00	0.90	0.00
Pd ²⁺				0.00	0.00	0.00	0.52	0.00	0.43	0.00	0.56	0.00
	0.63	0.45	0.50	0.28	0.56	0.35	0.85	0.50	0.80	0.54	1.00	0.50
Ag^+ Cd ²⁺	0.48	0.00	0.57	0.00	0.54	0.00	0.09	0.00	0.00	0.00	0.60	0.00
	0.67	0.46	0.60	0.57	0.59	0.50	1.00	0.85	0.86	0.80	0.62	0.56
In ³⁺	0.84	0.60	0.57	0.44	0.56	0.48	0.92	0.68	0.00	0.00	0.60	0.50
Sb ³⁺	0.62	0.45	0.53	0.40	0.57	0.50	1.00	0.88	0.17	0.00	0.61	0.00
Te ⁴⁺	0.53	0.00	0.50	0.00	0.45	0.00	1.00	0.85	0.00	0.00	0.54	0.00
Cs ⁺	0.06	0.00	0.12	0.01	0.00	0.00	0.11	0.00	0.17	0 ∙04	0.00	0.00
Ba ²⁺	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0 ∙12	0.01	0.00	0.00
La ³⁺	0.00	0.00	0.00	0.00	0.00	0.00	0.07	0.00	0 ·17	0.00	0.00	0.00
Ce ³⁺	0.00	0.00	0.00	0.00	0.00	0.00	0.08	0.00	0.18	0.00	0.00	0.00
Ce ⁴⁺	0.00	0.00	0.00	0.00	0 ∙00	0.00	0 ∙06	0.00	0 ·10	0.00	0.00	0.00
Hf⁴+	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.00	0.58
											0.18	0.00
]r⁴+	0.14	0.00	0.06	0.00	0.06	0.00	0·25	0·0 0	0.02	0.00	0·10	0.00
Pt ⁴⁺	0.71	0.48	0.55	0.20	0.60	0.52	0 ∙94	0 ∙77	0.60	0.20	0.60	0.20
Au³+	1.00	0.00	1.00	0.72	1.00	0.74	1.00	0 ∙94	1.00 0.00	0·90 0·00	1.00	0.17
Hg_{2}^{2+}	0.90	0.00	0.60	0.00	0 ∙86	0.64	1.00	0 ∙95	0·94 0·00	0.90	0.88	0.00
Hg ²⁺	0.94	0.61	0.61	0.54	0.81	0.60	0.90	0.00	1.00	0.92	0.82	0.61
Tl ⁺	0.26	0.00	0·11	0.00	0.01	0.00	0.22	0.00	0.13	0.92 0.00	0.82 0.11	
Pb ²⁺	0.20	0.14	0.21	0.00	0.00	0.00	0.47	0.00				0.00
Bi ³⁺	0.85	0·14 0·46	0.21	0.00	0·36 0·64	0.00			0.60	0.00	0.46	0.00
Th ⁴⁺	0.05	0.40	0.28	0.31			0.80	0.45	0.98	0.90	0.61	0.53
110 2+	0.06 0.65	0.00 0.43	0.00 0.45		0.00	0.00	0.07	0.00	0.09	0.00	0.00	0.00
UO2 ²⁺	0.03	0.43	0.42	0.24	0.46	0.32	0.90	0∙68	0 ∙56	0.00	0.63	0.34

Table I— $R_{\rm L}$ and $R_{\rm T}$ values of cations in some important solvent systems on tin(IV) tungstate papers

a					Solvent					
Cations		1		2	3				-	5
	$R_{\rm L}$	R _T	R_{L}	R _T	R _L	R_{T}	$R_{\rm L}$	R_{T}	$R_{\rm L}$	R_{T}
Be ²⁺	0.81	0.60	1.00	0.81	1.00	0.91	1.00	0.90	0.90	0.00
Mg ²⁺	0.96	0.82	0.95	0.80	1.00	0.90	0.80	0.57	1.00	0.93
Al ^{ă+}	0.81	0.33	0.91	0.20	1.00	0.98	0.64	0.37	0.46	0.00
K+	0·28	0.20	0.94	0.86	0.81	0.20	0.90	0.63	0.84	0.70
Ca ²⁺	0.20	0.16	0.97	0.81	0.98	0.83	0.70	0.40	0.80	0.00
Ti⁴+	0.30	0.00	0.63	0.00	0.07	0.00	0.00	0.00	0.00	0.00
V ⁴⁺	0.72	0.47	0.52	0.34	0.78	0.54	0.32	0.07	0.15	0.00
Cr ³⁺	0 ·98	0.77	1.00	0.90	0.96	0 ·81	0.17	0.00	0.25	0.00
Mn ²⁺	0.90	0.35	0.86	0.72	0.90	0.60	0.60	0.30	0.62	0.00
Fe ²⁺	0.73	0.54	0.87	0.00	0.90	0.00	0.60	0.00	0.00	0.00
Fe ³⁺	0.81	0.46	0.12	0.00	0.38	0.00	0.00	0.00	0.00	0.00
Co ²⁺	0 ·70	0.46	0.86	0.00	1.00	0.57	0.60	0.14	0.36	0.00
Ni ²⁺	0.70	0.36	1.00	0.62	0.99	0.77	0.63	0.44	0.71	0.09
Cu ²⁺	0 ·78	0.60	0.72	0.34	0.90	0.66	0.40	0.14	0.26	0.00
Zn ²⁺	0.97	0.00	0.80	0.61	0.90	0 ∙38	0.70	0.32	0.90	0.00
Ga ³⁺	0 ∙87	0.77	1.00	0.00	0.88	0.00	0.77	0.00	0.65	0.00
As ³⁺			0.00	0.00						
Rb+	0.32	0.21	0.85	0.57	0.90	0.61	0.66	0.43	0.74	0.57
Sr ²⁺	0.28	0.00	0.95	0.86	0.78	0.20	0.67	0.45	0.83	0.37
Y ³⁺	0.51	0.13	1.00	0.81	0.81	0.20	0.27	0.00	0.24	0.00
Zr ⁴⁺	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Nb ⁵⁺	0.27	0.00	0.00	0.00			1.00	0.90	0.00	0.00
Mo ⁶⁺	_		0.10	0.00	0.06	0.00	0.00	0.00	0.00	0.00
Ru³+	0.67	0.13	0.00	0.00	0.27	0,00	0.50	0.00	0.22	0.00
Pd ²⁺	1.00	0.00	1.00	0.00	1.00	0.00	1.00	0.00	1.00	0.00
Ag+	0.63	0.00	0.00	0.00	0.18	0.00	0.09	0.00	0.00	0.00
Cd ²⁺	0·38	0.18	0.62	0.42	0.88	0.20	0.60	0.14	0.77	0.00
In³+	0.82	0.61	0.17	0.00	0 ·48	0.00	0.00	0.00	0.10	0.00
Sb ³⁺	0.97	0.81	0.06	0.00	0·0 7	0.00	0.00	0.00	0.00	0.00
Te⁴⁺			0.00	0.00	0.07	0.00	0.00	0.00	0.00	0.00
Cs ⁺	0.00	0.00	0.82	0.58	0.85	0 ∙67	0.56	0.35	0.84	0.50
Ba ²⁺	0.16	0.00			0.90	0.81	0.43	0.27	0.84	0.16
La ³⁺	0.62	0.16	0.66	0.12	0.81	0 ∙50	0.30	0.00	0.13	0.00
Ce ³⁺	0.20	0.04	0.24	0.08	0.70	0.42	0.30	0.00	0.25	0.00
Ce ⁴⁺	0.40	0.00	0.20	0.00	0.00	0.00	0.32	0.00	0.51	0.00
W ⁶⁺	0.30	0.00	0.00	0.00			0.00	0.00	0.00	0.00
Ir ⁴⁺			0.00	0.00	1.00	0.80	0.00	0.00	0.25	0.00
Pt ⁴⁺		_	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Au ³⁺	0.92	0.75	0.26	0.00	0 .66	0.00	0.63	0.45	0.60	0.00
Hg ₂ ²⁺	1.00	0.90	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Hg ²⁺	1.00	0.93	0.74	0.54	0·15	0.00	0.84	0.00	0.10	0.00
TlŤ	0.00	0.00	0.44	0·1 8	0.26	0.36	0.30	0.00	0.31	0.06
Pb ²⁺	0.53	0 ·18	0.14	0.00	0.20	0.27	0.09	0.00	0.00	0.00
Bi ^{s+}	0.92	0.81	0.20	0.00	0.31	0.00	0.70	0.00	0.30	0.00
Th⁴+	0 ·20	0.00	0.18	0.00	0 ·13	0.00	0.00	0.00	0.00	0.00
UO_{2}^{2+}	0 ·76	0.46	0.36	0.00	0.45	0.10	0.16	0.00	0.10	0.00

TABLE II— R_{L} and R_{T} values of metal ions in some solvent systems on tin(IV) selenite papers

The charge on the ions separated was determined by electrophoresis on Whatman No. 1 paper with aqueous solvent systems used on selenite papers (Table VI).

DISCUSSION

The results show that papers impregnated with tin(IV) tungstate or selenite achieve fast, selective and specific separations with a solvent ascent of 110–150 mm. The

Cation separated	Solvent system	Ions which interfere	Time, min
$Zn^{2+}(0.94-0.87)$	5	Au ³⁺ , Hg ₂ ²⁺ , Hg ²⁺ , Bi ³⁺ , Cd ²⁺	60
Cd ²⁺ (0.86-0.80)	5	Au ⁸⁺ , Hg ²⁺ , Hg ²⁺ , Bi ³⁺ , Zn ²⁺	60
Au ³⁺ (1·00–0·74)	3	Hg ₂ ²⁺ and Hg ²⁺	35
Au ³⁺ (1.00-0.74)	2	Hg ² +	55
Ga ³⁺ (1·00-0·84)	1	Fe ²⁺ , Fe ³⁺ , Se ⁴⁺ , Au ⁸⁺ , Hg ₂ ²⁺ , Hg ²⁺ , Bi ³⁺	20

TABLE III—SEPARATION OF SINGLE CATIONS ON TIN(IV) TUNGSTATE PAPERS

Cation separated	Solvent system	Ions which interfere	Time, min
Au ³⁺ (1·000·80)	7(a)		40
Mg^{2+} (1.00–0.93)	5	Hg ²⁺ , Pd ²⁺ , Zn ²⁺	20
K ⁺ (0.81–0.63)	11	Hg ²⁺ , Pd ²⁺ , Au ³⁺ , Th ⁴⁺ , Nb ⁵⁺	20
Nb ⁵⁺ (1.00-0.90)	4	K ⁺ , Pd ²⁺ , Ga ³⁺ , Hg ²⁺ , Be ²⁺	20
Be ²⁺ (1.00-0.90)	4	K+, Pd ²⁺ , Ga ³⁺ , Hg ²⁺ , Nb ⁵⁺	20

TABLE	VSEPARATIONS ON TIN(IV) SELENITE PAPERS
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Solvent system	Separations achieved	Time, min
7(a)	Ga ³⁺ (0·77–0·65) → Tl ⁺	40
.,	Au^{3+} (1.00-0.86) $\rightarrow Ag^{+}$ (0.22-0.00)	
	\rightarrow Pt ⁴⁺ (0.63-0.45)	
	\rightarrow Pd ²⁺ (0.51-0.27)	
	Hg^{2+} (0.80–0.60) $\rightarrow Pb^{2+}$ (0.20–0.00)	
8	Cr^{3+} (0.16-0.00) $\rightarrow Co^{2+}$ (0.67-0.47)	20
	$\rightarrow Ni^{2+}$ (1.00–0.90)	

TABLE VI-ELECTROPHORETIC DETERMINATION OF THE CHARGE ON THE SPECIES IN SOME AQUEOUS SOLVENT SYSTEMS USED ON TIN(IV) SELENITE PAPERS

Solvent system	Positively charged	Negatively charged	Uncharged
2	Fe(III), Al		·
4	Ni, Ti(IV), Fe(III), Al,		
	Co(IV), Cr(III), Cu(II),		
	Ba, Sr, Mg		
6	Ce, Zr, Y, Th		
8	Tl(I), Cr(III), Ba, Sr,	Mg, Y	Ni, Co(II), La
	Ca, Be		
9	Tl(I), Cu(II), Cd		<u></u>
10	Fe(III), Cu(II), V(IV)	Tl(I), Mn(II), Ti	Ag, Th
11	Cs, Rb, Ca, As(III), Ni,	Mo(VI)	Hg(II)
	Cr(III), K		
12	Cr(III), Cs, Mg	V(IV), Cu(II), Zn, Pd(II), Al	UO2(II), Bi, Ti(IV)

papers are easily and quickly prepared and possible separations can almost always be predicted from $R_{\rm L}$ and $R_{\rm T}$ values. The more important aspects of chromatography on the tungstate papers are as follows.

(i) Out of 15 systems containing mixed solvents, best results are obtained with butanol + dioxan + 10M hydrochloric acid (6:2:2). The cations evidently migrate as chloro-complexes since the maximum R_t values are those of Cd²⁺, Sb³⁺, Fe³⁺, Fe²⁺ and Ga³⁺ which have a strong tendency to form chloro-complexes, whereas cations like Ba²⁺, Sr²⁺ and Ca²⁺, which form weak chloro-complexes, tend to be retained. The ions with high R_t values have small ionic radii and vice versa.

(ii) Hg^{2+} , Cd^{2+} , Zn^{2+} and Bi^{3+} have high R_t values in the ethyl methyl ketone + acetone + 1M hydrochloric acid (7:3:3) system and are easily separated from the other 41 metal ions tested. All four can form negatively charged chloro-complexes which would not be adsorbed by the ion-exchanger; rapid migration might also result from the high solubility of their chlorides in acetone.

(iii) The results for the acetonylacetone + acetone + 50% hydrochloric acid (6:3:1) system are very interesting. Cations such as Ga³⁺, In³⁺, Hg²⁺, Bi³⁺, Cu²⁺, Fe³⁺ and Co²⁺ probably migrate by forming negatively charged chloro-complexes. Similar results are obtained in the isopropanol + acetylacetone + 50% hydrochloric acid (6:3:1) system, for similar reasons. However, when in the latter solvent the hydrochloric acid is replaced by perchloric, the results are completely altered. Hg²⁺ now begins to tail owing to the lower solubility of its perchlorate. A similar change in behaviour is shown by Bi³⁺, Cd²⁺, Zn²⁺, UO₂²⁺, Pt⁴⁺ and Pd²⁺. All these cations migrate significantly and give compact spots in the hydrochloric acid medium but tail from the point of application when the perchloric acid medium is used. Ga³⁺, however, is an exception, giving a compact spot with $R_{\rm L}$ 1.00 and $R_{\rm T}$ 0.94, probably because of complexation by acetylacetone.

(iv) A number of systems containing perchloric acid were tried in order to study the chemistry of the cations rather than to achieve separations. For this purpose perchloric acid + chloroform + acetone systems were used, because acetone and chloroform do not strongly solvate metal ions. It was found that for non-complexing ions such as the alkali and alkaline earths metals, R_t values increase with electronegativity, whereas for complex-forming ions such as Ni²⁺, Co²⁺ and Mn²⁺ the reverse occurs. In this system Hg²⁺ has a higher R_t value than Cd²⁺ and Zn²⁺ owing to the high solubility of mercury(II) chloride in acetone. This explanation is confirmed by the fact that in 0.5M perchloric acid alone Hg²⁺ has a lower R_t value than Cd²⁺ and Zn²⁺ owing to the absence of an organic solvent in the system.

In perchloric acid systems the R_t values of all ions increase with electronegativity but in hydrochloric acid systems the reverse holds for complex-forming ions such as Ni²⁺, Mn²⁺, Zn²⁺, Cd²⁺ and Hg²⁺. A plot of the radii of hydrated ions vs. R_t value for Hg²⁺, Cd²⁺, Zn²⁺, Ba²⁺, Ca²⁺ and Mg²⁺ shows that the R_t values increase as the radii decrease. To find the cause of this, chromatography was performed on plain Whatman No. 1 papers; the R_t values were all close to 1.0. The solubility of the tungstates was then considered. It was found that tungstate solubilities decreased in the order Mg > Ca > Ba. The R_t value sequence is therefore most probably due to ion-pair formation between the ion and the matrix of the exchanger. A similar explanation applies to the low R_t value of Hg²⁺.

Cations may have zero R_t values if (i) the ion-exchanger has a high selectivity for

the cation concerned, (*ii*) they form a precipitate, e.g., hydroxide, chloride or bromide, with one of the components of the solvent system and hence remain at the point of application, or (*iii*) they have high adsorption on paper. To distinguish between these causes, chromatography was performed on plain Whatman No. 1 papers for those cations which had zero R_t value on ion-exchange papers. On mixing the cations with the solvent systems in test tubes precipitation was obtained in the following cases: Ag⁺ and Hg₂²⁺ in 0.1M ammonium chloride; Ag⁺, Hg₂²⁺ and W⁶⁺ in 1% EDTA solution and 6M hydrochloric acid; Ag⁺ in methanol + acetone + 0.1M hydrochloric acid (1:1:1) and in 0.1M hydrochloric acid; Hg_2^{2+} in 0.1M boric acid + 0.1M sodium hydroxide (pH 10). These cations have therefore zero R_t values owing to precipitation. The rest of the cations which had zero R, values on ion-exchange papers had also zero R_t values on Whatman No. 1 papers and in these cases this is due to low partition of the cation in the solvent system.

Since no work with selenite papers has been previously reported, more attention was given to their use with aqueous systems. These papers gave some remarkable separations, e.g., Zn²⁺-Cd²⁺, Rb⁺-Cs⁺, Nb⁵⁺ or Be²⁺ from numerous metal ions. Despite extensive work, these separations could not be achieved on tin(IV) tungstate or phosphate papers. Since the solvent ascent takes only about 20 mins the ionexchanger does not dissolve significantly and it is possible to use even moderately reactive systems. Such systems can not be used in column chromatography as the solubility of the ion-exchanger will be too great, owing to the longer time required. This is a decided advantage of ion-exchange paper chromatography.

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> Zusammenfassung-Es wurde gezeigt, daß mit den anorganischen Ionenaustauschern Zinn(IV)-wolframat und -selenit imprägnierte Papiere bei der Ionenaustauschchromatographie mehrerer Metallionengemische nützlich sind; geeignete Lösungsmittelsysteme wurden entwickelt und ihre Daten gemessen.

> Résumé—On a montré que les papiers imprégnés avec les échangeurs d'ions minéraux tungstate et sélénite d'étain(IV) sont utiles pour la chromatographie d'échange d'ions de plusieurs mélanges d'ions métalliques, et l'on a élaboré et estimé des systèmes de solvants convenables.

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ANALYSIS OF RADIOACTIVE METALS BY SPARK SOURCE MASS SPECTROMETRY

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Summary—A spark source mass spectrograph with photographic plate recording has been adapted for the analysis of plutonium and americium metals. Over seventy elements can be determined simultaneously in these metals. A comparison has been made between results obtained by mass spectrography and by conventional methods for impurity elements. The operations involved in handling radioactive materials in the mass spectrograph are also discussed.

IMPROVEMENTS in purification techniques and metal production technology have resulted in the production of radioactive metals, such as plutonium and americium, of a high degree of purity. The number of impurities present has been reduced, and the concentration of impurities contained has been lowered to a level that is below the detection limits of routine spectrographic methods. Analysis of the pure metal by emission spectrographic methods would require the use of separation and concentration techniques. This would mean increased analysis time and higher analytical costs.

A good determination of the degree of purity of a metal also requires that the concentration of many elements, that are not now routinely determined, be measured. Formerly, an element, difficult to determine, such as chlorine or sulphur, could be present to the extent of 20 ppm in the metal and be unimportant because there was a total of over 400 ppm of other impurities. Now, however, chlorine or sulphur may be one of the major impurities. It is, therefore, necessary to determine a greater number of elements in each sample.

The considerations above indicate that the use of the spark source mass spectrometer for this type of analysis would be desirable and feasible. A low level of detection limit is attainable, a large number of elements are detectable, the reported accuracy seems acceptable, and the probable increased cost of analysis appears justifiable. The equipment necessary for handling radioactive samples was therefore installed on a CEC 21-110 mass spectrometer.

Safe handling of radioactive metals

The dangers from the radioactivity of plutonium and americium are well known.¹ In addition, plutonium is also a highly toxic material. Plutonium has been termed one of the most toxic elements on which large scale work is now being performed. All non-solution work with these materials must be performed in a closed system so that no material is freed into the room atmosphere. This can be done with a glove-box or in an open-front box with controlled draught to keep loose material in the box.

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The major radioactive contamination of the mass spectrometer was in the source section. Provision had to be made for the sample holders to be removed for changing samples and all the resultant contamination contained. The electrode-positioning controls are on the sample holder, so these had to be manipulated inside the enclosure. The use of a completely enclosed box to contain the source section would have necessitated performing these complex operations through heavy rubber gloves. Therefore, an open-front box was designed to contain the source and permit working with surgeon's gloves. The box has proved to be satisfactory, with so far no escape of contamination. Only metal samples have been handled in this box; no powders have been analysed.

Samples are prepared for analysis in a standard glove-box. In addition to its radioactive and toxic characteristics, plutonium metal is also pyrophoric. The cutting and filing of the metal into shapes suitable for electrodes is therefore done in an argon atmosphere. Samples are then transferred to the source-box for loading into the instrument.

The source of the instrument became contaminated with the first plutonium sample sparked. An average of 3-4 mg of sample is consumed during each analysis, and most of this material remains in the source. It was also possible that enough plutonium was entering the instrument to constitute a hazard when the instrument was opened and the inside surfaces monitored with α -counting instruments. The only areas of significant radioactivity were the slit edges, back to and including the beam monitor. When the instrument is first vented, the slits may be removed and placed in a plastic bag with little chance of contamination. However, if the plutonium deposited is allowed to oxidize, the loose oxide will spread and be a health hazard.

The possible contamination of the photoplate was of prime interest because of handling difficulties if it were radioactive. If all the plutonium passing the beam monitor reached the plate, the calculated amount deposited there would be about 0.025 ng. The radioactivity from this amount of material would be four disintegrations per minute. Contamination determined in practice has been at the background level of the counting equipment. No contamination greater than one disintegration per minute has been detected on a developed plate, an undeveloped exposed plate, or in the developer and fixing solutions.

Continuous sampling of the laboratory air has shown that the method described is safe for the handling of radioactive metal samples for spark source analysis.

EXPERIMENTAL

Instrumental parameters

The instrument used for this work was a Consolidated Electrodynamics Corporation Model 21-110, Lot 3, double focusing mass spectrometer. One of the electrodes is at a potential of 13 kV positive with respect to earth. A 300 Hz pulse of 17 μ sec duration is applied to the other electrode for the spark analysis of the metal. Source conditions which were found to be difficult to reproduce from sample to sample were shape, distance to slit, and spark gap. These varying parameters probably contributed to the experimental error. The spectra of the samples were recorded on Ilford QII photoplates.

Plutonium standardization

There are very few certified standards of any material that contain impurities at the low levels desired for spark source analysis. A few copper metal standards and an aluminium standard were obtained and used in the initial development work. There are no certified plutonium metal standards at present. Fortunately, two samples of plutonium metal became available that had been analysed

several times by five USAEC contractors. A comparison could be made between the compiled results and the mass spectrographic results.

Analytical procedure

The visual method of estimating impurity concentration was used for most of the analyses. In this method, as described by Craig and Wolstenholme,^a a graded series of exposures is made of the same sample and the impurity concentrations (C_1) are calculated from the formula

$$C_{\rm i} = \frac{E_{\rm m} C_{\rm m} W_{\rm i} \, 10^6}{E_{\rm i} \, I_{\rm i} \, W_{\rm m}}$$

where the subscripts m and i represent matrix and impurity respectively, E is the beam monitor reading where the line of the element is just detectable, I_1 is the isotopic abundance (%) of the impurity isotope, W is atomic weight, and C_m is expressed in %. The concentration of the impurity will be in ppm by weight.

The plutonium samples to be analysed presented a problem in that the isotopic ratios of the various plutonium isotopes were not constant. To remove the need for isotopic analysis of all samples for the determination of C_m , an empirical E_m was used in the initial calculations. The work of Brown *et al.*,⁴ has shown that the basic ion sensitivity of a just detectable line is around 2×10^{-15} coulomb. This was verified from a few test plates, and the empirical value was used for the exposure level of the matrix in all subsequent visual calculations.

Sensitivity factors

For the initial results only the empirical formula was used, as all elemental sensitivities were assumed to be the same. Other workers,^{a,a,4} however, have shown that there are various factors influencing the recording of the ion on the photographic plate. Among them are emulsion response to mass, Z focusing, and matrix effects. All of these combine to result in different sensitivity factors for each element.

	Sensitivity		Sensitivity
Element	factor	Element	factor
Al	8.0	Mg	11.0
С	18.0	Mg Mn	8.0
Cr	5.4	Ni	8.0
Cu	8·0	Pb	18.0
Fe	7.2	Si	8.0
Ga	11.0	U	1.6
In	5.8	Zn	6.1

TABLE I.—RELATIVE SENSITIVITY FACTORS—VISUAL METHOD (Pu = 1.0)

Elemental sensitivity factors used in the mass spectrographic analysis of steels have been calculated by other workers^{5,6} from results obtained by analysing certified NBS and BISRA steel samples, but because there are no certified plutonium standards the sensitivity factors for plutonium analysis have to be obtained by a different method. A method that would combine most of the previously mentioned factors into a single factor was desirable. A programme was therefore initiated of sparking plutonium and other pure elements and recording their spectra under the same conditions. The only difference was that the spectra were recorded at small incremental increases in the beam monitor readings. By this method the exposure of a "just detectable" line could be more accurately estimated. The sensitivities of the various elements were then calculated relative to plutonium.

Table I contains the results of some of the elemental sensitivities that have been calculated. These factors should include most of the recording variables except for matrix effect. This method can thus also be used to determine which elements exhibit significant matrix effects. A good example of a large matrix effect is shown in the case of lead. The factor calculated from the pure lead photoplate was 2.6, a value which gave extremely high comparative answers when used in the analytical calculations. The sensitivity factor calculated for lead in both a copper matrix standard and in two NBS steel standards was 18, indicating that lead sensitivity was affected by a metal matrix. This factor was used in calculating the lead values in the plutonium samples. The gallium factor was calculated in the same manner.

Precision of measurements

Each of the plutonium metal samples was analysed a total of 16 times over a three-week period. A total of eight plates was taken. The metal electrodes used were from the same batches. Homogeneity of a metal at trace levels of impurities is difficult to ensure; this may account for the high relative standard deviation calculated for some of the elements.

RESULTS AND DISCUSSION

The two plutonium metal samples were analysed by the visual method. Results by spark source mass spectrography, both with and without sensitivity factors, are compared with emission spectrographic results in Table II. In both samples about

	Emission]	Mass spectrograph	лу
Element	spectrography ppm	Uncorrected ppm	Corrected ppm	Relative std. devn., %
Metal A				
Al	14	28	17	21
Cr	3	3	3	20
Cu	3 2	1	1	15
Fe	34	29	28	25
Ga	0.4	1	0.7	41
Mg	6	36	7	30
Mň	. 5	7	7	32
Ni	6	. 7	9	19
Pb	2	5	1.5	30
Si	30	31	10	30
Zn	4	18	17	22
Metal B				
Al	29	65	50	14
Cr	44	54	62	10
Cu	17	22	22	10
Fe	232	308	272	17
Ga	28	50	32	28
Mg	4	11	3	20
Mn	10	14	18	22
Ni	45	68	55	14
Pb	4	14	5	42
Si	80	105	85	15
Zn	15	19	15	16

TABLE II.—PLUTONIUM METAL ANALYSIS

90% of the mass spectrographic results are within a factor of two of the emission spectrographic results. The emission spectrographic results are the average of over 25 analyses for all elements except gallium and zinc. Only a few scattered results were available for these elements, as they are not requested determinations in this cooperative analysis program. The mass spectrographic results are the average of 16 analyses.

Sensitivity factors and impurity concentrations were also obtained by densitometric methods. A recording microphotometer was used to obtain chart tracings of ion lines of interest on the plutonium and pure element photoplates. Absorbance values were taken from the charts, and the area of the lines was calculated by the method of Owens.⁷ Values from the plutonium-239 spectral recording were then used to prepare a curve relating plutonium-239 line absorbance to exposure (beam monitor reading). A similar curve was prepared for area measurement.

The exposure necessary for the plutonium-239 line to give an absorbance, or area,

equal to that given by a second element line at a certain exposure was then obtained from this curve. The ratio of these exposures, corrected for isotopic abundance, was then termed the relative sensitivity of the second element. Five calculations were made for each element investigated. The average values obtained for some of these elements are shown in Table III. The increase in the factor with decrease in atomic weight was expected, but the curve was not as smooth as hoped.

TABLE III.-RELATIVE SENSITIVITIES BY

	DENSITOMETRIC METHODS						
Element	Relative sensitivity absorbance	Relative sensitivity area					
Pu	1.0	1.0					
Pt	1.4	1.6					
Zn	5.8	3.0					
Fe	11.3	2.6					
Cr	5.6	2.7					
Mg	12.9	4.0					
Mg C	25.7	8.0					

The corrections obtained by using the experimentally obtained densitometric factors are shown in Table IV. It also shows the errors that are present if these corrections are not used. The familiar general method of using the ratio of matrix and impurity exposure levels at some selected line transmission reading, usually about 40%, may give acceptable answers for impurities in some matrices such as iron, but not for impurities in plutonium. This is chiefly because of the large differences in

Impurity	Equal a	bsorbance	Equ	Emission	
element	Mass- corrected	Sensitivity- corrected	Calculated	Sensitivity- corrected	spectrographic, ppm
Metal A					
Zn	230	82	58	20	4
Fe	105	20	68	28	24
Cr	25	10	14	5	3
Mg	120	30	97	26	8
СŬ	585	110	755	100	95
Metal B					
Zn	116	42	78	28	15
Fe	1420	280	478	284	223
Cr	268	108	172	68	43
Mg	32	8	30	8	7
СŬ	450	85	486	65	145

TABLE IV.—ANALYSIS OF PLUTONIUM METAL SAMPLES BY DENSITOMETRIC METHODS

line profiles of the plutonium line at mass 239 and the major impurities which have mass numbers below 65. Although the equal absorbance values were corrected for the reported mass dependence of the Ilford QII emulsion, they are still considerably higher than those obtained by the area method. The method of calculating the absorbance factors included this value in the factor for each element, and this absorbance factor is applied instead of the mass dependence factor.

4

515

The absorbance method would be faster because fewer calculations are needed, but the area method yields results closer to the emission spectrographic and chemical results. Densitometric methods require more time per sample than the visual method of photoplate evaluation. The major purpose of the densitometric study was to prove the value of obtaining an ion density computer. Until this equipment is obtained, the visual method of sample analysis will be used. The large number of sample analyses being performed require that the faster method be used.

Americium analysis

Results obtained on the plutonium samples previously described, and on subsequent samples, indicated that comparatively good results could be obtained without the use of standards. The second radioactive metal analysed was again one for which no standards were available. This was americium.

		Sample 1		Sample 2			
Element	Mass spec.	Emission spec. A	Emission spec. B	Mass spec.	Emission spec. A	Emission spec. B	
Cr	60	50	<50	60	50	<50	
Fe	105	150	50	100	<50	50	
Ni	8	<50	<50	5	<50	<50	
Y	200	50	200	120	20	100	
Zn	4	<100	<100	2	<100	<100	
Eu	12	<12	<50	20	12	<50	
La	140	12	<50	110	50	100	
Sm	35	<25	<100	55	60	<100	
Tm	0.5	6	<50	0.2	<6	<50	
Yb	20	<1	<5	45	6	<5	
Ce, Dy Er, Gd, Ho, Lu, Nd, Pr, Tb	<0.5	<18	<75	<0.5	<18	<75	
CĨ	1000			390			
F	15		_	40			
Np	185			120			
ร่	8		_	2			
²⁴² M	600			40			

 TABLE V.—ANALYSIS OF AMERICIUM METAL (COMMON IMPURITIES) (All values are in ppm by weight)

The specially purified americium was to be used, if acceptable, for a half-life determination by calorimetric methods. This necessitated a knowledge of the purity of the metal, as this would enter into the half-life calculation. Spark source mass spectrographic and emission spectrographic methods were used to analyse the metal. Two different laboratories, using different methods, analysed the metal by the emission spectrographic technique. Results obtained for some of the more important impurities are compared in Table V.

The results compare quite well for the elements that were determined by all three methods. A determination of the rare earth elements is important in americium analyses as these are concentrated along with americium in the plutonium-americium separation. With the rare earths, a major advantage of the spark source method is the

lower limit of detection. The last five elements listed in the table are some that are not determined routinely by emission spectrographic methods. These impurities were quite important in the americium samples, as their added concentrations represented a high proportion of the total impurities. Chlorine was a major impurity in both of these americium metal samples. The impurity listed as mass 242 brings out an interesting feature of spark source analysis. In the method used for these analyses, it was not possible to determine the element represented by this isotope of 242 atomic mass units. However, the amount present could be calculated. Radiochemical work indicated later that this was plutonium-242 and also confirmed the presence of neptunium. The thermal effects of the high plutonium-242 content of americium sample number 1 made it unsuited for the americium half-life investigation.

CONCLUSIONS

Results so far obtained indicate that most of the requirements for analysis of pure radioactive metals have been met by spark source mass spectrographic analysis. This is summarized in Table VI.

Method requirement	Attainable by mass spectroscopy		
As many elements should be determined as is feasible.	Over 70 elements are determined by the one method.		
Low levels of detectability are needed.	Most of the elements can be routinely detected at the 0.1 ppm level.		
The accuracy must be adequate	Agreement within a factor of three is con- sidered adequate below 10 ppm at the present time.		
The cost of analysis must be justifiable.	A cost comparison of the mass spectro- graphic method and the other analytical methods is difficult to make, as many of the elements determined by the spark source method are not being routinely determined at this time. The total time of analysis, however, has been estimated to be reduced by about 60% by use of the spark source for total trace impurity analysis (the elements F, Na, S, and Cl are included in the spark source analysis time but not that of the other methods).		

TABLE	VI	-ANALYSIS	OF	PURE	RADIOACTIVE	METALS

The mass spectrographic method, using the instrumental parameters given in this paper, also has limitations. Spectral lines due to the various ions are closer together at the high mass end of the photoplate than at the low mass end. This can result, for ions of >230 amu, in a weak line of one ion being covered by a wide strong line due to an ion that is within one amu of the low level ion and present in far greater amounts. In the plutonium metal analysis, for example, the wide plutonium-239 matrix line makes it impossible to determined uranium-238 on the photoplate.

The small amount of sample actually used in the analysis makes it important that the analytical spark covers as much of the electrode surfaces as possible. If the spark should localize on one small area that is actually a grain of some segregated species, the analysis would represent that species and not the impurities of the bulk sample. The sparking, however, can be easily controlled by observing the sparking and making minor electrode positioning adjustments. This is done, during sparking, with controls external to the evacuated spark chamber.

The small amount of sample used is obviously advantageous in the analysis of the rare and expensive actinide metals and their compounds.

Acknowledgements-We wish to acknowledge the aid of L. A. DeSantis and R. E. Schlupp in operating the instrument and in developing the photoplates.

> Zusammenfassung-Ein Massenspektrograph mit Funkenquelle und photographischer Registrierung wurde zur Analyse von metallischem Plutonium und Americium angepaßt. In diesen Metallen können über siebzig Elemente gleichzeitig bestimmt werden. Die Ergebnisse des Massenspektrographen und konventioneller Methoden zur Bestimmung von Verunreinigungen wurden verglichen. Auch die Operationen, die bei der Handhabung radioaktiven Materials im Massenspektrographen notwendig sind, werden diskutiert.

> Résumé-On a adapté un spectrographe de mass à source d'étincelle avec enregistrement sur plaque photographique à l'analyse des métaux plutonium et américium. On peut déterminer simultanément plus de soixante-dix éléments dans ces métaux. On a effectué une comparaison entre les résultats obtenus par spectrographie de masse et par des méthodes usuelles pour les éléments à l'état d'impuretés. On discute aussi des opérations mises en jeu dans la manipulation de matériaux radioactifs dans le spectrographe de masse.

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SHORT COMMUNICATIONS

New chromogens of the ferroin type---V

Pyridylpyrimidines, bidiazines and other substituted derivatives of diazines

(Received 28 October 1968. Accepted 28 November 1968)

PREPARATION of a variety of pyridylpyrimidines and bidiazines and the spectrophotometric characteristics of their iron(II) chelates were reported recently by Lafferty and Case.¹ They concluded that the compounds are less sensitive as iron chromogens than the corresponding derivatives of 2,2'bipyridine and 2,2',2"-terpyridine. Chromogenic properties of the new ferroin-type compounds with respect to chelation of other metal ions, particularly copper and cobalt, were not investigated. The results of such a study are reported here, together with some redetermined spectrophotometric constants for the iron(II) chelates.

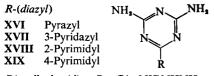
More recently, Case² described the synthesis of some pyrimidine, pyradazine and pyrazine derivatives that contain the ferroin group. The chromogenic reactions of these with iron(11), copper(I), and cobalt(II) have also been investigated and are reported here.

The new chromogens, identified below, will be referred to by roman numeral designation.

Pyridylpyrimidines

- 5-Methyl-2-(2-pyridyl)pyrimidine I
- Π 5-Phenyl-2-(2-pyridyl)pyrimidine
- 4-Phenyl-2-(2-pyridyl)pyrimidine 4-Phenyl-6-(2-pyridyl)pyrimidine ш
- IV
- v 4,6-Bis(2-pyridyl)pyrimidine
- VI 2,6-Bis(2-pyridyl)pyrimidine
- VП 4-Methoxy-2,6-bis(2-pyridyl)pyrimidine
- VIII 4-Hydroxy-2,6-bis(2-pyridyl)pyrimidine

2,4-Diamino-6-diazyl-1,3,5-triazines

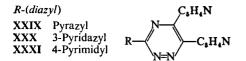


Diazylhydrazidines R—C(=NH)NHNH2

R-(diazyl)

XXIII Pyrazyl XXIV 3-Pyridazyl XXV 4-Pyrimidyl

3-Diazyl-5,6-bis(2-pyridyl)-1,2,4-triazines



Quinazolines

- IX 2-(2-Pyridyl)quinazoline
- х 2-(2-Pyridyl)-5,6,7,8-tetrahydroquinazoline
- 2,4-Bis(2-pyridyl)quinazoline XI
- XII 2,4-Bis(2-pyridyl)-5,6,7,8-tetrahydroquinazoline

Bidiazines

- XIII 3,3'-Bipyridazine
- 4,4'-Diphenyl-2,2'-bipyrimidine XIV
- XV Bipyrazine

2-Diazylbenzimidazoles

R-(diazyl)

XX	Pyrazyl
XXI	3-Pyridazyl
XXII	2-Pyrimidyl

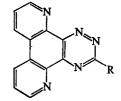


3-Diazyl-5,6-diphenyl-1,2,4-triazines

R-(diazyl) C₆H₅ XXVI Pyrazyl XXVII 3-Pyridazyl C₆H₅ XXVIII 4-Pyrimidyl

3-Diazyl-1,2,4-triazino[5,6-f][4,7]phenanthrolines

R-(diazyl) XXXII Pyrazyl XXXIII 3-Pyridazyl



EXPERIMENTAL

Samples of the 33 compounds, for which analytical and preparative details have been previously reported,^{1,2} were kindly provided by Dr. Francis H. Case of Temple University.

A description of the various standard solutions, pH buffers, reagents, and procedures used in this investigation appears in an earlier paper of this series.³ The method of continuous variations was used to determine spectrophotometrically the nature and stability of certain of the iron(II) complexes.

RESULTS AND DISCUSSION

The spectral properties of the iron(II), copper(I), and cobalt(II) chelates are listed in Table I. Of the thirty-three chromogens studied, XXVI and XXVII are the most sensitive for iron, and IX is the most sensitive for copper. None are particularly outstanding as cobalt chromogens. More sensitive chromogens for iron and copper are known,³ and it is unlikely that any of those studied here will prove popular as chromogenic reagents.

It is concluded that a diazine moiety is an inferior chromophoric element in comparison to either a triazine^{3,5,6} or a pyridine⁷⁻⁹ ring when incorporated as a part of the ferroin chromophore group. Furthermore, the complexes are less stable (Table II).

	Iroi	n(II)	Сорј	per(I)	Coba	lt(II)
Chromogen	λ, nm	8	λ , nm	3	λ , nm	ε
I	488	6800	423	2700	†	†
п	525	7000*	425	4600	Ť	Ť
ПІ	531	10800	425	4200	ŧ	Ť
IV	569	7600*	487	3400	Ť	t
v	571	7800*	488	6400	Ť	Ť
VI	550	9700	425	170†	487	896
VII	563	10600	†	† .	456	368
VIII	525	10900	ŧ	Ť	†	†
IX	442	11470	481	8900	Ť	t
Х	488	6200	437	5500	t	Ť
XI	658	10900	481	4600	ŧ	t
XII	582	10500	438	2500	460	1580
ХШ	517	6350	473	5700	†	†
XIV	*	*	403	5200	ŧ	Ť
XV	512	1700*	460	1500	t	Ť
XVI	†	+	457	1400	÷	Ť
XVII	÷	÷	457	3600	÷	Ť
XVIII	÷ ·	÷	430	3640	t	Ť
XIX	÷	÷ ·	450	2700	÷	ŧ
XX	600	8800	†	†	462‡	380‡
XXI	590	8100	Ť	÷	÷ .	t .
XXII	516	2300	Ť	÷	÷	Ť
xxm	535	7800	t	÷	÷	÷
XXIV	525	14800	Ť	÷	+	Ť
XXV	537	3000	÷	ŧ	÷	Ť
XXVI	536	19600	472	2730	÷	t
XXVII	542	19000	588	6900	506	930
XXVIII	550	10400	475	2400	525	450
XXIX	580	6800	507‡	4000	455±	1800‡
XXX	584	12900	507	4800	450‡	6000‡
XXXI	593	7000	512	2600	450‡	5400‡
XXXII	581	15800	531	8300	537	610
XXXIII	583	15900	525	7100	537	4000

TABLE I.—SPECTRAL CHARACTERISTICS OF THE IRON(II), COPPER(I), AND COBALT(II) CHELATES

* Poor stability; absorbance not linear with concentration

† Colours and spectra of chelate and chromogen are very similar.

‡ Wavelength not at maximum but at a shoulder.

Chromogen	Fe:L	log K'	
XXVI	1:3	9.7	
XXVII	1:3	12.3	
XXVIII	1:3	8.3	
XXIX	1:2	7.5	
XXX	1:2	9.1	
XXXI	1:2	7.3	
XXXII	1:3	11-1	
XXXIII	1:3	14.3	

TABLE II.—MOLE RATIOS AND CONDITIONAL FORMATION CONSTANTS OF SOME OF THE IRON(II) CHELATES

As expected, chromogens XVI-XIX failed to give the characteristic ferroin colour reaction with iron(II) salts. They possess amino groups on carbon atoms contiguous to the ferroin chromophore groups, and methyl and other bulky substituents at such positions in closely related compounds are known to cause steric hindrance in formation of tris-chelated octahedral complexes of iron(II) and cobalt(II) but not in formation of bis-chelated tetrahedral complexes of copper(I).¹⁰

Consideration of the structures of chromogens XXIX-XXXIII reveals that they should be capable of acting without steric hindrance as either bidentate or terdentate ligands to give respectively tris- and bis-chelates of iron(II). They differ from 2, 2',2"- terpyridine, which in chelation with iron(II) must either serve as a terdentate ligand to form a bis-chelate or suffer serious steric hindrance from bulky unco-ordinated pyridyl groups when attempting to form a tris-chelate. The continuous variation results for XXXII and XXXIII were surprising. Both behave preferentially as bidentate ligands towards iron(II). This is probably a consequence of both steric and electronic effects. Certain chelate rings apparently involve less physical strain than others, and donor atoms undoubtedly have greater basicities in some ferroin groupings than in others.

The conditional formation constants (Table II) indicate that pyridazyl groups confer greater stability on the iron(II) complexes than do either pyrimidyl or pyrazyl groups. This is consistent with the relative order of basicities: pyridazine $(pK_a = 2.24) > pyrimidine (pK_a = 1.23) > pyrazine (pK_a = 0.51)$. The relative stabilities of the pyrimidyl and pyrazyl ferroin complexes do not follow the expected trend; however, the differences are not great and may be obscured by experimental uncertainties in the conditional formation constants.

Acknowledgement—John W. Hook III assisted in the measurements of conditional formation constants, Dr. F. H. Case furnished samples of the new compounds, and the G. Frederick Smith Chemical Company provided financial support.

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Summary—Spectrophotometric studies of the reactions of iron(II), copper(I) and cobalt(II) with 33 new compounds have demonstrated that the chromogenic properties of diazyl groups are inferior to those of triazyl or pyridyl groups when incorporated into the ferroin chromophore group. The metal complexes of the diazyl derivatives are less stable than those of the corresponding pyridyl and triazyl derivatives. Conditional formation constants of the iron(II) chalates of some representative diazyl derivatives indicate that pyridazyl groups impart greater stabilities than pyrimidyl or pyrazyl groups. Five of the new chromogens have structures that suggest they can chelate iron(II) without steric hindrance, either as bidentate or as terdenate ligands. Although the terdentate mode would ordinarily be expected, two of the five were found to act preferably as bidentate ligands.

Zusammenfassung—Spektrophotometrische Untersuchungen der Reaktionen von Eisen(II), Kupfer(I) und Kobalt(II) mit 33 neuen Verbindungen zeigten, daß die farbbildenden Eigenschaften von Diazylgruppen denen von Triazyl- oder Pyridylgruppen unterlegen sind, wenn

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Short communications

man sie in den Ferroinchromophor einbaut. Die Metallkomplexe der Diazylderivate sind weniger stabil als die der entsprechenden Pyridylund Triazylderivate. Bildungskonstanten der Eisen(II) chelate einiger ausgewählter Diazylderivate deuten darauf hin, daß Pyridazylgruppen größere Stabilität verleihen als Pyrimidyloder Pyrazylgruppen. Fünf von den neuen Chromogenen haben Strukturen, die vermuten lassen, daß sie Eisen(II) ohne sterische Hinderung entweder zwei- oder dreizähnig chelieren können. Obwohl man normalerweise die dreizähnige Chelatbildung erwarten würde, fand man bei zweien unter den fünf, daß die vorzugsweise als zweizähnige Liganden fungieren.

Résumé—Des études spectrophotométriques des réactions des fer(II), cuivre(I) et cobalt(II) avec 33 nouveaux composés ont démontré que les propriétés chromogènes des groupes diazyle sont inférieures à celles des groupes triazyle ou pyridyle lorsqu'ils sont incorporés dans le groupe chromophore ferroïne. Les complexes métalliques des dérivés diazyle sont moins stables que ceux des dérivés correspondants pyridyle et triazyle. Les constantes de formation conditionnelles des chélates du fer(II) avec quelques dérivés diazyle types montrent que les groupes pyridazyle communiquent de plus grandes stabilités que les groupes pyrimidyle ou pyrazyle. Cinq des nouveaux chromogènes ont des structures qui suggèrent qu'ils peuvent chélater le fer(II) sans empêchement stérique, à l'état de ligands à deux ou trois attaches. Quoique le mode à trois attaches devrait être ordinairement attendu, on a trouvé que deux de ces cinq composés se comportent préférentiellement comme ligands à deux attaches.

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Infrared determination of calcium or lithium nitrate in acetone solution

Determination of calcium or lithium in the presence of strontium or barium

(Received 12 September 1968. Accepted 30 October 1968)

CALCIUM has been determined in the presence of strontium by conversion of both into the nitrates, treatment with acetone to dissolve the calcium nitrate, filtration of the insoluble strontium nitrate, and determination of the calcium gravimetrically (after evaporation of the acetone) or by difference.¹⁻³ The method has apparently not been applied to the determination of calcium in the presence of barium, although barium nitrate is also insoluble in acetone.

It is proposed that calcium in the presence of strontium or barium be determined by treatment of the nitrates with acetone, filtration, and infrared determination of calcium nitrate by measuring the nitrate peak at about 825 cm⁻¹. The same technique has been applied to the determination of lithium in the presence of strontium or barium.

EXPERIMENTAL

Apparatus

The dry-box used consisted of a cardboard box and top about $10 \times 6 \times 4$ in., containing a $\frac{1}{2}$ -in. thick layer of "Drierite" covered by a platform consisting of a piece of cardboard with a $\frac{1}{4}$ -in.

diameter hole in each in.²; there were two inlet holes in the top for the glass tubes conducting the dry air.

Reagents

Acetone. Reagent grade, ACS specification.

Anhydrous calcium nitrate. Heat $Ca(NO_3)_2$ ·4H₂O in an uncovered weighing dish on the hot-plate at gentle heat until most of the water is driven off, dry in an oven at 170° for 6 hr, cover, and store over anhydrous magnesium perchlorate in a desiccator.

Anhydrous lithium nitrate. Dry reagent grade LiNO₃ in an oven at 170° for 2 hr, cover, and store over anhydrous magnesium perchlorate in a desiccator.

Calibration curves

Prepare standard solutions (~ 1.0 g weighed to ± 0.1 mg, dissolved in acetone and diluted to 50.0 ml) of calcium and lithium nitrates. Dilute 1, 2, 3 and 4-ml portions to the mark in 5-ml volumetric flasks, with acetone. Record the spectra (0.4-mm sodium chloride cells) from 860 to 800 cm⁻¹ and measure the peak heights at 824 cm⁻¹ for calcium and 827 cm⁻¹ for lithium. Plot calibration curves.

Calcium or lithium in the presence of strontium or barium

The calcium, lithium, strontium and barium must be in the form of nitrates. The oxides and carbonates (and oxalates after ignition) can be converted into nitrates by treatment with nitric acid (1 + 1), evaporation to dryness, addition of water, and re-evaporation to dryness. Use an amount of sample that will contain 1-80 mg of calcium or lithium nitrate and up to about 0-2 g of strontium or barium nitrate. Dry the nitrates at 170° for 2 hr and cool over anhydrous magnesium perchlorate in a desiccator. Add 20 ml of acetone, break up any lumps by use of a policeman, wash down the policeman with a little acetone, and remove it. Cover the beaker with a watch-glass, insert a small stirring rod, and allow to stand for 2 hr with occasional stirring. Filter through a sintered glass crucible of fine porosity (tared if strontium or barium is to be determined). Transfer the precipitate to the crucible with acetone and wash it several times with acetone.

If the strontium or barium is to be determined, dry the crucible at 130° for 1 hr, cool in a desiccator, and weigh as $Sr(NO_3)_2$ or $Ba(NO_3)_2$.

In a dry-box evaporate the filtrate to about 2 ml with a stream of air dried by passage through anhydrous magnesium perchlorate. Then immediately wash the solution into a 5-ml volumetric flask with acetone and dilute to the mark with acetone. Record the spectrum from 860 to 800 cm⁻¹ and measure the absorbance of the peak at 824 cm⁻¹ (calcium) or 827 cm⁻¹ (lithium).

RESULTS AND DISCUSSION

The spectra of nearly saturated acetone solutions of calcium and lithium nitrate and of acetone were obtained over the range 4000–667 cm⁻¹, in 0.028, 0.2 and 0.4-mm cells. The peaks are listed in Table I. The best peak seemed to be at 824 cm⁻¹ for calcium nitrate and 827 cm⁻¹ for lithium nitrate. A 0.4-mm cell was used for the quantitative procedure in order to obtain good sensitivity.

Wave num	ber, <i>cm</i> ⁻¹	
Calcium nitrate	Lithium nitrate	Nature
737	734	weak, sharp
824	827	medium, sharp
1032	1037	weak, sharp
1314	1325	strong, ill-defined owing to acetone interference
1420	1405	strong, ill-defined owing to acetone interference

TABLE I.—PEAKS FOR CALCIUM NITRATE AND LITHIUM NITRATE IN ACETONE SOLUTION

Calcium nitrate and lithium nitrate in acetone solution have covalent characteristics, so the peaks are not due to the nitrate ion as such. It is known that nitrate in the ionic state has four fundamental vibrations in the infrared while nitrate in the covalent state has six.⁴

Water interferes by lowering the base-line in the region of 825 cm⁻¹ and causing low results. This interference from water makes it necessary to use a dry-box and dry air for the evaporation. Otherwise the cooling effect of the vaporization and the hygroscopicity of the acetone and nitrates will

cause condensation of moisture from the air. The effect of moisture precludes the use of a steam-bath for the evaporation.

Typical results are shown in Table II.

Add	ed, g	Four	nd, <i>g</i>
Ca(NO ₃)	Sr(NO ₈) ₂	Ca(NO ₃) ₂	Sr(NO ₃) ₂
0.0768	0.2301	0.0755	0.2297
0.0610	0.0521	0.0610	0.0519
0.0105	0.1010	0.0110	0.1002
0.0077	0.0054	0.0071	0.0021
0.0017	0.0014	0.0015	0.0010
Ca(NO ₃) ₂	Ba(NO ₈) ₂	$Ca(NO_3)_2$	$Ba(NO_3)_2$
0·0749	0.2332	0.0765	0.2316
0.0208	0.0217	0·0 496	0.0212
0.0120	0.1009	0.0120	0.1004
0.0055	0.0049	0.0023	0.0046
0.0010	0.0012	0.0009	0.0013
LiNO ₃	Sr(NO ₃) ₂	LiNO ₃	$Sr(NO_3)_2$
0.0799	0.2102	0.0792	0.2099
0.0576	0.0510	0.0550	0.0216
0.0111	0.0165	0.0111	0.0123
0.0055	0.0022	0.0056	0.0055
0.0024	0.0026	0.0022	0.0023
LiNO ₃	Ba(NO ₃) ₂	LiNO ₃	Ba(NO ₃) ₂
0.0774	0.2009	0.0762	0.2014
0.0598	0.0570	0.0576	0.0557
0.0126	0.0121	0.0115	0.0116
0.0043	0.0029	0.0041	0.0024
0.0034	0.0022	0.0032	0.0020

TABLE II.-RESULTS FOR SYNTHETIC MIXTURES

Interferences

Sodium and potassium nitrates are slightly soluble in acetone and produce a slight but significant interfering peak. Magnesium nitrate is very soluble in acetone and produces a strong interfering peak. The method cannot be used for the determination of magnesium nitrate because water cannot be removed from hydrated magnesium nitrate without loss of some nitrogen dioxide.

If the method is to be applied to mixtures of calcium and magnesium a preliminary separation is necessary, *e.g.*, by oxalate precipitation. Three samples containing respectively $5 \cdot 5$, $2 \cdot 2$ and $1 \cdot 1$ mg of calcium nitrate, with $5 \cdot 1$ mg of magnesium nitrate in each, were taken and calcium oxalate was filtered off, ignited, and converted into the nitrate, which was then determined. The amounts of calcium nitrate found were $5 \cdot 2$, $2 \cdot 4$ and $0 \cdot 9$ mg.

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Summary—A method is proposed for the infrared determination of calcium or lithium in the presence of strontium or barium. A mixture of the nitrates is treated with acetone which dissolves only the calcium or lithium nitrate. The strontium or barium nitrate is filtered off. The filtrate is evaporated to about 2 ml with a stream of dry air and then diluted to 5 ml with acetone. The infrared spectrum is scanned from $860 \text{ to } 800 \text{ cm}^{-1}$ and the nitrate peak at 824 cm^{-1} for calcium and 827 cm^{-1} for lithium is measured. The recommended range is 1-80 mg of calcium or lithium nitrate in the presence of up to about 200 mg of strontium or barium nitrate.

Zusammenfassung—Ein Verfahren zur Infrarot-Bestimmung von Calcium oder Lithium neben Strontium oder Barium wird vorgeschlagen. Ein Gemisch der Nitrate wird mit Aceton behandelt, das nur Calciumoder Lithiumnitrat löst. Strontium- oder Bariumnitrat wird abfiltriert. Das Filtrat wird mit einem trockenen Luftstrom auf etwa 2 ml eingeengt und mit Aceton auf 5 ml verdünnt. Das Infrarotspektrum wird von 860-800 cm⁻¹ registriert und die Nitratbande bei 824 cm⁻¹ für Calcium und 827 cm⁻¹ für Lithium gemessen. Empfohlen werden 1-80 mg Calcium-oder Lithiumnitrat neben bis zu 200 mg Strontium- oder Bariumnitrat.

Résumé—On propose une méthode pour le dosage infra-rouge du calcium ou du lithium en présence de strontium ou de baryum. On traite un mélange des nitrates à l'acétone qui dissout seulement le nitrate de calcium ou de lithium. Le nitrate de strontium ou de baryum est séparé par filtration. On évapore le filtrat à 2 ml environ par un courant d'air sec puis dilue à 5 ml par l'acétone. Le spectre infra-rouge est examiné de 860 à 800 cm⁻¹ et l'on mesure le pic du nitrate à 824 cm⁻¹ pour le calcium et 827 cm⁻¹ pour le lithium. Le domaine recommandé est de 1-80 mg de nitrate de calcium ou de baryum pouvant atteindre 200 mg.

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Liquid-liquid extraction of tungsten(VI) with mesityl oxide

Application to an alloy steel

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MESITYL oxide (4-methyl-3-pentene-2-one) has been used in this laboratory for the extraction of transition elements. These studies have been extended to tungsten(VI), which can be extracted with 75% mesityl oxide in isobutyl methyl ketone (IBMK). It can then be stripped with ammonia and determined photometrically as the thiocyanate complex. The method is simple and rapid and has been successfully applied to an alloy steel.

EXPERIMENTAL

Reagents

Mesityl oxide.

Stock solution of sodium tungstate, $\sim 0.8\%$ w/v, standardized by the oxinate method, and diluted as required for working solutions.

Potassium thiocyanate solution, 50% w/v.

Tin(II) chloride solution, 20% w/v in concentrated hydrochloric acid.

General procedure

A 2-ml portion of sodium tungstate solution containing 430 μ g of tungsten(VI) was taken in a separatory-funnel. Enough hydrochloric acid and lithium chloride were added to make their concentrations 1M and 12M respectively in a total volume of 25 ml. The aqueous phase was then extracted with 10 ml of 75% mesityl oxide solution in IBMK for 2 min. The layers were allowed to separate, and tungsten(VI) was stripped from the organic layer by shaking first with 10 ml of 0.5M ammonia and then 5 ml of distilled water. To the extract about 25 ml of concentrated hydrochloric acid, 5 ml of 20% tin(II) chloride solution and 0.5 ml of 12% titanium(III) chloride solution were added and mixed well. After addition of 1.5 ml of 50% potassium thiocyanate solution and dilution

to 50 ml, the absorbance of the yellow solution was measured photometrically at 420 nm against water, within 2 hr.¹

RESULTS AND DISCUSSION

In the presence of 12M lithium chloride as salting-out agent, extraction was found to be complete from 1-4M hydrochloric acid.

The concentration of mesityl oxide was varied from 19% (1.62*M*) to 100% (8.70*M*) with IBMK as the diluent, and the hydrochloric acid concentration was varied from 0.1 to 4.0*M* in the presence of 12*M* lithium chloride. The results (Table I) show that it is quite possible to extract tungsten(VI) quantitatively even with 75% mesityl oxide. Various other solvents such as chloroform, carbon tetrachloride, benzene, toluene, xylene, n-butanol and isobutyl acetate were also tried as the diluent. The extraction was incomplete with all except xylene, toluene and IBMK. IBMK was preferred as it permits clear separation of the two phases.

The chlorides of lithium, magnesium and aluminium were tried as salting-out agents (Table II)

Mesityl oxide concentration, %	Initial [HCl], <i>M</i>	Extraction, %	Distribution ratio
19	0.1	46.2	2.14
(1·62 <i>M</i>)	0.2	52.8	2.79
	0.5	61-1	3.92
	1	69.4	5.77
	2-3	75.0	7.50
	4	80.6	10-35
30	0.1	56-9	3.30
(2·61 <i>M</i>)	0.2	58.3	3.49
	0.5	63.9	4.42
	1	72.2	6.66
	2	77.8	8.74
	1 2 3	79-2	9.44
	4	83-3	12.49
60	0.1-0.2	69.4	5.77
(5·22M)	0.2	75.0	7.50
	1–2	94 ·4	42.46
	3–4	97-2	87.38
75	0.1-0.2	77.8	8.74
(6·52M)	0.5	86-1	15.49
	14	100-0	x
100	0.1	80.6	10.35
(8·70M)	0.2	83.3	12.49
	0.5	94.4	42.46
	1-4	100.0	œ

TABLE I.-DISTRIBUTION RATIO AS THE FUNCTION OF ACIDITY

Tungsten(VI) = 430 μ g in presence of 12*M* LiCl Mesityl oxide = 75% in IBMK

with 75% mesityl oxide in IBMK and 0.5-4.0M hydrochloric acid. The results showed that for quantitative extraction of tungsten(VI) at 1M hydrochloric acid concentration it is necessary to use 12M lithium chloride as the salting-out agent.

Variation of shaking-time from 30 sec to 3 min showed that a minimum of 2 min shaking is needed for complete extraction.

A number of representative ions were carried through the procedure and tested for interference. The tolerance limits (Table III) represent the weight ratios of ion to tungsten at which the error in tungsten determination is <2%. Ions showing strong interference are copper, mercury, ruthenium, antimony, iridium, molybdate, selenite, tellurite and fluoride. The relative standard deviation (10 variates) was $\pm 1.2\%$. The extraction and determination take about 40 min.

Salting-out agent	Initial [HCl], <i>M</i>	Extraction, %	Distribution ratio
LiCl, 6M	0.5	31.9	1.17
· ·	1	34.7	1.32
	2	44.4	1.90
	3	63.9	4.42
	4	76-4	8.12
8 <i>M</i>	0•5–1	34.7	1.32
	2 3	7 7·8	8∙74
	3	80.6	10.35
	4	88.9	19-98
10 <i>M</i>	0.2	52-8	2.79
	1	69.4	5.77
	2	91.6	27·4 7
	3-4	94•4	42.46
12 <i>M</i>	0-5	86.1	15-49
	1-4	100-0	œ
MgCl ₂ , 1 <i>M</i>	1	22.2	0.71
	1 2 3	27-8	0.96
	3	31.9	1.17
	4	38-9	1.59
2 <i>M</i>	1	34.7	1.32
	2	38-9	1.59.
	2 3 4	46-2	2.14
	4	72·2	6.66
AlCl ₂ , 1 <i>M</i>	1	23.6	0.77
	1 2 3	31.9	1.17
	3	41.7	1.78
	4	61-1	3.92
1•5M	1	33-3	1.24
	1 2 3	38-9	1.59
	3	58.3	3.49
	4	66.7	4.99

Tungsten(VI) = $430 \ \mu g$ Mesityl oxide = 75% in IBMK

Application to an alloy steel

Dissolve a known weight (~ 0.5 g) of alloy steel in 9 ml of concentrated sulphuric acid and 50 ml of water. After the initial reaction is over, heat the solution and oxidize it carefully with 10 ml of nitric acid and evaporate to fumes. Finally dilute it to 250 ml in a volumetric flask. Take a 2-ml aliquot of this solution in a separatory-funnel and add hydrochloric acid to give a concentration of 3.5*M*. Shake with 10 ml of 100% mesityl oxide for 10 min to remove iron;⁴ under these conditions tungsten(VI) is not extracted. Evaporate the aqueous phase to about 5 ml. Add hydrochloric acid and lithium chloride to make their concentrations 1*M* and 12*M* respectively. Shake the resulting solution for 2 min with 75% mesityloxide in IBMK. Allow the layers to separate. Strip tungsten(VI) from the organic phase as described above and determine it photometrically as the thiocyanate complex, at 420 nm.

Short communications

Foreign ion	Source	Tolerance limit, ion/W, w/w	Foreign ion	Source	Tolerance limit, ion/W, w/w
Pb ²⁺	PbCl _a ·2H _a O	5	Ca ²⁺	CaCl ₂ ·2H ₂ O	2.5
Tl+	Tl ₂ SO ₄	2.5	Sr ²⁺	SrCl ₂ ·6H ₂ O	5
Cu ²⁺	CuSO ₄ ·5H ₂ O	0	Ba ²⁺	BaCl ₂ ·2H ₂ O	10
Hg ²⁺	HgCl ₂	0	Sb ³⁺	SbCl ₃ ·3H ₂ O	0
Cď ²⁺	CdCl ₂ ·6H ₂ O	2.5	Os ³⁺	Na ₃ OsO ₄	0.2
Bi ³⁺	Bi(NO ₈) ₈ ·5H ₈ O	2.5	Ir ⁸⁺	IrCl ₃	0
Pt ⁴⁺	H ₂ PtCl ₆ ·6H ₂ O	2.5	Mo ⁶⁺	(NH4)6M07O24·4H2	0 0
Ru ³⁺	RuCl ₈ ·3H ₈ O	0	CN-	KCN	0.5
Pd²+	PdCl ₂ ·2H ₂ O	2.5	S ₂ O ₃ ²⁻	Na ₂ S ₂ O ₃ ·5H ₂ O	5
Rh³+	RhCl ₃ ·3H ₂ O	1.5	HPO42-	Na ₂ HPO ₄ ·12H ₂ O	2.5
Cr ³⁺	Cr ₂ (SO ₄) ₃ ·18H ₂ O	10	VO3-	NH ₄ VO ₃	1.5
Fe ³⁺	FeCl ₃ ·6H ₂ O	2.5	Tartrate	Tartaric acid	2.5
Au ⁸⁺	HAuCl ₄ XH ₂ O	0-5	Citrate	Citric acid	2.5
Be ²⁺	$Be(NO_3)_2$	10	Oxalate	H ₂ C ₂ O ₄ ·2H ₂ O	0.5
Th⁴+	Th(NO ₃) ₄ ·4H ₂ O	5	Ascorbate	Ascorbic acid	2.5
Zr ⁴⁺	Zr(NO ₃) ₄	2.5	Malonate	Malonic acid	0.2
Ce ³⁺	$Ce_2(SO_4)_3$	5 5	Acetate	CH ₃ COONH ₄	5
U ⁶⁺	UO ₂ (NO ₃) ₂ ·6H ₂ O	5	EDTA	EDTA	2.5
Zn ²⁺	ZnSO ₄ ·7H ₂ O	5	SeO ₃ ²⁻	Na ₂ SeO ₃	0
Mn ²⁺	MnCl ₃ ·6H ₂ O	5 5	TeO ₃ ²⁻	Na ₂ TeO ₃	0
Co ²⁺	CoCl ₂ ·6H ₂ O	5	F-	NaF	0
Ni ²⁺	NiSO4·7H2O	5	SO4 ²	Na ₂ SO ₄ ·10H ₂ O	35

TABLE III.-EFFECT OF DIVERSE IONS

Tungsten(VI) = 215 μ g in the presence of 1*M* HCl and 12*M* LiCl. Mesityl oxide = 75% in IBMK.

The results from the duplicate analysis of alloy steel No. 2735 (Bureau of Analysed Samples Ltd.) were 13.6 and 13.6% of tungsten (certificate value 13.65%).

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Summary—A new and simple method has been developed for the rapid extraction of tungsten(VI) with mesityl oxide. Quantitative extraction occurs from solutions 1M in hydrochloric acid and 12M in lithium chloride (as the salting-out agent) with 75% mesityl oxide in isobutyl methyl ketone. Tungsten is finally determined photometrically as the thiocyanate complex in the aqueous phase. Tungsten-(VI) can be extracted and determined satisfactorily in the presence of several elements. The method is shown to be applicable to an alloy steel.

Zusammenfassung—Eine neue und einfache Methode zur schnellen Extraktion von Wolfram(VI) mit Mesityloxid wurde entwickelt. Die Extraktion ist quantitativ aus Lösungen, die 1*M* Salzsäure und 12*M* Lithiumchlorid (als Aussalzmittel) enthalten, mit 75% Mesityloxid in Isobutylmethylketon. Wolfram(VI) wird zum Schluß in der wäßrigen Phase als Rhodanidkomplex photometrisch bestimmt. Wolfram(VI) kann in Gegenwart mehrerer Elemente zufriedenstellend extrahiert und bestimmt werden. Es wird gezeigt, daß sich das Verfahren auf einen legierten Stahl anwenden läßt.

Résumé—On a élaboré une méthode nouvelle et simple pour l'extraction rapide du tungstène(VI) avec l'oxyde de mésityle. L'extraction quantitative a lieu à partir de solutions 1M en acide chlohydrique et 12M en chlorure de lithium (comme agent de relargage) avec l'oxyde de mésityle à 75% en méthylisobutylcétone. On dose finalement le

Short communications

tungstène photométriquement sous forme de son complexe thiocyanique dans la phase aqueuse. On peut extraire et déterminer le tungstène(VI) de façon satisfaisante en la présence de plusieurs éléments. On montre que la méthode est applicable à un alliage d'acier.

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Glass electrode measurements of sodium in albumin solutions*

(Received 8 July 1968. Accepted 5 October 1968)

SINCE the initial work of Eisenman, Rudin and Cosby¹ on sodium-selective glass electrodes, several studies have been made comparing sodium-electrode and flame photometric determination of the the sodium content of various biological fluids. Friedman, Wong and Walton,² and Portnoy and Gurdjian,^{3,4} made their own small electrodes from Corning NAS₁₁₋₁₈ glass; Moore and Wilson⁵ used two commercially available sodium electrodes. All investigators reported no indication of glass poisoning by any of the constituents in the samples they analysed.

The present work is limited to some observations on the behaviour of one commercially available sodium electrode in bovine albumin solutions during the course of a study to obtain supporting results for a model for ultrafiltration to be published separately. Since these electrodes are now manufactured by several companies, they are readily available, and because of the expected increase in their use, it is hoped that these observations will be pertinent.

EXPERIMENTAL

A Beckman Research Model pH meter was used for the potential measurements. The sodium electrodes were the Corning NAS₁₁₋₁₈ glass membrane electrodes. The calomel electrode was the Beckman 5-in. fibre junction electrode. Sodium analyses were made with a lithium internal standard flame photometer (Instrumentation Laboratory Inc., Model 143). Solutions were made up in demineralized water, with reagent grade chemicals. The albumin was Pentex crystallized bovine albumin lot 13. Agar-salt bridges were made by dissolving 2% of Bactoagar (Difco Laboratories) in the appropriate salt solutions. Polyethylene tubing 2.5 mm i.d. was used for the bridge. Special sample tubes were made by drawing the ends of 20-mm borosilicate glass test-tubes into rounded cones that closely fitted the bulbs of the electrodes.

Two procedures were employed to determine the difference in sodium activity between an albumin solution and its ultrafiltrate. In the first the solutions were placed in separate containers electrically joined by means of a salt bridge. The potential difference between two sodium electrodes, one immersed in each solution, was then measured. The second procedure was to measure the potential difference between a single sodium electrode and a calomel electrode immersed in the same solution. For checking their responses, the two sodium electrodes were first immersed in the same solution. For checking their responses, the two sodium electrodes were first immersed in the same sodium chloride solution and the potential difference noted. They were then checked for Nernst response by the first procedure with two known sodium chloride solutions (usually one 0-16 molal and the other 0-08 molal made up to the same ionic strength with potassium nitrate). The potential was regarded as at equilibrium if it was unaffected by stirring the solution and it remained constant for 30 min. When the second procedure was used, the calomel electrode was connected by an agar-saturated potassium chloride bridge to the solution to be measured in order to prevent clogging of the fibre junction by protein; the criteria for equilibrium were the same as in the first procedure.

For determining sodium levels of unknown solutions a standard curve of potential vs. log concentration was constructed. The equation obtained for the curve was

$$E(mV) = 53.45 + 65.8 \log C$$

where C is the molal concentration of sodium chloride in a solution of ionic strength 0.16.

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RESULTS

Effect of depth of immersion

Very erratic results led to the observation that the depth of immersion of the sodium electrode was quite critical. After the bulb was immersed to its narrowest portion, further immersion caused no change. Table I summarizes the results for the potentials of the sodium electrode in a 0.14 molal

TABLE I.—EFFECT OF DEPTH OF IMMERSION ON POTENTIAL		
Potential, m		
+6.7		
−0 ·7		
-2.3		

sodium chloride solution, measured against a calomel electrode. Essentially the same behaviour was noted for the two sodium electrodes used. In the special sample tubes, 1 ml of solution was sufficient to cover the bulb of the electrode completely.

Effect of aging of solutions

The difference in potential between an albumin solution and its ultrafiltrate, whether measured directly with two sodium electrodes or by difference by the second procedure, was close to zero when measured reasonably soon after completion of ultrafiltration (14 samples gave 0.30 ± 0.10 mV). However, the differences as well as the potentials of the individual solutions were found to change if there were any prolonged exposures at room or higher temperatures (Table II). The first three samples had various periods of aging. Measurements on sample 4 were made soon after completion of ultrafiltration, and again on the original solution after it has been stored for one month in a refrigerator.

	e.m.f. vs. calomel, mV	Difference, (sac-ultrafiltrate), mV	[Na], molal	
			e.m.f.	Flame photometry
1. Sac*	7.50	0.82	0.200	0.193
Ultrafiltrate	6.65		0.194	0.184
2. Sac*	-11.75	3.40	0.102	0.094
Ultrafiltrate			0.091	0.082
Direct difference [†]		3.00		
3. Sac*	17-55	8.20	0.275	0.197
Ultrafiltrate	9.05	0.20	0.211	0.183
Direct difference [†]		8.70		
4. Sac‡	+0.82	0.15	0.126	0.163
Ultrafiltrate†	+1.00	-0.12	0.159	0.151
Direct difference [†]		0.20		
Direct difference [†] (4hr later)		1.30		
5. Albumin solution§	-0.50		0.153	0.160

TABLE II.-EFFECT OF AGING OF SOLUTIONS ON POTENTIAL

* Measurements at least 2 weeks after samples were prepared.

† Two sodium electrodes.

‡ Measurements within 2 hr after ultrafiltration.

§ Original solution of sample 4, one month later.

DISCUSSION

Careful standardization was necessary in order to obtain reproducible results. The bulbs of the sodium electrodes were completely immersed, and the response was checked by placing the electrodes in the same solution as well as in separate solutions of the same and different concentrations. This effect of depth of immersion has not been previously reported.

Short communications

Although the meter could be read to 0.05 mV, the repeatability of a potential measurement was within 0.2 mV. The potential difference between two sodium chloride solutions of different concentrations usually agreed within 0.2 mV when measured by either procedure. However, such was not the case when one of the solutions contained albumin. As seen in column 3 of Table II, the differences determined by the two methods show a wider deviation for the same solutions.

Considerable drifting occurred when an electrode was placed in a new solution, and 10–20 min were required for a steady potential to be attained. The presence of albumin in solution caused an even slower approach to a steady potential. Friedman, Wong and Walton,² and Portnoy and Gurjian,^{3,4} reported using equilibration times of several minutes after changing solutions. However, they used hand-made electrodes which were much smaller than the commercial electrodes used in the present work.

No extensive study on the aging process was carried out other than to establish its presence and to determine how it might be prevented. In most of the early experiments a number of circumstances cast doubt on the validity of potential measurements made soon after ultrafiltration. These samples were kept in the refrigerator most of the time but had been brought to 37° for potential measurements on several occasions. In general it was noted that the samples which gave the greatest deviation of the differences deviate considerably from the expected nearly zero value, and the sodium levels calculated from the individual solution potentials are considerably greater than the levels found by flame photometry.

In the experiment where the measurements were made reasonably soon after ultrafiltration it may be seen that the sodium potential difference between the sac and ultrafiltrate increased from 0.5 to 1.3 mV in an interval of 4 hr when the samples were placed in a thermostat at 37° . On the other hand, the sodium activity as indicated by the potential measurement on the refrigerated original solution one month later was essentially the same as that of the sac contents. This observation was taken as an indication that refrigeration was an effective means of preventing undesirable changes in the albumin solution. In contrast to the measurements on the aged solutions, the electrode sodium levels were lower than the flame photometric values for the fresh solutions and refrigerated samples.

It seems apparent that continued exposure of albumin solutions at room temperature results in the formation of some substance that affects the potential of the electrode system. Two obvious sites of the effect are the surface of the glass electrode and the liquid junction between the solution and the agar-salt bridge. However, sufficient information is not available to determine whether the effect occurs at one or both of these sites.

It will be noted that the values are expressed in molal units (moles per kg of water) in the present work. Most of the flame photometry values for serum are reported in mole/l., and are lower than the values obtained by electrode. Moore and Wilson⁵ noted that when they corrected their flame photometry values for protein content (conversion to molal units), the electrode value was lower. If a correction for 93% water content for serum is used, the flame photometer value obtained by Friedman, Wong and Walton² increases from 137.9 meq/l. to 148.3 meq/100 g of water as compared to the electrode result of 146.8. Our own value of 0.153 molal found by electrode for a 5% albumin solution was lower than the 0.160 molal found by flame photometry.

The usual explanation for the lower value found by electrode is that the activity is being measured and that the activity coefficient of the solution is affected by the protein. Another explanation of this effect could be that there is some type of protein binding of the sodium, since the effect of the protein on the ionic strength is not sufficient to account for the decrease in sodium activity.

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Summary—Measurements of the sodium level of albumin solutions and their ultrafiltrates were made with commercially available sodiumsensitive glass electrodes. The potential of the electrode was found to vary considerably with the depth of immersion. The potentials of albumin solutions which were allowed to remain at room temperature or higher for any length of time were found to increase, and in time gave unrealistic levels of sodium activity. An albumin solution stored in a refrigerator for a month did not show this effect. The sodium levels of albumin solutions as determined by the electrode were lower than the flame photometric values for the same solutions.

Zusammenfassung—Der Natriumgehalt von Albuminlösungen und ihren Ultrafiltraten wurde mit käuflichen natriumempfindlichen Glaselektroden gemessen. Es wurde gefunden, daß das Potential der

Short communications

Elektrode mit der Eintauchtiefe beträchtlich variiert. Die Potentiale von Albuminlösungen, die beliebige Zeit bei Zimmer- oder hoherer Temperatur belassen wurden, steigen an und gaben mit der Zeit unrealistische Werte der Natriumaktivität. Eine einen Monat im Kühlschrank aufbewahrte Albuminlösung zeigte diesen Effekt nicht. Die mit der Glaselektrode ermittelten Natriumgehalte von Albuminlösungen waren niedriger als die an den selben. Lösungen flammenphotometrisch bestimmten.

Résumé—On a effectué des mesures de la teneur en sodium de solutions d'albumine et de leurs ultra-filtrats avec des électrodes de verre sensibles au sodium commercialement disponibles. On a trouvé que le potentiel de l'électrode varie considérablement avec la profondeur d'immersion. On a trouvé que les potentiels de solutions d'albumine qu'on a laissé reposer à température ordinaire ou plus élevée pendant un temps quelconque crosisent, et donnent dans le temps des valeurs non réelles de l'activité du sodium. Une solution d'albumine convserée dans un réfrigérateur pendant un mois ne montre pas cet effet. Les teneurs en sodium de solutions d'albumine déterminées par l'électrode sont inférieures aux valeurs obtenues par photométrie de flamme pour les mêmes solutions.

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Determination of hydrazine by gas evolution

(Received 9 September 1968. Accepted 2 October 1968)

HYDRAZINE and its compounds are used extensively as industrial chemicals, rocket fuels, and in hydrazine-oxygen fuel cells. Numerous methods have been proposed for the determination of these compounds but the majority are based on the titration of hydrazines, either as reducing agents or as bases.¹ Other methods which have been used include coulometry,^{3,3} chronopotentiometry,⁴ turbidimetry,⁵ and colorimetry.⁶⁻⁹ Most of the titration procedures require 20-100 mg of hydrazine per determination, whereas the electrical and colorimetric techniques use μg amounts.

Quantities of hydrazine in the 1-10 mg range have been determined by measuring the volume of nitrogen evolved on oxidation of the hydrazine. The published methods have used iodate,¹⁰ ferricyanide,^{11,13} and lead (IV) and (II, IV) oxides¹³ to produce the gas. Other oxidants proposed include copper(II)14 and the oxides of copper(II),15 manganese(IV),15 silver(I)16 and silver(II).17,18

The suitability of the oxides of silver for this purpose has now been investigated. The resultant analytical procedure, described in this paper, proved comparable with alternative methods.

Reagents

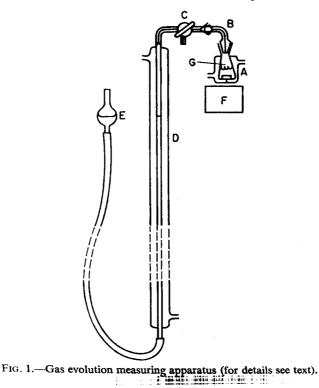
EXPERIMENTAL

Silver(I) oxide of low carbonate content was prepared by adding 0.1M barium hydroxide through a filter into a slight excess of 0.2M silver nitrate under an atmosphere of nitrogen. The silver nitrate solution was prepared with freshly boiled distilled water which had been previously purged with pure nitrogen gas. The precipitate of silver(I) oxide, after filtration and washing with carbonate-free water, was dried under vacuum over phosphorus pentoxide. The ground product was stored in a desiccator over potassium hydroxide pellets.

Silver(II) oxide was prepared by the method of Hammer and Kleinberg¹⁹ and was stored similarly to the silver(I) oxide. The carbonate contamination of this compound has been found to be less than 0.5% Ag₂CO₃ for a freshly prepared product containing 98% ÅgO.

Hydrazine sulphate stock solutions were prepared by dissolving a sample of the salt which had been recrystallized twice from distilled water. Hydrazine samples of lower purity were prepared by recrystallizing hydrazine sulphate from solutions containing either sodium sulphate or potassium nitrate, and these were used for comparing the method with other published procedures.

Buffer solutions were prepared from analytical reagent grade chemicals in the usual manner, a phosphate buffer being used for pH 6.8, and an acetate buffer for pH 6.5.



Apparatus

The gas evolution method was tested in the apparatus shown in Fig. 1. The apparatus consists of a water-jacketed reaction vessel (A) of 60 ml capacity connected through a removable capillary tube (B) and 3-way stop-cock (C) to a water-jacketed 5-00-ml gas burette (D), reading to 0-01 ml. The gas burette is fitted with a levelling bowl (E). The reaction mixture in the vessel (A) is stirred by means of a magnetic stirrer (F) and the apparatus is maintained at constant temperature by circulating water from a thermostatically controlled constant temperature bath fitted with a Braun Thermomix unit.

Recommended procedure

Prepare a stock solution of the hydrazine sample and add an aliquot of this solution, containing 5-6 mg of hydrazine, to approximately 15 ml of 0.5M buffer solution (phosphate or acetate) contained in the reaction vessel. The total volume should not be greater than 25 ml. Stir the mixture to ensure thermal equilibrium with the circulating water which should preferably be maintained within 1° of ambient temperature. Weigh 0.1 g of silver(1) oxide into a plastic boat and, after stopping the stirrer, float the boat and contents on the surface of the reaction mixture. Replace the removable capillary tube and close the apparatus to the atmosphere by adjusting the 3-way stop-cock. Allow sufficient time for the enclosed gases to equilibrate thermally then level the liquid in the gas burette with the aid of the levelling bowl and 3-way stop-cock. Start the stirrer to sink the boat and contents, and measure the maximum volume of gas evolved. The amount of hydrazine present in the reaction mixture is given by

$$N_2H_4(mg) = 0.514 \frac{PV}{T}$$
,

where P = partial pressure of nitrogen evolved (mmHg), *i.e.*, atmospheric pressure – water vapour pressure; V = volume of wet gas evolved (ml); T = temperature of circulating water in apparatus (°K).

RESULTS AND DISCUSSION

Earlier studies indicated that the rate of reaction is pH-dependent and as protons are released during the reaction adequate buffering is essential. At pH < 6 the reaction rate at room temperature is too slow for practical purposes. At pH > 7 low nitrogen yields were observed, possibly owing to some aerial oxidation of the hydrazine test solution.

Two buffer systems were therefore examined in detail; a phosphate system adjusted to pH 6.8 and an acetate system buffered at pH 6.5. Acetate ions form a weak complex with silver ions and total gas evolution was complete in 8–10 min. The phosphate ion forms a sparingly soluble compound with silver ions and the time required to liberate the gas fully from these solutions was 20 min. Silver ions are involved in the reaction mechanism¹⁶ hence the presence of anions which form sparingly soluble compounds reduces the rate of reaction. For example, a 0.1M chloride concentration in the two buffer solutions reduced the amount of gas evolved in the stated time periods to 50% and 15% respectively of the total yield. At concentrations less than 0.5M, nitrate and sulphate ions had no effect on the yield. Some studies were made with a maleate buffer system but the experimental results were consistently 2–5% low.

The effect of varying the buffer concentration, the pH, the total volume, the amount of hydrazine present, the weight of silver oxide added, and the temperature, on the efficiency of the gas evolution method, were all examined.

Silver(II) oxide was found to be an unsuitable oxidant under all conditions. To avoid side-reactions with silver(I) oxide the amount of excess of reagent has to be restricted. The amount of oxide added should not exceed 1.4 (acetate buffer) or 2 (phosphate buffer) times the amount theoretically required. The use of silver(I) oxide samples containing large amounts of carbonate impurity is not recommended, as a sample containing 2-3% Ag₈CO₈ gave results which were 1-2% high. The rate of reaction decreases with decreasing hydrazine concentration, increasing ionic strength,

The rate of reaction decreases with decreasing hydrazine concentration, increasing ionic strength, and decreasing temperature, and consequently, low analytical results were obtained in the presence of high concentrations of acetate ions, on dilution of the sample with large volumes of buffer, and at low temperatures. Increasing the temperature did not successfully overcome the kinetic problems, since the errors associated with vapour pressure corrections become more pronounced with increased temperature.

The results obtained when samples were analysed by the recommended procedure and three other procedures selected from the literature are shown in Table I. These results are the average of at least eight determinations, the standard deviations recorded being determined in the usual way.

Method		N_2H_4 . $H_2SO_4,\%$,)
Method	Sample I	Sample II	Sample III
Gasometric method (acetate buffer)	100·7 ± 0·4	77.5 ± 0.2	89·8 ± 0·5
Gasometric method (phos- phate buffer)	100.1 ± 0.4	76.5 ± 0.3	89·8 ± 0·3
Acid-base potentiometric ti- tration method ²⁰	98·4 ± 0·4	$76{\cdot}2\pm0{\cdot}2$	$89{\cdot}2\pm0{\cdot}1$
Indirect iodate titration method ²¹	$100{\cdot}3\pm0{\cdot}2$	77·5 \pm 0·2	$90{\cdot}3\pm0{\cdot}2$
Dichromate colorimetric method ²²	$102{\cdot}2\pm0{\cdot}6$	$79{\cdot}0\pm0{\cdot}3$	92.7 ± 0.5

It can be observed that the two gas evolution procedures yielded values which compare favourably with the two titration methods, the results obtained with an acetate-buffered solution being, in general, slightly higher than those obtained with a phosphate-buffered solution. The acid-base potentiometric titration gave results which were lower than those obtained by the gas evolution and indirect iodate methods. With pure hydrazine sulphate the titration result was 2% low (Sample I). The colorimetric method, based on the reduction of dichromate ions, gave results which were consistently high by 2-3%. This method requires calibration with a standard hydrazine solution and the reaction between hydrazine and the dichromate appears to be non-stoichiometric and slightly dependent on reaction conditions.

All gasometric procedures have limitations. For example, special apparatus is required and this restricts the method to a small range of hydrazine concentrations. The technique is sensitive to changes in experimental conditions and the procedure is comparatively slow. However, for the analysis of hydrazine solutions the alternative techniques are each subject to some limitations, and, as shown in this study, the gas evolution method is just as satisfactory for mg quantities of hydrazine.

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Summary—A method is proposed for the determination of mg amounts of hydrazine based on the measurement of the volume of nitrogen evolved after oxidation with silver(I) oxide.

Zusammenfassung—Eine Methode zur Bestimmung von Milligrammengen Hydrazin wird vorgeschlagen. Dabei wird das Stickstoffvolumen gemessen, das nach Oxidation mit Silber(I)-oxid entwickelt wird.

Résumé—On propose une méthode pour le dosage de l'hydrazine en quantités de l'ordre du mg basée sur la mesure du volume d'azote dégagé après oxydation par l'oxyde d'argent (I).

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Thermometric titrimetry

Studies of the cerium(IV) oxidation of α -mercaptocarboxylic acids

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RECENT studies in these laboratories^{1,2} have dealt with attempts to correlate the thermodynamic and kinetic parameters involved in metal-ion oxidations of organic substrates. Although kinetic^{3,4} and analytical⁵ investigations of cerium(IV) oxidation reactions are well established, little information is available on the thermodynamics of such reactions. Provided the reaction rates are sufficiently fast, enthalpimetric titration can be used to determine not only the stoichiometry of a particular reaction but its overall heat. Jordan and Ewing⁶ have measured the heat of reaction of cerium(IV) with iron(II), titanium(III) and ferrocyanide but no results are available for cerium(IV) oxidation of organic substrates. The reactions with α -mercaptocarboxylic acids are complete within a few msec under the conditions used¹ and so represent ideal systems for study.

EXPERIMENTAL

All materials used were of analytical reagent grade. The stock ammonium sulphatocerate solutions were standardized with iron(II) ammonium sulphate, with ferroin as indicator. Thiomalic acid, 99.7% pure, was used without recrystallization, but thiolactic acid and thioglycollic acid were redistilled at reduced pressure under nitrogen. Titration of the thiol group with iron(III)⁷ showed the acids to be more than 99% pure.

Experiments were carried out at various hydrogen ion concentrations. The α -mercapto acid was placed in the reaction cell, diluted to 50 ml with oxygen-free water and titrated with the oxidant (generally 100 times more concentrated than the acid solution, to keep the volume changes small, <2%).

Reaction products were shown to be the disulphides¹ which have also been prepared by iodine oxidation⁸ of the substrates. Infrared spectra of the products from both methods showed them to be identical.

The titration assembly was of conventional design, the rectangular perspex reaction cell of 150 ml capacity being surrounded by ~150-mm thick expanded polystyrene for heat insulation. A Vibronix stirrer (Shandon Scientific Co.,) ensured thorough mixing and the titrant was delivered at an adjustable but constant rate by a synchronous motor via a micrometer syringe the tip of which was below the level of the solution in the cell. Heat changes were detected by a $5-k\Omega$ thermistor in a bridge circuit, the output being relayed to a Honeywell multispeed 10-mA chart-recorder.

The instrument was calibrated with the hydrochloric acid-sodium hydroxide neutralization and checked with the iron(II)-cerium(IV) reaction, the value obtained for the latter being -27.0 ± 0.7 kcal/mole, compared with -27.0 kcal/mole previously obtained.⁶

RESULTS AND DISCUSSION

The initial steps of these oxidations have previously been shown to take place rapidly¹ and direct titration indicated that further slower oxidation steps take place, the total amount of cerium(IV) required being 8 moles per mole of α -thiol, the time taken being up to 3 days depending on temperature and acidity. With ferroin used as indicator the first reaction required more than 1 mole of cerium(IV) per mole of thiol (see Table I).

TABLE I			
	Ratio Ce(IV)/a-thiol		
a-Thiol	visual	thermometric	
Thiomalic acid	1.30	1.32	
Thiolactic acid	1.12	1.14	
Thioglycollic acid	1.16	1.18	

The curves obtained in thermometric titrations showed marked deviations from those normally derived. A typical example is shown in Fig. 1, where AB represents the base-line (heat loss from the solution to the surroundings) and at B the titrant was added. The rate of evolution of heat was constant for about 60% of the reaction $(B \rightarrow C)$. The curve then deviated slightly at C but remained fairly linear to D where a sharp change was recorded. DE represents the excess of reagent. The volume of titrant added from B to D, V_t , yielded the stoichiometries of the reactions of the three α -thiols (Table I).

Such stoichiometries are unexpected since the formation of disulphide would suggest a reaction (RSH = thiol)

$$Ce^{4+} + RSH \rightarrow Ce^{3+} + RS^{\cdot} + H^{+}$$

where 1 mole of each reagent is required.

By extrapolation of *BC* and *DE* the volume V_{\bullet} (Fig. 1) was obtained, which corresponded to 1:1 stoichiometry within 1% in all three cases.

Titrations with methyl acrylate present

The results suggested that the radicals produced reacted further with cerium(IV). To investigate this, titrations were carried out in the presence of methyl acrylate. Sharp changes in slope were

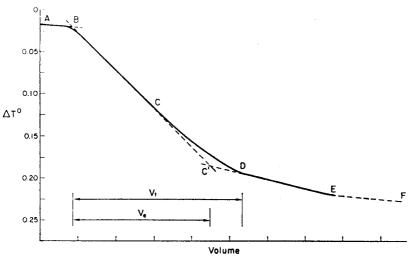


FIG. 1.—Enthalpimetric titration of 1.93×10^{-4} mole of thiolactic acid with cerium(IV) in 0.50M H₂SO₄.

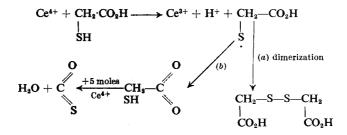
Each volume division represents 0.2280 ml. Addition rate, 2.5 ml/min. Effects due to the secondary reaction (*EF*) were obtained by measuring the heat changes as a function of time after addition of oxidant has ceased at *E*.

recorded at the beginning and end of the titrations but the titration branch showed some curvature. This may be caused by polymerization in the neighbourhood of the sensing device. Overall heat changes in these systems were 10-20 times as great as those normally recorded. The curvature did not affect the measurement of titrant consumed. In all three cases the stoichiometry found was 1:1 within 1%.

Measurements of ΔH

The secondary oxidations interfere with the calculation of ΔH in the normal way. In order to calculate the heat of reaction for the first oxidation step it is necessary to assume that (a) the second oxidation starts after the completion of the first reaction and (b) the oxidation rate for the second reaction is constant during the addition of the excess of oxidant and for about 30 sec after addition has ceased, *i.e.*, while the fourth portion of the enthalpogram (*EF* in Fig. 1) is being traced. Since the first reaction occurs at a rate several orders of magnitude greater than that of the second and all the curves referring to excess of reagent are linear (except at very low acidities [H⁺] < 0.1*M*), even if the assumptions are not valid the results will still be essentially correct. To calculate ΔH , the following procedure was adopted: slopes *BC*, *DE*, and *AB* were measured (Fig. 1) and the heat contribution of the second oxidation reaction was obtained by measuring the heat changes (*EF*) occurring after the addition of titrant had ceased. The ΔH for the reaction was then calculated from slopes BC' - (ED + EF - AB). Table II lists the ΔH values obtained in this way, together with those derived without allowance for the side-reaction. Good agreement is seen over the acidity range used (0.2-1.2*M*) and differences in ΔH at 20° and 25° are within experimental error.

To date we have not been able to characterize fully the side-reaction involving the radical, although the inhibition of the reaction in the presence of methyl acrylate would suggest a possible isomerization followed by further (very fast) redox reaction with the cerium(IV). A possible scheme for thioglycollic acid might be:



The requirements of stoichiometry are met if the reaction is considered to proceed 97% via path (a) and 3% via path (b). The fact that for thiomalic acid, which has two carboxylic groups, the deviation in V_t (Table I) is twice that for the other acids which are monocarboxylic, would suggest that these groups are involved in the side-reaction.

It is of interest to note that this is the only method of obtaining the heat of reaction for these

	Moles reseted	TOC	III SO I M	$-\Delta H_{\text{uncorr}},$	$-\Delta H_{\rm corr},$
	Moles reacted T	T°C	[H₂SO₄], <i>M</i>	kcal/mole	kcal mole
Thiolactic acid	2.213×10^{-4}	20.2	0.7	37.8	38.7
		20.4	0.6	37.4	37.9
		20.0	0.2	35.0	38.9
		20.2	0.2	30.5	37.4
		20.5	0.2	26.7	39.6
	$1.476 imes 10^{-4}$	19.8	1.2	38.0	38.4
		20.2	0.5	37-2	38.2
		22.4	0.2	35.3	38.1
		25.1	0.2	31.3	38.7
		21.3	0.2	35.2	37.8
			Mean	$\Delta H_{\rm corr} = -38$	4 ± 0.5 kcal/mole
Thioglycollic acid	1.841×10^{-4}	20 ·1	0.5	39.5	40.0
07		20.5	0.5	38.3	40 ·7
		21.2	0.2	37.1	40.2
		20 ·7	0.2	37.3	39.6
		20.0	0.5	38.4	40.0
		20.4	0.2	34.5	39.8
		20.4	1.2	38.3	41.5
		19.6	1.2	39.8	40.3
		22.8	0.2	35.4	40.2
		24.0	0.5	34.1	41.5
			Mean	$\Delta H_{\rm corr} = -40$	4 ± 0.6 kcal/mole
Thiomalic acid	$1.730 imes 10^{-4}$	20.3	0.3	37.9	40.4
		20.1	0.2	38.4	40.0
		20.8	0.2	37.1	39.8
		20 ·1	1.2	37.7	40.1
	$2.184 imes10^{-4}$	20.6	0.7	38.4	39.5
		20.7	0.5	37.8	40.9
		20.7	0.5	37.6	39.9
		20.9	0.5	37.2	39.0
		20.1	0.2	36.5	39.8
		20.1	0.2	36.8	40.5
			Mear	$\Delta H_{\rm corr} = -40$	0 ± 0.4 kcal/mole

TABLE II.—HEATS OF REACTION

systems since it is only through the titration that the secondary reactions which occur can be identified and corrected for.

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Summary—The cerium(IV) oxidation of thioglycollic, thiolactic and thiomalic acids has been examined by thermometric titration. The titration curves indicate stoichiometries of more than 1 mole of cerium(IV) per mole of α -thiol, suggesting possible side-reactions. In the presence of methyl acrylate, however, the expected ratio is observed. The overall heat of each reaction has been derived. Only with a titration method of this kind where allowance can be made for side-reactions can the heats of reaction for these systems be measured.

Zusammenfassung—Die Oxidation von Thioglycolsäure, Thiomilchsäure und Thioäpfelsäure mit Cer(IV) wurde mit thermometrischen Titrationen verfolgt. Die Titrationen deuten auf Verhältnisse von mehr als einem Mol Cer(IV) pro Mol α -Thiol, was auf die Möglichkeit von Nebenreaktionen hinweist. In Gegenwart von Methylacrylat beobachtet man hingegen das erwartete Verhältnis. Die Gesamtwärmetönung jeder Reaktion wurde ermittelt. Nur mit einer Titrationsmethode dieser Art, wo für Nebenreaktionen korrigiert werden kann, lassen sich die Reaktionswärmen dieser Systeme messen.

Résumé—On a examiné par titrage thermométrique l'oxydation par le cérium (IV) des acides thioglycolique, thiolactique et thiomalique. Les courbes de titrage montrent des stoechiométries de plus d'une mole de cérium(IV) par mole d'a-thiol, suggérant des réactions secondaires possibles. En la présence d'acrylate de méthyle, toutefois, on observe le rapport attendu. On a déduit la chaleur globale de chaque réaction. On ne peut mesurer les chaleurs de réaction de ces systèmes qu'avec une méthode de titrage de cette sorte, où l'on peut tenir compte des réactions secondaires.

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Logarithmic converter for atomic-absorption spectrometry

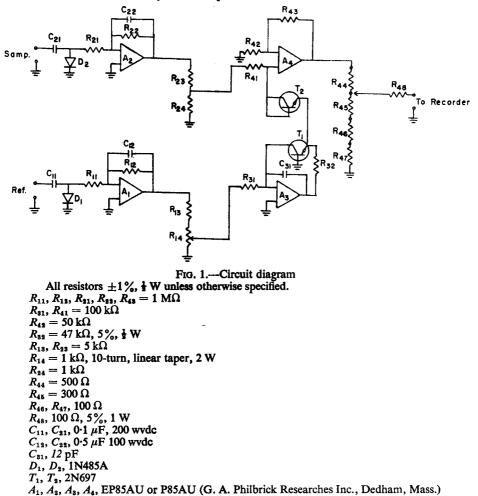
(Received 12 August 1968. Accepted 7 November 1968)

IN ATOMIC-ABSORPTION spectrometry, as in classical absorption spectrophotometry, the Beer-Lambert law describes the relationship between sample concentration and absorbance. Since the most commonly employed transducer, the photomultiplier, responds linearly to intensity, it is necessary to convert its output into logarithmic form to utilize the light absorption data for analysis. Usually the conversion is effected manually, by means of tables, or automatically, by measuring the output with a recorder of which the slidewire or gearing is logarithmic. Manual methods are tedious and slow, while mechanical conversion suffers from an inherently limited dynamic range.

Short communications

Recently, the logarithmic relationship between the current through a semiconductor junction and the voltage across it has been used to effect logarithmic conversion. Although any semiconductor diode will show logarithmic response, the largest dynamic range is exhibited by silicon transistors in which the emitter-base junction is used, while the collector-base junction is effectively short-circuited.^{1,2} Such devices show a logarithmic response over 7–9 orders of magnitude.

This paper describes a logarithmic converter designed for use with the Perkin-Elmer Model 303 atomic-absorption spectrophotometer and incorporating signal-conditioning devices appropriate to that instrument. Since the Perkin-Elmer instrument is a double-beam device, the converter described computes the ratio of the intensity of the sample beam to that of the reference beam.



The inputs to the converter are the separated sample and reference beam signals taken at the outputs of the cathode followers in the signal separator assembly in the instrument.³ The signals are two out-of-phase square-waves at high d.c. levels. They are conveniently available on most versions of the instrument at external terminals labelled TP-5 and TP-6 and at octal sockets available for connection of accessories supplied by the manufacturer. Because the output is taken from cathode followers and because the logarithmic converter draws only a few μ A of current, the logarithmic converter and the manual nulling circuits of the instrument do not interact and may be used simultaneously.

Construction

A circuit diagram of the instrument is shown in Fig. 1. The operational amplifiers are manufactured by Philbrick Researches, Inc., Dedham, Mass. and powered by a Philbrick Researches

PR-30 power supply. The output is fed into a Honeywell Electronik 15 recorder (1-50 mV, full scale, as required). Other recorders and null potentiometers have been used with the instrument and found satisfactory.

Description

The reference and sample input channels are identical and only the reference channel will be discussed. Capacitor C_{11} and diode D_1 pass the a.c. component of the spectrophotometer output and clamp its positive end to 0.5 V. The resulting square-wave is passed through the inverter-filter, (amplifier 1) which converts it into a positive d.c. signal. The filter may be considered to be a slowly discharging integrator, the time constant of which is too long to allow complete discharge during one cycle of the square-wave. The smoothed inverted sample and reference beams are fed into a logarithmic ratio circuit, a standard analogue computer circuit with an output proportional to the logarithm of the ratio of the input voltages.⁴ The potentiometer, R_{14} , is a zero control used to balance the sample

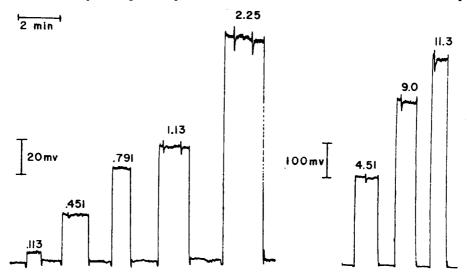


FIG. 2.—Response of logarithmic amplifier. Aqueous Ca(ClO₁)₂ solution, 0.113-11.3 ppm calcium. Air-acetylene flame. Note scale-change for solutions more concentrated than 2.25 ppm calcium.

and reference beams when no sample is in the flame. Since the input square-wave has a magnitude of about 6 V, attenuation of both signals is necessary and is effected by the voltage dividers on the outputs of the filters $(R_{23} + R_{24} \text{ and } R_{13} + R_{14})$.

Amplifier 3 is a conventional logarithm-taking circuit.^{1,3} Its output is bucked against transistor T_2 , the voltage across which is proportional to the logarithm of the current through it. Thus, the non-inverting input of amplifier 4 is maintained at a potential proportional to the difference in the logarithms of the two input voltages. Since the output voltage is proportional to the potential difference between the inputs, this difference is multiplied by the amplifier in the conventional way and appears at the output terminal. The output is taken through a 100-ohm resistor to protect the amplifier against accidental shorting of its output terminals.

Performance

Figure 2 illustrates the performance of the logarithmic converter. Solutions of calcium perchlorate were employed for these measurements. Absorbance was measured at 422.6 nm, a calcium hollow-cathode lamp being used as source. The slope of the response curve is 1.36 mV per 0.001 absorbance and is observed to at least 90% absorption. This corresponds to a change of 6 mV for a solution showing 1% absorbance. For the calcium system used here the slope of the response curve is 58 mV/ppm of calcium up to about 1 ppm, decreasing to 52 mV/ppm at 10 ppm.

mV/ppm of calcium up to about 1 ppm, decreasing to 52 mV/ppm at 10 ppm. Because of the ratio configuration of the circuit, a change of 30% in the gain of the photomultiplier causes less than a 1% change in the output of the logarithmic amplifier. The instrument baseline drifts slowly, however, because of fluctuations in flame conditions, for which the instrument cannot compensate. The logarithmic converter requires about 2.6 sec to respond to a step increase or decrease in absorbance. This slow response is caused by the active filters, which have time constants of about 0.5 sec. A 0.5-sec time constant is necessary to achieve the desired smoothing of the square wave, to a ripple factor of less than 1%. However, slow response is desirable, since it helps filter out some of the noise inherent in atomic-absorption spectrometric measurements. It is possible to increase the filtering action further by increasing the size of capacitors C_{12} and C_{22} , but this does not appear to be necessary.

DISCUSSION

A major shortcoming of the transistor as a logarithmic conversion device is its relatively high temperature sensitivity, about $0.3\%/deg.^1$ The converter described here does not incorporate temperature compensation, but this could be readily effected by simple modifications to the feedback circuit of amplifier 3. Since thermistors have a negative temperature coefficient of resistance, a fixed resistor plus thermistor in place of the feed-back resistor in amplifier 4 would attenuate the gain of the amplifier to compensate for the temperature dependence of the transistor transfer functions. In practice, the temperature fluctuations encountered in the normal laboratory in the course of the working day are not sufficiently great to affect the performance of the converter seriously. Normally, a precision of 1-2% relative is acceptable for atomic-absorption work and room temperature fluctuations of at least $\pm 3^\circ$ are tolerable.

The converter would show an even wider dynamic range than it does if the relatively constant reference signal were fed to amplifier 4 and the sample signal to amplifier 3. However, the response range is more than adequate for atomic-absorption spectrometry, since a working concentration range of more than a 100-fold is seldom employed. The configuration employed here gives a negative output signal, a useful feature for the recorder employed by us. Interchange of the functions of amplifiers 3 and 4 would give a positive output signal, which is desirable for some recorders.

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Summary—A logarithmic converter using a silicon transistor in the feed-back loop of an operational amplifier circuit, and suitable for use with a double-beam atomic-absorption spectrometer, is described.

Zusammenfassung—Ein logarithmischer Umsetzer wird beschrieben. Er enthält einen Silicium-Transistor in der Rückkopplungsschleife eines Operationsverstärkerkreises und eignet sich zum Gebrauch in Verbindung mit einem Zweistrahl-Atomabsorptionsspektrometer.

Résumé—On décrit un convertisseur logarithmique utilisant un transistor au silicium dans la boucle de rétroaction d'un circuit amplificateur opérationnel et convenant à l'emploi avec un spectrométre d'absorption atomique à douvbe faisceau.

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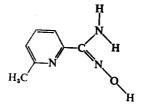
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6-Methyl-2-pyridinecarboxamide oxime, a reagent for copper

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THE blocking effect of substituents in positions adjacent to the nitrogen atoms of ferroin reagents (1,10-phenanthroline, 2,2'-bipyridyl) renders the molecules non-reactive towards iron(II) and confers

on them extraordinary specificity for copper (I).¹ In attempting to extend this blocking effect to 2,4,6-tripyridyl-s-triazine, an extraordinarily sensitive reagent for iron,^{2,3,4} we failed to obtain the desired 2,4,6'-tri(6'-methylpyridyl)-s-triazine, but did isolate a compound identified as 6-methyl-2-pyridinecarboxamide oxime (**R**) which yields an intensely yellow compound with copper (I). The



molar absorptivity is reasonably high ($\varepsilon = 7.2 \times 10^{\circ}$) and the specificity good (only palladium interferes) but in neither respect is the reagent superior to neocuproine ($\varepsilon = 7.95 \times 10^{\circ}$) or bathocuproine ($\varepsilon = 13.9 \times 10^{\circ}$). On the other hand the compound is easy to prepare.

EXPERIMENTAL

6-Methyl-2-pyridinecarboxamide oxime

To 8.4 g of hydroxylammonium chloride dissolved in 25 ml of water and adjusted to pH 5-6 with sodium carbonate were added 15.1 g of 2-cyano-6-methylpyridine dissolved in 75 ml of 95% ethanol. The mixture was kept at 80-85° for 1 hr and then cooled to 40° and a stream of air was passed over the surface of the liquid until the volume of the solution was reduced to about 25 ml. Water was added until the crude product began to precipitate. After further standing the solid was filtered off, thoroughly washed with water, recrystallized three times from hot benzene and then dried for 24 hr at 60° under reduced pressure. White crystals; m.p. 138° with some sublimation before melting. Found: C 55.6%, H 6.1%, N 27.8%, m.w.⁶ 146; calculated for C₄H₆N₃O: C 55.62%, H 6.00%, N 27.80%, m.w. 151:2. The NMR spectrum showed four bands, at $\delta = 9.19$, 7.60, 5.86 and 2.5. Integration showed 1, 3, 2 and 3 hydrogen atoms, respectively, the positions corresponding to a hydroxyl hydrogen atom, three asymmetric ring hydrogen atoms, two amino hydrogen atoms, and three identical methyl group hydrogen atoms respectively. The spectrum is thus in agreement with that expected for 6-methyl-2-pyridinecarboxamide oxime.

Reaction with copper(I)

The yellow copper(I) compound of **R** is completely formed in aqueous solution over the pH range 4.5-7. The system conforms to Beer's law up to $10^{-4}M$ copper, the molar absorptivity being 7.2×10^3 at 405 nm, the wavelength of maximum absorption. The copper compound can be completely extracted into isoamyl alcohol in two extractions. The compound is stable in aqueous and in isoamyl alcohol solutions. Spectrophotometric titration at 405 nm showed formation of a CuR₂ compound.

6-Methyl-2-pyridinecarboxamide oxime is quite specific for copper. Mercury, cobalt, zinc, manganese, lead, nickel, tungsten and platinum, at the 500-µg level, when treated with hydroxyl-ammonium chloride, buffer of pH 5.5, and reagent, give no colour; bismuth gives a white precipitate, presumably the oxychloride, and molybdenum gives a slight yellow colour. The determination of copper can be carried out in the presence of 100 times as much iron if the copper compound is extracted into isoamyl alcohol. The most serious interference is from palladium which forms a yellow compound, the molar absorptivity being about 5.0×10^8 at the wavelength of maximum absorbance, 355 nm.

Determination of copper in blood and liver

Attempts to determine copper in serum with 6-methyl-2-pyridinecarboxamide oxime following treatment with an equal volume of 1.2M hydrochloric acid and precipitation of the protein with 20% trichloracetic acid gave incomplete and irregular recovery of added copper. Results obtained by first wet-washing the organic material with nitric and perchloric acids were satisfactory. It proved necessary to fume adequately to remove all traces of nitric acid. Perchloric acid does not interfere, as the colour formation is complete in the presence of even large amounts of sodium perchlorate.

Procedure. Digest the sample of serum or blood, 10 ml, or of liver, 2.50 g (wet basis), with 2.5 ml of sulphuric acid, 10 ml of nitric acid and 1 ml of perchloric acid. Add additional amounts of a mixture of nitric and perchloric acids (4:1) until all of the organic matter is destroyed. Heat the

mixture until fumes of sulphuric acid appear and then cool. Add water, and heat until fumes appear again. The resulting solution is nearly colourless. Dilute with water, adjust the pH to 5-6 with 10M sodium hydroxide, and then dilute to a definite volume. Take an aliquot of the solution equivalent to 5 ml of the whole blood or 0.5 g of the liver and dilute it to 25 ml with water and add 5 ml of 2Macetic acid-sodium acetate buffer, pH 5.5 (from which the copper impurity has been removed by treatment of 1 l. with 5 ml of 10% hydroxylammonium chloride solution and 5 ml of 0.1% reagent solution and extraction with 10 ml of isoamyl alcohol), 5 ml of 10% hydroxylammonium chloride solution (from which the copper impurity has been removed by treating 11. with 5 ml of 0.1% reagent solution and extracting with 10 ml of isoamyl alcohol), and 5 ml of 0.1% reagent solution. Extract with first 5 ml and then 2.5 ml of isoamyl alcohol, place the extracts in a 10-ml volumetric flask and dilute to the mark with ethanol. Measure the absorbance of this solution at 405 nm. Prepare a calibration curve in a similar manner.

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Summary-6-Methyl-2-pyridinecarboxamide oxime (R) forms a yellow compound with copper(I), the molar absorptivity being $7\cdot 2\times 10^3$ at the wavelength of maximum absorption, 405 nm. The copper compound, CuR_{1} , forms completely over the pH range 4.5-7 and is easily extracted into isoamyl alcohol. R is highly specific for copper, the methyl group neighbouring the ring nitrogen atom preventing reaction with iron and other metals.

Zusammenfassung-6-Methyl-2-pyridincarboxamidoxim (R) bildet eine gelbe Verbindung mit Kupfer(I) mit dem molaren Extinktionskoeffi-zienten $7,2 \cdot 10^{\circ}$ bei ihrem Absorptionsmaximum 405 nm. Die Kupferverbindung CuR₂ bildet sich im pH-Bereich 4,5-7 vollstandig und läßt sich leicht in Isoamylalkohol extrahieren. R ist hochspezifisch für Kupfer; die Methylgruppe in der Nachbarschaft des Ringstickstoffs verhindert eine Reaktion mit Eisen und anderen Metallen.

Résumé-La 6-méthyl 2-pyridinecarboxamide oxime (R) forme un composé jaune avec le cuivre (I), le coefficient d'absorption moléculaire étant 7,2 \times 10⁸ à la longueur d'onde du maximum d'absorption, 405 nm. Le composé de cuivre, CuR₂, se forme totalement dans le domaine de pH 4,5-7 et est aisément extrait en alcool isoamylique. R est hautement spécifique du cuivre, le groupement méthyle au voisinage de l'atome d'azote du cycle empêchant la réaction avec le fer et d'autres métaux.

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Polarography of uranium(VI) and lead(II) complexes with L-glutamine

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THE DL- and L-glutamine complexes of nickel, cobalt(II) and copper(II) have been investigated by Ritsma et al. and the stability constants determined.¹ Perkins has studied the effect of amino-acid structure on the stabilities of the complexes formed with mercury, beryllium, zinc and cadmium.²

The present paper describes a polarographic study of the uranium(VI) and lead(II) complexes with L-glutamine.

EXPERIMENTAL

Apparatus

The polarograph and techniques used have been described previously.³ The dropping mercury electrode had m = 2.08 mg/sec and t = 4.02 sec in air-free 0.6M sodium nitrate at an applied potential of -0.5 V vs. the S.C.E. with 732-mm mercury column height. All measurements were made at $25 \pm 0.01^{\circ}$.

The pH of solutions was adjusted with nitric acid or potassium hydroxide and checked with a pH-meter.

Reagents

Uranyl nitrate (0.01M) and lead nitrate (0.01M) stock solutions were prepared and analysed as described previously.^{4,5} L-Glutamine (research grade) solutions were freshly prepared before use.

Triton X-100 (0.003% solution for nitrate and 0.001% for perchlorate supporting electrolytes) was used as maximum suppressor for the uranium(VI) system, but no suppressor was needed for the lead system.

RESULTS AND DISCUSSION

Because perchlorate is a very weak complexing agent, uranyl perchlorate and sodium perchlorate (as supporting electrolyte) were used exclusively in our earlier polarographic work.^{6,7} However, precipitation of potassium perchlorate in the calomel electrode of the pH-meter and in the polarographic cell interferes with pH measurement and changes the ionic strength of the polarographic solutions. For this reason, sodium nitrate was tried as supporting electrolyte, and found satisfactory. As shown, *e.g.*, in curve I of Fig. 1, for solutions 10⁻⁹M in uranyl nitrate, 0·3–1·5M in sodium nitrate

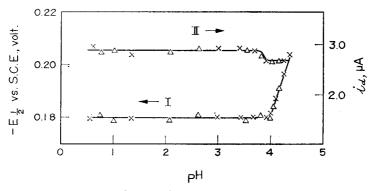


FIG. 1.—Effect of pH on the wave parameters of uranium(VI). $\times 1.0 \times 10^{-3}M$ UO₃(NO₃)₃, 0.6M NaNO₃, 0.003% Triton X-100; $\Delta 1.0 \times 10^{-3}M$ UO₃(ClO₄)₂, 0.15M NaClO₄, 0.0015% Triton X-100 I—Half-wave potential; II—diffusion current.

and containing 0.003% Triton X-100, $E_{1/2}$ remains constant at -0.180 V vs. the S.C.E. below pH 4.0, identical with the first half-wave potential of the simple uranyl ion, indicating that no complexation occurred. Between pH 4.0 and 4.4, $E_{1/2}$ varies with pH, having a slope of 0.060 indicating that one hydroxyl group is attached to the uranyl ion.

Nature of the reduction

All the polarographic solutions examined were $10^{-3}M$ in uranyl nitrate or lead nitrate and 0.6M in sodium nitrate (as supporting electrolyte). The solubility of glutamine limited the maximum ligand concentration to 0.25M. The pH ranges covered were 0.6-5.2 for the uranyl system and 0.6-8.5 for the lead system. Above these pH ranges, even with maximum ligand concentration, precipitation occurred, or an ill-defined wave was obtained.

The slopes of the conventional log plot fall in the ranges 0.057-0.060 for the uranyl system (Table I) and 0.028-0.031 for the lead system (Table II). These values were in good agreement with the theoretical values for the reversible one-electron reduction of the uranyl ion and two-electron reduction of lead.

Ligand conc., M	pН	$-E_{1/2} vs. S.C.E.,$	i _d , μΑ	$-\Delta E_{\rm d.e.}/\Delta \log \frac{i}{i_{\rm d}-i}$
0.03	1.50	0.180	2.70	0.057
	2.59	0.183	2.63	0.059
	3.42	0.186	2.60	0.028
	4.79	0.215	1.01	0.057
0.02	1.95	0.184	2.76	0.057
	2.92	0.195	2.70	0.060
	3.95	0 ·197	2.60	0.059
	4.38	0.208	2.34	0.028
0.10	1.02	0.180	2.83	0.057
	2.08	0.194	2.70	0.028
	3.90	0.204	2.44	0.028
	4.65	0.222	2.03	0.059
	5.28	0.244	0.70	0.060
0.20	0.60	0.180	2.96	0.059
	1.70	0.197	2.90	0.058
	2.78	0.218	2.20	0.059
	4.08	0.222	2.20	0.059
	5.28	0.263	0.95	0.028
0.25	0.60	0.180	2.93	0.057
1 - 1 - 1	1.45	0-192	2.75	0.028
	2.50	0.222	2.55	0.059
	4.50	0.240	2.05	0.057
	5.22	0.266	1.40	0.060

TABLE I.—POLAROGRAPHIC CHARACTERISTICS OF URANYL-GLUTAMINE COMPLEXES

10⁻³M UO₂(NO₃)₂, 0.6M NaNO₃, 0.003% Triton X-100.

TABLE II.--POLAROGRAPHIC CHARACTERISTICS OF LEAD-GLUTAMINE COMPLEXES

Ligand conc.,		$-E_{1/2}$ vs. S.C.E.,	i _d	$-\Delta E_{\rm d.e.}/\Delta \log \frac{i}{i_{\rm d}-i}$
M	рН	V	$\mu \mathbf{A}$	$-\Delta L_{\rm d.e.}/\Delta \log_{\rm i_d} - i$
0.10	0.60	0.403	5.62	0.029
	2.30	0.408	5.41	0.030
	5.18	0.407	5.45	0.028
	6.40	0.418	5.20	0.029
	7.59	0.441	3.85	0.029
0.20	1.80	0.405	5.25	0.031
	2.40	0.407	5.15	0.030
	4.60	0.408	5.10	0.030
	6.60	0.429	4.79	0.029
	8.00	0.467	4.35	0.029
0.25	0.55	0.402	5.51	0.030
	2.25	0.408	5.30	0.029
	4.60	0.410	5.09	0.028
	6.00	0.423	4.79	0.029
	7.05	0.442	4.26	0.029
	8.48	0.490	3.64	0.029

10⁻³ M Pb (NO₃)₂, 0.6M NaNO₃.

The diffusion current was found to be proportional to the square root of the height of the mercury column, proving that the electrode reactions for both systems were diffusion-controlled. The temperature coefficients of half-wave potential and diffusion current were less than the limiting ranges, $\pm 1 \text{ mV/deg}$ and 2%/deg respectively.

Uranyl-glutamine complex

A plot of half-wave potential vs. pH is shown in Fig. 2. It breaks into three sections at pH 2.5 and 4.1. Below pH 2.5 the slope in each curve increases with increasing ligand concentration and

reaches a largest value of 0.028 at ligand concentration 0.25*M*. This shows that one hydrogen ion is consumed for every two uranyl ions reduced. That $E_{1/2}$ is independent of pH between pH 2.5 and 4.1 indicates that no hydrogen ion participates in the electrode reaction in this pH range. Above pH 4.1 the curves show a uniform slope 0.036, proving that one hydroxyl ion is involved for every two uranyl ions reduced.

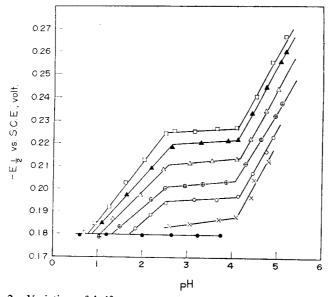


FIG. 2.—Variation of half-wave potential with pH for uranyl-glutamine complex. $1\cdot 0 \times 10^{-3}M$ UO₂(NO₃)₂, $0\cdot 6M$ NaNO₃, $0\cdot 003\%$ Triton X-100 and various ligand concentrations: • 0; × $0\cdot 03M$; \bigcirc $0\cdot 05M$; \oplus $0\cdot 10M$; \triangle $0\cdot 15M$; \blacktriangle $0\cdot 02M$; \Box $0\cdot 25M$.

Figure 3 shows the relation of $E_{1/2}$ to ligand concentration. The difference in number of ligands co-ordinated to uranium(VI) and uranium(V), (p-q), can be determined from the slope of $E_{1/2}$ vs. log C_G . At pH > 2.5 and $C_G > 0.11M$ the slopes are 0.056, corresponding to (p-q) = 1. However, at pH < 2.5 and $C_G > 0.11$ or at any pH values when $C_G < 0.11M$ the slopes show (p-q) < 1 (C_q is the total glutamine concentration).

In order to determine the metal-ligand ratio, potentiometric and conductometric titrations were performed. The formation of a 1.2 complex was proved when the ligand was in excess; below pH 2.5 only a 1:1 complex was found conductometrically.

Glutamine is a neutral amino-acid with $pK_{COOH} = 2.17$, $pK_{NH_s} = 9.13$ and isoelectric point at pH 5.56.⁸ Therefore, in the pH range investigated in this work, the predominant ligand species must be a dipolar molecule rather than the glutamine anion.

In the light of the discussion above, the complex species and electrode reactions can be formulated as follows. At pH < 2.5, both species UO_2^{+2} and UO_2G^{+2} co-exist and undergo the electrode reaction

$$UO_2^{+2} + UO_2G^{+2} + H^+ + 2e = 2UO_2^+ + HG^+$$

At 2.5 < pH < 4.1 with $C_G > 0.11M$, $UO_2G_2^{+2}$ is formed and the equation is

$$UO_2G_2^{+2} + e = UO_2G^+ + G$$

At $4 \cdot 1 < pH < 5 \cdot 2$ with $C_G > 0 \cdot 11M$, one hydroxyl group is attached to the uranyl ion, forming the UO₂(OH)G₂⁺ complex; the electrode reaction is

$$UO_2(OH)G_2^+ + e = UO_2G^+ + OH^- + G$$

Lead-glutamine complex

Figure 4 shows the effect of pH on the wave parameters. Below pH $2\cdot 0$ no complex is formed. Between pH 2 and 5, the slope is zero, *i.e.*, no hydrogen ion is involved in the reaction. Between

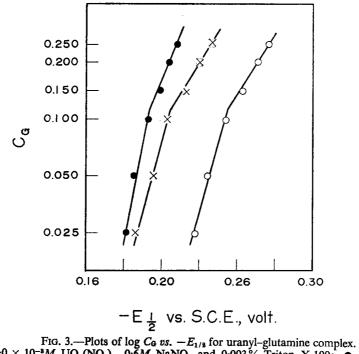


FIG. 3.—Plots of log C₆ vs. $-E_{1/8}$ for uranyl-glutamine complex. 1.0 × 10⁻³M UO₅(NO₅)₅, 0.6M NaNO₅ and 0.003% Triton X-100; • pH 2.00; × pH 3.50; \bigcirc pH 4.95

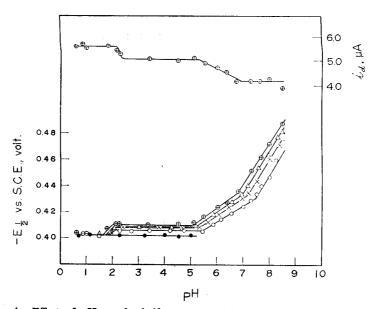


FIG. 4.—Effect of pH on the half-wave potential and diffusion current for lead-glutamine complex.
1.0 × 10⁻³M Pb(NO₃)₃, 0.6M NaNO₈ and various ligand concentrations: ● 0;
○ 0.10M; × 0.15M; △ 0.20M; ⊕ 0.25M

Short communications

pH 5 and 7, the slope 0.014 was regarded as due to the partial hydroxylation of lead ions; above pH 7.0, the hydroxylation was completed with one hydroxyl ion attached to each lead ion, as evidenced from the slope 0.032. The pH values of the break-points depend on the ligand concentration; the higher the ligand concentration, the lower the pH value at which the break occurs, which is attributed to the fact that the higher ligand concentration favours the complexation of the lead ion. The stepwise decrease in diffusion current and the accordance of pH at break-points for i_d -pH plots and for $E_{1/2}$ -pH plots provide further support for our suggestions.

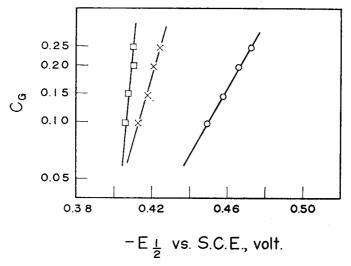


FIG. 5.—Plots of log $C_{\rm G}$ vs. $-E_{1/2}$ for lead-glutamine complex. 1·0 × 10⁻³M Pb(NO₃)₂, 0·6M NaNO₃; \Box pH 3·0; × pH 6·0; \bigcirc pH 8·0

The dependence of $E_{1/2}$ on the ligand concentration in various pH ranges is shown in Fig. 5, from which the number of ligands co-ordinated to lead is determined. The slopes 0.056 for pH 7.0-8.5 and 0.027 for pH 5.0-7.0 reveal the lead-glutamine ratios to be 1:2 and 1:1, respectively. Thus, the complex species and electrode reactions would be given as follows.

$$\begin{aligned} &7 \cdot 0 < pH < 8 \cdot 5; \ Pb(OH)G_{a}^{+} + 2e + Hg = Pb(Hg) + 2G + OH^{-} \\ &5 \cdot 0 < pH < 7 \cdot 0; \ Pb(OH)G^{+} + 2e + Hg = Pb(Hg) + G + OH^{-} \\ &2 \cdot 0 < pH < 5 \cdot 0; \ PbG^{+2} + 2e + Hg = Pb(Hg) + G \end{aligned}$$

The half-wave potential of a complex $Pb(OH)_m G_n^{2-m}$ at 25° obeys the equation:

$$(E_{1/2})_c = (E_{1/2})_s + \frac{0.059}{2} \log K_c - \frac{0.059}{2} n \log [G] - \frac{0.059}{2} m \log [OH^{-1}]$$

where

$$K_{c} = \frac{[Pb^{+s}][G]^{n}[OH^{-}]^{n}}{[Pb(OH)_{m}G^{s-m}]}$$

If

$$pK_{NH_3}^+ > pH \gg pK_{COOH}$$

$$[G] = \frac{C_{G} \cdot [\Pi^{+}]}{[\Pi^{+}] + K_{NH_{3}}^{+}}$$
$$-\log [OH^{-}] = 14 - pH$$

$$pK_{c} = \frac{(E_{1/2})_{s} - (E_{1/2})_{c}}{0.0295} - n \log C_{G} + (n - m) pH + n \log (K_{NH_{g}} + [H^{+}]) + 14m$$

At pH 7.0-8.5, n = 1.9 and m = 1.1 then, $pK_c = 10.16 \pm 0.04$ (Table III).

pН	[Ligand], M	$(E_{1/2})_{\rm s} - (E_{1/2})_{\rm c}, V$	p <i>K</i> e
7.4	0.10	0.029	10.16
	0.15	0.037	10.16
	0.20	0.045	10.14
	0.25	0.020	10.13
8 ∙0	0.10	0.048	10.18
	0.15	0.026	10.18
	0.20	0.060	10.15
	0.25	0.069	10.14
8.4	0.20	0.076	10.20
	0.25	0.081	10.19
			av. 10.16 ± 0.04

TABLE III.—Dissociation constant of Pb(OH)G₂⁺ at 25°C, μ 0.6

 $(E_{1/2})_s = -0.403 \text{ V vs. S.C.E.}$

Acknowledgement-The authors thank the National Council of Science for financial support of this work.

Chemical Engineering Department Cheng Kung University Tainan, Taiwan China

TSAI-TEH LAI MON-CHAO CHEN

Summary-The complexes of uranium(VI) and lead(II) with Lglutamine were investigated polarographically. For uranium(VI), the complexes UO_2G^{+2} , $UO_2G_2^{+2}$ and $UO_2(OH)G_2^+$ were identified at pH < 2.5, pH 2.5-4.1 and pH 4.1-5.2 respectively. With lead(II), complexes PbG+2, Pb(OH)G+ and Pb(OH)G2+ were formed at pH 2.0-5.0, pH 5.0-7.0, and pH 7.0-8.5, respectively. The concentration dissociation constant of $Pb(OH)G_2^+$ was found to be $pK_c = 10.16 \pm$ 0.04 at ionic strength 0.6.

Zusammenfassung-Die Komplexe von Uran(VI) und Blei(II) mit l-Glutamin wurden polarographisch untersucht. Mit Uran(VI) wurden bei pH < 2.5; 2.5–4,1 und 4.1–5.2 die Komplexe UO₂G²⁺, UO2G22+ bzw. UO2(OH)G2+ identifiziert. Mit Blei(II) wurden bei pH 2,5-5,0; 5,0-7,0 und 7,0-8,5 die Komplexe PbG²⁺, Pb(OH)G⁺ bzw. $Pb(OH)G_2^+$ gebildet. Die auf Konzentrationen bezogene Dissoziationskonstante von Pb(OH)G₂⁺ betrug bei der Ionenstärke $0,6 \ pKc = 10,16 \pm 0,04.$

Résumé—On a étudié polarographiquement les complexes de l'uranium (VI) et du plomb(II) avec la l-glutamine. Pour l'uranium(VI), les complexes $UO_{9}G^{3+}$, $UO_{2}G_{9}^{3+}$ et $UO_{2}(OH)G_{2}^{+}$ ont été identifiés à pH < 2,5, pH 2,5–4,1 et pH 4,1–5,2 respectivement. Avec le plomb(II), les complexes PbG⁺³, Pb(OH)G⁺ et Pb(OH)G₂⁺ ont été formés à pH 2,0– 5,0, pH 5,0-7,0 et pH 7,0-8,5 respectivement. On a trouvé que la constante de dissociation de concentration de Pb(OH)G₂⁺ est de $pK_{a} = 10,16 \pm 0,04$ à la force ionique 0,6.

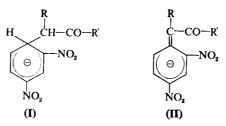
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Sur une colorimétrie des alcoylamines, guanidines et ammoniums quaternaires par la réaction de Janovsky

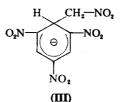
(Reçu le 14 Octobre 1968. Accepté le 21 Octobre 1968)

LA RÉACTION colorée que fournit le *m*-dinitrobenzène en solution acétonique alcaline, décrite par Janovsky,^{1,2} est liée à la présence d'un méthylène activé.³ Il est maintenant bien établi qu'il se forme en premier lieu un composé d'addition (I), irréversiblement oxydé en (II) s'il y a un excès de dérivé dinitré [conditions de Zimmermann^{4,5}].⁶⁻¹⁰



Le *m*-dinitrobenzène peut être remplacé par l'acide dinitro-3,5 benzoïque,^{11,13} le trinitro-1,3,5 benzène¹³⁻¹⁶ ou l'acide picrique.^{14,17} D'autres dérivés méthyléniques réagissent également; Ashworth et Gramsch¹⁸ ont ainsi accédé à la colorimétrie des nitroalcanes par action du *m*-dinitrobenzène et de potasse aqueuse.

En général, le développement de la coloration nécessite l'intervention d'une base forte. Selon nos essais, avec le trinitro-1,3,5 benzène en solution dans le nitrométhane, l'alcalinité d'une alcoylamine suffit pour provoquer la condensation. Bien que nous n'ayons pas isolé le produit de la réaction, il est raisonnable d'admettre que la coloration, dont l'intensité est proportionnelle à la quantité d'amine mise en jeu, est due à l'anion (III).



Par addition d'oxyde d'argent au milieu réactionnel, on peut également doser les chlorhydrates d'amines et de guanidines et les chlorures d'ammoniums quaternaires.

Le spectre d'absorption offre deux maximums à 453 et 565 nm. Le premier, plus important, est difficilement exploitable par suite de l'intense absorption du témoin des réactifs à cette longueur d'onde. La solution présente aussi une fluorescence rouge relativement peu sensible (excitation 546 nm, émission 625 nm). On pourrait, par exemple, déterminer de la sorte entre 12 et 50 μ g de dibenzylamine.

Les arylamines sont très peu réactives (densité optique = 0,05 pour 2 mg d'aniline) ainsi que la pyridine (densité optique = 0,2 pour 2 mg) avec laquelle la coloration continue de se développer pendant plusieurs heures.

PARTIE EXPERIMENTALE*

Réactif

Solution à 0,2% de trinitro-1,3,5 benzène dans le nitrométhane. Ce réactif doit être conservé à l'abri de la lumière.

Mode opératoire

A 0,2 ml de solution éthanolique de chlorhydrate d'amine ou de chlorure d'ammonium quaternaire, on ajoute 5 mg environ d'oxyde d'argent et 0,2 ml de réactif. On agite simultanément tous les tubes pendant 2 mn d'un mouvement oscillant régulier puis dilue par 3 ml de nitrométhane et filtre. Lecture immédiate à 565 nm.

Short communications

Amine	Prise d'essai pour obtenir une densité optique de 0,3 (cuve de 10-mm) μg
Amines libres	
n-Butylamine	6,8
Di-n-butylamine	9
Triéthylamine	7,5
Chlorhydrates et chlorures	
Méthylamine	5,2
Ethylamine	8
Di-n-butylamine	12,5
Dibenzylamine	25
Triméthylamine	13
Triéthylamine	10,5
Emétine	45
Morphine	50
Prométhazine	30
Guanidine*	7
Paludrine	22
Acétylcholine	18
Triméthylbenzylammonium (iodure)	25

TABLEAU I

*Résultats peu reproductibles.

Si l'on opère à partir de 0,2 ml de solution éthanolique d'alcoylamine libre, on ajoute 0,2 ml de réactif, laisse reposer pendant 1,5 mn à température ordinaire puis dilue par 3 ml de nitrométhane avant d'effectuer la lecture.

Note: Ce mémoire était sous presse lorsque nous avons eu connaissance d'un travail tout récent de C. A. Fyfe (Can. J. Chem., 1968, 46, 3047). L'auteur y démontre, par étude du spectre RMN, que le condensat obtenu par action de la triéthylamine sur le 1,3,5-trinitrobenzène en solution dans le nitrométhane a bien la structure que nous proposons ici.

Centre de Recherches Roussel-Uclaf 93-Romainville, France

> Résumé—En présence d'une alcoylamine, d'une guanidine ou d'un hydroxyde d'ammonium quaternaire libérés de leurs sels par l'oxyde d'argent, le nitrométhane se condense sur le trinitro-1,3,5 benzène selon la réaction de Janovsky pour former un composé rouge qui autorise la colorimétrie de la base azotée.

J. BARTOS

Summary—In the presence of an alkylamine, a guanidine or a quaternary ammonium hydroxide, liberated from their salts by the action of silver oxide, nitromethane reacts with 1,3,5-trinitrobenzene, yielding a red compound which allows the colorimetric determination of the nitrogenous base.

Zusammenfassung—In Gegenwart eines Alkylamins, eines Guanidins oder eines quatären Ammoniumhydroxids, die aus ihren Salzen durch Silberoxid freigesetzt werden, reagiert Nitromethan mit 1,3,5-Trinitrobenzol zu einer roten Verbindung, was die kolorimetrische Bestimmung der Stickstoffbase erlaubt.

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* Avec M^{me} C. Colombat.

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LETTER TO THE EDITOR

Computer calculation of the interference of ammonium salts in Mohr's method for the determination of chloride

Sir,

The interference of ammonium salts in Mohr's method for the determination of chloride has been studied experimentally by Block and Waters,¹ and theoretically by Wänninen,³ who used the method of conditional constants.³ The ionic equilibria involved can, however, be more comprehensively treated by use of the computer program HALTAFALL.^{4,5}

In this letter Block and Waters² and Wänninen's experimental values for the relative errors are compared with the results calculated by the computer. In all cases 30.4 mg of chloride in 60 ml of solution were titrated with v ml of 0.1M silver nitrate. The pH and the total concentrations of chromate and ammonium ions were varied. The values taken for stability and solubility constants were those used by Wänninen.² The results are shown in Fig. 1.

The free concentrations of Ag⁺ and CrO₄²⁻ are printed by the program for different values of v. The volume at the end-point, v_{end} , is then estimated as the value of v when $[Ag^+]^2[CrO_4^{2-}] = 10^{-11.3}$, and the relative error can easily be obtained as $E_{rel} = 100(v_{end} - v_{eq})/v_{eq} %$, where v_{eq} refers to the

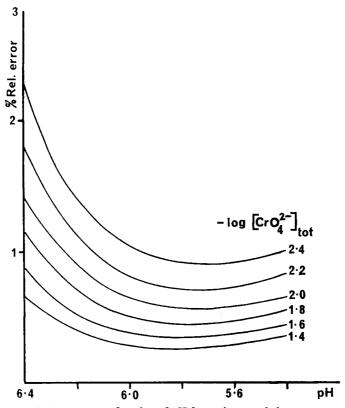


FIG. 1.-Relative error as a function of pH for various total chromate concentrations.

equivalence point. The amount of solid silver chromate required to give a visible precipitate can be estimated by means of a blank and need not be considered further.

		Et	rors, %, calculated fr	om	
NH_4NO_3 added, g	рН	Conditional constants ²	HALTAFALL ⁴ output data	Experimental data ¹	
0.1	6.75	0.3(0.3)*	0.3	0	
0.3	6.79	0.8(0.5)	0.6	0.3	
0.6	6·72	1.3(0.9)	1.0	1.0	
1	6.61	1.8(1.3)	1.4	1.7	
1.5	6.61	3.4(2.4)	2.6	3.0	
2	6.60	5.5(3.9)	4.1	3.3	

TABLE I.—CALCULATED AND EXPERIMENTAL ERRORS AT DIFFERENT AMMONIUM CONCENTRATIONS FOR THE TITRATION OF 30.4 mg of chloride in 60 ml of solution with v ml of 0.1M silver NITRATE AND AN INITIAL TOTAL CHROMATE CONCENTRATION OF $10^{-2.36}M$

* Figures in parentheses are calculated with corrected values for the total ammonium concentration.

The error in the calculation of total concentration of each component (H, CrO₄, Ag, Cl, NH₃) is 0.05% and even if all errors accumulate, the error in our concentration calculations cannot be more than $\pm 0.2\%$ (pH is constant for each set of calculations). Further information concerning the form of input data tapes used for the calculations can be obtained from this department.

In Table I, our calculated relative errors are compared with those calculated by Wänninen and those obtained experimentally by Block and Waters. The discrepancy between the errors calculated

TABLE II.—CALCULATED AND EXPERIMENTAL ERRORS (%) FOR THE TITRATION OF A SOLUTION CONTAINING 30.4 mg of chloride and 2 g of ammonium nitrate in 60 ml at different pH values and total chromate concentrations

Total		pH 6∙4			pH 6·2		pH	pН	pН	рН
[Cr(VI)] <i>M</i>	cond. const.	comp.	exp.ª	cond. const.	comp.	exp. ³	6.0 comp.	5∙8 comp.	5.6 comp.	5·4 comp.
10-2-4	2.9	2.30	4.4	1.5	1.38	1.9	1.04	0.90	0.91	1.01
10-2.2	2.5	1.82	3.6	1.3	1.11	1.5	0.82	0.70	0.73	0.82
10-2-0	1.9	1.43	2.2	1.0	0.90	1.3	0.64	0.57	0.28	0.66
10-1.8	—	1.15			0 ·70		0.51	0.44	0.47	0.55
10-1.6		0.86	—		0.51		0.40	0.35	0.37	0.44
10-1.4		0.64			0.38		0.28	0.27	0.29	0.36

by Wänninen and by the computer is probably due to an erroneous calculation of the total concentration of ammonium ion. The values in parentheses have been recalculated by us by Wänninen's method but with correct values of the total ammonium concentration. They agree satisfactorily with the errors calculated by the computer as well as with the experimental values.

One advantage of the computer method is that a wide range of variables can be examined rapidly. In order to find the optimum conditions for the titration of chloride in the presence of an initial total ammonium concentration of 0.416*M*, we have extended the concentration ranges of hydrogen ion and chromate to pH 5.4-6.4 and $10^{-1.4}-10^{-8.4}M$ respectively. The results are shown in Table II.

At decreasing $\vec{p}H$ values the formation of HCrO₄ and Cr₂O₇²⁻ cannot be neglected. This can be seen from Fig. 2. The optimum pH is 5.8; at higher pH interference is predominately due to ammonia while at lower pH the formation of HCrO₄⁻ and Cr₂O₇²⁻ increases the relative error. For a given pH the accuracy increases with increasing total chromate concentration since the precipitation

of silver chromate starts, in all cases, after the equivalence point. In practice there is, of course, an upper limit to the total chromate concentration.

upper mini to the total chromate concentration. A buffer capacity curve (Fig. 2) for a total chromate concentration of $10^{-1.8}M$ was calculated to see whether it is possible to keep the pH approximately constant during the titration. It can be seen that the indicator system itself has a fairly good buffering effect in the pH range considered.

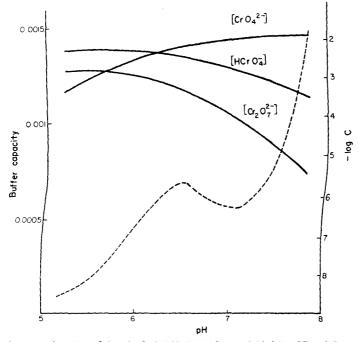


FIG. 2.—The titration of 68 ml of $10^{-0.44}M[NH_3]_{tot}$ and $10^{-1.86}M[CrO_4^{2-}]_{tot}$ with v ml of 10N OH⁻. The dashed curve represents the buffer capacity as a function of pH and the full curve represents the logarithmic concentration of the different chromium species as a function of pH.

We should like to thank Professor David Dyrssen for valuable discussions and Mrs Susan Jagner, M.A., fil. lic., for revising the English text. We are also indebted to His Majesty the King of Sweden, who gave us free computer time through "Statskontoret".

Department of Analytical Chemistry University of Gothenburg 402 20 Göteborg 5, Sweden 27 September 1968

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T. Anfält D. Jagner

NOTICES

INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

ANALYTICAL CHEMISTRY DIVISION

The Analytical Chemistry Division is administered by the Division Committee, the present members being:

Professor P. W. West, U.S.A. (President) Professor W. Kemula, Poland (Vice-President) Professor I. P. Alimarin, U.S.S.R. Professor R. Belcher, U.K. Professor C. Duval, France. Professor C. Duval, France. Professor L. Erdey, Hungary. Professor T. Fujinaga, Japan. Professor D. N. Hume, U.S.A. Professor D. N. Hume, U.S.A. Professor H. Kaiser, Germany. Mr. R. W. Fennell (Secretary), Materials Department, Royal Aircraft Establishment, Farnborough, Hants., U.K.

The bulk of the scientific work of the Division is done by the seven Commissions, whose terms of reference are the study of topics of international scientific or technical significance requiring agreement, regularization, standardization or codification within the sphere of their respective expertise.

Brief summaries of the work currently being done by these Commissions follow. Requests for further information or suggestions for future projects should be addressed to the appropriate Commission Secretary or, in case of doubt, to the Division Secretary.

Commission 1. Analytical Reactions and Reagents

Chairman: Professor H. Malissa Institut für Analytische Chemie und Mikrochemie Technische Hochschule, Getreidemarkt 9, A-1060 WIEN, Austria.

At the present time, this Commission is concerned entirely with standardization of analytical methods required by the European Economic Community with whom IUPAC has a working agreement.

Commission 2. Microchemical Techniques and Trace Analysis Chairman: Dr. W. Schöniger (Switzerland) Secretary: Dr. R. Lévy, Service central de Microanalyse du CNRS,

2, Rue H.-Dunant,

94 Thiais, France.

Studies are being carried out, on an international basis, on the elemental analysis of organic materials, in particular:

(a) carbon and hydrogen, especially in compounds containing heteroelements

(b) fluorine

(c) nitrogen, based on the Dumas method

(d) metals, excluding simple residue procedures.

Notices

In addition, known sources of errors in microanalysis are being collated and studies being made on the purification of chemicals used for micro and trace analysis and on mass absorption coefficients used in electron beam microanalysis.

Commission 3. Analytical Nomenclature

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Chairman: Professor R. Belcher (U.K.)
Secretary: Professor T. S. West,
Department of Chemistry,
Imperial College,
Kensington,
London, S.W.7, U.K.
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Internationally acceptable nomenclature, definitions and symbols are being sought in the following areas of analytical interest—

(a) liquid-liquid distribution (solvent extraction)

- (b) automatic analysis
- (c) ion exchange

(d) chromatography

- (e) scales of working
- (f) mass spectrometry
- (g) contamination phenomena in analytical precipitation.

The Commission is also compiling a list of trivial names of analytical reagents and examining the need for primary standards other than acid-base standards. Other projects under consideration are the concept of a selectivity index and the presentation of analytical methods for publication.

Commission 4. Spectrochemical and Other Optical Procedures

Chairman: Professor H. Kaiser (Germany) Secretary: Professor V. A. Fassel, Department of Chemistry, Iowa State University, Ames, Ia. 50010, U.S.A.

The Commission is concentrating its efforts on nomenclature, symbols and usage in atomic spectrochemical analysis. The first part of its report, dealing with atomic-emission spectroscopy, is being completed and work is proceeding to cover:

- (a) flame atomic-absorption and atomic-fluorescence spectroscopy
- (b) X-ray fluorescence spectroscopy (including X-ray microprobe techniques)
- (c) excitation source descriptions and parameters
- (d) terms and concepts related to rigorous determination of detection limits.

Pending the standardization of concepts and procedures for establishing detection limits, a project on the compilation of lists of minimal detectable concentrations is in abeyance.

Commission 5. Electroanalytical Chemistry

Chairman: Professor I. M. Kolthoff (U.S.A.) Secretary: Dr. P. Zuman, Department of Chemistry, University of Birmingham, P.O. Box 363, Birmingham 15, U.K.

The purification and purity of solvents and reagents of interest in electroanalytical chemistry is a continuing project of the Commission. Other projects include:

- (a) the compilation of physico-chemical data in non-aqueous media
- (b) the production of polarographic data cards and critical evaluation of polarographic procedures
- (c) studies on solid electrodes
- (d) the revision of tables of oxidation-reduction potentials.

Commission 6. Equilibrium Data

Chairman: Professor Y. Marcus (Israel) Secretary: Dr. F. J. C. Rossotti, Inorganic Chemistry Laboratory, South Parks Road, Oxford, U.K.

The Commission is actively engaged on the compilation and revision of data under the following headings:

- (a) stability constants
- (b) distribution and solubility constants
- (c) ion-exchange equilibrium constants
- (d) stability constants of complexes.

Commission 7. Analytical Radiochemistry and Nuclear Materials

Chairman: Dr. G. B. Cook (U.K.) Secretary: Dr. W. W. Meinke, National Bureau of Standards, Chemistry Division, Washington, DC 20234, U.S.A.

Studies are being made on:

- (a) the purity of commercial radioactively labelled preparations
- (b) the use of radioactive methods in analytical chemistry
- (c) national regulations for the use of small quantities of radioisotopes
- (d) reference materials for activation analysis.

The limits of reliability in the analysis of nuclear materials and the results of an intercomparison of laboratory methods for the determination of uranium are being studied. Multi-lingual nomenclature and basic reference reports are also being studied.

GERMANY

The German Society of Clinical Chemistry will organize a meeting in Hannover (Germany), 13-14 March 1969 on Automation and Data Processing in Clinical Chemistry.

For further information contact Prof. Dr. I. Trautschold, Medizinische Hochschule Hannover, Klinische Biochemie, 3000 Hannover, Osterfeldstraße 5, Germany.

INTERNATIONAL CONFEDERATION FOR THERMAL ANALYSIS

At the Second International Conference on Thermal Analysis, held on 18–23 August 1968, an international association was formally established under the title of International Confederation for Thermal Analysis (ICTA). The main function of this body will be to keep interested scientists in touch with developments in this interdisciplinary branch of science through the issue of periodic news letters at least three a year), to promote international understanding and co-operation in thermal analysis, and to organize periodic conferences at which problems can be discussed. The next conference will be held in Switzerland in 1971.

Membership is open to all interested individuals, institutions and companies on payment of the appropriate annual subscription. In return, members will receive the newsletters, circulars, etc., of ICTA, and will be able to attend, participate, in, and vote at conferences on payment of a reduced conference fee.

Further information on membership may be had from the Secretary, Mr. J. A. Hill, Xerox Corporation, P.O. Box 1540, Rochester, N.Y. 14603, U.S.A., or the Treasurer, Dr. R. C. Mackenzie, The Macaulay Institute, Craigiebuckler, Aberdeen, Scotland.

Talanta, 1969, Vol. 16, p. 562. Pergamon Press. Printed in Northern Ireland

ERRATUM

In Fig. 1 of the paper by M. Ashraf, M. A. Siddiqui and M. K. Bhatty, *Talanta*, 1968, 15, 559, the diameter of the "*N*-tube" should be 18 mm and not 28 as shown.

Talanta, 1969, Vol. 16, pp. i to ii. Pergamon Press. Printed in Northern Ireland

PAPERS RECEIVED

- Verwendung mäßig dissoziierter Komplexe bei spektralphotometrischen Bestimmung-II. Reaktionen von Arsenazo III mit Uranyl: J. BORÁK, Z. SLOVÁK and J. FISCHER. (25 September 1968)
- Verwendung mäßig dissoziierter Komplexe bei spektralphotometrischen Bestimmung—III. Reaktionen von Arsenazo III mit Thorium: Z. SLOVÁK, J. BORÁK and J. FISCHER. (25 September 1968)
- Characterization of materials by qualitative neutron activation analysis: B. T. KENNA and P. E. HARRISON. (17 January 1969)
- A simple low-power, reduced pressure microwave plasma source for emission spectroscopy: D. N. HINGLE, G. F. KIRKBRIGHT and R. M. BAILEY. (19 January 1969)
- Analytical utility of two-metal ternary complexes of alizarin fluorine blue: Spectrophotometric determination of nickel: M. A. LEONARD and F. I. NAGI. (27 January 1969)
- Determination of manganese by precipitation as manganese ammonium phosphate from homogeneous solution: É. BUZÁGH-GERE and L. ERDEY. (28 January 1969)
- Solvent extraction of chromium(VI) with tributylphosphate: Direct spectrophotometric determination in the organic phase: A. A. YADAV and S. M. KHOPKAR. (28 January 1969)
- Amperometric determination of Tl(I), Co(II), Bi(III), Se(IV) and Te(IV) with 1-methyl-2,4-dithiobiuret: G. S. DESHMUKH and R. K. NANDI. (28 January 1969)
- Solvent extraction and spectrophotometric determination of vanadium(V) with N-p-tolyl-2-furanacryloand N-phenyl-2-furanacrylohydroxamic acids: D. C. BHURA and S. G. TANDON. (28 January 1969)
- Spectrophotometric determination of vanadium with anthranylhydroxamic acid: Néstor MAGGIO and GUIDO CONCHA. (29 January 1969)
- Radiochemical separations by the ring-oven technique—IV. The system ¹⁴⁴Ce/¹⁴⁴Pr: D. KLOCKOW and R. G. BÖHMER. (29 January 1969)
- Reaction of Hg(II) and Xylenol Orange—I. Qualitative spectrophotometric study of the buffering media: F. BURRIEL-MARTÍ, A. CABRERA-MARTÍN, J. L. PERAL-FERNÁNDEZ and S. VICENTE-PÉREZ. (29 January 1969)
- Rapid spectrophotometric determination of cobalt after extraction with oximidobenzotetronic acid: G. S. MANKU, A. N. BHAT and B. D. JAIN. (30 January 1969)
- Determination of cobalt and zinc in high-purity niobium, tantalum, molybdenum and tungsten metals by atomic-absorption spectrophotometry after separation by extraction: ELSIE M. DONALDSON, D. J. CHARETTE and VERA H. E. ROLKO. (3 February 1969)
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- Spectrophotometric determination of vanadium(V) with N-(o-sulphobenzoyl)-N-phenylhydroxylamine (sodium salt): S. P. BHARGAVA and N. C. SOGANI. (11 February 1969)

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- 1. J. B. Austin and R. H. H. Pierce, J. Am. Chem. Soc., 1955, 57, 661.
- 2. S. T. Yoffe and A. N. Nesmeyanov, Handbook of Magnesium-Organic Compounds, 2nd Ed., Vol. 3, p. 214. Pergamon Press, Oxford, 1956.
- 3. R. J. Winterton in C. L. Wilson and D. W. Wilson, Comprehensive Analytical Chemistry, Vol. IB, p. 238. Elsevier, Amsterdam, 1960.
- 4. A. B. Smith, The Effect of Radiation on Strength of Metals. A.E.R.E., M/R 6329, 1962.
- 5. W. Jones, Brit. Pat. 654321, 1959.

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SUMMARIES FOR CARD INDEXES

Inorganic analysis in organic solvents-III. Adsorption characteristics of metal chelate compounds on aluminas and silica gels: M. P. T. BRADLEY and D. A. PANTONY, *Talanta*, 1969, 16, 473 (Department of Metallurgy, Imperial College, London, S.W.7.)

Summary—The general adsorption characteristics of 8-quinolinol, actioporphyrin, β -diketone and 8-quinolinethiol chelates of metals are described. These, with adsorption isotherm studies, indicate that the mechanism is of a chemisorption type with, in the case of oxo-chelating agents, high heats of adsorption. It appears that hydrogen-bonding to Brønsted sites on the adsorbents is an essential feature of the process, and that multilayers of adsorbate are readily formed. This observation is supported by rate studies which show that the adsorption is a two-stage process with a break at a point corresponding to monolayer coverage. Both stages are diffusion controlled with relatively low probability. Infrared and X-ray diffraction studies, although of limited value, support these conclusions. The requirements of more generally applicable chelating agents and adsorbents for analytical purposes are discussed and predicted.

An investigation into the use of **platform** were for allicate analysis: B. G. RUSSELL, JUDY D. SPANGENBERG and T. W. STEELE, *Talanta*, 1969, 16, 487 (National Institute for Metallurgy, Yale Road, Milner Park, Johannesburg, S. Africa.)

Summary—The amount of platinum dissolved from platinum apparatus used for dissolving silicate materials to obtain solutions for analysis has been determined. The study included apparatus made from an alloy containing 95% platinum and 5% gold. The affinity of iron and platinum was investigated, together with the problem of removing iron from platinum after the latter has been contaminated during fusions. The behaviour of platinum in a classical scheme for the analysis of silicate materials was investigated and the distribution of the platinum in various precipitates established. Platinum has been found to interfere in commonly used methods for the determination of silica, aluminium, iron, titanium, calcium and magnesium.

НЕОРГАНИЧЕСКИЙ АНАЛИЗ В ОРГАНИЧЕСКИХ РАСТВОРИТЕЛЯХ—III. АДСОРБЦИОННЫЕ ХАРАКТЕРИСТИКИ ХЕЛАТОВ МЕТАЛЛОВ НА ОКИСЯХ АЛЮМИНИЯ И СИЛИКАГЕЛЯХ:

M. P. T. BRADLEY and D. A. PANTONY, Talanta, 1969, 16, 473.

Резюме даны общие адсорбционные характеристики хелатов металлов 8-оксихинолина, етиопорфирина, β -дикетона и 8-оксихинолинтиола. Эти данные вместе с изучением адсорбционных изотерм указывают на механизм типа хемисорбции с высокими теплотами адсорбции в случае оксохелатообразующих соединений. Кажется что образование водородных связей с центрами Бренстеда на адсорбентах представляет собой существенную особенность процесса и что легко образуются многомолекулярные слои адсорбата. Это наблюдение подкреплено изучением скорости реакции из которого видно что адсорбция представляет собой двухфазный процесс показывающий инфлексию в точке, соответствующей мономолекулярном слою. Обе фазы контроллированы относительно низкой вероятностью. Изучение методами инфракрасной спектроскопии и диффракции рентгеновских лучей подкрепляет эти выводы, хотя они имеют только ограниченное значение. Обсуждены и предсказаны требования для общеприменимых хелатообразующих агентов и адсорбентов для анализа.

ИСПОЛЬЗОВАНИЕ ПЛАТИНОВЫХ СОСУДОВ В АНАЛИЗЕ СИЛИКАТОВ

B. G. RUSSELL, JUDY D. SPANGENBERG and T. W. STEELE, Talanta, 1969, 16, 487.

Резюме—Определено количество платины растворенное из платиновых сосудов использованых для растворения силикатных материалов с целью приготовлять растворы для анализа. Исследование включает сосуды из сплава содержащего 95% платины и 5% золота. Изучено сродство железа и платины вместе с проблемой устранения железа от платины после загрязнения при плавлении. Изучено поведение платины в классической схеме анализа силикатных материалов и определено распределение платины в различных осадках. Платина влияет на обыкновенные методы определения двуокиси кремния, алюминия, железа, титана, кальция и магния. Some vicinal dioximes as gravimetric reagents: L. S. BARK and D. BRANDON, *Talanta*, 1969, 16, 497 (Analytical Chemistry Laboratories, University of Salford, Salford 5, U.K.)

Summary—A series of 3,3-substituted indane-1,2-dionedioximes has been synthesized and their reactions with transition metals have been investigated. From the results obtained it is suggested that the selectivity of such dioximes, as gravimetric reagents, is not a function of the dioxime grouping but is due to metal-metal bonding in the complex.

Separation of metal ions on tin(IV) tunstate and selenite papers: MOHSIN QURESHI, K. N. MATHUR and A. H. ISRAILI, *Talanta*, 1969, 16, 503 (Chemical Laboratories, Aligarh Muslim University, Aligarh, U.P., India.)

Summary—Papers impregnated with the inorganic ion-exchangers tin(IV) tungstate and selenite have been shown to be useful for ion-exchange chromatography of several metal ion mixtures, and suitable solvent systems have been developed and evaluated.

Analysis of radioactive metals by spark source mass spectrometry: A. J. JOHNSON, A. KOZY and R. N. MORRIS, *Talanta*, 1969, 16, 511 (Analytical Development Group, Chemistry-Physics Research and Development, The Dow Chemical Company, Rocky Flats Division, P.O. Box 888, Golden, Colorado 80401, U.S.A.)

Summary—A spark source mass spectrograph with photographic plate recording has been adapted for the analysis of plutonium and americium metals. Over seventy elements can be determined simultaneously in these metals. A comparison has been made between results obtained by mass spectrography and by conventional methods for impurity elements. The operations involved in handling radioactive materials in the mass spectrograph are also discussed.

НЕКОТОРЫЕ ВИЦИНАЛВНЫЕ ДИОКСИМИ В КАЧЕСТВЕ ГРАВИМЕТРИЧЕСКИХ РЕАГЕНТОВ:

L. S. BARK and D. BRANDON, Talanta, 1969, 16, 497.

Резюме---Синтезирован ряд 3,3-замещенных индан-1,2диондиоксимов и исследованы их реакции с переходными металлами. Полученные результаты показывают что селективность таких диоксимов в качестве гравиметрических реагентов на зависит от группировки диоксима но от связы металл-металл в комплексе.

РАЗДЕЛЕНИЕ ИОНОВ МЕТАЛЛОВ НА БУМАГАХ ПРОПЫТАННЫХ ВОЛЬФРАМАТОМ И СЕЛЕНИТОМ ОЛОВА(IV):

MOHSIN QURESHI, K. N. MATHUR and A. H. ISRAILI, Talanta, 16, 503.

Резюме Бумага пропытанная неорганическими ионообменниками вольфраматом и селенитом олова(IV) оказвлась полезном в ионообменной хроматографии некоторых смес ионов металлов; разработаны и испытаны подходящие системы растворителей.

АНАЛИЗ РАДИОАКТИВНЫХ МЕТАЛЛОВ МЕТОДОМ МАСС-СПЕКТРОМЕТРИИ С ИСКРОВЫМ ИСТОЧНИКОМ:

А. J. JOHNSON, A. Kozy and R. N. MORRIS, *Talanta*, 1969, 16, 511. Ревюме—Масс-спектрометр с искровым источником пользующийся записыванием на фотографической пластинке применен в анализе металлического плутония и америция. Можно одновременно определять свыше семьдесят элементов в этих металлах. Ревультаты анализа металлических примесей полученные масс-спектрометрическим методом сравнены с результатами анализа обыкновенными методами. Обсуждены так же операции манипулирования радиоактивных материалов в масс-спектрометре. New chromogens of the ferroin type—V. Pyridylpyrimidines, bidiazines, and other substituted derivatives of diazines: ALFRED A. SCHILT and WAYNE E. DUNBAR, *Talanta*, 1969, **16**, 519 (Department of Chemistry, Northern Illinois University, DeKalb, Illinois 60115, U.S.A.)

Summary—Spectrophotometric studies of the reactions of iron(II), copper(I) and cobalt(II) with 33 new compounds have demonstrated that the chromogenic properties of diazyl groups are inferior to those of triazyl or pyridyl groups when incorporated into the ferroin chromophore group. The metal complexes of the diazyl derivatives are less stable than those of the corresponding pyridyl and triazyl derivatives. Conditional formation constants of the iron(II) chalates of some representative diazyl derivatives indicate that pyridzyl groups impart greater stabilities than pyrimidyl or pyrazyl groups. Five of the new chromogens have structures that suggest they can chelate iron(II) without steric hindrance, either as bidentate or as terdenate ligands. Although the terdentate mode would ordinarily be expected, two of the five were found to act preferably as bidentate ligands.

Infrared determination of calcium or lithium nitrate in acetone solution: Determination of calcium or lithium in the presence of strontium or barium: GEORGE NORWITZ and DAVID E. CHASAN, *Talanta*, 1969, 16, 522 (Frankford Arsenal, Philadelphia, Pa 19137, U.S.A.)

Summary—A method is proposed for the infrared determination of calcium or lithium in the presence of strontium or barium. A mixture of the nitrates is treated with acetone which dissolves only the calcium or lithium nitrate. The strontium or barium nitrate is filtered off. The filtrate is evaporated to about 2 ml with a stream of dry air and then diluted to 5 ml with acetone. The infrared spectrum is scanned from $860 \text{ to } 800 \text{ cm}^{-1}$ and the nitrate peak at 824 cm^{-1} for calcium and 827 cm^{-1} for lithium is measured. The presence of up to about 200 mg of strontium or lithium nitrate.

НОВЫЕ ХРОМОГЕНЫ ТИПА ФЕРРОИНА—3. ПИРИДИЛПИРИМИДИНЫ, БИДИАЗИНЫ И ДРУГИЕ ЗАМЕЩЕННЫЕ ПРОИЗВОДНЫЕ ДИАЗИНОВ:

ALFRED A. SCHILT and WAYNE E. DUNBAR, Talanta, 1969, 16, 519.

Резюме-Спектрофотометрическое изучение реакций железа-(II), меди(I) и кобальта(II) с 33 новыми соединениями показало что хромогенные свойства диазилгрупп плохи в сравнении с триазил-или пиридилгруппами, когда включены в структуру хромофорной группы ферроина. Комплексы металлов диазилдериватов менее устойчивые чем комплексы соотвествующих пиридил-или триазилдериватов. Условные константы образования хелатов железа(II) некоторых репрезентативных диазилдериватов показывают что пиридазилгруппы дают стабильность больше чем стабильность полученная пиримидил-или пиразилгруппами. Структуры нять из новых хромогенов позволяют образование хелатов железа(II) без пространственного затруднения, в форме двойних или тройних лигандов. Хотя нормально ожидать тройную форму, два из пять реагировали предпочтительно как тройние лиганлы.

ОПРЕДЕЛЕНИЕ НИТРАТА КАЛЬЦИЯ ИЛИ ЛИТИЯ В АЦЕТОНОВОМ РАСТВОРЕ МЕТОДОМ ИНФРАК-РАСНОЙ СПЕКТРОСКОПИЙ: ОПРЕДЕЛЕНИЕ КАЛЬЦИЯ ИЛИ ЛИТИЯ В ПРИСУТСТВИИ СТРОНЦИЯ ИЛИ БАРИЯ:

GEORGE NORWITZ and DAVID E. CHASAN, Talanta 1969, 16, 522.

Резюме—Предложен метод инфракрасной спектроскопии для определения кальция или лития в присутствии стронция или бария. Смесь нитратов обрабатывают ацетоном который растворяет только нитрат кальция или лития. Нитраты бария или стронция укланяют фильтрованием. Фильтрат выпаривают до 2 мл с струей сухого воздуха и затем разбавляют до 5 мл ацетоном. Снимают инфракрасный спектр в области 860 до 800 см⁻¹ и измеряют нитратовый пик про 824 см⁻¹ для кальция и при 827 см⁻¹ для лития. Рекоммендованный диапазон—1-80 мг нитрата кальция или лития в присутствии до 200 мг нитрата стронция или бария. Liquid-liquid extraction of tungsten(VI) with mesityl oxide—Application to an alloy steel: V. M. SHINDE and S. M. KHOPKAR, *Talanta*, 1969, 16, 525 (Department of Chemistry, Indian Institute of Technology, Bombay-76, India).

Summary—A new and simple method has been developed for the rapid extraction of tungsten(VI) with mesityl oxide. Quantitative extraction occurs from solutions 1M in hydrochloric acid and 12M in lithium chloride (as the salting-out agent) with 75% mesityl oxide in isobutyl methyl ketone. Tungsten is finally determined photometrically as the thiocyanate complex in the aqueous phase. Tungsten-(VI) can be extracted and determined satisfactorily in the presence of several elements. The method is shown to be applicable to an alloy steel.

Glass electrode measurements of sodium in albumin solutions: T. Y. TORIBARA and LARYSA KOVAL, *Talanta*, 1969, 16, 529 (Department of Radiation Biology and Biophysics, University of Rochester School of Medicine and Dentistry, Rochester, New York 14620, U.S.A.)

Summary—Measurements of the sodium level of albumin solutions and their ultrafiltrates were made with commercially available sodiumsensitive glass electrodes. The potential of the electrode was found to vary considerably with the depth of immersion. The potentials of albumin solutions which were allowed to remain at room temperature or higher for any length of time were found to increase, and in time gave unrealistic levels of sodium activity. An albumin solution stored in a refrigerator for a month did not show this effect. The sodium levels of albumin solutions as determined by the electrode were lower than the flame photometric values for the same solutions.

Determination of hydrazine by gas evolution: C. P. LLOYD and W. F. PICKERING, *Talanta*, 1969, 16, 532 (Department of Chemistry, University of Newcastle, New South Wales, Australia.)

Summary—A method is proposed for the determination of mg amounts of hydrazine based on the measurement of the volume of nitrogen evolved after oxidation with silver(I) oxide.

ЖИДКОФАЗНАЯ ЭКСТРАКЦИЯ ВОЛЬФРАМА(VI) С МЕЗИТИЛОКСИДОМ—ПРИМЕНЕНИЕ МЕТОДА НА ЛЕГИРОВАННУЮ СТАЛЬ:

V. M. SHINDE and S. M. KHOPKAR, Talanta, 1969, 16, 525.

Резюме—Разработан новый несложный метод быстрого извлечения вольфрама(VI) с мезитилоксидом. Количественное извлечение получается из растворов 1M в соляной кислоте и 12M в литийхлориде (в качестве высаливающего агента) с 75% ным раствором мезитилоксида в изобутилметилкетрне. Вольфрам(VI) конечно определяют фотометрическим методом в форме роданидового комплекса в водной фазе. Вольфрам(VI) можно извлекать удовлетворительно в присутствии ряда элементов. Методом можно пользоваться для анализа легированной стали.

ОПРЕДЕЛЕНИЕ НАТРИЯ В РАСТВОРАХ АЛЬБУМИНА СТЕКЛЯННЫМ ЭЛЕКТРОДОМ:

T. Y. TORIBARA and LARYSA KOVAL, Talanta, 1969, 16, 529.

Резюме—Опрелеена концентрация натрия в растворах альбумина и их ультрафильтратах с использованием коммерческих натрийчувствительных стеклянных электродов. Напряжение электрода в значительной мере изменялось в зависимости от глубины погружения. Напряжение растворов альбумина держанных через данные периоды времени при комнатной или повышенной температурах повышалось, и после определенного времени получены нереальные уровни активности натрия. Держанный в рефрижераторе в течение одного месяца раствор альбумина не показывал этот эффект. Результаты определения натрия в растворах альбумина с использованием электрода были ниже чем величины полученные пламенно-фотометрическим методом в тех же растворах.

ОПРЕДЕЛЕНИЕ ГИДРАЗИНА НА ОСНОВЕ ВЫДЕЛЕНИЯ ГАЗА:

C. P. LLOYD and W. F. PICKERING, Talanta, 1969, 16, 532.

Резюме—Предложен метод определения миллиграммовых количеств гидразина, основывающийся на измерении объема азота выделенного после окисления окисью серебра(I).

Thermometric titrimetry. Studies of the cerium(IV) oxidation of α -mercaptocarboxylic acids: W. A. ALEXANDER, C. J. MASH and A. MCAULEY, *Talanta*, 1969, 16, 535 (Department of Chemistry, University of Strathclyde, Glasgow, C.1, Scotland.)

Summary—The cerium(IV) oxidation of thioglycollic, thiolactic and thiomalic acids has been examined by thermometric titration. The titration curves indicate stoichiometries of more than 1 mole of cerium(IV) per mole of α -thiol, suggesting possible side-reactions. In the presence of methyl acrylate, however, the expected ratio is observed. The overall heat of each reaction has been derived. Only with a titration method of this kind where allowance can be made for side-reactions can the heats of reaction for these systems be measured.

Logarithmic converter for atomic-absorption spectrometry: MICHAEL D. MORRIS and JAMES B. ORENBERG, *Talanta*, 1969, 16, 539 (Department of Chemistry, Pennsylvania State University, University Park, Pennsylvania 16802, U.S.A.)

Summary—A logarithmic converter using a silicon transistor in the feed-back loop of an operational amplifier circuit, and suitable for use with a double-beam atomic-absorption spectrometer, is described.

6-Methyl-2-pyridinecarboxamide oxime, a reagent for copper: JOHN R. PEMBERTON and HARVEY DIEHL, *Talanta*, 1969, 16, 542 (Department of Chemistry, Iowa State University, Ames, Iowa 50010, U.S.A.)

Summary—6-Methyl-2-pyridinecarboxamide oxime (R) forms a yellow compound with copper(I), the molar absorptivity being 7.2×10^3 at the wavelength of maximum absorption, 405 nm. The copper compound, CuR₂, forms completely over the pH range 4.5–7 and is easily extracted into isoamyl alcohol. R is highly specific for copper, the methyl group neighbouring the ring nitrogen atom preventing reaction with iron and other metals.

ИЗУЧЕНИЕ ОКИСЛЕНИЯ α-МЕРКАПТОКАРБО-НОВЫХ КИСЛОТ ЦЕРИЕМ(IV) МЕТОДОМ ТЕРМОМЕТРИЧЕСКОЙ ТИТРАЦИИ:

W. A. ALEXANDER, C. J. MASH and A. MCAULEY, Talanta, 1969, 16, 535.

Резюме—Окисление тиогликолевой, тиомолочной и тиояблочной кислот с церием(IV) изучено методом термометрической титрации. Кривие титрования показывают стехиометрическое отношение больше чем одного моля церия(IV) на моль α -тиола, указывающее на возможные побочные реакции. Между тем в присутствии метилакрилата получается ожиданное отношение. Рассчитана общая теплота каждой реакции. Только метод титрования лого типа, который принимает в расчёт побочные реакции, позволает определять теплоты реакции этих систем.

ЛОГАРИФМИЧЕСКИЙ КОНВЕРТЕР ДЛЯ АТОМНО-АБСОРБЦИОННОЙ СПЕКТРОМЕТРИИ:

MICHAEL D. MORRIS and JAMES B. ORENBERG, Talanta, 1969, 16, 539.

Резюме—Описан логарифмический конвертер имеющий кремневый транзистор в возвращающей петле действующей цепи усилителя, который может быть применен с двухлучным атомно—абсорбционным спектрометром.

6-МЕТИЛ-2-ПИРИДИНКАРБОКСАМИДОКСИМ— РЕАКТИВ ДЛЯ МЕДИ:

JOHN R. PEMBERTON and HARVEY DIEHL, Talanta, 1969, 16, 542.

Резюме—6-Метил-2-пиридинкарбоксамидоксим (R) образует желтое соединение с медью(I), которого молярное светоноглощение 7,2 $\times 10^3$ при длины волны максимального поглощения 405 нм. Соединение меди CuR₂ полностью образуется в области pH 4,5–7 и легко извлекается изоамиловым спиртом. R является высокоизбирательным реактивом для меди, метиловая группа, смежная атому азота в кольце предупреждая реакцию с железом и другими металлами. Polarography of uranium(VI) and lead(II) complexes with L-glutamine: TSAI-TEH LAI and MON-CHAO CHEN, *Talanta*, 1969, 16, 544 (Chemical Engineering Department, Cheng Kung University, Tainan, Taiwan, China.)

Summary—The complexes of uranium(VI) and lead(II) with L-glutamine were investigated polarographically. For uranium(VI), the complexes $UO_2G_{1^*}$, $UO_2G_{2^{+3}}$ and $UO_3(OH)G_2^+$ were identified at pH < 2.5, pH 2.5–4.1 and pH 4.1–5.2 respectively. With lead(II), complexes PbG⁺², Pb(OH)G⁺ and Pb(OH)G⁺ were formed at pH 2.0–5.0, pH 5.0–7.0, and pH 7.0–8.5, respectively. The concentration dissociation constant of Pb(OH)G⁺ was found to be $pK_c = 10.16 \pm 0.04$ at ionic strength 0.6.

Sur une colorimétrie des alcoylamines, guanidines et ammoniums quaternaires par la réaction de Janovsky: J. BARTOS, *Talanta*, 1969, 16, 551 (Centre de Recherches Roussel-Uclaf, 93-Romainville, France.)

Summary—In the presence of an alkylamine, a guanidine or a quaternary ammonium hydroxide, liberated from their salts by the action of silver oxide, nitromethane reacts with 1,3,5-trinitrobenzene, yielding a red compound which allows the colorimetric determination of the nitrogenous base.

ИЗУЧЕНИЕ КОМПЛЕКСОВ УРАНА(VI) И СВИНЦА(II) С L-ГЛУТАМИНОМ ПОЛЯРОГРАФИЧЕСКИМ МЕТОДОМ:

TSAI-TEH LAI and MON-CHAO CHEN, Talanta, 1969, 16, 544.

Резюме—Изучены полярографическим методом комплексы урана(VI) и свинца(II) с L-глутамином. Для урана обнаружены комплексы UO₂G⁺³, UO²G₂⁺² и UO₂(OH)G₂⁺ при pH < 2,5, pH 2,5–4,1 и pH 4,1–5,2 соответственно. Свинец(II) образовал комплексы PbG⁺², Pb(OH)G⁺ и Pb(OH)G₂⁺ при pH 2,0–5,0, pH 5,0–7,0 и pH 7,0–8,5 соответственно. Определена константа диссоциации Pb(OH)G₂⁺ pK_o = 10,16 ± 0,04 при ионной силе 0,6.

КОЛОРИМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ АЛКОИЛАМИНОВ, ГУАНИДИНОВ И ЧЕТВЕРТИЧНЫХ АММОНИЕВИХ СОЕДИНЕНИИ С ИСПОЛЗОВАНИЕМ РЕАКЦИИ ЯНОВСКОГО:

J. BARTOS, Talanta, 1969, 16, 551.

Резюме—В присутствии алкоиламина, гуанидина или четвертичного аммониевого основания, выделенных из их солей действием окиси серебра, нитрометан реагирует с 1,3,5тринитробензолом образуя красное соединение позволяющее колориметрическое определение азотного основания.

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Contents

Editorial	471
M.P.T.BRADLEY and D.A.PANTONY, Inorganic analysis in organic solvents-III. Adsorption char- acteristics of metal chelate compounds on aluminas and silica gels	473
B.G.RUSSEL, JUDY D.SPANGENBERG and T.W.STEELE: An investigation into the use of platinum ware for silicate analysis	48
L.S.BARK and D.BRANDON: Some vicinal dioximes as gravimetric reagents	497
MOHSIN QURESHI, K.N.MATHUR and A.H.ISRAILI: Separation of metal ions on tin(IV) tungstate and selenite papers	563
A.J.JOHNSON, A.KOZY and R.N.MORRIS: Analysis of radioactive metals by spark source mass spectrometry .	51
Short Communications	
A.A.S.CHILT and W.E.DUNBAR: New chromogens of the ferroin type—V. Pyridylpyrimidines, bidiazines and other substituted derivatives of diazines	51.
G.NORWITZ and D.E.CHASAN: Infrared determination of calcium or lithium nitrate in acetone solution. Determination of calcium or lithium in the presence of strontium or barium	522
V.M.SHINDE and S.M.KHOPKAR: Liquid-liquid extraction of tungsten(VI) with mesityl oxide. Application to an alloy steel	525
T.Y.TORIBARA and LARYSA KOVAL: Glass electrode measurements of sodium in albumin solutions .	529
C.P.LLOYD and W.F.PICKERING: Determination of hydrazine by gas evolution	532
W.A.ALEXANDER, C.J.MASH and A.MCAULEY: Thermometric titrimetry. Studies of the cerium(IV)	
oxidation of α -mercaptocarboxylic acids	535
oxidation of α-mercaptocarboxylic acids . M.D.Morris and J.B.Orenberg: Logarithmic converter for atomic-absorption spectrometry	535 539
M.D.MORRIS and J.B.ORENBERG: Logarithmic converter for atomic-absorption spectrometry	539
M.D.MORRIS and J.B.ORENBERG: Logarithmic converter for atomic-absorption spectrometry J.R.PEMBERTON and H.DIEHL: 6-Methyl-2-pyridinecarboxamide oxime, a reagent for copper TSAI-TEH LAI and MON-CHAO CHEN: Polarography of uranium(VI) and lead(II) complexes with L-glutamine J.BARTOS: Sur une colorimétrie des alcoylamines, guanidines et ammoniums quaternaires par la	539 542 544
M.D.MORRIS and J.B.ORENBERG: Logarithmic converter for atomic-absorption spectrometry J.R.PEMBERTON and H.DIEHL: 6-Methyl-2-pyridinecarboxamide oxime, a reagent for copper TSAI-TEH LAI and MON-CHAO CHEN: Polarography of uranium(VI) and lead(II) complexes with L-glutamine J.BARTOS: Sur une colorimétrie des alcoylamines, guanidines et ammoniums quaternaires par la réaction de Janovsky	539 542
M.D.MORRIS and J.B.ORENBERG: Logarithmic converter for atomic-absorption spectrometry J.R.PEMBERTON and H.DIEHL: 6-Methyl-2-pyridinecarboxamide oxime, a reagent for copper TSAI-TEH LAI and MON-CHAO CHEN: Polarography of uranium(VI) and lead(II) complexes with L-glutamine J.BARTOS: Sur une colorimétrie des alcoylamines, guanidines et ammoniums quaternaires par la réaction de Janovsky Letter to the Editor	539 542 544
M.D.MORRIS and J.B.ORENBERG: Logarithmic converter for atomic-absorption spectrometry J.R.PEMBERTON and H.DIEHL: 6-Methyl-2-pyridinecarboxamide oxime, a reagent for copper TSAI-TEH LAI and MON-CHAO CHEN: Polarography of uranium(VI) and lead(II) complexes with L-glutamine J.BARTOS: Sur une colorimétrie des alcoylamines, guanidines et ammoniums quaternaires par la réaction de Janovsky	539 542 544
M.D.MORRIS and J.B.ORENBERG: Logarithmic converter for atomic-absorption spectrometry J.R.PEMBERTON and H.DIEHL: 6-Methyl-2-pyridinecarboxamide oxime, a reagent for copper TSAI-TEH LAI and MON-CHAO CHEN: Polarography of uranium(VI) and lead(II) complexes with L-glutamine J.BARTOS: Sur une colorimétrie des alcoylamines, guanidines et ammoniums quaternaires par la réaction de Janovsky Letter to the Editor T.ANFÄLT and D.JAGNER: Computer calculation of the interference of ammonium salts in Mohr's	539 542 544 551
M.D.MORRIS and J.B.ORENBERG: Logarithmic converter for atomic-absorption spectrometry J.R.PEMBERTON and H.DIEHL: 6-Methyl-2-pyridinecarboxamide oxime, a reagent for copper TSAI-TEH LAI and MON-CHAO CHEN: Polarography of uranium(VI) and lead(II) complexes with L-glutamine J.BARTOS: Sur une colorimétrie des alcoylamines, guanidines et ammoniums quaternaires par la réaction de Janovsky Letter to the Editor T.ANFÄLT and D.JAGNER: Computer calculation of the interference of ammonium salts in Mohr's method for the determination of chloride	539 542 544 551 555
M.D.MORRIS and J.B.ORENBERG: Logarithmic converter for atomic-absorption spectrometry J.R.PEMBERTON and H.DIEHL: 6-Methyl-2-pyridinecarboxamide oxime, a reagent for copper TSAI-TEH LAI and MON-CHAO CHEN: Polarography of uranium(VI) and lead(II) complexes with L-glutamine J.BARTOS: Sur une colorimétrie des alcoylamines, guanidines et ammoniums quaternaires par la réaction de Janovsky Letter to the Editor T.ANFÄLT and D.JAGNER: Computer calculation of the interference of ammonium salts in Mohr's method for the determination of chloride.	539 542 544 551 555 559
M.D.MORRIS and J.B.ORENBERG: Logarithmic converter for atomic-absorption spectrometry J.R.PEMBERTON and H.DIEHL: 6-Methyl-2-pyridinecarboxamide oxime, a reagent for copper TSAI-TEH LAI and MON-CHAO CHEN: Polarography of uranium(VI) and lead(II) complexes with L-glutamine J.BARTOS: Sur une colorimétrie des alcoylamines, guanidines et ammoniums quaternaires par la réaction de Janovsky Letter to the Editor T.ANFÄLT and D.JAGNER: Computer calculation of the interference of ammonium salts in Mohr's method for the determination of chloride . Notices	539 542 544 551 555 559

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