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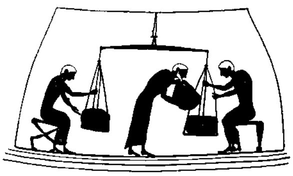

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CO-ORDINATION OF THE NO GROUP

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(*Received* 18 *March* 1959, *revised paper received* 17 *July* 1959)

Summary—The evidence indicates that nitric oxide normally co-ordinates as a charged ion. Complexes containing the neutral molecule such as $[Fe^{II}(CN)_5NO]^{3-}$, derived from the compound sodium pentacyanoammine ferrate^{II} which is widely used in analytical chemistry and in which the odd electron is still localised on the ligand, exist as unstable, transient compounds only.

ON the basis of its electronic structure, which contains one unpaired electron, we would expect nitric oxide to form co-ordination compounds in three ways. These are:

(1) By loss of the odd electron, followed by co-ordination of the $\overset{+}{NO}$ ion.

(2) By gain of an electron, followed by co-ordination of the $\overset{-}{NO}$ ion.

(3) By co-ordination of the neutral NO group, through a co-ordinate covalency involving two electrons from the N atom.

Examples of both (1) and (2) are well established, particularly the former. Thus the structure of sodium nitroprusside as $Na_2[Fe^{II}(CN)_5\overset{+}{N}O]$ (the N atom having lost an electron) has been deduced from its diamagnetism, from its conversion to $Na_4[Fe^{II}(CN)_5\overset{-}{N}O_2]$ by alkali and from its relation to the compounds $Na_4[Fe^{II}(CN)_6]$ and $Na_3[Fe^{II}(CN)_5{\cdot}CO]$. It should, however, be mentioned that recent infra-red studies[1] point to it being a resonance hybrid, with the iron tending to the Fe^{III} and even the Fe^{IV} state. Compounds of the type $Co(NO)(CO)_3$ are also accepted as containing the $\overset{+}{NO}$ ion.

Evidence for the existence of complexes containing the $\overset{-}{NO}$ ion is more scanty, but the diamagnetism of the pink ion $[Co^{III}(NH_3)_5{\cdot}\overset{-}{NO}]^{2+}$ is ascribed to its containing tervalent Co and the $\overset{-}{NO}$ ion, this salt being similar to the chloropentammine salts in which the chlorine is bound covalently to tervalent Co. Sidgwick thought the structure of the compound iron tetranitrosyl to be $[Fe(NO)_3]^- \overset{+}{NO}$, but Griffiths, Lewis and Wilkinson[2] consider that its infra-red spectrum points to three of the NO groups co-ordinating as $\overset{+}{NO}$ and the other as $\overset{-}{NO}$.

A number of authors have assumed the existence of compounds in the third class, but it appears that very little experimental evidence can be adduced for their existence. Mattern and Gill[3] state that pentacyano-iron complexes such as $Na_3[Fe^{II}(CN)_5{\cdot}NH_3]$ react with nitric oxide to form structures containing the ion $[Fe(CN)_5{\cdot}NO]^{3-}$, this being one of the few cases in which NO replaces a neutral group without change of charge, which implies that the iron is in the Fe^{II} state. They say that the complexes are yellow in neutral but violet in acid solution and cite the work of Manchot, Merry and Woringer,[4] and also of Baudisch.[5]

Baudisch[5] explains the reactions into which nitroprusside enters after exposure to light by stating that the NO group has become extremely reactive. This he considers is due to the photo-reaction,

$$[Fe^{III}(CN)_5NO]^{2-} \rightarrow [Fe^{II}(CN)_5\overset{+}{N}O]^{3-}$$

and he states that the unpaired electron is attached to the N of the NO group, although why he should denote this by $\overset{+}{N}O$ is not clear.

Bearing in mind, however, that the accepted structure of nitroprusside is $Na_2Fe^{II}(CN)_5\overset{+}{N}O$ and that any change in the valency state of the iron would involve an electron gain by the $\overset{+}{N}$ of the $\overset{+}{N}O$ ion, we would expect this activated intermediate to have the structure $Na_2[Fe^{III}(CN)_5{\cdot}NO]$.

This would be paramagnetic, as Baudisch reports, although he appears to associate paramagnetic properties with the Fe^{II} state. Baudisch presents no experimental evidence for the existence of the transitory paramagnetic compound, however, and he never succeeded in isolating it.

Blanchard,[6] also quoting Manchot, states that the tervalent ion $[Fe^{II}(CN)_5{\cdot}NO]^{3-}$ can be prepared but that it is unstable and goes over spontaneously to the nitroprusside anion.

Sidgwick[7] refers to nitroso-prussi compounds with the probable structure $M_3[Fe(CN)_5{\cdot}NO]$ which he considers to contain ferric iron bound covalently to a nitroso group, *i.e.* $>Fe^{III}{-}N{=}O$. He states that these compounds are prepared by the action of nitric oxide on aqueous solutions of pentacyano-aquo or ammine-ferrates^{II}, *i.e.* of the type $Na_3[Fe^{II}(CN)_5{\cdot}H_2O]$, but the papers[8] which he quotes do not mention the isolation of such compounds. He also states that the colour changes which these compounds supposedly undergo ("dark yellow in neutral solution, purple in acid solution") support his postulate of nitroso structure, as the latter can exist in a dimeric colourless state and a blue or green monomeric one.

Hofmann[8] merely suggests that in the reaction between nitric oxide and what he calls "prussid-natrium" (probably the compound $Na_3[Fe^{II}(CN)_5{\cdot}H_2O]$), an intermediate compound "most probably $Na_3[Fe(CN)_5{\cdot}NO]$" is formed, which is then transformed quantitatively into sodium nitroprusside. He also observes that when in the intermediate stage, the yellow neutral solution gives the characteristic violet colour on testing with sulphides, but also becomes violet on acidification. This hypothetical intermediate containing a neutral NO group and the iron presumably in the Fe^{II} state, has never been isolated.

Manchot, Merry and Woringer,[4] who studied the absorption of nitric oxide by the pentacyano-ammine ferrate^{II} $Na_3[Fe^{II}(CN)_5{\cdot}NH_3]$ also postulated the intermediate formation of the same compound. They termed it a ferrous nitroprusside, this being an obvious stage in the formation of a ferric nitroprusside (as sodium nitroprusside was then thought to be) under oxidising conditions.

Krasna and Rittenberg[9] suggest the intermediate formation of the ion $[Fe^{II}(CN)_5{\cdot}NO]^{3-}$ during the reduction of nitroprusside with hydrogen in the presence of the enzyme hydrogenase, but the results on which they base this are somewhat imprecise. They deduce the structure of the products from the reaction of the solution with "neutral iodine" and suggest that the solution of nitroprusside, which turns first blue and then brown, is reduced according to the equation

$$[Fe^{II}(CN)_5\overset{+}{N}O]^{2-} \rightarrow [Fe^{II}(CN)_5NO]^{3-} \rightarrow [Fe^{II}(CN)_5NOH]^{3-}$$

Krasna and Rittenberg state that "2 equivalents of neutral iodine are required to oxidise the N at the oxidation level of NOH to nitrite" and that "oxidation of the blue compound to $[Fe^{II}(CN)_5NO_2]^{-4}$ would require 2 equivalents of neutral iodine per mole of hydrogen consumed. They do not discuss the chemistry of these novel reactions, however, and in addition, the stoichiometry of the latter is somewhat doubtful. Furthermore, a complex ion containing the nitroxyl radical has never previously been reported.

Koltoff and Toren[10] state that polarographic reduction of the nitroprusside ion gives three waves, the first one of which can be explained in terms of a one electron reduction to the ion $[Fe^{II}(CN)_5{\cdot}NO]^{3-}$.

The co-ordination compound, sodium pentacyano-ammine ferrate^{II}, is widely used in analytical chemistry, because of the colours which it gives with many organic compounds. Its preparation and use in this connection is described by Fearon[11] and is based on Hoffmann's work. Freshly prepared, it is a pale yellow solid with the formula $Na_3[Fe^{II}(CN)_5{\cdot}NH_3]{\cdot}xH_2O$, but on exposure of the aqueous solution to light and air, it becomes brown and able to react with compounds ranging from thiourea to phenylhydrazine. During an investigation of its reaction with N-nitroso compounds, the present author found that an intense purple colour was obtained with traces of nitrous acid. This suggested the possible formation of a complex of the type suggested by Sidgwick, in view of the fact that nitrous acid oxidises simple ferrous salts with formation of nitric oxide, which could conceivably enter the complex anion in this case. All attempts to isolate the supposed purple complex failed, however, and it was eventually concluded that the purple colour was due to the formation of the compound $Na_2[Fe^{III}(CN)_5{\cdot}H_2O]$, the nitrous acid merely oxidising the compound $Na_2[Fe^{II}(CN)_5{\cdot}H_2O]$, formed by hydrolysis of the original ammine compound.

With regard to other compounds which may contain a neutral NO group, there is again very little concrete evidence. Hückel[13] states that the black paramagnetic ion $[Co(NH_3)_5{\cdot}NO]^{2+}$ exemplifies the co-ordination of NO as a neutral group, the Co atom being bivalent, but Milward, Wardlaw and Way,[14] in their original paper on the paramagnetic properties of the compound, considered it to be a resonance hybrid of the structure

$$[5NH_3,\ \overset{=}{Co}—\overset{+}{N}\equiv\overset{+}{O}]^{2+} \longleftrightarrow [5NH_3,\ \overset{-}{Co}=\overset{+}{N}=O]^{2+}$$

Its exact structure is still in doubt.

Cambi and Szego[15] considered that measurements of magnetic susceptibility pointed to the existence of the red Roussin salt $K_2Fe_2S_2(NO)_4$ as a dimer in which one of the iron atoms is bivalent and the other tervalent, three of the NO groups being in the complex as univalent radicals and the other as a molecule. Ewens,[16] however, considers that these and similar compounds contain a Fe–Fe link and that each NO group contributes three electrons to the corresponding Fe atom.

Moeller,[17] referring to the same compound, also states that Manchot's view that it contains co-ordinated nitrosyl groups is in accord with the general tendency of nitric oxide to transfer an electron and co-ordinate.

The strongest experimental evidence for the co-ordination of NO as a neutral molecule appears in a recent paper by Griffith, Lewis and Wilkinson.[18] Their measurements of the magnetic susceptibility of solutions of sodium pentacyanoammine ferrate^{II} which have absorbed nitric oxide until the ratio Fe : NO is unity, indicate a moment corresponding to somewhat less than one unpaired electron. This corresponds to the co-ordination of the neutral molecule, the odd electron remaining localised on the ligand. They offer no explanation of the moment being less than that corresponding to one unpaired electron, however, (this being unusual for hexa-co-ordinated iron compounds), and also state that the complex cannot be isolated.

These authors also remark that measurements of the magnetic susceptibility of aqueous solutions of the corresponding ferrous sulphate-nitric oxide complex point to the formulation of the penta-aquonitrosyl ferrate ion as

$$[Fe^{I}(H_2O)_5NO]^{2+}$$

Although at first sight this ion would appear to contain iron^{II} co-ordinated with a neutral NO molecule, the nitric oxide has actually donated three electrons to the ferrous iron.

Most of the experimental evidence therefore points to the co-ordination of NO as an ion. The existence of compounds such as $M_3[Fe(CN)_5{\cdot}NO]$, containing a neutral NO group, appears to be hypothetical, what evidence there is pointing to their extreme instability and formation as transient intermediates only. This would be in accord with the fact that the odd electron would still be localised on the ligand, and the molecule would therefore be as reactive as that of nitric oxide itself.

Acknowledgements—The author wishes to thank British Nylon Spinners Limited for permission to publish, Dr. D. R. Williams for helpful criticism of the paper, and the translating staff of the Department for translating the original papers referred to in the text.

Zusammenfassung—Aus bisherigen Befunden ist der Schluss zu ziehen, dass das Stickoxyd gewöhnlich in Form des geladenen Ions Koordinierung eingeht. Komplexe welche das neutrale Molekül enthalten und in welchen sich das ungepaarte Elektron noch auf dem Liganden befindet, wie z.B. $[Fe^{II}(CN)_5NO]^{3-}$, werden nur als unbeständige Zwischenprodukte aus dem in der analytischen Chemie vielfach zur Anwendung kommenden Natrium Pentacyanoammineferrat (II) gebildet.

Résumé—Sur la base des données disponibles on déduit que l'oxyde nitrique se coordine généralement sous forme de son ion chargé; des complexes comme, par exemple, le $[Fe^{II}(CN)_5NO]^{3-}$, qui contiennent la molecule neutre et dans lesquels l'éléctron impair se trouve encore sur le ligand, n'ont qu'une existence temporaire sous forme de produits intermediaires, derivés du pentacyano-ammine ferrate (II) de sodium, composé qui a un usage universel dans l'analyse chimique.

REFERENCES

[1] E. F. G. Herington and W. Kynaston, *J. Chem. Soc.*, 1955, 3555.
[2] W. P. Griffith, J. Lewis and G. Wilkinson, *ibid.*, 1958, 3993.
[3] J. A. Mattern and S. J. Gill, *Chemistry of the Co-ordination Compounds*, Ed. by J. C. Bailar, Reinhold, N.Y., 1956, p. 537.
[4] W. Manchot, E. Merry and P. Woringer, *Ber.*, 1912, **45**, 2869.
[5] O. Baudisch, *Science*, 1948, **108**, 443.
[6] A. A. Blanchard, *Chem. Revs.*, 1940, **26**, 418.

[7] N. V. Sidgwick, *The Chemical Elements and their Compounds*, Oxford Univ. Press, 1950, p. 1360.

[8] K. A. Hofmann, *Z. anorg. Chem.*, 1896, **12,** 146: W. Manchot, E. Merry and P. Woringer, *loc. cit.* L. Cambi and T. Ricci, *Atti. Rev.*, 1930, [6] **11,** i. 443.

[9] A. I. Krasna and D. Rittenberg, *J. Amer. Chem. Soc.*, 1955, **77,** 5295.

[10] I. M. Kolthoff and P. E. Toren, *ibid.*, 1953, **75,** 1197.

[11] W. R. Fearon, *Analyst*, 1946, **71,** 562.

[12] D. Davidson, *J. Amer. Chem. Soc.*, 1928, **50,** 2622.

[13] W. Hückel, *Structural Chemistry of Inorganic Compounds* (tr. Long), Elsevier Publishing Co., Amsterdam, 1951, Vol. II, p. 516.

[14] J. L. Milward, W. Wardlaw and W. J. R. Way, *J. Chem. Soc.*, 1938, 233.

[15] L. Cambi and L. Szegó, *Atti. Rev.*, 1931, [6], **13,** 168.

[16] R. V. G. Ewens, *Nature*, 1948, **161,** 530.

[17] T. Moeller, *J. Chem. Educ.*, 1946, **23,** 441, 542; 1947, **24,** 149.

[18] W. P. Griffith, J. Lewis and G. Wilkinson, *loc. cit.*

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STUDIES ON URONIC ACID MATERIALS—II[1]

THE VARIATION IN COMPOSITION OF GUM NODULES FROM *COMBRETUM LEONENSE*

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(*Received* 16 *May* 1959)

Summary—Several gum nodules from the Nigerian tree *Combretum leonense* have been individually investigated. The amount of material present in each nodule has permitted a study of the variation in constitution of both crude and purified forms of the gum. The variations found are much greater than can be explained by analytical error. They are considered to indicate that inter-nodule differences in fine structure exist.

IN certain fields of carbohydrate chemistry, *e.g.* those dealing with starch[2,3,4] and with glycogen,[5] sampling procedures require strict attention when material for investigation of fine structure is being selected. Even if strict control of botanical variety and strain proves possible, variations in growth and maturity caused by seasonal effects are difficult to control, and wide variation in chemical composition can occur.[6] Several extensive studies of such effects, *e.g.* in some varieties of seaweed,[7] barley,[8] grasses and clovers[9,10] have now been reported.

Severe sampling difficulties exist in the study of plant gums. Usually the gum is taken from the tree bark in small nodules which can vary greatly in colour and general appearance. Any guarantee of constancy of originating botanical species is difficult to obtain, particularly when collection overseas is arranged. Furthermore, gum is normally exuded to minimise bacterial attack at localised sites where superficial injury from a variety of possible causes has been sustained at some unknown time. Thus nodules from the barks of a number of trees may possibly vary greatly in maturity and chemical composition, even although each of the trees was authentically of the same botanical species.[11]

Consequently, when a batch of nodules collected in such a way is purified by precipitation in acidified alcohol from aqueous solution, a complex mixture of different polymeric carbohydrate systems may result. Although early studies[12] showed that damson gum from several trees grown in different districts was "essentially a homogeneous chemical entity," recent work has suggested that gum ghatti may be heterogeneous[13] and that sisal pectic acid[14] may contain a series of closely related molecular species.

There have been few investigations of inter-nodule variation. Torto[15] analysed one nodule of gum from *Fagara Xanthoxyloides* for acetyl and methoxyl content, and stated that specimens prepared from nodules from different trees did not show significant variations in optical rotations and equivalent weights; this was claimed to indicate the essential homogeneity of the gum. In a study of the gum from *Brachychiton diversifolium*, three separate nodules were powdered, dried, and analysed for ash, nitrogen, methoxyl and acetyl content: it was deduced that the nodules were "not significantly different in composition".[16]

A sample of the gum from *Combretum leonense** was observed to contain a number of unusually large clean nodules, each approximately the size of a walnut. This appeared to make possible a study of the composition of each nodule.† This paper gives the results of an attempt to investigate the composition of each nodule as fully as the amount of material available permitted.‡

Initially, the six largest, whole nodules, whose weight varied from 8–12 grams, were selected for study. They were alike in appearance, being dark brown in colour with characteristic surface markings, and had a marked odour of acetic acid. The nodules, numbered I–VI, were individually ground to a coarse powder. It was immediately observed that nodules I, III and V gave a pale yellow powder, whilst that from the others was a dark reddish-brown.

EXPERIMENTAL

Analytical methods

(*a*) Moisture contents were found by heating to constant weight at 103°.

(*b*) % ash was found by heating in a muffle at 550°; constant weight was reached in 4 hours.

(*c*) % nitrogen was found by a semi-micro Kjeldahl method.

(*d*) Acetyl contents were determined by the Weisenberger method.[22]

(*e*) Anderson's apparatus[1] was used to determine uronic acid contents.

(*f*) Free titratable acidity was found by direct titration with 0·0247*N* sodium hydroxide to phenolphthalein end-point in a stream of CO_2-free nitrogen.

(*g*) Viscosity measurements were made using a suspended-level dilution viscometer (Polymer Consultants Ltd; water = 184 secs) in a thermostat constant to 0·01°; results are expressed using g/ml as concentration units.[23]

Autohydrolysis experiments

The quantity (calculated on an ash-free, dry weight basis) of each nodule to give 100 ml of a 1% (w/v) solution was dissolved in a standard flask. The solutions were transferred to clean, dry flasks which were placed in a boiling water bath after being fitted with short reflux condensers. Aliquots (2 ml) were withdrawn at intervals by pipette (considerably lengthened above the graduation mark) introduced *via* the reflux condenser, which was fitted with an anhydrone guard-tube except when withdrawals were being made.

Paper partition chromatography

This was carried out on Whatman No. 1 paper at 20° with the upper layers of the following systems (v/v): (*A*) butan-1-ol–benzene–pyridine–water (5 : 1 : 3 : 3); (*B*) pyridine/ethyl acetate/acetic acid/water (5 : 5 : 1 : 3).[24] Sugars were located by heating after spraying with either saturated aqueous aniline oxalate solution or with a solution of *p*-anisidine hydrochloride in butan-1-ol. All sugars were identified by comparison with reference sugars run on the same chromatograms.

Quantitative estimation of sugars

This was by the Somogyi method;[25] D-ribose was used as reference sugar after being shown absent in the gum. In the autohydrolysis experiments, total free reducing sugars were calculated as arabinose, which was the main sugar liberated.

Electrophoresis

The electrophoresis of neutralised solutions of purified nodules VII and VIII was attempted (Shandon Universal Filter Electrophoresis Apparatus) using 300 volts for 2–6 hours in 0·05*M* borate

* Collected in Nigeria in 1952, and kindly provided by Dr. R. J. McIlroy.

† Dr. G. O. Aspinall kindly provided several nodules for this purpose, although the total weight of gum available was not large.

‡ The structure of the gum is now being studied in this Department by Dr. Aspinall.

buffer at pH 8 on (*a*) 20 × 5 cm paper strips (Whatman No. 1), (*b*) glass-fibre paper. No movement was observed on the paper strips: small mobilities ($<0{\cdot}5$ cm after 6 hours) were obtained on the glass-fibre paper, but no separation of components could be detected. Electrophoresis for 6–18 hours on glass-fibre paper in 2*M* alkali[13] resulted in movements of 3–4 cm as a continuous smear, from which no conclusive result could be obtained.

Studies on crude material

Table I shows the results of duplicate determinations of the moisture, ash, nitrogen, methoxyl, acetyl and uronic acid content of the crude powdered material from each nodule. Results of analyses of the ash are also shown.* Chloride, sulphate and phosphate were all absent; carbonate, formed during ashing, was found to account for 55 % of the ash from nodule VI.

Table II shows the values for pH, free titratable acidity, total free reducing sugars, and flow-time number obtained from aliquots of aqueous solutions (1 % w/v, corrected for moisture and ash content) of each powdered nodule. Each 1 % solution was then autohydrolysed at 98°. At intervals, up to a

TABLE I.—DETERMINATIONS ON CRUDE POWDERED MATERIAL

	Nodule					
	I	II	III	IV	V	VI
% Moisture	14·9 14·9	15·3 15·6	14·0 14·0	15·5 15·6	17·1 16·9	14·9 14·9
% nitrogen	0·13 0·14	0·06 0·07	0·16 0·16	0·05 0·05	0·11 0·13	0·12 0·12
% methoxyl	nil	nil	nil	nil	nil	nil
% acetyl	5·1 5·2	6·2 6·2	4·4 4·4	5·9 5·9	6·3 6·2	3·0 3·0 3·1
% Uronic acid anhydride	15·4 15·7	18·7 19·0	15·9 16·0	18·9 19·0	17·7 17·8	15·1 15·4
% Ash	2·56 2·54	4·03 3·96	2·38 2·43	3·79 3·83	3·02 3·12	1·71 1·69
Composition of ash (as parts per million)						
Ca	235,000	235,000	205,000	257,000	257,000	270,000
Na	5,200	5,200	4,700	3,700	3,000	4,400
K	136,000	91,000	180,000	127,000	136,000	37,400
Mg	n.d.	n.d.	n.d.	n.d.	n.d.	84,000
Cu	166	59	538	56	82	272
Mn	25,000	11,400	17,400	17,100	13,400	18,400
Fe	4,800	1,240	2,310	1,200	1,200	1,540
Ba	680	590	620	630	550	540
Sr	1,590	1,290	1,490	1,560	1,170	1,060

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* We are greatly indebted to Dr. R. L. Mitchell, Macauley Institute for Soil Research, Aberdeen, who obtained from the small quantities of ash available the values for Cu, Mn, Fe, Ba and Sr.

TABLE II.—DETERMINATIONS ON 1 % AQ. SOLUTIONS OF CRUDE MATERIAL

	Nodule					
	I	II	III	IV	V	VI
% cold water insoluble	0·3	0·5	0·6	0·2	0·2	0·3
pH	4·25	4·30	4·10	4·25	4·20	4·10
Free titratable acidity	0·378	0·374	0·324	0·426	0·398	0·354
(*ml* 1*N* NaOH per gram)	0·374	0·384	0·330	0·404		
Hence apparent equiv. wt.	2645	2645	3125	2380	2500	2820
% Free reducing sugars	0·74	1·02	0·72	2·10	0·74	0·90
(Somogyi,[25] as arabinose)		1·02	0·84	2·16		
Flow-time at 26·4°	468	491	425	620	449	366
(water = 184 secs)	466	491	429	618	451	364
Hence $(t - t_0)/t_0$	1·52	1·73	1·32	2·41	1·45	1·00

total of 360 hours, aliquots were withdrawn for determination of total reducing power and total free acidity; the values found are shown in Figs. 1 and 2 respectively. Table III shows the ratios of free sugars present after 70 and 168 hours' autohydrolysis; values of the flow-time number were also found at 70 hours. Hydrolysis with H_2SO_4 (2*N*) at 100° for 24 hours was incomplete, but formic acid (90 %) in a sealed tube at 100° for 5 hours gave complete hydrolysis. Within the limits of experimental error, the ratios of the sugars found were the same for each of the samples, *viz.* arabinose/galactose/rhamnose = 9/10/1.

Studies on purified material

Preliminary purification experiments were carried out on nodules I and V, which were the largest samples remaining. After dissolution in cold distilled water, the solutions were poured into 3 volumes of acidified ethanol (0·1*N* with respect to HCl). The white curdy gum precipitate was removed by centrifuge. After one such precipitation, the material from nodule I contained 0·04 %*N* and 0·11 % ash; two precipitations of the material from nodule V gave purified gum having 0·03 %*N* and 0·02 % ash. Since re-precipitations and ash determinations at this level consume considerable quantities of material, it was decided to accept this as a reasonable standard of purification. Each of the remaining nodules was therefore precipitated twice, and, to conserve material, it was assumed that their values of %*N* and % ash would be similar to those found for V.

After removal by centrifugation, the precipitated material was dried by immersion in acetone for 10 days: the acetone was changed daily and the gum was progressively ground to a fine powder. Samples I and V were then placed in a vacuum pistol at 60° over P_2O_5 for 1 hour, then stored in a vacuum desiccator for 14 days. After this treatment, oven drying to constant weight at 103° showed 6·83 % "moisture" in sample I and 4·64 % in V. Purified samples II, III, IV and VI were dried, after acetone dehydration as before, under vacuo at 80° for 48 hours in an attempt to decrease the moisture content; oven drying to constant weight at 103°, however, showed 5·25 %, 4·86 %, 5·73 % and 6·20 % "moisture" for these samples respectively. Since these values were surprisingly high, further drying experiments were carried out on small quantities of each sample. Using an infra-red quantitative technique,[17] it was found that both water and acetone (or any other organic solvent used for precipitation or preliminary dehydration) were retained up to temperatures at which decomposition of the gum began (about 135°) as indicated by slight browning and the start of evolution of CO_2. To augment the material available, a further two nodules (numbers VII and VIII) were obtained; after two

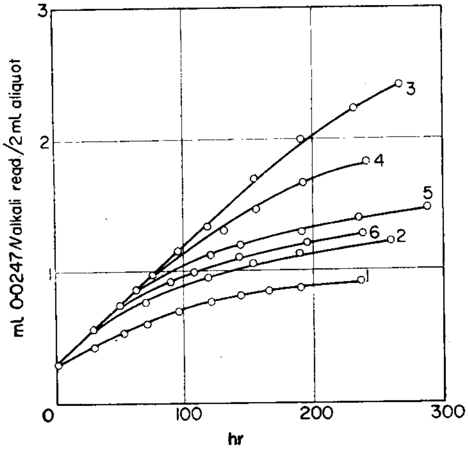

FIG. 1.—Increase in total free acidity on autohydrolysis.

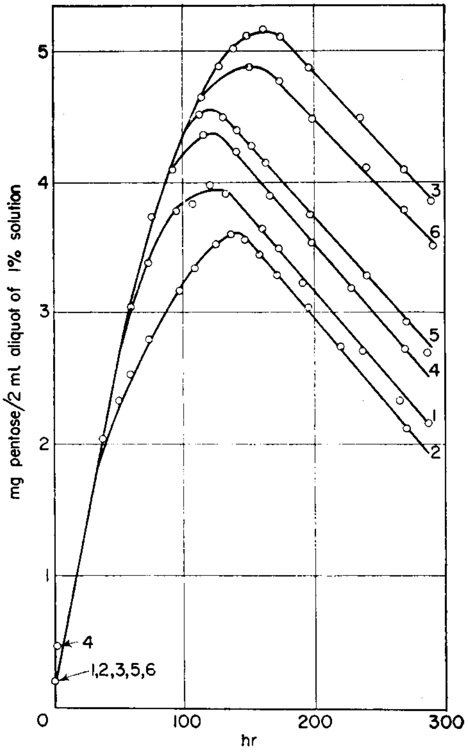

FIG. 2.—Increase in total free reducing power on autohydrolysis.

TABLE III.—DETERMINATIONS ON 1 % AQ. SOLUTIONS AFTER AUTOHYDROLYSIS

		Nodule					
		I	II	III	IV	V	VI
After 70 *hours:*							
$(t - t_0)/t_0$		0·04	0·02	0·07	n.d.	0·10	0·06
ratio of sugars	hexose disacch.	1	1	1	n.d.	1	1
	pentose disacch.	1	1	1	n.d.	1	1
	galactose	1·6	1·2	1·5	n.d.	1·5	1·6
	arabinose	12	10	20	n.d.	15	20
	rhamnose	1	1	1	n.d.	1	1
After 168 *hours:*							
ratio of sugars	hexose disacch.	1	1	1	1	1	1
	pentose disacch.	1	1	1	1	1	1
	galactose	2	2	2	2	2	2
	arabinose	15	12	14	10	13	13
	rhamnose	1	1	1	1	1	1

TABLE IV.—DETERMINATIONS ON PURIFIED MATERIAL

	Nodule							
	I	II	III	IV	V	VI	VII	VIII
% nitrogen	0·04 0·03	n.d.	n.d.	n.d.	0·03 0·03	n.d.	0·04	0·06 0·07
% acetyl	2·9 2·8	3·4 3·3	3·3	2·9 2·9	4·3 4·4	1·7 1·7	3·0 2·9	3·6
% uronic acid anhydride	15·3 15·5	19·2 19·3	15·2 15·4	19·7 19·6	18·1 18·4	14·9 14·9	19·2 19·4	20·1 19·9
Results from 1 % *aq. solutions*:								
% Free reducing sugars	0·21	n.d.	n.d.	n.d.	0·28	n.d.	n.d.	n.d.
Free titratable acidity*	0·882	1·058	0·868	1·106	1·060	0·856	1·072	1·149
Hence equivalent wt.	1133	945	1152	904	943	1168	933	870
Hence % uronic† acid anhydride	15·5	18·6	15·3	19·4	18·6	15·1	18·9	20·2
Limiting flow-time‡ number	0·63	0·76	n.d.	0·98	0·68	n.d.	0·61	0·67

* as mls. 1·0*N* NaOH per gm
† if all acidity due to uronic acid groups
‡ at 25·0° in 1 % NaCl solution.

precipitations in acidic ethanol, the purified material was redissolved, dialysed against distilled water for 3 days, then isolated by freeze drying. The resultant material was found (*a*) to lose 1 % of water on drying to constant weight at 103°, and (*b*) to retain a further 1 % of water up to the temperature at which decomposition began. Robson[18] has reported that freeze drying for 500 hours is required to remove *all* traces of moisture from glucose–gelatine solutions. A full account of the dehydration and solvent retention studies made will be given in a later communication.

Determinations of nitrogen, acetyl, and uronic acid content were made on the purified samples, the results (corrected for the moisture contents reported above) being shown in Table IV, which also gives the results of determinations of free reducing sugars and free titratable acidity made on 1 % (w/v) aqueous solutions. Calculation of the equivalent weight of the gum acid, based on the free titratable acidity value, shows that, in each case, the uronic acid content accounts for the total acidity found.

Before studying the viscosity behaviour of each purified sample, the polyelectrolyte effect was investigated. Fig. 3 shows that 1 % salt solution gives adequate suppression of the polyelectrolyte effect. The limiting flow-time number of the purified samples was subsequently found at 25·0° in 1 % sodium chloride solution; the viscosity curves obtained are shown in Fig. 4. Use of a zero shear viscometer (Polymer Consultants Ltd.) showed that Newtonian behaviour was given by an 0·5 % solution of sample VIII in 1 % sodium chloride.

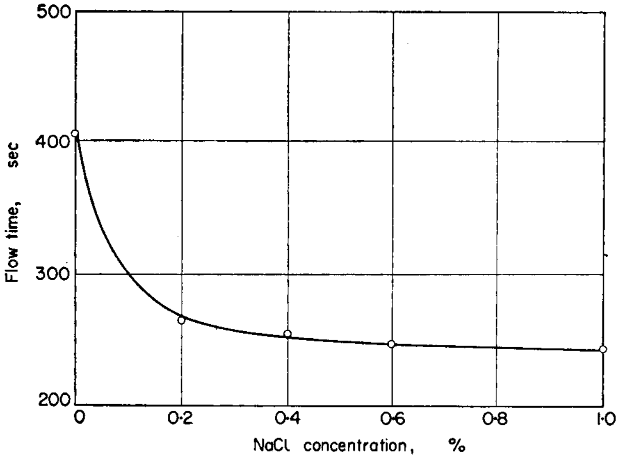

FIG. 3.—Decrease in electroviscous effect.

When a plant gum is purified by acidic ethanol precipitation from aqueous solution (which may, as in this case, have pH = 4) some form of auto-degradation or fractionation could possibly occur. Such an effect would become increasingly serious as the number of re-precipitations—and consequently the percentage of free-acid groups—was increased. To investigate this possibility, the twice precipitated material from nodule VII (curve VII(*a*), Fig. 4) was given two further purifications. During each of these, the possibility for degradation to occur was increased by storing the aqueous solution at 40° for 1 hour before precipitation in ethanol. (In the original precipitations, no heating was employed, and addition to ethanol was made as soon as solution was achieved). Since the material recovered from these treatments gave viscosity curve VII(*b*) in Fig. 4, no degradation of this gum apparently occurs whilst it is in the free acid form during purification processes. The effect of dilute alkali was also tested. An aqueous solution (1 % w/v) of the gum was neutralised to phenolphthalein end-point; a calculated excess of alkali was then added to make the solution 0·1N with respect to

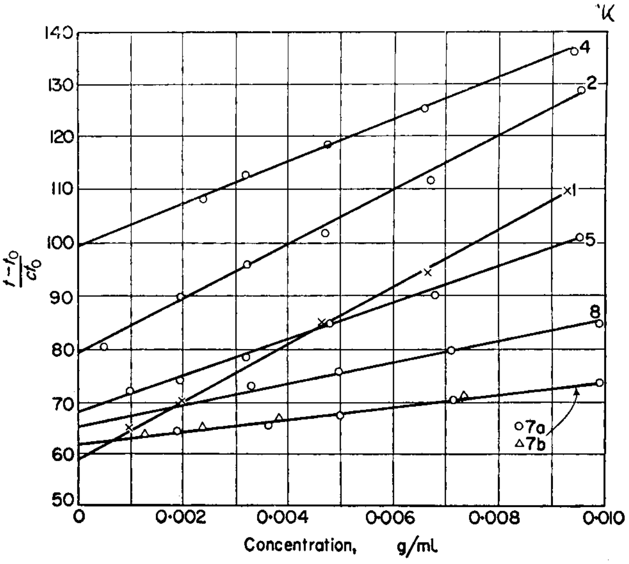

FIG. 4.—Viscosity curves for purified samples.

NaOH. The limiting flow-time number of this solution was determined at 25·0° on portions of the solution (*a*) *immediately*, (*b*) *after storage* at 25·0° for 72 hours. No difference in viscosity behaviour, before and after storage, was detectable.

No tendency for fractionation to occur was observed when the ethanol used in precipitations was varied from 2 to 5 volumes. After centrifugation of the main precipitate, the supernatants were stored at 0° for several days; no further material precipitated. No precipitation of neutral material was given on addition to the supernatants of borate + "cetavlon".[19] Electrophoresis experiments on nodules VII and VIII were inconclusive. (see above).

DISCUSSION

The available material was used to obtain, as far as possible, information supplementary to that which will be obtained in the structural study now in progress on the bulk material. Each of the samples was remarkably homogeneous; good replicates, as shown in the tables, being obtainable without difficulty. Each nodule, however, differed strikingly in composition from each of the others. In view of the reproducibility of results obtained in each of the analytical procedures used, the internodule differences are greater than could be ascribed to any possible experimental error, and are considered to be significant. In only one procedure—determination of the ratio of sugars liberated on complete hydrolysis—was it not possible to distinguish between each nodule; the error involved in such a determination is, however, at best ±5% and is more probably ±10%.

Correlations between the properties of the nodules are difficult. The nodules cannot easily be assigned to sub-groups; a gradation between the maximum and minimum values of each analysis appears to be given. That the nodules are broadly similar in essential detail is not surprising, considering the care with which they were selected for study from a batch. Yet, in the crude material, 100% variation occurred in the nitrogen, ash, and acetyl contents. Calculation shows that, in the crude material, about 50% of the uronic acid carboxyl groups are in the free acid form.

In the purified samples, considerable variations occur in the acetyl and uronic acid anhydride contents, and in the viscosity behaviour. The acetyl contents shown in Table IV are stable in solution under the precipitation conditions used; when stored in the solid state, however, the purified material develops a strong odour of acetic acid, a behaviour reminiscent of the original nodules. The nitrogen content of the crude material was reduced, but not completely eliminated, by the purification process used. Re-precipitations were found to reduce ash contents significantly, but little reduction in residual nitrogen content was achieved. Small residual nitrogen contents persist in other carbohydrate systems[20] despite extensive attempts at purification; their significance remains in doubt.[21]

In only one case (nodule III) is the uronic acid content of the purified sample significantly smaller than that of the crude material. This is difficult to explain since, on a dry weight basis, purification should lead to increased uronic acid content unless some sort of fractionation has occurred. Agreement between the uronic acid values found directly and by calculation from the neutralisation equivalent is good, and strengthens the evidence that the variation from 14·9% to 20·1% is real. Such a variation must reflect fine structural differences; the inter-nodule variation in viscosity and acetyl content, and the kinetic differences found in the autohydrolysis experiments support this indication.

The variations found are sufficiently great to emphasise the need for more careful sampling procedures than have generally been used in the past. It is hoped at an early date to extend the present investigation by securing for study* a number of gum nodules obtained (*a*) from the bark of one tree as a result of several injuries made simultaneously and (*b*) from the barks of a number of trees, all of the same species, as the result of one similar injury inflicted simultaneously on each of them.

Acknowledgments—We thank the Rockefeller Foundation and Messrs Imperial Chemical Industries Ltd. for grants, and the Department of Scientific and Industrial Research for a maintenance allowance (to N. J. K.).

Zusammenfassung—Gummitropfen vom Baume Combretum leonense aus Nigeria wurden individuell untersucht. Die Mengen verschiedener Substanzen in einzelnen Tropfen wurden als stark variierend gefunden und gestatteten Rückschlüsse auf Verschiedenheiten in der Zusammensetzung sowohl von Roh- als auch gereinigtem Latex. Verschiedenheiten der Zusammensetzung waren weitaus grösser als dass sie hätten durch Schwankungen der Analysenwerte erklärt werden können. Der Schluss wurde gezogen, dass sie durch Unterschiede in der feineren Stuktur der Tropfen verursacht werden.

Résumé—Les auteurs ont étudié individuellement différents nodules de gomme provenant de l'arbre nigérien, Combretum leonense. La quantité de matière présente dans chaque nodule a permis une étude de la variation de la constitution des deux formes: brute et purifiée de la gomme. On trouve des variations beaucoup plus grandes que ne l'expliquerait l'erreur analytique. On considère que ces variations indiquent qu'il existe des différences internodules dans la structure fine.

REFERENCES

[1] Part 1: D. M. W. Anderson, *Talanta,* 1959, **2,** 73.
[2] G. A. Gilbert, *Die Stärke,* 1958, **10,** 95.
[3] A. H. A. de Willigen and P. W. de Groot, *Korte Ber Proefsta Aard appelwerwerk,* 1947, **7,** 2. (See *Chem. Abs.,* 1949, **43,** 2005h).
[4] G. L. Doremus, F. A. Creshaw and F. H. Thurber, *Cereal Chem.,* 1951, **28,** 308.
[5] A. M. Liddle and D. J. Manners, *J. Chem. Soc.,* 1957, 3432.
[6] E. L. Hirst, *Proc. Chem. Soc.,* 1958, 177.
[7] A. Haug and A. Jensen, *Norwegian Institute of Seaweed Research, Reports* Nos. 4, 14.
[8] G. Harris and I. C. McWilliam, *J. Inst. Brewing,* 1957, **63,** 210.
[9] R. Waite and J. Boyd, *J. Sci. Food and Agric.,* 1957, **8,** 422.
[10] E. L. Hirst, D. J. Mackenzie and C. B. Wylam, *ibid.,* 1959, **10,** 19.
[11] E. L. Hirst and J. K. N. Jones, in *Modern Methods of Plant Analysis,* Edited by Paech and Tracey, Vol. II, p. 275.
[12] *Idem, J. Chem. Soc.,* 1938, 1174.
[13] B. A. Lewis and F. Smith, *J. Amer. Chem. Soc.,* 1957, **79,** 3929.
[14] G. O. Aspinall and A. Cañas-Rodriguez, *J. Chem. Soc.,* 1958, 4020.
[15] F. G. Torto, *Nature,* 1957, **180,** 864.
[16] E. L. Hirst, E. E. Percival and R. S. Williams, *J. Chem. Soc.,* 1958, 1942.
[17] D. M. W. Anderson, *Analyst,* 1959, **84,** 50.
[18] E. M. Robson, *Vacuum,* 1956, **4,** 60.
[19] H. Palmstierna, J. E. Scott and S. Gardell, *Acta Chem. Scand.,* 1957, **11,** 1792.
[20] D. M. W. Anderson and C. T. Greenwood, *J. Sci. Food and Agric.,* 1955, **6,** 587.
[21] A. W. Arbuckle and C. T. Greenwood, *J. Chem. Soc.,* 1958, 2626.
[22] E. Weisenberger, *Mikrochem. ver. Mikrochim Acta,* 1947, **33,** 51.
[23] I.U.P.A.C. nomenclature, *J. Polymer Sci.,* 1952, **8,** 257.
[24] F. G. Fischer and H. Dorfel, *Z. physiol. chem.,* 1955, **302,** 186.
[25] M. Somogyi, *J. Biol. Chem.,* 1945, **160,** 69.

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* By the kind co-operation of Dr. H. R. Fletcher, Regius Keeper, Royal Botanic Garden, Edinburgh.

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THE APPLICATION OF THE CATHODE RAY POLAROGRAPH TO THE ANALYSIS OF EXPLOSIVES

THE DETERMINATION OF MERCURY FULMINATE*

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(*Received* 9 *July* 1959)

Summary—The polarographic behaviour of mercury fulminate has been described, and it is possible to determine this compound polarographically.

THE polarographic behaviour of mercury fulminate has not yet been reported in literature. The simplicity of analytical procedures using the Cathode Ray Polarograph[1,2,3] suggests the value of its application to the determination of this explosive. Consequently, a method has been developed for the rapid determination of mercury fulminate. The method is based on the anodic oxidation and cathodic reduction of mercury fulminate in a pyridine/potassium nitrate basic electrolyte. Mercury fulminate is soluble in pyridine[4] which also acts as as essential part of the base electrolyte in the polarography of fulminic acid.

EXPERIMENTAL

Mercury fulminate was prepared as stated by Davis.[4] It was purified from oxides of mercury by recrystallization from ammonium hydroxide.

The determination was carried out in the following way: 250 mg of sample were placed in a 100-ml flask, dissolved in 50 ml pyridine and made up to the mark with N potassium nitrate. 0·04, 0·08, 0·12, 0·16 and 0·20 ml of this solution were transferred to 10-ml flasks and brought up to the mark with a base electrolyte consisting of 10% pyridine and 90% N potassium nitrate; thus the concentrations of mercury fulminate in the flasks were 10, 20, 30, 40 and 50 μg/ml. The polarograms were determined using 5 ml of each solution, with starting potentials of −0·5 V for anodic oxidation and −0·05 V for cathodic reduction, and the scale factor was 1·0 in each case. The wave heights, as recorded in Table I, were observed to be directly proportional to the concentration of mercury fulminate. Typical anodic and cathodic waves are shown in Figs. 1 and 2.

TABLE I

Concentration of $Hg(ONC)_2$, μg/ml	Wave height, *divisions*	
	Anodic	Cathodic
10	6·5	9
20	13	18·5
30	19·5	25
40	25·5	36
50	32·5	45

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* Presented at a joint meeting of the Scottish Section of the Society for Analytical Chemistry and the Polarographic Society, held at The Queen's University, Belfast on 26 June 1959.

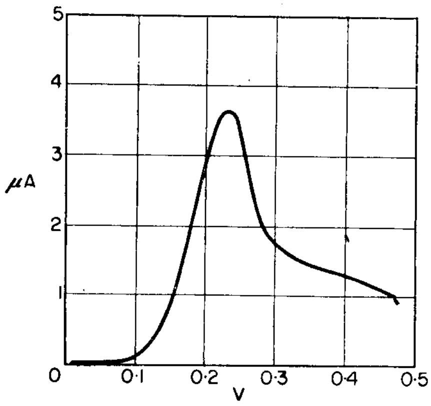

FIG. 1.—Reduction wave of ONC′
40 μg/ml $Hg(ONC)_2$

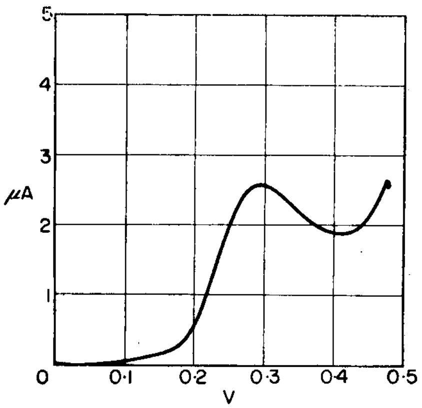

FIG. 2.—Oxidation wave of ONC′
40 μg/ml $Hg(ONC)_2$

Determination of mercury fulminate in explosive primers

To extend this observation for practical application, (to the determination of mercury fulminate in explosive primers), a series of synthetic samples was prepared containing 20, 40, 50, 60 and 80% of mercury fulminate in potassium chlorate, and the percentage of introduced mercury fulminate was determined using the sample containing 50% as "standard" for comparison.

Weights of mercury fulminate, 40, 80, 100, 120, and 160 mg, were introduced into 100-ml flasks, dissolved in 50 ml pyridine, 160, 120, 100, 80 and 40 mg. of potassium chlorate were added respectively, and the solutions were made up to the mark with *N* potassium nitrate; 0·1 ml of each solution was transferred into a 10-ml flask and made up to the mark with base electrolyte (pH 8·8). The polarograms were determined on a 5-ml aliquot of each solution as before, using cathodic reduction, and a scale factor of 1·5. The results are recorded in Table II.

TABLE II

% $KClO_3$ introduced	% $Hg(ONC)_2$ introduced	% $Hg(ONC)_2$ found
80	20	20·6
60	40	38·9
50	50	50·0
40	60	61·1
20	80	79·2

The effect of the addition of lead (as nitrate), sodium azide, mercuric mercury, cyanide, cyanate and copper was next investigated. The addition of lead nitrate, sodium azide or mercuric chloride produce no interference with the formation of red/ox fulminic waves. The addition of cyanide results in the formation of red/ox waves with shapes identical to the waves of fulminic acid, but with peak potentials differing by 100 mV. In consequence the determination of both substances using direct current is not possible; but working with derivative current, the separation of both waves is easily obtained, thus indicating the possibility of the simultaneous determination of both cyanide and fulminate, as indicated by Figs. 3–6. Cyanate is neither oxidisable nor reducible and so has no effect on the determination of fulminate. Copper produces an extremely interesting behaviour. The addition of 1 μg of copper to 100 μg of fulminate depresses the wave height of fulminate by 15%. Further additions of 1 μg of copper decrease the wave height approximately by 15% until the ratio of copper to fulminates is 1 : 5, when the reduction wave of fulminate is completely removed, and the formation of two copper waves is observed with a starting potential of −0·3 V. This indicates that quantitative

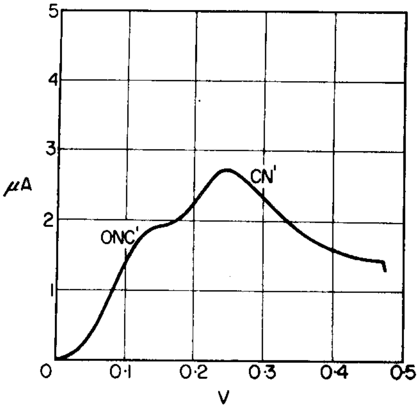

FIG. 3.—Reduction waves of ONC′ and CN′
Direct current
7 μg/ml ONC′ : 3 μg/ml CN′

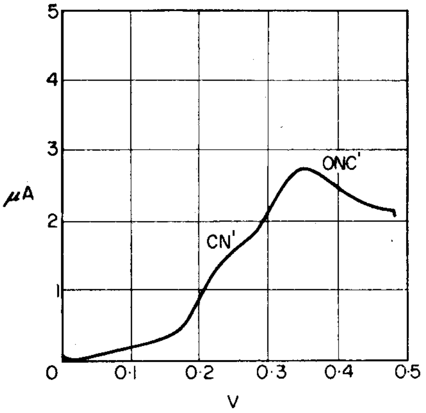

FIG. 4.—Oxidation waves of ONC′ and CN′
Direct current
7 μg/ml ONC′ : 3 μg/ml CN′

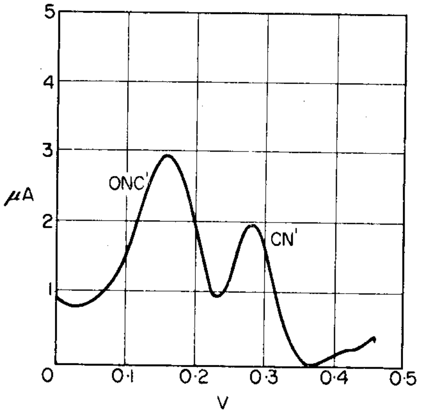

FIG. 5.—Reduction waves of ONC′ and CN′
Derivative current
7 μg/ml ONC′ : 3 μg/ml CN′

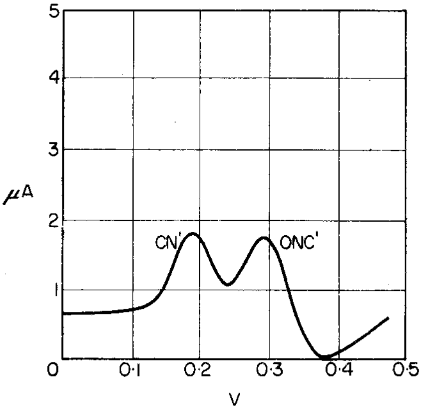

FIG. 6.—Oxidation waves of CN′ and ONC′
Derivative current
7 μg/ml ONC′ : 3 μg/ml CN′

estimation of fulminate cannot be carried out in presence of copper. However, providing the copper content is known, it is possible to determine the fulminate concentration by means of calibration graphs.

DISCUSSION

Fulminic acid is an isomeric form of oxycyanic acid. To the different characteristics, *i.e.* the toxic and explosive property of the one and the non-toxic and non-explosive property of the other, is now added differing polarographic behaviour. The polarographic behaviour of fulminates is similar to that of cyanides. The oxidation of cyanides has been investigated by Kolthoff[5] and the mechanism of the electrode reaction was suggested as being

$$2CN^- + Hg \rightarrow Hg(CN)_2 + 2e^-$$

Similarly the oxidation of fulminates should be

$$2ONC^- + Hg \rightarrow Hg(ONC)_2 + 2e^-.$$

No previous work has been published concerning the reduction of cyanides, but the occurrence of reduction has been proven by the present work. The mechanism of the reduction of cyanides and fulminates remains doubtful.

Acknowledgement—The author wishes to express his thanks to the Directors of Southern Instruments Limited for permission to publish this paper.

Zusammenfassung—Das polarographische Verhalten von Quecksilberfulminaten sowie dessen polarographische Bestimmung werden beschrieben.

Résumé—Le comportement polarographique du fulminate de mercure a été décrit. Il est possible de doser ce composé par polarographie.

REFERENCES

[1] G. F. Reynolds and H. M. Davis, *Analyst*, 1953, **78,** 314.
[2] H. M. Davis and J. E. Seaborn, *Electronic Eng.*, 1953, **25,** 314.
[3] J. Hetman, *Dechema-Monographien*, 1959, **31,** 167.
[4] T. L. Davis, *Chemistry of Powder and Explosives*, John Wiley & Sons, Inc., New York, 1956.
[5] I. M. Kolthoff and C. S. Miller, *J. Amer. Chem. Soc.*, 1941, **63,** 1405.

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THE SEPARATION AND DETERMINATION OF ALUMINIUM, GALLIUM, INDIUM AND THALLIUM BY PARTITION CHROMATOGRAPHY

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Summary—A method is described for the chromatographic separation and determination of small amounts of aluminium, gallium, indium and thallium. The chlorides of the metals are separated using a solvent-mixture containing phenol : methanol : conc. hydrochloric acid (50 : 30 : 20 W : V : V). Each substance is detected by a single spraying reagent—8-hydroxyquinoline—and the amount of element present estimated semi-quantitatively by visual comparison with standards.

Investigation of the conditions for the removal of the metal oxinates from the paper into an organic solvent has permitted the determination of the elements spectrophotometrically.

A NUMBER of methods have been suggested for the separation of two or more of the elements of Group IIIB of the Mendeleef Periodic Table.[1] Many techniques have been used for separation of elements in this group. In an interesting paper Steinbach and Freiser[2] have examined the extraction of the acetyl acetonates of aluminium, gallium and indium from iron. They suggest a possible separation of these metals by solvent extraction at different pH values. A different approach is that of Klement and Sandmann[3] who separated indium and gallium on cation-exchanger Dowex-50. Gallium has also been separated from aluminium as the thiocyanate by a solvent containing ether and tetrahydrofuran.[4]

One of the most extensive investigations in the separation of this group of elements is that by Arden *et al.*,[5] who separated aluminium, gallium, indium and zinc by partition chromatography using *n*-butanol-hydrochloric acid as the solvent-mixture. Attempts by us to include thallium were found to be unsuccessful.

From the literature survey it appeared that a complete separation of all four elements of the Group had not been successfully achieved. These elements are becoming increasingly important, occurring in small amounts in aluminium alloys and various minerals. Bassett and Tompkins[6] attempted the determination of all four elements in uranium-bearing materials. Aluminium was determined colorimetrically with haemotoxylin or alizarin, but attempts to determine gallium, indium and thallium were wholly unsuccessful.

An important condition in the determination of these elements appears to be the complete separation of one from another. It seemed likely that by careful investigation of solvents or solvent-mixtures, partition chromatography would offer the best and simplest method of separating the elements. This paper, therefore, reports the investigations carried out and the results obtained.

PRELIMINARY INVESTIGATIONS

In 1957, Magee and Headridge[7] reporting results on the chromatographic separation of the alkali metals, suggested that a solvent-mixture containing phenol as complexing agent might give a separation of aluminium, gallium, indium and thallium. A wide range of solvent mixtures were therefore prepared to investigate the action of phenol, in the presence of alcohols and acids. With simple phenol-methanol mixtures, "bearding" occurred. On the addition of acid to these mixtures the bearding disappeared and separation, with good banding, was obtained. The best mixture was found to be one containing phenol-methanol and concentrated hydrochloric acid. Chromatograms with 200 μg of each element were prepared, over a wide range of solvent-mixture components. The Rf values of the most promising are shown in Table I.

TABLE I

No	Phenol	Methanol	Conc. HCl	Rf Values			
				Al	Ga	In	Tl
1	33	33	33	0·18 (±0·04)	0·66 (±0·06)	0·26 (±0·04)	0·43 (±0·03)
2	40	30	30	0·52 (±0·04)	0·80 (±0·05)	0·52 (±0·05)	0·74 (±0·03)
3	25	40	30	0·48 (±0·05)	0·91 (±0·05)	0·53 (±0·04)	0·74 (±0·04)
4	50	30	20	0·10 (±0·03)	0·76 (±0·06)	0·24 (±0·06)	0·50 (±0·06)
5	40	50	10	0·20 (±0·05)	0·68 (±0·05)	0·28 (±0·05)	0·51 (±0·04)
6	20	40	40	0·55 (±0·06)	0·90 (±0·06)	0·50 (±0·04)	0·75 (±0·05)
7	10	50	40	0·70 (±0·05)	0·84 (±0·05)	0·72 (±0·05)	0·77 (±0·05)
8	40	10	50	0·25 (±0·05)	0·55 (±0·06)	0·27 (±0·06)	0·45 (±0·04)

In the solvent-mixtures No. 3–10 each constituent of the phenol-methanol-concentrated hydrochloric acid mixture was varied over the range 20–50%. It can be seen that the separation of gallium, indium and thallium is achieved in every case, but the separation of indium from aluminium is more difficult. This separation was investigated separately and it was found that a large amount of phenol with almost equal quantities of acid and methanol was the most effective. The solvent-mixture used in subsequent work was No. 4 containing phenol : methanol : conc. hydrochloric acid (50 : 30 : 20 : W : V : V).

Development of spraying reagents

Most workers who have investigated these elements by chromatography developed aluminium and gallium with aluminon,[8] indium with dithizone and thallium with an aqueous solution of potassium iodide.[7]

In paper chromatography, however, it is obviously a great asset if a single spraying reagent can be used. Experiments were therefore carried out to find such a reagent. Gallium and indium have been detected by spraying the paper strips with a 5% solution of 8-hydroxyquinoline in methanol : chloroform : water (85 : 10·5% V : V)[7] and then hanging the strips in an atmosphere of ammonia. Under ultra-violet light these elements fluoresce brilliant yellow. Investigations were carried out with this reagent and it was found that, if the chloroform concentration is increased to an amount equal to methanol, the paper sprayed with a 5*N* aqueous solution of ammonia and then with a 8-hydroxyquinoline reagent, aluminium, gallium, indium and thallium may be detected as yellow bands. Aluminium, gallium and indium also give a brilliant fluorescence under ultra-violet light. The composition of the spraying reagent used throughout was a 5% W : V solution of 8-hydroxyquinoline in methanol : chloroform : water (48 : 48 : 4 V : V : V).

Detailed procedure

1. Place the solvent-mixture, phenol-methanol-conc. hydrochloric acid (50 : 30 : 20 W : V : V) in the solvent-trough of the Shandon Chromatank at least one hour before the experiment is started. A beaker containing the solvent-mixture should be placed at the bottom of the tank.
2. Cut sheets of Whatman No. 1 filter paper into 16-cm strips.
3. At distances of 2·5, 4 and 6 cm from the top, rule lines across the strip and bend the paper along the first of these lines.
4. Along the 6-cm line place 0·01 ml of the metal chloride test solution. Three such spots may be accommodated on the paper by placing them 4 cm in from the edge and allowing the same distance between spots. Leave the spots to dry in air and insert the strip into the chromatographic vessel in such a way that all below the 4-cm marks hang vertically.
5. Allow the solvent-mixture to run down the paper to the 40-cm mark. This takes about 16 hours.
6. Remove the strip from the trough and allow it to hang in air for about 30 minutes. Heat in an oven at 80° for 15 minutes. The paper is now ready for spraying.
7. Attach the strip to the strip-holder and spray with the 8-hydroxyquinoline reagent.
8. Hang the strip in an ammonia-saturated atmosphere at 80° for 10 minutes.
9. Wash the strip with hot water to remove excess 8-hydroxyquinoline.
10. Dry in an oven at 120° for about 2 hours.
11. Examine the strips under ultraviolet light. Aluminium, gallium and indium will be observed as brilliant yellow, fluorescing bands with the following Rf values: aluminium 0·10; gallium 0·76; indium 0·24; thallium 0·50.

Notes:

1. Although in the procedure just outlined it is recommended that the strip should be examined under ultraviolet light, it was found, in practice, that aluminium, gallium, indium and thallium, down to the minimum amount, may be detected by the naked eye.
2. For the semi-quantitative estimation of thallium it was found convenient to amend the procedure. If the strip containing thallium is heated to 150° for 10 minutes, the thallium position becomes a vivid purple, due possibly to the formation of a complex of the metal with the phenol on the paper. If desired, a set of standards may be prepared in this way and used for the estimation of thallium.
3. The oxinates of the metals should be kept out of contact with light as much as possible since they tend to be photo-sensitive. Aluminium, gallium and indium show signs of decomposition in 10 hours whereas thallium oxinate breaks down in 5 hours.

Standard and limits of detection

Using the procedure outlined a number of standards were prepared. For all the metals a range of 20 μg up to at least 500 μg may be detected. The minimum amount (20 μg) of any element can be successfully separated and detected in the presence of the maximum amount of any other or combination of the other elements.

As a test of the validity of the proposed scheme synthetic mixtures of "unknown" composition were analysed by one of us (I. A. P. S.). The results are shown in Table II. The estimated amounts are in micrograms.

For estimation purposes, the bands, developed in the recommended manner, were compared with a set of standards. The areas and intensities of the bands increase with increasing amounts of the elements. Where the amounts detected differ from the amount present, the latter are shown in parentheses.

TABLE II

No.	Al	Ga	In	Tl
1	25	30(50)	400	70(50)
2	450(500)	50(25)	—	—
3	50(25)	500	—	—
4	—	—	30(25)	450(500)
5	—	30(25)	470(500)	—
6	25(50)	30(50)	25	25
7	120(150)	125(150)	—	100(150)
8	200(250)	250	50(25)	—
9	—	350(400)	25	70(50)
10	450(400)	—	50(75)	—

The determination of aluminium, gallium, indium and thallium

The success of the separation and the satisfactory manner in which the semi-quantitative estimations were obtained suggested the possibility of quantitative determination of the elements. Since, after detection, all the metals are present as oxinates, it appeared hopeful that the metal oxinates might be extracted quantitatively from the paper.

The metal oxinates are of the form $X(C_9H_6ON)_3$ and show chelate linkages within the molecule which are completely satisfied by co-ordinate number six, normally shown by this group of metals. It therefore appeared highly probable that they would dissolve, under suitable conditions, in a solvent such as chloroform. It would then be possible to carry out a spectrophotometric determination on the solution.

Gallium: Moeller and Cohen[9] have investigated the absorption spectra of chloroform solutions of gallium oxinate and have shown that strong absorption peaks occur at 335, 320 and 392·5 mμ. In this investigation, the authors point out that the precipitation of gallium oxinate in aqueous solution is complete above pH 3·10. It appeared likely that the same conditions of pH would apply to precipitation on the paper and the following procedure was used:

Spray the paper with a 5% solution of 8-hydroxyquinoline in *ethanol*, followed by a 5*N* aqueous ammonia solution. This treatment was found to raise the pH to approximately 6. Dry the strip in the oven for 10 minutes at 75°. Cut a 3-cm square of paper around the metal oxinate band. This keeps the excess of 8-hydroxyquinoline to a uniform minimum. Wash the square of paper with 3 × 10-ml portions of boiling water to remove excess oxine. Dry in an oven for 1½ hours at 120°. To extract the metal complex from the paper place it in a separatory funnel along with 5 ml of hot conc. hydrochloric acid and shake for 5 minutes. After dilution to 25 ml and adjustment of the pH to 4·5, shake the solution containing the gallium oxinate with 2 × 4-ml amounts of chloroform. Dry the combined extracts over sodium sulphate and make the volume up to 10 ml with chloroform.

For the extraction of gallium oxinate completely from aqueous solution into chloroform, careful control of pH conditions is necessary. Sandell[10] states that complete extraction can only take place in the range 2·6–3·0. Lacroix[11] claims that it is complete at pH 2·0, while Moeller and Cohen[9] favour the range 3·0–7·0. Numerous experiments carried out to investigate the extraction showed that pH 4·5 gave the optimum extraction and this pH was used in the subsequent work.

The absorption spectrum of the chloroform solution of the metal complex, prepared as described showed a strong absorption peak at 390 mμ which was used in all subsequent work.

Indium: The precipitation of indium was carried out in the same way as for gallium by spraying with a 5% solution of 8-hydroxyquinoline in ethanol. This method did not, however, give reproducible results and it was found more satisfactory to use a 5% solution of 8-hydroxyquinoline in chloroform. The best method for the development and extraction of indium was devised as follows:

Develop the indium band on the paper by spraying with a 5% solution of 8-hydroxyquinoline in chloroform. Re-spray with 2*N* aqueous ammonia solution. Dry in an oven at 75° for 10 minutes. Cut out the indium oxinate band (keeping the size 3 cm^2 as for gallium). Wash with 3 × 10-ml portions of hot water. Finally, dry in an oven for 1½ hours at 120°. Shake in a separatory funnel with 5 ml of conc. hydrochloric acid to remove the complex from the paper. Dilute the acid extract to about 25 ml and adjust the pH to 4·0 to ensure complete extraction. Shake with 2 × 3-ml portions of chloroform. Dry the combined extracts over sodium sulphate and make up the volume to 10 ml with chloroform.

The absorption spectrum of the chloroform solution of the metal complex prepared in this way showed a strong absorption peak at 395 mμ which was used in all subsequent work.

Thallium: Thallium oxinate was developed and extracted in a very similar manner to gallium, since complete precipitation occurs in the range pH 3·0–8. The following procedure was used:

Spray the strip of paper with a 5% solution of 8-hydroxyquinoline in ethanol and then with 2*N* aqueous ammonia. Dry in an oven at *20° for ½ hour.* Cut out the thallium oxinate band from the paper (keeping the size 3 cm^2 as for gallium), wash with 3 × 10-ml portions of hot water. Dry in an oven for 1½ hours at 120°. Shake in a separatory funnel with 5 ml of hot conc. hydrochloric acid. Adjust the pH, after dilution to 25 ml, to a value between 7 and 8. Extract with 2 × 3-ml portions of chloroform. Dry the combined extracts over sodium sulphate and make the volume up to 10 ml with chloroform.

The absorption spectrum of the chloroform solution of the metal complex prepared in this way showed a strong absorption peak at 400 mμ which was used in all subsequent work.

Note: Photochemical decomposition of thallium oxinate occurs readily in daylight. It should, therefore, be developed and extracted in red light.

Aluminium: The oxinate of aluminium was prepared and extracted in the same way as that of indium:

Spray the strip with a 5% solution of 8-hydroxyquinoline in chloroform, followed by 2*N* ammonia solution. Dry the strip in an oven at 75° for 20 minutes. Cut out the aluminium oxinate band from the paper (keeping the size 3 cm^2 as for gallium) and wash with 3 × 10-ml portions of hot water. Dry at 120° for 1½ hours. Shake in a separatory funnel with 5 ml of conc. hydrochloric acid. Adjust the pH to about 6·0 to give complete extraction into chloroform. Extract with 2 × 3-ml portions of chloroform. Dry the combined extracts over sodium sulphate and make the volume up to 10 ml with chloroform.

The absorption spectrum of the chloroform solution of the metal complex prepared in this way showed a strong absorption peak at 385 mμ which was used in all subsequent work.

The analysis of synthetic mixtures

Using the procedures described calibration curves were prepared for each metal over the range 20–500 μg. In all cases Beer's law was obeyed.

To test the validity of the method a number of "known" mixtures was analysed by one of us (I. A. P. S.). The results expressed in micrograms, are recorded in Table III. Where experimental results differ from the amount actually present, the latter are shown in parentheses.

TABLE III

No.	Al	Ga	In	Th
1	300	—	60(50)	105(100)
2	460(450)	—	50(25)	—
3	250	225(200)	—	65(50)
4	—	40(30)	450	30(20)
5	55(50)	—	245(250)	255(250)
6	—	—	50	480(500)
7	500	—	50(30)	—
8	250	258(250)	25	—
9	—	400	30(25)	60(50)
10	155(150)	140(150)	—	150

Small deviations that occur in the above results are thought to be due most likely, not to the method, but rather to the error inherent in the measuring of small volumes by means of the micro-pipettes and in making up the "unknowns".

For the aluminium the determinations are very good. Gallium and indium also give very satisfactory values. The results for thallium are, perhaps, the least satisfactory. This may be due in part to the fact that thallium oxinate is light-sensitive, and superficial decomposition may occur.

Although the upper limit is given as 500 μg, experiments have shown that this may be increased to 1 mg for gallium, indium and thallium. Aluminium and indium are the bands closest to one another on the chromatogram and, if the ratio of one to the other is increased beyond 25·1, the bands tend to touch.

The behaviour of other elements with the solvent-mixture was investigated. The Rf values of some of them are as follows:

Copper 0·25; iron 0·40; cadmium 0·33; nickel 0·15; chromium 0·15; zinc 0·35.

It will be seen from these figures that many important elements will not interfere with the separation, so that the method may be capable of wider application.

Zusammenfassung—Eine Methode zur papierchromatographischen Trennung und nachfolgenden Bestimmung kleiner Mengen von Aluminium, Gallium, Indium und Thallium wird beschrieben. Die Chloride der Metalle werden getrennt mittels einer Mischung von Phenol: Methanol: conc. Salzsäure (50 : 30 : 20 g/ml/ml). Alle Ionen werden mit einem einzigen Sprühreagens, nämlich Oxin, nachgewiesen. Die Mengen können halbquantitativ durch Vergleich der erhaltenen Flecken mit denen von Standardlösungen erzeugten bestimmt werden.

Die Metalloxinate können mittels organischer Lösemitteln vom Papier gelöst und spectrophotometrisch bestimmt werden.

Résumé—Les auteurs décrivent une méthode de séparation chromatographique et de dosage de faibles quantités d'aluminium, de gallium, d'indium et de thallium. On sépare les chlorures métalliques en utilisant un mélange de solvants contenant du phénol, du méthanol, de l'acide chlorhydrique concentré (50, 30, 20, P.V.V). Chaque substance est décelée par une simple pulvérisation d'oxine, et on dose semi-quantitativement la quantité d'élément présent par comparaison visuelle avec des étalons.

L'étude des conditions pour séparer du papier les oxinates métalliques dans un solvant organique a permis le dosage des éléments par spectrophotométrie.

REFERENCES

[1] G. Charlot and D. Bezier, *Analyse Quantitative Minerale*, 3 edition, Masson et C^{ie}, Paris 1955 p. 548: J. A. Scherrer, *J. Research Nat. Bur. Standards*, 1935, **15**, 585: E. Gastinger, *Z. analyt. Chem.*, 1953, **140**, 245.

[2] J. F. Steinbach and H. Freiser, *Analyt. Chem.*, 1954, **26**, 375.

[3] R. Klement and H. Sandman, *Z. analyt. Chem.*, 1955, **145**, 326.

[4] H. Specker and E. Bankmann, *ibid.*, 1956, **149**, 97.

[5] T. V. Arden, *et al.*, *Nature*, 1948, **162**, 691.

[6] L. G. Bassett and F. S. Tompkins, *Analyt. Chem. Manhattan Project*, 1950, 382.

[7] R. J. Magee and J. B. Headridge, *Analyst*, 1957, **82**, 95.

[8] T. V. Arden, *et al.*, *loc. cit.*

[9] T. Moeller and A. J. Cohen, *Analyt. Chem.*, 1950, **22**, 686.

[10] E. B. Sandell, *Analyt. Chem.*, 1947, **19**, 63: *Ind. Eng. Chem. Anal.*, 1941, **13**, 844.

[11] S. Lacroix, *Analyt. Chim. Acta*, 1947, **1**, 260.

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A STUDY OF THE CONDITIONS FOR THE DETERMINATION OF BORON WITH DIANTHRIMIDE

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Summary—The reaction between boric acid and dianthrimide in concentrated sulphuric acid has been studied from an analytical point of view using a statistically planned experimental design. Certain interactions between the different factors affecting the reaction that have not previously been taken into account were found to be significant. Thus, the reaction rate is affected by both the acid and the dianthrimide concentrations. The temperature at which the reaction is carried out affects the absorbance less at higher acid concentrations. Suitable analytical conditions are described.

THE analytical laboratory at the Swedish Institute for Metal Research has for a long time used a method for the determination of boron in iron and low-alloy steel based originally on a method given by Rudolph and Flickinger.[1] Boron is determined colorimetrically using quinalizarin without any preliminary separations. It has been found possible to replace the quinalizarin with 1:1'-iminodianthraquinone (dianthrimide) which has a greater sensitivity as well as other favourable properties. A preliminary method has now been in use for two or three years with good results but a systematic investigation of the dianthrimide method seemed desirable. The results of this investigation are described in two papers, this dealing with problems connected with the colorimetric determination of boric acid and a following[2] dealing with the application of the method to the determination of boron in steel.

A. CHOICE OF REAGENT

The determination of boric acid in microgram quantities requires in general the use of colorimetric methods. Curcumin is the best known reagent and probably also the most sensitive. However it requires extensive preliminary separations and the conditions must be standardised very carefully. It was therefore considered less suitable for the present purpose.

Almost all other reagents that have been used for boron are anthraquinone derivatives. The reaction between these and boric acid takes place in strong sulphuric acid solution but with proper precautions this need not cause any great practical difficulties. Many anthraquinone derivatives are very selective and have sufficiently high sensitivity for the concentration range involved. Of these quinalizarin and to a lesser extent carminic acid have been most widely used for the determination of boron in steel. This group of compounds also includes dianthrimide and the substituted hydroxyanthraquinones investigated by Cogbill and Yoe.[3]

A comparison was made of the sensitivities of quinalizarin, carminic acid and dianthrimide. The results are shown in Table I. They are expressed in $\mu g/cm^2$ as suggested by Sandell[4] and it is therefore possible to compare the results directly with those obtained by Cogbill and Yoe.

As shown in the table, dianthrimide is considerably more sensitive than quinalizarin and carminic acid. Comparison with the results obtained by Cogbill and Yoe shows that it is also somewhat more sensitive than the best reagents of the substituted hydroxyanthraquinones.

Like quinalizarin and carminic acid, dianthrimide is strongly coloured in sulphuric acid solution. The absorption maximum is however below 400 mμ and the absorption at the boron complex maximum at 620 mμ is rather small. This is a considerable advantage over quinalizarin which has absorption maxima at wavelengths very close to that of the boron complex maximum. Since a large excess of reagent is usually required for high sensitivity a high reagent absorption at the wavelength of measurement can be very troublesome. Carminic acid and most of the substituted hydroxyanthraquinones have more favourable properties in this respect than quinalizarin.

TABLE I.—SENSITIVITIES OF BORON REAGENTS

Reagent	Method	Sensitivity (μg/cm^2)
Quinalizarin	AOAC[5]	0·003
Carminic acid	Hatcher–Wilcox[6]	0·002
Dianthrimide	Method recommended	0·0006

With boric acid quinalizarin gives calibration curves that show considerable deviations from Beer's law and the useful concentration range is relatively small. Dianthrimide and carminic acid on the other hand give linear calibration curves.

Since preliminary investigations showed also that the colour reaction of boric acid with dianthrimide is relatively free from interference this appeared to be a suitable reagent for further examination. Probably some of the new reagents developed by Yoe and co-workers would also be suitable for this purpose.

B. DIANTHRIMIDE AND ITS BORON COMPLEX

The reaction between boric acid and dianthrimide is very slow at room temperature. For analytical purposes it is therefore essential to heat the reaction solution. Prolonged heating especially at temperatures over 90° gives rise to discoloration of the solutions, probably due to partial degradation of the reagent. A corresponding though less marked change in colour occurs if the reagent solution while in storage is exposed to sunlight. The green colour disappears and the solution becomes yellowish brown. However, although a reagent solution after standing for 5 days in sunlight absorbed strongly in the 400–550 mμ region it showed only a slight increase in the absorption at 620 mμ where the analytical measurements were made. Solutions of the reagent kept in the dark and protected against access of air could be stored for several months.

Attempts were made to determine the empirical formula of the boron dianthrimide complex in solution using the mole ratio method of Yoe and Jones[7] and a modified method of continuous variation.[8]

In the mole ratio method the concentration of dianthrimide was kept constant at $1{\cdot}00 . 10^{-4}M$ while the concentration of boric acid was varied within the range $1{\cdot}00 . 10^{-5}M$–$1{\cdot}00 . 10^{-3}M$. The solutions contained 90·5 % by weight of sulphuric acid and were heated in an oven for 18 hours at 70°. The results obtained indicated a mole ratio of 1 : 1 but are somewhat uncertain since the complex appears to have a low stability constant. The absorption was still increasing at a boron : reagent ratio of 10 : 1.

In the continuous variation method (Job's method) a solution of *a* ml of $2{\cdot}00 \,.\, 10^{-4}$ *M* boric acid was mixed with 30-*a* ml of dianthrimide solution of the same molar concentration. In this experiment *a* was varied between 0 and 30; the solutions contained 90·3 % by weight of sulphuric acid and were heated for 48 hours at 70°. The absorbance was measured at 460, 520, 540, 580 and 620 mμ.

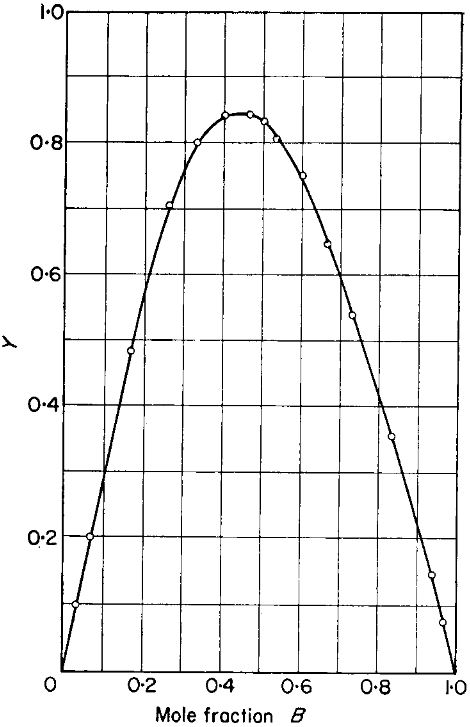

FIG. 1.—Determination of the empirical formula of the boron complex in solution using the method of continuous variation. Wavelength 620 mμ.
Y = absorbance$_{obs}$ − absorbance$_{calc}$ assuming no reaction

Fig. 1 shows the absorbance of the boron complex at 620 mμ plotted as a function of the mole fraction of boric acid. The maximum lies at a mole fraction 0·47 corresponding to a reagent-boron mole ratio of 1·1 : 1. The other wavelengths measured also gave maxima at the same mole fraction. It thus appears probable that there is only one coloured complex and that it is composed of equal numbers of boric acid and dianthrimide molecules.

C. SYSTEMATIC INVESTIGATION OF SUITABLE ANALYTICAL CONDITIONS

Dianthrimide (MW 429·41) is a rather new reagent for boron and the reaction has not yet been examined in full detail. Several modifications of the original method[9] have been described giving different acid and reagent concentrations, heating temperatures and heating times. A detailed study of the effect of these different factors seemed desirable. Since the effects of the individual factors were probably not independent of the other factors it seemed also desirable to use a factorial experiment design. Evaluation of the experimental results would then provide a statistical basis to show which of the effects of the different factors and interactions between the factors were significant and had a real effect on the results.

The levels of the different factors were selected as follows:

Sulphuric acid concentration (% by weight): 95·0, 92·5, 90·0, 87·5, 85·0, 82·5 and 80·0.
Reagent concentration (mg of dianthrimide/ml): 0·100, 0·200 and 0·400.
Boron concentration (μg boron/ml): 0·500, 1·000 and a boron-free blank solution.
Temperature (°C): 60, 80 and 100.

Since the reaction rate is strongly dependent on the temperature a series of different heating times were chosen for the different temperatures as follows:

Temp, °C	Time, *min*
60	120, 240, 480, 960
80	120, 240, 480
100	15, 30, 60, 120

Measurements were made at each temperature using all combinations of the other factors.

Solutions containing 1·000 and 2·000 μg B/ml and with 95·0, 90·0, 85·0 and 80·0% by weight of sulphuric acid were made up using boric acid (H_3BO_3 p.a. Merck). A third solution without boron was made up for each of these acid concentrations.

The reagent solutions were prepared by dissolving 0·200, 0·400 and 0·800 g of dianthrimide (Merck) in sulphuric acid (1000 ml) of the four concentrations given above.

The boron and reagent solutions were stored with protection against atmospheric moisture and the reagent solutions were kept in the dark. The sulphuric acid solutions were prepared by mixing 97% acid with the calculated amount of a diluted acid. The concentrations were determined by acidimetric titration with 0·25*M* NaOH and adjusted to the required level.

The reaction solutions were heated at 60° and 80° in a thermostat-controlled water bath and at 100° in boiling water. The reaction was carried out in Pyrex Erlenmeyer flasks (Jobling) which after repeated treatment by heating in concentrated sulphuric acid did not give off boron in amounts sufficient to interfere with the analyses.

For each determination, boron solution (10 ml) and reagent solution (10 ml) of the same acid concentration were transferred to a 50 ml Erlenmeyer flask with a ground glass stopper. The mixture was heated for a given time at a given temperature in the water bath and then cooled rapidly to 20° in cold water. The absorbance of the solution at 620 mμ was then measured in a 1-cm cell against a boron-free blank with the same reagent and acid concentrations using a Beckman model B spectrophotometer. Acid concentrations of 92·5, 87·5 and 82·5% by weight were obtained by using a reagent solution with the next higher acid concentration and a boron solution with the next lower acid concentration. The amount of heat evolved on mixing and the deviation from the required concentration are very slight.

The results obtained from 396 absorbance measurements were evaluated by analysis of variance. Since no replications were made the highest order interactions were used to estimate the error. The results for the 80% acid concentration were excluded from this calculation, as a complete set of measurements at this level could not be made because it was not possible to dissolve 0·8 g of dianthrimide in 1000 ml of sulphuric acid of this concentration.

Some diagrams have been given to illustrate the results of analytical interest obtained from these factorial experiments. As expected the analysis of variance showed that all the effects of the factors varied were significant and that a number of interactions between the factors were also significant.

Heating time

The reaction rate is of course affected by the heating temperature and it was found that the time required for the reaction to reach equilibrium was four times as long at 80° as at 100°. Of greater interest is the marked influence on the reaction rate of the acid and reagent concentrations.

Fig. 2 shows the absorbance as a function of the heating time for different acid concentrations at 100°. Each point in the diagram represents a mean value for the six combinations of boron and reagent concentrations. It is clearly apparent that an increased acid concentration is accompanied by a strong reduction in the reaction rate. In 85% sulphuric acid equilibrium is reached after only 15 minutes heating while in 95% sulphuric acid the reaction is not complete after 2 hours heating. The results for 60° and 80° were similar.

Fig. 3 shows the absorbance as a function of the heating time for different reagent concentrations at 100°. Each point in the diagram represents a mean value of the absorbances for the twelve combinations of boron and acid concentrations. It is clear that an increase in the reagent concentration increases the rate of reaction.

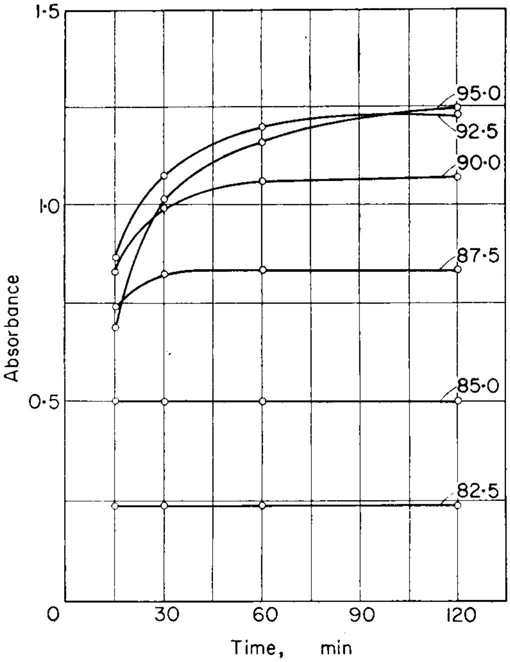

FIG. 2.—Absorbance of the boron complex as a function of the heating time at different acid concentrations (% by weight). Temp. 100°.

The boron concentration on the other hand does not appear to have any effect on the reaction rate. The ratio of the absorbances for the two boron concentrations was the same for different heating times. It should therefore be possible in making a boron determination to interrupt the reaction at any given time before equilibrium was reached but this can hardly be of any great practical interest.

The discussion below of the dependence of the absorbance on other factors will deal only with heating times for which it can be presumed that the reaction will be complete.

Temperature

Baron,[10] in an investigation of the use of dianthrimide for the determination of boron in plant material, found that the same absorbance is obtained when the colour reaction is done at 70°, 85° or at 100° while in a recently published investigation[11] it is stated that temperature variations of only a few degrees can give erroneous results. Our experiments showed that the temperature had a significant effect on the absorbances obtained but that this effect was dependent on the acid concentration. Fig. 4 shows an example of this. At the two highest acid concentrations the absorbance was the same at all three temperatures but if the acid concentration was reduced to 90% or lower the absorbance fell appreciably with the heating temperature. This effect was always greater at lower reagent concentrations. In 90% sulphuric acid at 100° the absorbance was 11% lower than at 80° for the lowest

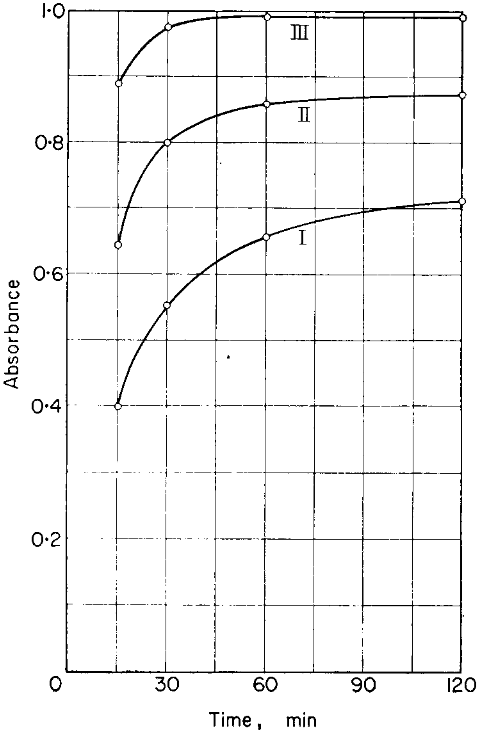

FIG. 3.—Absorbance of the boron complex as a function of the heating time at different dianthrimide concentrations. (I 0.1, II 0.2, III 0.4 mg/ml.) Temp. 100°.

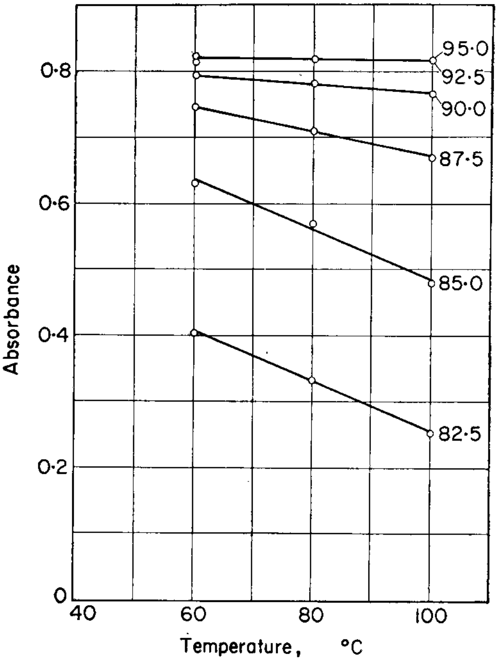

FIG. 4.—Absorbance of the boron complex at different temperatures and acid concentrations (% by weight). Boron 0.5 μg/ml. Dianthrimide 0.4 mg/ml.

reagent concentration but the corresponding value for the highest reagent concentration was 2%. At the lowest reagent concentration the effect of the temperature was already noticeable in 92·5% acid.

It was mentioned earlier that the reagent is discoloured by prolonged heating at higher temperatures, presumably due to degradation. At low acid concentrations such a degradation of the reagent can be expected to reach appreciable values before the reaction between boric acid and dianthrimide is complete.

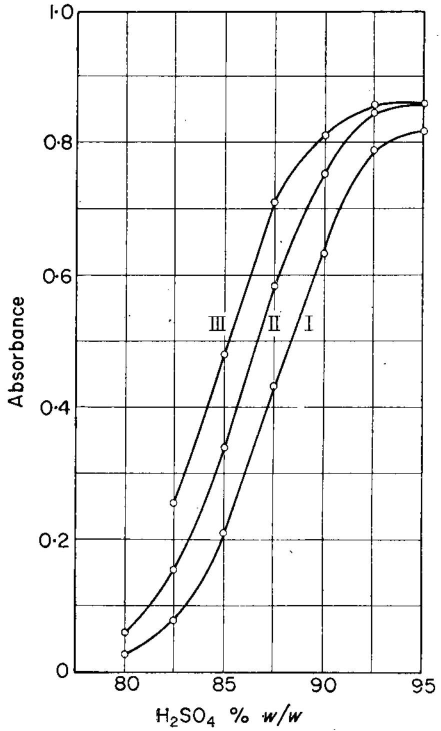

FIG. 5.—Absorbance of the boron complex at different acid and dianthrimide concentrations. I 0.1, II 0.2, III 0.4 mg dianthrimide/ml. Boron 0.5 μg/ml. Temp. 100°. Heating time 120 min.

Sulphuric acid concentration

As in the use of other anthraquinone derivatives it is essential to have a high sulphuric acid concentration. Fig. 5 shows how the absorbance of the boron complex increases with the acid concentration. This increase is rather large at acid concentrations less than 90% and this should therefore be taken as a minimum for analytical use; above this minimum the variations due to any changes in the acid concentration are smaller the higher the reagent concentration. MacDougall and Biggs found the same tendency in the determination of boron with quinalizarin.[12]

If the concentration of the acid is reduced from 92·5 to 90% the heating temperature begins to affect the result, as is shown in Fig. 4. The consequent decrease in the absorbance is only half as great at 60° as at 100°.

Reagent concentration

As discussed above there is reason to suppose that dianthrimide and boric acid react in a ratio of 1 : 1 and that a large excess of reagent is required for Beer's law to apply. In this investigation the molar ratio between reagent and boron has been varied between 2·5 and 20·2. Fig. 5 shows that the absorbance increases with the reagent concentration but that at the highest acid concentrations there is only a very small increase when the reagent concentration is increased from 0·2 to 0·4 mg/ml.

Calculation from the results obtained of the ratio of the absorbances at the lower and the higher boron concentrations for increasing reagent concentrations gives the values 0·532, 0·512 and 0·502. Only the last of these values indicates a direct proportionality to the boron concentrations. This means that the reagent/boron ratio must be of the order of 10 if a linear calibration curve is to be obtained.

D. DISCUSSION OF THE RESULTS

The optimum conditions for an analytical method are not determined by high sensitivity alone. It is also important that moderate variations in the conditions should have as little effect as possible on the results. The factorial experiment showed that both these requirements could be satisfied. Suitable conditions were found to be: Dianthrimide 0·4 mg/ml; sulphuric acid 93–95% by weight; boron 0·3–1·0 μg/ml; heating time at 100°, 1–1·5 h; or, for instance at 80°, 4–5 h.

The choice of reagent concentration is a question of judgement. At 0·2 mg/ml the sensitivity is almost as high as at 0·4 mg/ml. The lower concentration is more advantageous from the point of view of the reagent absorption but at the higher concentration the sulphuric acid concentration can be allowed to vary over a wider range. Although the dianthrimide reagent absorbs comparatively little at 620 mμ the high concentration gives a quite appreciable blank. The reagent absorption is proportional to the concentration but also increases significantly with the acid concentration. It is therefore essential to use high precision in adding the reagent. Particularly at low boron concentrations, however, the disadvantages of a high blank can outweigh the advantage of lower sensitivity to small variations in the conditions that is obtainable at high reagent concentrations. It may then be desirable to reduce the reagent concentration but the mole proportion of dianthrimide to boron should not be much less than 10. The longer heating times this requires can be reduced in certain cases by carrying out the reaction in a small volume and then diluting with sulphuric acid to the desired volume.

The sulphuric acid concentration can be varied within the specified range and a little to either side without affecting the results. Supplementary experiments showed that there was no advantage to be gained by increasing the acid concentration over 95% by weight. The sensitivity slowly decreases and there will also be a further reduction in reaction speed and a greater reagent absorption. Baron reached somewhat different conclusions on the effect of the acid concentration. He obtained an appreciably lower sensitivity in concentrated sulphuric acid (s.g. 1·84) than in solutions with a lower acid concentration. It could however be questioned whether the heating period of 5 hours at 70° used by Baron was sufficient to reach equilibrium at the highest acid concentrations.

The absorbances for the boron concentrations given, when measured against a reagent blank in 1-cm cell, fall within a range of 0·5–1·7 which is suitable for the photometer used (Beckman B). However most photometers work best at lower absorbances and with these it is necessary to use a lower boron concentration.

The heating temperature can be selected arbitrarily within the range investigated, 60–100°, but at 60° the rate of reaction is inconveniently low. The times given must be increased if an oven is used instead of a waterbath since temperature equilibrium is reached more slowly. Unnecessarily long heating at the highest temperatures should be avoided since the reagent gradually decomposes causing a decrease in the accuracy of the determination.

The conditions found most suitable in this investigation can be used for boron determination after separation of the boron by distillation. The alkaline residue must then of course be free from organic material. In other methods of separation such as electrolysis with a mercury cathode and ion-exchange the sample is usually in the form of a solution in weak sulphuric acid. Concentration of this solution by evaporation to fumes of sulphuric acid leads to loss of boron. If however the solution is made $2M$ in sulphuric acid it can be evaporated at 100° without noticeable loss of boron. An example of the use of this method for the determination of boron in steel is given in a following paper.[2]

Acknowledgement—The author wishes to express his thanks to Dr. Axel Johansson, Royal Institute of Technology, Stockholm, for valuable discussions.

Zusammenfassung—Die Reaktion zwischen Borsäure und Dianthrimid in konzentrierter Schwefelsäure wurde vom analytisch-chemischen Standpunkte aus statistisch untersucht. Es wurde gefunden, dass das Zusammenwirken verschiedener, früher nicht berücksichtigter Faktoren die Reaktion in signifikanter Weise beeinflusst. So z.B. wird die Reaktionsgeschwindigkeit sowohl durch die Konzentration der Schwefelsäure als auch die des Dianthrimids beeinflusst. Die Temperatur, bei der die Reaktion abläuft, hat auf die Absorption weniger Einfluss bei hoher Säurekonzentration. Brauchbare analytische Bedingungen werden mitgeteilt.

Résumé—La réaction entre l'acide borique et la dianthrimide dans l'acide sulfurique concentré a été étudiée d'un point de vue analytique en utilisant une méthode expérimentale contrôlée statistiquement. Certaines interactions entre différents facteurs affectant la réaction dont on n'avait pas tenu compte précédemment, se sont révélées significatives. Ainsi, la vitesse de la réaction est influencée par les concentrations et de l'acide et de la dianthrimide. La température à laquelle a lieu la réaction affecte moins l'absorption aux plus hautes concentrations d'acide. On décrit des conditions analytiques appropriées.

REFERENCES

[1] G. A. Rudolph and L. C. Flickinger, *Steel*, 1943, **112**, 114.
[2] L. Danielsson, *Talanta*, 1959, **3**, 203.
[3] E. C. Cogbill and J. H. Yoe, *Analyt. Chim. Acta*, 1955, **12**, 455.
[4] E. B. Sandell, *Colorimetric Determination of Traces of Metals*. Interscience N.Y., 2nd Ed., 1950, p. 49.
[5] *Official Methods of Analysis*. Ass. Off. Agr. Chem. Washington, D.C., 7th Ed., 1950.
[6] J. T. Hatcher and L. V. Wilcox, *Analyt. Chem.*, 1950, **22**, 567.
[7] J. H. Yoe and A. L. Jones, *Ind. Eng. Chem. Analyt.*, 1944, **16**, 111.
[8] W. C. Vosburgh and G. R. Cooper, *J. Amer. Chem. Soc.*, 1941, **63**, 437.
[9] G. H. Ellis, E. G. Zook and O. Baudisch, *Analyt. Chem.*, 1949, **21**, 1345.
[10] H. Baron, *Z. analyt. Chem.*, 1954, **143**, 339.
[11] B.I.S.R.A., Methods of Analysis Committee, *J. Iron Steel Inst.*, 1958, **189**, 227.
[12] D. MacDougall and D. A. Biggs, *Analyt. Chem.*, 1952, **24**, 566.

Talanta, 1959, Vol. 3, pp. 147 to 150. Pergamon Press Ltd. Printed in Northern Ireland

ANALYTICAL APPLICATION OF XYLENOL ORANGE—IV*

A SPECTROPHOTOMETRIC STUDY OF THE FERRIC XYLENOL ORANGE COMPLEX

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Summary—The purplish red ferric Xylenol Orange complex has been studied spectrophotometrically. It offers a reasonably sensitive and selective reaction for determining ferric iron. But it requires a rather narrow acidity (0.04 to 0.05*N*) for maximum colour development. It is a 1 : 1 complex and has a formation constant of 5×10^5 under the conditions studied.

XYLENOL Orange forms a purplish red coloured complex with ferric iron in an acid medium. The coloured complex tends to fade upon standing, however, it offers a very sensitive colour reaction for iron. This paper reports the conditions for the colour formation of the complex, its composition, its formation constant, and the interference.

APPARATUS AND REAGENTS

Standard iron solution

A $1.79 \times 10^{-2}M$ ferric nitrate nonahydrate was prepared in 0.01*N* perchloric acid solution and standardized by EDTA. A solution of $1.79 \times 10^{-4}M$ iron in 0.05*N* perchloric acid was made by appropriate dilution of the stock solution.

Other apparatus and reagents are the same as those reported previously.[1]

EXPERIMENTAL

Calibration curve

Pipette 5 to 50 μg of iron into a 25-ml volumetric flask. Add 4 ml of 0.05% Xylenol Orange in 0.05*N* perchloric acid, dilute to volume with 0.05*N* perchloric acid and mix. Measure the absorbance after 15 minutes at 550 mμ using the reagent blank. Beer's law is followed. The molar absorptivity was found to be 26,600.

RESULTS

Absorption spectra

The spectra for Xylenol Orange and its ferric complex are shown in Fig. 1. The maximum absorption of the complex is at 550 mμ.

Effect of acidity

Fig. 2 shows that the optimum perchloric acid concentration for the colour formation of the ferric Xylenol Orange complex is 0.04 to 0.06*N*. Above 0.075*N*, the absorbance drops sharply. The ferric Xylenol Orange complex requires a low and very narrow acidity range as compared with the Xylenol Orange complexes of zirconium and hafnium. Hydrochloric acid may also be used giving a similar curve to perchloric acid. Sulphate showed somewhat of a masking effect on complex formation. It was noticed that at the higher acidity, the complex faded rather rapidly.

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* Part III, *Talanta*, 1959, **3**, 81.

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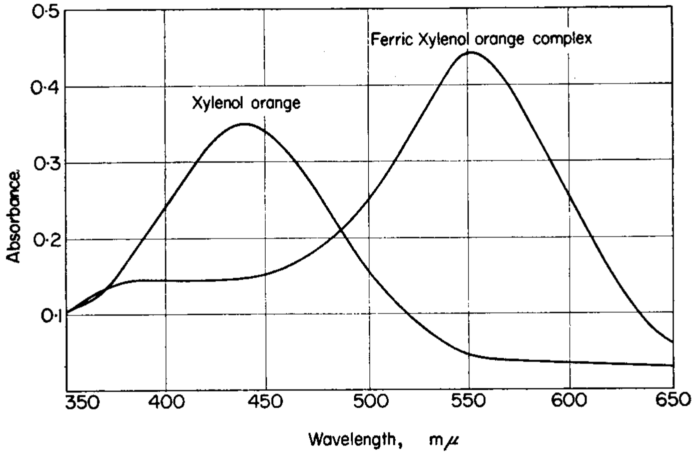

Fig. 1.

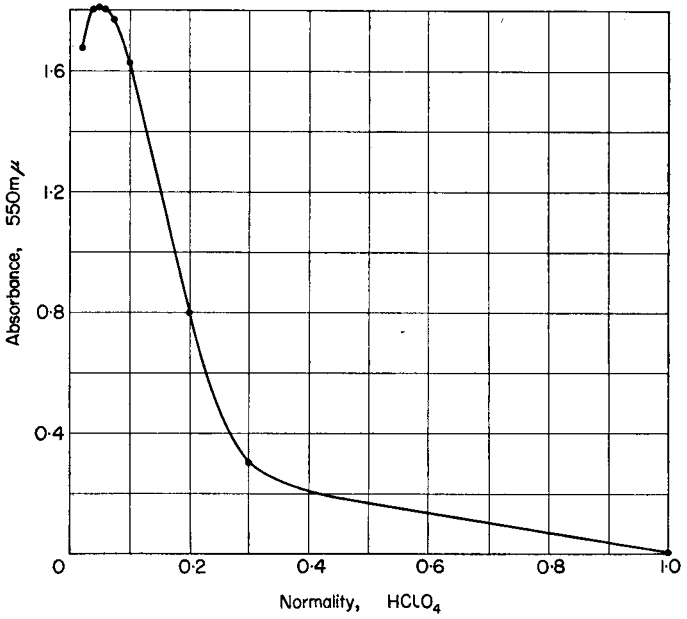

Fig. 2.

The absorbance measurements were made 15 minutes after addition of Xylenol Orange.

Effect of amount of Xylenol Orange

Fig. 3 shows that for 50 μg of iron, 3 to 4 ml of 0.05% Xylenol Orange solution are required. As happened with zirconium and hafnium, large amounts (more than 4 ml of 0.05%) of Xylenol Orange tend to decrease the absorbance.

Interference

Only a few metals in 0.2*N* sulphuric acid medium form a red or purplish colour with Xylenol Orange.[1] Table I indicates the extent of the effect of these interfering

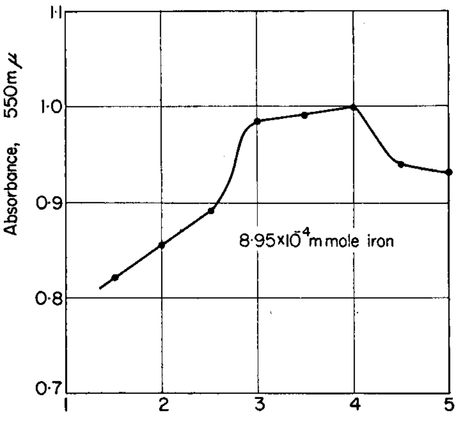

FIG. 3.

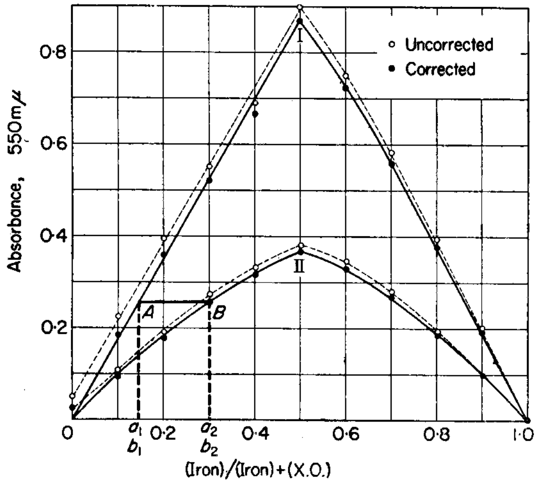

FIG. 4.

metals and of some anions. Some of the interfering metals can be completely or partially masked by the masking agents.

Complex formation

Like zirconium and hafnium, ferric iron also forms a 1 : 1 complex with Xylenol Orange as indicated by Job's method (Fig. 4). The formation constant was calculated from the curves shown in Fig. 4, based on the method used previously.[2] It was found to be 5×10^5 in 0.05*N* perchloric acid.

As compared with the complexes of zirconium and hafnium, the iron Xylenol Orange complex requires a lower and narrower acidity, shows a maximum absorption at longer wave length, and forms a slightly weaker complex (also 1:1). However, this dye ($E_{max} = 26{,}600$) offers a higher sensitivity for iron than other commonly known iron reagents such as *o*-phenanthroline ($E_{max} = 11{,}100$) and bathophenanthroline

TABLE I.—EFFECT OF FOREIGN IONS

Taken: 20 μg iron

Ion	Amount added	Iron recovered, %	Remarks
Fluoride	0.1 mmole	64.6	
	0.1 mmole	97.8	0.25 mmole Be^{II} added
	0.1 mmole	99.7	1.0 mmole Be^{II} added
Chloride	10 mmoles	99.0	
Citrate	0.17 mmole	89.3	
	0.1 mmole	98.1	
Orthophosphate	0.15 mmole	97.0	
Sulphate	0.3 mmole	98.4	
	3.1 mmole	85.0	
H_2O_2	1 ml. 30%	108.1	
Bismuth	1×10^{-4} mmole	100.0	10 mmoles chloride added
Molybdenum	0.008 mmole	99.0	1 ml. 30% H_2O_2 added
Zirconium	0.01 mmole	216.5	1 ml. 30% H_2O_2 added
Niobium	0.01 mmole	98.4	
Tin^{II}	0.01 mmole	333.1	
	0.001 mmole	143.6	
	0.0001 mmole	102.9	
Tin^{IV}	0.01 mmole	456.0	1 ml. 30% H_2O_2 added
	0.001 mmole	180.0	1 ml. 30% H_2O_2 added
	0.0001 mmole	112.6	1 ml. 30% H_2O_2 added
	0.001 mmole	205.5	no H_2O_2 added
	0.0001 mmole	105.8	

($E_{\max} = 22{,}400$). It is expected that this dye would find many applications where a highly sensitive reaction for iron is desired. For example this proposed method would be useful in determining traces of iron in nickel-iron thin film (permalloy).

Zusammenfassung—Der purpur rote ferritische Xylenol Orange Komplex ist spektrophotometrisch untersucht worden. Er liefert eine ziemlich empfindliche und selektive Reaktion zur Bestimmung von Eisen. Die Äzidität muss jedoch in engen Grenzen (0.04 bis 0.06*N*) gehalten werden um maximale Farbbildung zu erhalten. Es handelt sich um einen 1 : 1 Komplex mit einer Bildungs-konstante von 5×10^5 unter den untersuchten Bedingungen.

Résumé—Le complexe ferrique rouge-pourpre du Xylenol Orange a été étudié par spectrophotométrie. Il donne une reaction assez sensible et selective pour la détermination du fer. Mais il nécessite une bande d'acidité étroite (0.04 á 0.06*N*) pour obtainer le maximum de coloration. Il a un rapport de complexe 1 : 1 et une constante de formation de 5×10^5 dans les conditions étudiées.

REFERENCES

[1] K. L. Cheng, *Talanta*, 1959, **2**, 61.

[2] *Idem*, *ibid.*, 266.

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ORGANIC ANALYSIS—XX*

MICROESTIMATION OF BLOOD SUGAR WITH 5-HYDROXY-1-TETRALONE

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(*Received* 21 *July* 1959)

Summary—Blood sugar is estimated with 0·02 ml of blood, measuring the fluorescence produced with 5-hydroxy-1-tetralone in sulphuric acid.

IN the previous papers of this series, it was shown that 5-hydroxy-1-tetralone gave, when heated in sulphuric acid,[1] a green fluorescence sensitively and selectively with hexoses, oligosaccharides, and polisaccharides which contained hexose unit in their molecule, and that the fluorescence intensity had a linear correlation with the concentration of glucose in definite conditions.[2] The fluorescent compound produced in this reaction was also isolated in crystalline form, and its probable structure was forwarded as benzonaphthenedione.[3] This paper describes the microestimation of blood sugar with the reagent.

EXPERIMENTAL

Reagents

Trichloroacetic acid solution—5 g of trichloroacetic acid, JIS† 1 st. grade, was dissolved in 100 ml of water.

*5-Hydroxy-*1*-tetralone solution*—100 mg of 5-hydroxy-1-tetralone was dissolved in 400 ml of conc. sulphuric acid, JIS 1 st. grade, and stored in a refrigerator.

Standard glucose solution—Stock solution was prepared by dissolving 100 mg of dried glucose in sufficient 0·21 % aqueous solution of benzoic acid to measure 100 ml. Glucose solution, 10 μg/ml, was freshly prepared by diluting 1 ml of the stock solution to 100 ml with water.

Fluorescence intensity

This was measured by a Hitachi L-3 fluorometer attached to a Type EPU-2 spectrophotometer with a glass cell of 10-mm optical length. The ultraviolet light, emitted from a high-pressure mercury lamp, was passed through a filter of 365 mμ.

Procedure

0·02 Ml of blood was pipetted with a dried Sahli's pipette for haemoglobin estimation, and the outside of the pipette was wiped with defatted and moistened deerskin. The blood was introduced into 0·5 ml of water placed in a micro centrifuge tube, and the inside of the pipette was rinsed several times with the water. The contents were mixed and haemolysed, 0·5 ml of 5 % trichloroacetic acid was added, mixed, and set aside for 5 minutes. The mixture was diluted with 0·98 ml of water to measure 2 ml, and centrifuged. Two aliquots of 0·5 ml of the supernatant clear solution were pipetted into glass-stoppered test-tubes, and 2 ml of 0·025 % reagent solution was added to each tube under ice cooling. The mixture was then heated in a boiling water bath for 40 minutes, cooled in ice water, and diluted with 7·5 ml of water before measuring its fluorescence intensity.

At the same time, two aliquots of 0·5 ml of 10 μg/ml glucose solution and two aliquots of 0·5 ml of water were treated in the way described, to act as standard and blank solutions.

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* Part. XIX: *Chem. Pharm. Bull.* (*Tokyo*), 1959, **7**, in press.

† Japanese Industrial Standards.

The relative fluorescence intensity was measured at 532 mμ, adjusting the intensity of the solution obtained from 10 μg/ml glucose to 50%. Two values for each aliquot were averaged unless unexpected error occurred. The calibration curve was obtained by combining two intensities of blank and standard solutions (Fig. 1). Blood sugar in mg/dl was calculated by multiplying the number of μg/ml by 10, which was obtained from the calibration line.

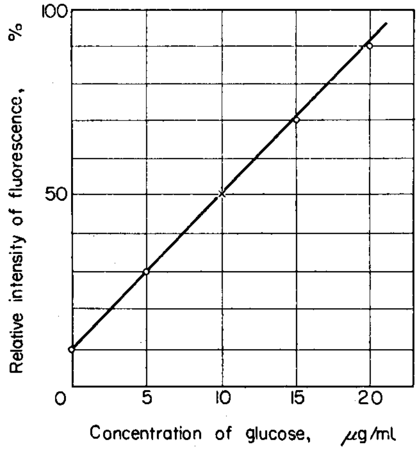

FIG. 1.—Calibration curve.

TABLE I.—FLUORESCENCE INTENSITY* OF DEVELOPED BLOOD, DEPROTEINISED BY THREE METHODS

	Deproteinising method								
	$Zn(OH)_2$ method			Na_2WO_4 method			CCl_3COOH method		
Blood	1	2	3	1	2	3	1	2	3
Deproteinised soln, 0·5 *ml* + H_2O, 0·5 *ml*	47·0	47·5	48·0	46·5	49·0	48·5	50·8	51·5	51·5
Deproteinised soln, 0·5 *ml* + 20 *μg/ml* glucose 0·5 *ml*	81·5	82·0	83·2	81·3	83·5	83·7	87·3	86·8	88·0
Blank, H_2O, 1 *ml*	8·3	8·5	8·5	9·0	8·5	8·5	9·0	8·5	8·5

* The intensity produced from 1 ml of 20 μg/ml glucose was taken as standard 100.

RESULTS AND DISCUSSION

Deproteinization of blood was successfully carried out with zinc hydroxide,[4] sodium tungstate,[5] and trichloroacetic acid without influence upon the fluorescence (Table I). But the last reagent was simple to use, and gave a larger value of blood sugar than the others, which coincided with the value obtained by Hagedorn's method.[6] The concentration of trichloroacetic acid showed no influence upon the fluorescence in a range of 0·05–0·3% in the final solution.

A large amount of glycerol gave the same fluorescence with the reagent,[1] and in consequence the influence of glyceride in blood was studied. A deproteinised blood solution was divided in two portions. One portion was defatted by extracting for 3 hours with ether, and was then developed with the reagent and compared with the other. The same value for the fluorescence intensity was observed in each solution. Other substances in blood which gave a fluorescence with sulphuric acid, showed no influence upon the intensity. They showed a faint blue fluorescence when a deproteinised blood solution was heated with 80% by volume of sulphuric acid and diluted with water, but the fluorescence intensity was negligible at the wavelength of 532 mμ.

TABLE II.—BLOOD SUGAR VALUES (*mg*/100 *ml*)

Blood	1	2	3	4	5	6	7	8
Present method	89	88	102	96	81	89	103	75
Hagedorn's method	91	89	100	98	82	92	102	73

TABLE III.—RECOVERY TEST

Blood sugar values,* μg/ml.	Glucose added, μg	Glucose found, μg	Recovery, %
5·3	2·5	7·8	100
5·3	5·0	10·2	98
5·2	2·5	7·6	96
5·2	5·0	9·9	94
2·1	5·0	7·1	100
2·1	10·0	12·3	102
2·9	5·0	7·7	96
2·9	10·0	12·9	100
2·3	4·0	6·6	107
2·3	10·0	12·3	100

* The amount of glucose in 1 ml of deproteinised blood.

The calibration curve was based on the fluorescence intensities of standard and blank solutions. Other intensities of the fluorescence produced by glucose solutions were almost on the line in a range of 0–20 μg/ml. But if the concentration of glucose exceeds this range, the development of fluorescence should be carried out with a diluted solution.

The values of blood sugar found are shown in Table II, and almost agree with those obtained by Hagedorn's method, though the latter gives the amount of reducing sugar, and can not be exactly compared with the present method.

A recovery test was carried out by adding a known amount of glucose to the water, by which the measured blood was haemolysed. The results showed an average rate of 97·3%, and the maximum error of 7%.

Sources of errors

5-Hydroxy-1-tetralone reacts in sulphuric acid with polysaccharides such as cellulose, and therefore contamination with cotton dust may cause a large error. The reagent solution should be stored in a glass-stoppered bottle covered with a small beaker. Pipette and test-tubes should be quite clean before the development of fluorescence. Moistened deerskin is satisfactory for use in the wiping of pipette. The fluorescence intensity increases with rising temperature, and should be read at 15–25°.

Zusammenfassung—Blutzucker wurde in 0·02 ml Blut bestimmt durch Messen der Fluoreszenz, die mit 5-Oxy-I-tetralon in Schwefelsäure entsteht.

Résumé—Le sucre dans le sang a été évalué dans 0,02 ml de sang par mesure de la fluorescence obtenue avec l'hydroxy 5 tetralone 1 dans l'acide sulfurique.

REFERENCES

[1] T. Momose and Y. Ohkura, *Pharm. Bull.* (*Tokyo*), 1956, **4,** 209.
[2] *Idem, Chem. Pharm. Bull.* (*Tokyo*), 1959, **7,** 31.
[3] *Idem, ibid.*, 1958 **6,** 412.
[4] M. Somogyi, *J. Biol. Chem.*, 1945, **160,** 69.
[5] O. Folin and H. Wu, *ibid.*, 1919, **38,** 81.
[6] H. C. Hagedorn and B. N. Jensen, *Biochem. Z.*, 1923, **135,** 46.

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SPECTROPHOTOMETRIC DETERMINATION OF THORIUM WITH NEOTHORONE

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Summary—In the spectrophotometric method for the determination of thorium with Neothorone, the peak of the absorption spectrum of the thorium-Neothorone solution against a Neothorone blank solution lies between 570 mμ and 580 mμ. A suitable pH for the sample solution in the determination is 2, when the colour of the thorium-Neothorone solution ceases to change about one hour after colour development. Besides several ions reported already, anions such as nitrate and citrate ions also interfere with the colour reaction between thorium and Neothorone.

INTRODUCTION

NEOTHORONE (*o*-arsonophenylazochromotropic acid) (NT) was proposed by Ishibashi and Higashi[1] as a chromogenic reagent for thorium (Th). At the present time, it is increasingly important in the colorimetric determination of Th[1,2] and F (indirect method),[3] because of its excellent sensitivity and selectivity. Furthermore this reagent can be used for the determination of U,[4,5] Be[6] and In,[7] and the behaviour of NT with respect to metallic ions has been studied in the considerable detail.[4,8]

The present authors report here new information regarding the spectrophotometric method for the determination of Th employing NT.

EXPERIMENTAL

Reagents

(1) Standard $ThCl_4$ solution; dissolve commercial $Th(NO_3)_4$ in water and purify the solution by ion-exchange using alginate,[9] precipitate the hydroxide with ammonia and dissolve the hydroxide in hydrochloric acid. Standardise the stock solution thus prepared titrimetrically by EDTA. It contains 5·5 mg of Th per ml. It was diluted to a suitable concentration for each experiment.

(2) 0·1% NT solution; dissolve 0·1 g of guaranteed reagent NT in water and dilute to 100 ml.

(3) Buffer solutions; prepare the following buffer solutions from guaranteed reagents;

pH 1: [KCl 4·7 g + Conc. HCl 10·5 ml] per 250 ml.
pH 2: [KCl 4·7 g + Conc. HCl 1·1 ml] per 250 ml.
pH 4: [1*N* HAc 100 ml + 1*N* NaAc 25 ml] per 250 ml.
pH 6: 125 ml of [1*N* HAc 10 ml + 1*N* NaAc 160 ml] per 250 ml.
pH 8: [NH_4Cl 6·5 g + 1*N* NH_4OH 3·8 ml] per 250 ml.

Apparatus

A Beckman Model DU Spectrophotometer with a self-recording apparatus constructed by the authors[10] was used for the measurement of absorbancy.

General procedure

For the determination of Th in aqueous solution, the following procedure was used. Pipette 1 ml of 0·1% NT solution, 5 ml of buffer solution of pH 2 and an aliquot of the sample solution containing less than 150 μg of Th into a 25 ml measuring flask; make up the volume of the solution to 25 ml with water. Allow the solution to stand for one hour or more, and measure the absorbancy in 1-cm cell at 580 mμ against either water or the blank reference solution.

All measurements were carried out at room temperature which ranged from 10° to 15°, such a temperature range having no appreciable influence on the absorbancy in these experiments.

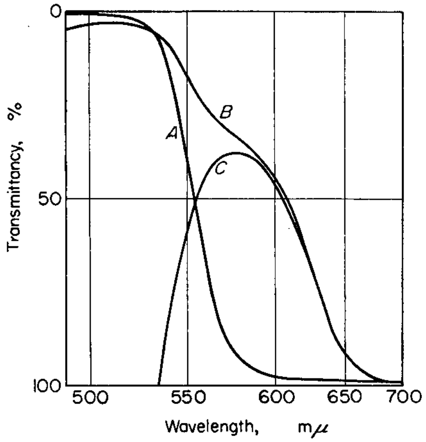

FIG. 1.—Absorption spectra.

A: NT blank solution against water.
B: Th–NT solution against water.
C: Th–NT solution against NT blank solution.

RESULTS AND DISCUSSION

Absorption spectra

The absorption spectra of a NT blank solution and a Th–NT solution against water, and of a Th–NT solution against NT blank solution at pH 2 are shown in Fig. 1 in which the ordinate represents percent transmittancy. The peak of the absorption spectrum of Th–NT solution against a NT blank solution lies between 570 mμ and 580 mμ. The peak has been reported at 600 mμ,[1] 570 mμ[3] and 580 mμ.[5]

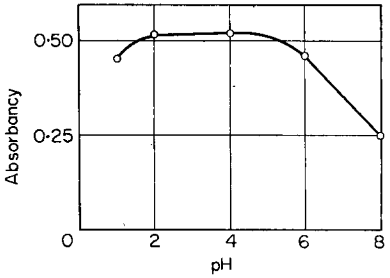

FIG. 2.—Effect of pH upon the absorption of Th–NT solution against a NT blank solution at pH 2, 580 mμ.

Effect of pH

The effect of pH upon the absorbancy of a Th–NT solution at 580 mμ is shown in Fig. 2 in which the ordinate represents the absorbancy of the solution against NT blank solution. The absorbancy has constant maximum intensity over a pH range from 2 to 4, agreeing with the results obtained by Matsuyama *et al.*[5]

Fig. 3 gives the absorption spectra of NT blank solution against water at various values pH; the curves move towards longer wave lengths with increase in pH.

Composition of the TH–NT complex

The absorbancy of Th–NT solution at 600 mμ was measured, the volume of 0·1 % NT solution added to a fixed volume of Th solution being varied. The results are shown in Fig. 4 in which the abscissa represents the mol ratio of NT to Th. The complex is apparently composed of 1 mol Th and 2 mol NT, and 1 ml of 0·1 % NT solution is therefore sufficient for less than 150 μg of Th.

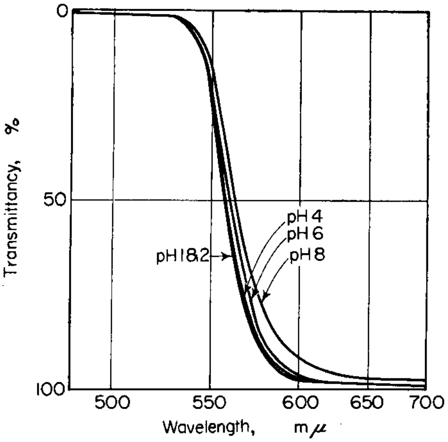

FIG. 3.—Effect of pH upon the absorption spectra of a NT blank solution against water.

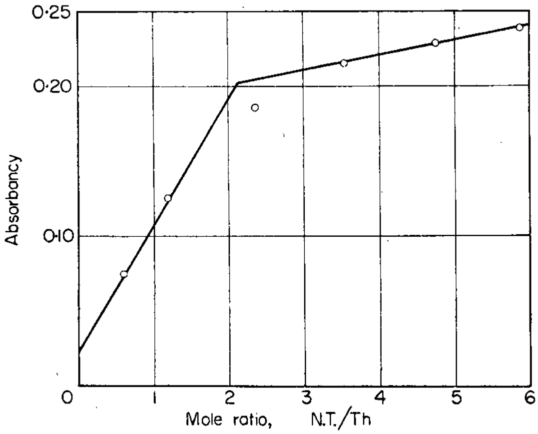

FIG. 4.—Effect of mol ratio of NT to Th upon the absorbance of Th–NT solution at pH 2, 600 mμ.

Stability of colour

It has been reported that the colour of Th–NT solution is lasting and stable. But according to the present results this is doubtful. The relationship between absorbancy at 600 mμ and time at various pH values is shown in Fig. 5. In general, the colour change of the solution is obvious during the initial period of reaction; the absorbancy of a solution of lower pH reaches a constant value after the lapse of about one hour, but at higher pH there is a continuous change of absorbancy over several hours.

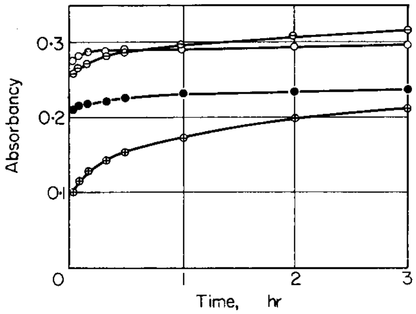

FIG.5.—S tability of the colour of Th–NT solution at 600 mμ.
⊙ pH 1: ○ pH 2: ⊖ pH 4: ⊕ pH 8.

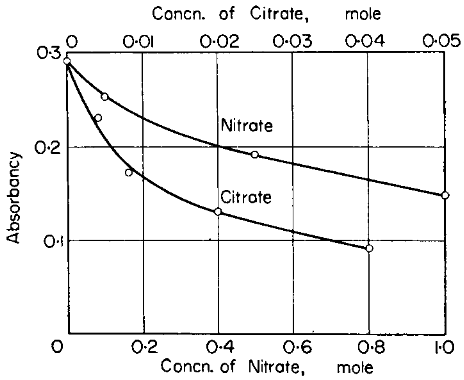

FIG. 6. —Interference of citrate and nitrate with the colour of Th–NT solution at pH 2, 580 mμ.

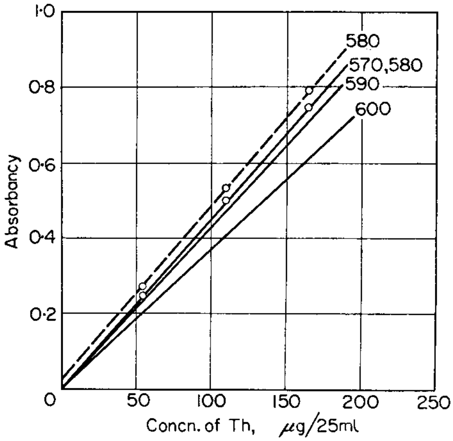

FIG.7.—Calibration curves at pH 2.
– – – – against water.
——— against NT blank solution.

Interfering ions

Ishibashi and Higashi[1] have reported that Zr, Ti, Ce, UO_2, Fe, F, PO_4, SO_4, C_2O_4, etc. interfere with the colour formed by Th. Our experiments also indicate that nitrate and citrate interfere. The magnitude of the interference of varying concentrations of these ions is shown in Fig. 6.

Calibration curve

Calibration curves at pH 2 are shown in Fig. 7. The curve is linear in the concentration range from 0 to 150 μg of Th per 25 ml, at any wave length from 570 mμ to 600 mμ, either against water or NT blank solution. At other values of pH the curve is also linear, but the absorbancy varies with time. Therefore, the measurement of the absorbancy for the determination of Th should be carried out at pH 2 and at 580 mμ.

Acknowledgement—The authors are grateful for a grant from the Ministry of Education, Japan.

Zusammenfassung—Das Absorptionsmaximum bei der spektrophotometrischen Bestimmung von Thorium mit Neothoron liegt zwischen 570 und 580 mμ, wenn gegen eine Neothoron-Blindlösung gemessen. Als geeignet für die Bestimmung wurden Arbeiten in einer Lösung von pH = 2 gefunden. Unter dieser Bedingung wurde Konstanz des Absorptionswertes eine Stunde nach Entwickeln der Färbung erzielt. Neben anderen schon berichteten Ionen wurden auch noch Nitrat- und Zitration für die Farbreaktion als störend gefunden.

Résumé—Dans la méthode spectrophotométrique de dosage du thorium avec la néo-thorone, le maximum du spectre d'absorption de la solution contenant le thorium et la néo-thorone par rapport à la solution témoin de néo-thorone se produit pour une longueur d'onde comprise entre 570 mμ et 580 mμ. On trouve qu'un pH de 2 pour la solution échantillon est convenable pour le dosage; de cette manière la couleur du complexe cesse de se modifier environ une heure après le début du développement de la couleur. De même que différents ions déjà mentionnés, des anions tels que nitrate et citrate perturbent la réaction colorée.

REFERENCES

[1] Y. Ishibashi and S. Higashi, *Japan Analyst*, 1955, **4,** 14; 1956, **5,** 135.

[2] T. Nozaki, *J. Chem. Soc. Japan, Pure Chem. Sec.*, 1955, **76,** 996.

[3] K. Emi and J. Hayami, *ibid.* 1955, **76,** 1291.

[4] S. Shibata and T. Matsumae, *Bull. Chem. Soc. Japan*, 1958, **31,** 377; 1959, **32,** 279.

[5] H. Matsuyama *et al.*, *J. Chem. Soc. Japan, Pure Chem. Sec.* 1958, **79,** 958.

[6] S. Shibata *et al.*, *Bull. Chem. Soc. Japan*, 1958, **31,** 888.

[7] T. Matsumae, *Japan Analyst*, 1959, **8,** 167.

[8] K. Emi *et al.*, *J. Chem. Soc. Japan, Pure Chem. Sec.*, 1958, **79,** 681.

[9] T. Takahashi and S. Miyake, *Bull. Chem. Soc. Japan*, 1959, **32,** 879.

[10] *Idem*, *J. Chem. Soc. Japan, Ind. Chem. Sec.*, 1959, **62,** 636.

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THE POLAROGRAPHIC DETERMINATION OF NITROGLYCERINE*

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(*Received* 26 *May* 1959)

Summary—The application of the cathode-ray polarograph for the determination of nitroglycerine in certain double base propellant compositions and blasting explosives is described. Employing an alcoholic aqueous solution of tetramethyl ammonium iodide as base solution, only one wave is seen on the conventional polarograph. When the cathode-ray polarograph is used, however, three peaks are clearly seen; these occur at —0·25, —0·45 and —0·75 V (referred to the mecury pool). Nitroglycerine is readily obtained in the ether extract of propellant compositions by measuring the peak height at —0·75 or —0·25 V.

In the case of blasting explosives, in addition to nitroglycerine, dinitroglycol and mononitrotoluene may be present in the ether extract. Dinitroglycol gives two peaks which occur at —0·45 and —0·75 V, thus coinciding with the two later peaks of nitroglycerine. Further, the isomers of mononitrotoluene give peaks which occur very near to nitroglycerine (—0·75 V). In view of this, it is necessary to use the first peak for nitroglycerine, namely that which occurs at —0·25 V. Accuracies of the order of ±2% are obtained.

A METHOD has already been described for the detremination of dibutyl phthalate in propellant compositions, using the cathode-ray polarograph.[1] In this connection it was shown that owing to interference by the large preceding wave of nitroglycerine at the sensitivity required, the orthodox polarograph could not be used for the determination of dibutyl phthalate. Whitnack *et al.*[2] have described a method for the polarographic determination of nitroglycerine in double base powders using a Sargent recording polarograph, presumably based on orthodox polarography. They use a base solution of tetramethyl ammonium chloride in a solution containing 75% alcohol. They refer only to a single wave which is used for quantitative measurement. In an earlier paper,[3] Whitnack studied the polarographic reduction of polynitrate esters; employing alcoholic solutions varying from 60–95% alcohol be obtained only one clearly visible wave. The work described here has confirmed that only one wave is obvious, extending over a very wide voltage range; close examination of the wave does, however, suggest that more than one wave may be present and this has now been shown to be so. The cathode-ray polarograph (Southern Instruments Ltd.) reveals the presence of three clearly defined reduction steps.[1]

Employing the cathode-ray polarograph, in a base solution comprising 0·05M tetramethyl ammonium iodide in 50% aqueous methanol solution, nitroglycerine gives three peaks at —0·25, —0·45 and —0·75 V (vs. mercury pool). Propellant compositions of the type shown in Table I have been analysed for nitroglycerine using the height of the third peak (—0·75 V) as a means of quantitative assessment. Certain propellants (*loc. cit.*) contain substances which reduce around —0·75 V so that in such

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cases the peak at —0·25 V must be used. This peak is not so convenient to use as it is less well defined and more subject to interference by oxygen, but it overcomes the problem of interference by other peaks produced from substances which show peaks in the vicinity of the main peak of nitroglycerine.

It was found that up to a certain level there was enhancement of the nitroglycerine peak height by the dibutyl phthalate in common with that already described for enhancement of the dibutyl phthalate by nitroglycerine,[1] but there was no effect on the blank in the determination of nitroglycerine which was due only to the base solution.

The work has been extended to the determination of nitroglycerine in blasting explosives, for which, compositions are given in Table V. The ether extract from these explosives usually contains in addition to nitroglycerine, also nitroglycol. Glycol is added to glycerine to the extent of about 20% and it is this mixture which is nitrated to give "nitroglycerine 'C'." The only other constituent of the ether extract from some types of explosives which gives a polarographic wave is mononitrotoluene. Nitroglycol gives two well defined waves on the cathode-ray polarograph. These occur at peak potentials of —0·45 V and —0·75 V, namely they are coincident with the two later peaks of nitroglycerine. For this reason it is necessary to use the wave occurring at —0·25 V peak potential for the determination of nitroglycerine. Whitnack *et al.* report only one wave for dinitroglycol;[3] this is most probably because of the difficulty of detection by orthodox polarography. When the value for amount of dinitroglycol present is required, it is a simple matter to use either the —0·45 V or the —0·75 V peaks for further measurement and deduct the height which would be obtained for the nitroglycerine present by multiplying the height of the —0·25 V peak by a predetermined factor. A peak for mononitrotoluene occurs at —0·8 V so that in its presence it is only possible to use the —0·45 V peak in addition to that at —0·25 V.

Comparison with chemical methods has shown excellent agreement for propellants containing between 2 and 35% nitroglycerine in the presence of dibutyl phthalate and, in the case of the lower percentage, also in the presence of a nitro-amine body.

Blasting explosives containing 10–27% "nitroglycerine 'C' " and in some cases about 2% mononitrotoluene have been successfully analysed for nitroglycerine and nitroglycol.

A. PROPELLANTS

Method

1. *Reagents:*

Ether: pure dry ether.

Methanol: pure anhydrous methanol.

Standard nitroglycerine:

- (a) *Stock solution:* Dissolve 1 g of *pure* nitroglycerine 'A' in 500 ml methanol in a standard flask.
- (b) *Dilute solution:* Dilute 8 ml of the stock solution to 50 ml with methanol in a standard flask. This solution contains 320 μg nitroglycerine per ml.

0·1*M tetramethyl ammonium iodide solution:* Dissolve 2 g of tetramethyl ammonium iodide which has been recrystallised 5 times from water in 100 ml of distilled water.

2. *Extraction procedure:* Weigh accurately about 1 g of the sample into a sintered-glass crucible (porosity G. 3) and extract with ether in a suitable extraction unit for six hours (alternatively pure methylene chloride may be used). Evaporate the resulting solution to dryness in a current of dry air, taking the usual precautions for handling materials containing nitroglycerine. Dissolve the residue in methanol and dilute it to 100 ml in a standard flask. Dilute 10 ml of this solution to 100 ml with methanol and use the resulting solution for the polarographic determination of nitroglycerine. When

the amount of nitroglycerine in the sample falls below about 5%, this second dilution should be omitted.

3. *Polarography using the cathode-ray polarograph:* (*a*) For samples which are free from ether soluble substances which may reduce to give peaks near to the third peak of nitroglycerine, the peak occurring at —0·75 V may be used for the estimation of the nitroglycerine. The propellants of composition shown in Table I (A and B) may be examined in this way.

(*a*) Transfer 5 ml of the methanol solution containing the nitroglycerine into a suitable glass stoppered flask, add 5 ml of methanol followed by 10 ml of the tetramethyl ammonium iodide solution. Thoroughly mix the solutions and transfer a suitable amount to a polarographic cell. The concentration of nitroglycerine in the cell should be of the order of 25–150 µg per ml. Place the cell in position in the water bath (at 25°) of the polarograph stand and connect it to a nitrogen bubbler containing equal volumes of methanol and water. Pass a stream of oxygen free nitrogen in the usual manner for a period of 5 minutes in order to remove oxygen. Disconnect the nitrogen and after choosing a suitable sensitivity setting, polarograph the solution using a start potential of —0·40 V. A well defined peak will appear at —0·75 V. Measure the wave height as the vertical height from the base line to the peak (see Fig. 1(*b*)). Repeat the whole procedure, taking 5 ml of the appropriate standard nitroglycerine solution instead of the 5 ml of methanol. Finally, carry out a blank determination on a solution containing equal volumes of methanol and the tetramethyl ammonium iodide solution. In each case take the mean of three determinations.

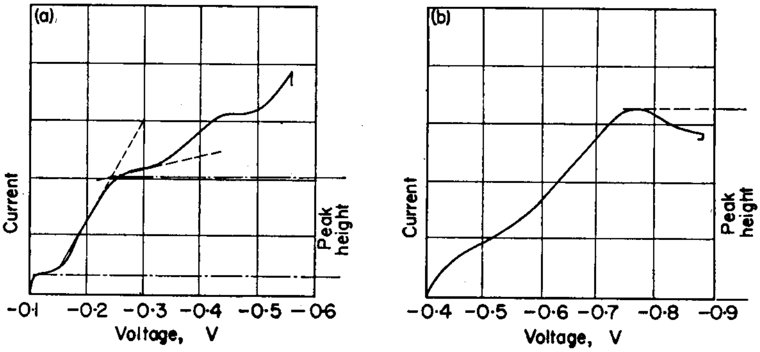

FIG. 1.—Polarograms obtained from nitroglycerine using the cathode ray polarograph and showing methods of measuring peak heights: (a) with start potential —0·1 V, (b) with start potential —0·4 V.

(*b*) If the sample contains substances which reduce near to the third wave of the nitroglycerine it is necessary to choose an earlier wave for measurement. Thus certain nitro-amine bodies which are used as stabilisers may cause interference. Using a start potential of —0·1 V the wave due to nitroglycerine, appearing as a shoulder at a potential of —0·25 V approximately is measured by the procedure shown in Fig. 1(*a*). The determination is completed in the manner described in 3(*a*) above. Since interference by oxygen is very significant at the lower voltage of —0·25 V (Fig. 2) at least 10 minutes are required for de-oxygenation.

(*c*) Calculation of results when the dilute (see 1(*b*) above) standard solution of nitroglycerine is used.

Let a = the peak height of the unknown solution from which the blank has been deducted.

Let b = the peak height of the unknown plus the standard solutions corrected as above.

The concentration C in µg/ml of nitroglycerine in the cell is given by:

$$C = \frac{a \times 80}{b - a}$$

(employing standard solution of nitroglyceine = 320 µg/ml).

From the weight of sample taken and the extent of dilution of the ether extract with methanol and knowing the volume of this methanol solution used, calculate the percentage nitroglycerine in the sample.

EXPERIMENTAL

1. *The examination of nitroglycerine using the conventional polarograph*

Whitnack *et al.* have carried out extensive investigations of the polarography of nitroglycerine and polynitrate esters.[3] In the method described for the determination of nitroglycerine[2] in double base powders they employed a base solution comprising tetramethyl ammonium chloride in 75 % alcohol solution and polarographed over the range −0·0 to −1·60 V and measured the height of the wave so obtained. Under the conditions used only a single wave is obtained.

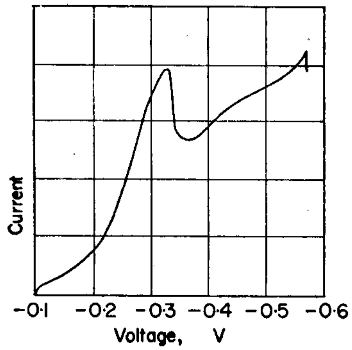

Fig. 2.—Polarogram obtained from nitroglycerine using the cathode ray polarograph showing interference by dissolved oxygen due to insufficient degassing.

Work carried out by us with a similar base solution and using Tinsley model polarograph confirmed that there is one readily distinguishable wave considerably drawn out over the voltage −0·1 to −1·3 (using a base solution of 0·05M tetramethyl ammonium iodide in alcohol solution). Gelatine (0·1 % solution) was used as maximum suppressor. When Methyl Red (as employed by Whitnack) was used as maximum suppressor it was not possible to obtain a complete wave owing to the presence of a maximum at −0·45 V which was apparently derived from the base solution and could not be readily eliminated. Figs. 3(*a*) and (*b*) show polarograms for the determination of nitroglycerine using (*a*) Methyl Red, (*b*) gelatine as maximum suppressors. Similar results were obtained both for 50 % and 75 % alcoholic solutions. As already reported in a previous paper[1] this large preceding wave for

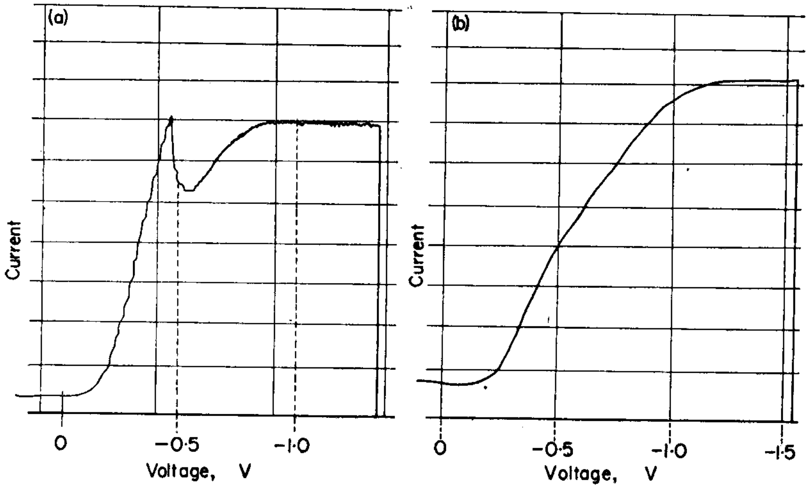

Fig. 3.—Polarograms obtained from nitroglycerine using the Tinsley polarograph.
Sensitivity = 100, damping = 10
Maximum suppressor used: (a) methyl red, (b) gelatine.

nitroglycerine causes marked interference with the reduction of dibutyl phthalate for the determination of which it is not therefore practicable to devise a routine procedure (see Figs. 4 and 5).

Although only one wave is readily discernible on the orthodox polarograph, when the cathode-ray polarograph is used, three waves are obtained with peaks occurring at −0·25, −0·45 and −0·75 V (vs. mercury pool).

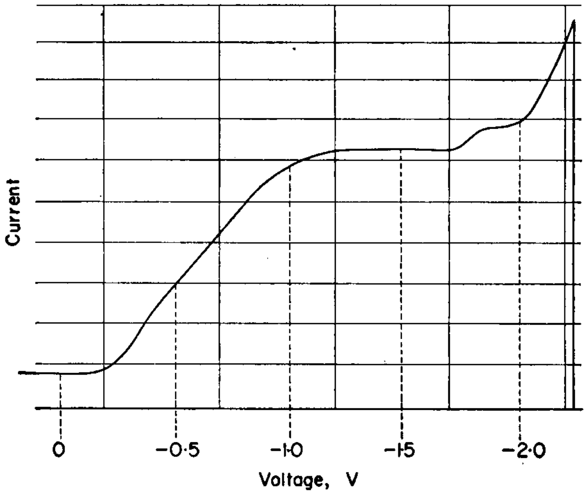

FIG. 4.—Polarogram obtained from a mixture of nitroglycerine and dibutyl phthalate using the Tinsley polarograph. Sensitivity = 150, damping = 10.

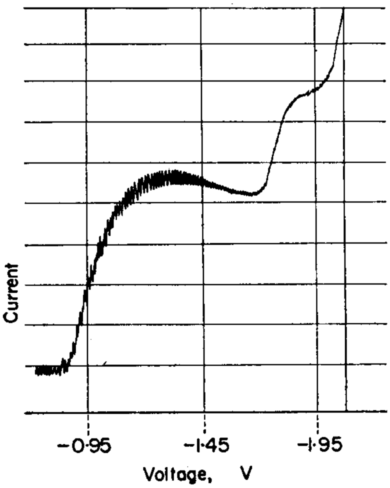

FIG. 5.—Polarogram obtained from a mixture of nitroglycerine and dibutyl phthalate using the Tinsley polarograph. Sensitivity = 30, damping = 10.

2. *Results using the cathode-ray polarograph*

The determination of nitroglycerine in double base propellants: Throughout the work which follows, the cathode-ray polarograph manufactured by Southern Instruments Ltd. was used and the solution employed for polarography consisted of 10 ml methanol containing the nitroglycerine together with an equal volume of 0·1*M* aqueous tetramethyl ammonium iodide. By choosing a suitable start potential, any one of the three waves with peaks at −0·25, −0·45 and −0·75 V, may be used for measurement of the peak height although the later wave occurring at —0·75 V gives the best defined peak (see Fig. 1(*a*) and (*b*)).

Examples showing the composition of double base propellants are given in Table I. The ether extract from propellants of Type A and B contain dibutyl phthalate, ethyl centralite and mineral jelly as well as the nitroglycerine, but only the dibutyl phthalate in addition to nitroglycerine give polarographic waves.

TABLE I.—APPROXIMATE COMPOSITIONS OF TYPICAL DOUBLE BASE PROPELLANTS

Propellant	A	B	C
Nitrocellulose	49·75	56·5	76·0
Nitroglycerine	34·50	19·5	2·5
Ethyl centralite	6·5	1·0	—
Dibutyl phthalate	8·0	—	—
Mineral jelly	0·25	0·25	—
Potassium nitrate	1·0	1·0	—
Triacetin	—	21·75	—
Other constituents including nitro-amine stabiliser	—	—	21·5

(*a*) *The effect of dibutyl phthalate on the wave and peak potential of nitroglycerine:* It was found that just as the presence of nitroglycerine affected the determination of dibutyl phthalate[1] so dibutyl phthalate caused enhancement of the height of the nitroglycerine peak and a change in peak potential. It was shown that a progressive increase in concentration of dibutyl phthalate from 0 to 250 μg per ml of base solution caused a progressive change in the peak potential of the third step from —0·75 to —0·85 V which remained constant with further increase in concentration of dibutyl phthalate.

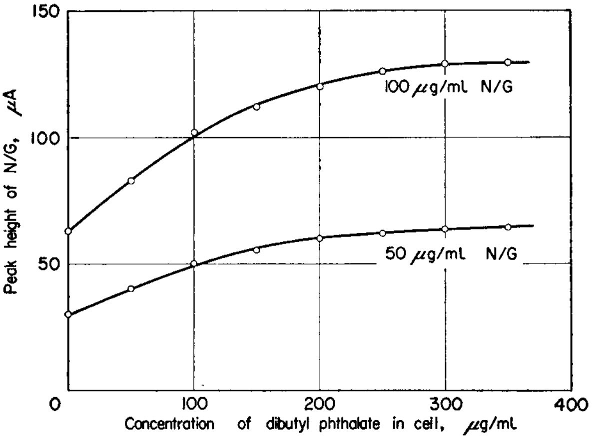

FIG. 6.—The effect of dibutyl phthalate on the peak height of nitroglycerine.

The enhancing effect of dibutyl phthalate on the nitroglycerine peak at —0·75 V reached a maximum at about 250–300 μg per ml of base solution (see Fig. 6). Unlike previous work on the determination of dibutyl phthalate when nitroglycerine had a marked effect on the value of the blank, it was found that dibutyl phthalate had no effect on the value of the "nitroglycerine" blank.

(*b*) *The determination of nitroglycerine in synthetic solutions and propellant samples:* Base solutions were made up in the manner described so that they contained 80 μg of dibutyl phthalate per ml and various concentrations of nitroglycerine. Employing the procedure described under A, the amounts of nitroglycerine were then determined and results are given in Table II. Samples of double base propellants (mechanites) were analysed by the standard routine procedure using reduction by ferrous ammonium sulphate and by the polarographic method; results are shown in Table III and it is seen that a good measure of agreement is obtained.

(*c*) *Special case of propellant containing a "reducible" stabiliser:* It may happen that instead of ethyl centralite a nitro-amine compound may be present as stabiliser (see sample C, Table I) and if this has a reduction peak close to that of the main nitroglycerine peak it is obviously necessary to use either the peak occurring at −0·45 V or −0·25 V. The peak at −0·25 V was taken as it was more clearly defined than the later peak. The measurement of the peak height is clearly demonstrated in Fig. 1(*a*). The low peak potential of −0·25 V makes it essential to ensure that oxygen is thoroughly removed from the solution and therefore a longer period of at least 10 minutes degassing must be given (see Fig. 2). Table IV shows results obtained by the method described in A, 3(*b*) employing samples containing nitroglycerine of the order of 2–3%.

TABLE II.—THE DETERMINATION OF NITROGLYCERINE IN MECHANITE TYPE SYNTHETIC SOLUTIONS

Nitroglycerine added (μg/ml)	Nitroglycerine found (μg/ml)
200	197
240	241
280	275
320	316
360	354
400	398

TABLE III.—THE DETERMINATION OF NITROGLYCERINE IN MECHANITE SAMPLES

Nitroglycerine recovered, %	
(*a*) By polarograph	(*b*) By ferrous-titanous method
34·3	34·4
34·2	34·4
30·0	30·2
29·9	30·2
34·3	34·3
34·3	34·5

B. BLASTING EXPLOSIVES

Method

These methods deal with blasting explosives which normally contain nitroglycerine together with dinitroglycol in contrast to the pure nitroglycerine used in propellants. Thus there is the problem of estimating nitroglycerine in the presence of dinitroglycol. In some cases nitrotoluene may be present. Dinitroglycol gives two peaks which coincide with the last two peaks of nitroglycerine and nitrotoluene gives a peak which is very near to the third peak of nitroglycerine.

1. *Reagents:* The reagents are similar to those given under A but the standard nitroglycerine

solution should be prepared from "nitroglycerine" as used in the manufacture, namely prepared from the nitroglycerine-dinitroglycol mixture.

Standard mononitrotoluene solution: The material used in the actual explosive may be a mixture of the isomers and so the standard solution is best made up from a current plant sample of mononitrotoluene.

Dissolve 0·25 g of the mononitrotoluene in 250 ml of methanol in a standard flask. Dilute 2 ml of this solution to 100 ml in a standard flask. This solution contains 20 μg/ml mononitrotoluene.

2. *Extraction procedure:* Weigh accurately about 1 g of the sample into a sintered-glass crucible, (porosity G.3) and extract in a suitable extraction unit for two hours. Employing suitable precautions evaporate the resulting solution almost to dryness, dissolve the residue in methanol and dilute the resulting solution in such a way as to give a final convenient concentration of nitroglycerine of say about 300 μg/ml. For example, if the explosive contained about 16% nitroglycerine the residue would be dissolved in 100 ml of methanol in a standard flask. 20 ml of this solution would then be diluted to a further 100 ml with methanol and the resulting solution used for the determination of nitroglycerine.

TABLE IV.—THE DETERMINATION OF NITROGLYCERINE IN PROPELLANT POWDERS CONTAINING A NITRO-AMINE STABILISER

Nitroglycerine recovered, %	
(*a*) By polarograph	(*b*) By ferrous-titanous method
2·93	2·84
2·95	2·84
2·30	2·2
2·32	2·2
2·64	2·6
2·59	2·6

3. *Polarography using the cathode-ray polarograph:* (*a*) Samples of the type shown in Table V(Y) which are free from mononitrotoluene:

(i) Assuming that the composition of the nitroglycerine-dinitroglycol mixture incorporated in the explosive is known: Determine the "nitroglycerine" by the method described for propellants under A, but instead of using a standard nitroglycerine solution use a standard solution of the known mixture of nitroglycerine and dinitroglycol.

(ii) If the composition of nitrated glycerine and glycol mixture is not known then it is necessary to use the first peak occurring at —0·25 V. The procedure is as described for propellants (see A). The same method can, of course, be used when the composition of nitroglycerine-dinitroglycol as described above, is known.

(*b*) For samples of blasting explosives which contain mononitrotoluene (see Table V, X and Z).

A peak for mononitrotoluene occurs in the vicinity of the final peak for nitroglycerine and the only reliable method for estimating the nitroglycerine under these conditions is to use its —0·25 V peak. The determination is carried out precisely as described above.

EXPERIMENTAL

The determination of nitroglycerine in blasting explosives

There are two groups of blasting explosives with which this work is concerned, namely those containing mononitrotoluene and dinitroglycol (see Table V) in addition to nitroglycerine and those in which mononitrotoluene is absent (see Table V). Employing the standard base solution comprising 0·05M tetramethyl ammonium iodide in 50% methanol, peak potentials as follows were obtained: nitroglycerine: —0·25, —0·45 and —0·75 V; dinitroglycol: —0·45, —0·75 V; mononitrotoluenes: —0·67, —0·80 and —0·82 V. The types of waves obtained are shown in Fig. 1 and Fig. 7 (nitroglycol is similar). The wave due to mononitrotoluene is typical of the type produced by a reversible reduction on the cathode ray polargraph. Adopting the method shown in Fig. 1 for the measurement of peak heights, it was shown that for each substance the peak heights were proportional to the amount of substance present. This applied equally to the three peaks for nitroglycerine and to both peaks of the dinitroglycol.

TABLE V.—APPROXIMATE COMPOSITIONS OF TYPICAL BLASTING EXPLOSIVES

Explosive	X	Y	Z
'C' nitroglycerine*	27·5	10·5	16·0
B.S. nitrocellulose	1·0	—	0·5
Mononitrotoluene	1·5	—	1·0
Ammonium nitrate	31·0	70·7	42·5
Sodium chloride	29·4	10·0	28·0
Oat husk meal	1·1	—	—
China clay	4·0	—	5·0
Diammonium phosphate	0·5	—	—
Alcohol	0·3	—	—
Woodmeal	—	6·7	2·0
Woodflour	—	2·1	—
"Cellofas" B	—	—	0·5
Calcium stearate	—	—	0·5
Barytes	4·0	—	4·0

* Nitroglycerine-nitroglycol mixture prepared from glycerine containing 20% ethylene glycol.

(*a*) *The determination of nitroglycerine in the presence of dinitroglycol:* Blasting explosives differ from propellants in that glycerine containing ethylene glycol is used instead of pure glycerine for nitration and the "nitroglycerine" so prepared is used in the preparation of the explosive. In addition some compositions contain mononitrotoluene as a mixture of the isomers. The only polarographically reducible compounds in the ether extract (see B, 2) of the explosive are nitroglycerine, and dinitroglycol and mononitrotoluene when present. Since the nitroglycerine: dinitroglycol ratio used in the manufacture is usually known, provided mononitrotoluene is absent, it is possible to use the third peak occurring at —0·75 V for the determination of nitroglycerine. Alternatively, by using the early peak occurring at —0·25 V (see Fig. 1) the nitroglycerine can be determined directly in the presence of both dinitroglycol and mononitrotoluene. Results obtained with synthetic mixtures of

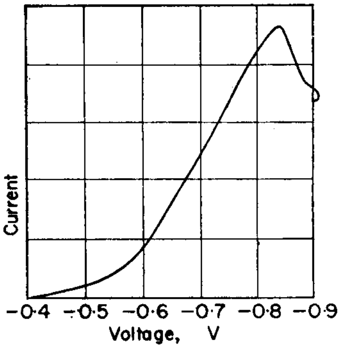

FIG. 7.—Polarogram obtained from mononitrotoluene using the cathode ray polarograph. Peak potentials: ortho = —0·80 V, meta = —0·67 V, para = —0·82 V.

TABLE VI.—DETERMINATION OF NITROGLYCERINE IN THE PRESENCE OF DINITROGLYCOL

Nitroglycerine added, µg/ml, base solution	Nitroglycerine found, µg/ml	Error %
100	98	−2
200	195	−2·5
300	296	−2
400	410	+2·5
500	492	−1·6

TABLE VII.—DETERMINATION OF NITROGLYCERINE IN THE PRESENCE OF DINITROGLYCOL AND MONONITROTOLUENE

Nitroglycerine added, µg/ml base solution	Nitroglycerine found, µg/ml	Error %
100	97	−3
200	197	−1·5
300	304	+1·3
400	394	−2
500	492	−1·6

TABLE VIII.—THE DETERMINATION OF NITROGLYCERINE IN BLASTING EXPLOSIVES

Nitroglycerine determined by difference method, %		Nitroglycerine determined by polarograph, %	
1	2	1	2
10·5		10·3, 10·4	
	16·1		16·3, 16·4, 16·5
	27·7		27·3, 27·4

1—mononitrotoluene absent
2—nitrotoluene present.

various amounts of nitroglycerine in the presence of 40 µg dinitroglycol per ml of base solution are shown in Table VI.

(*b*) *The determination of nitroglycerine in the presence of dinitroglycol and mononitrotoluene:* The procedure described above, using the peak for nitroglycerine occurring at −0·25 V was used for the determination of nitroglycerine in the presence of both dinitroglycol and mononitrotoluene. Since the mononitrotoluene used in the manufacture consisted of a mixture of the three isomers, the same mixture was used as a standard in the preparation of synthetic solutions used for testing the method

In the actual polarographic determination, the method of standard addition was employed as there was a slight enhancing effect of the nitroglycerine peak by the mononitrotoluene. It was found that the peak potentials for the isomers of mononitrotoluene ranged from −0·67 to −0·82 V.

Table VII shows results obtained for various amounts of nitroglycerine in the presence of 40 μg dinitroglycol and 5 μg mononitrotoluene per ml of base solution. These are the amounts which would be expected in the amount of solution taken from the diluted ether extract of the sample (see B, 2).

(*c*) *The determination of nitroglycerine in blasting explosives:* Table VIII shows results which were obtained for the determination of nitroglycerine in blasting explosives of the types shown in Table V.

Zusammenfassung—Es wird die Anwendung des Kathodenstrahl-Polarographen zur Bestimmung von Nitroglycerin in einigen doppel basischen Treibstoffmischungen und Sprengstoffen beschrieben. Bei Anwendung von einer alkoholisch-wässrigen Lösung von Tetramethyl ammonjodid als Grundlösung kann man nur eine Welle in üblichen Polarographen sehen. Wenn man aber den Kathodstrahl-Polarographen benützt, können deutlich drei Spitzen gesehen werden: diese erscheinen bei −0,25, −0,45 und −0,75V (bezogen auf den Quecksilber-Pool). Nitroglycerin erhält man leicht in Äther-Extrakt von Treibstoffmischungen durch Messung der Wellehöhe bei −0,75 oder −0,25V. Im Falle der Sprengstoffe können sowohl Nitroglycerin als auch Dinitroglykol und Mononitrotoluol in Äther-Extrakt anwesend sein. Die Dinitroglykol gibt zwei Wellen die bei −0,45 und −0,75V erscheinen, und so übereinstimmen mit den zwei späteren Wellen von Nitroglycerin. Weiters, geben die Isomere von Mononitrotoluol Spitzen welche sehr nahe bei den Spitzen von Nitroglycerin erscheinen. In Hinblick dieser Tatsache ist es notwendig für Nitroglycerin die erste Spitze zu benützen, diese die bei −0,25V erscheint.

Die Genauigkeit läuft in der Grössenordnung von ±2%.

Résumé—On décrit l'application du polarographe à rayons cathodiques au dosage de la nitroglycérine dans des mélanges propulsifs à deux constituants de base et dans les explosifs "soufflants". En utilisant une solution hydroalcoolique d'iodure de tétraméthylammonium comme électrolyte support, on observe, sur le polarographe classique, une seule vague. Sur le polarographe à rayons cathodiques on décèle nettement trois pics; ceux-ci se placent à −0,25, −0,45 et −0,75 V (par rapport à la napde de mercure). On dose facilement la nitroglycérine dans l'extrait à l'éther du mélange propulsif(———) en mesurant la hauteur du pic à −0,75 ou à −0,25 V.

Dans le cas des explosifs "soufflants", on trouve dans l'extrait à l'éther, outre la nitroglycérine, du dinitroglycol et du mononitrotoluène. Le dinitroglycol donne deux pics à −0,45 V et −0,75 V, coïncidant ainsi avec les deux derniers pics de la nitroglycérine. De plus, les isomères du mononitrotoluène donnent des pics qui apparaissent très près de celui de la nitroglycérine (−0,75 V). En conséquence, il est nécessaire d'utiliser le premier pic pour la nitroglycérine, c'est-à-dire celui qui apparaît à −0,25 V.

On obtient une précision de ±2 pour cent.

REFERENCES

[1] A. F. Williams and D. Keynon, *Talanta*, 1959, **2**, 79.
[2] G. C. Whitnack, M. M. Mayfield and E. St. C. Gantz, *Analyt. Chem.*, 1955, **27**, 899.
[3] G. C. Whitnack, J. M. Nielsen and E. St. C. Gantz, *J. Amer. Chem. Soc.*, 1954, **76**, 4711.

DISCUSSION

Mr. E. TYRRALL asked whether the reactions corresponding to the three peaks in the nitroglycerine polarogram had been identified. Mr. WILLIAMS replied by indicating that no detailed study had so far been made of the reduction steps involved, but it was possible that each of the three peaks could be due to each of the nitrogroups, although it was possible that they may be reduction steps in any one of the nitrogroups.

Mr. A. O. PEARSON asked whether three peaks are obtained for trinitrotoluene. In his reply, Mr. WILLIAMS referred Mr. PEARSON to the work of J. Pearson (*Trans. Farad. Soc.* 1948 **44,** 683) who had studied that particular reduction and obtained three peaks in both acid and alkaline media.

Mr. E. TYRRALL asked, as an outcome of comments by Mr. HETMAN, whether a suggested cyclic isomer of nitroglycerine was established or was it merely a guess. Mr. WILLIAMS indicated that it could be largely guesswork.

Mr. H. Y. STRAIN wanted to know whether aliphatic nitrates such as those derived from erythritol or mannitol, containing a number of nitrogroups, had been examined to see whether their behaviour was similar. Mr. WILLIAMS replied by pointing out that some work would almost certainly have been carried out on the polarograph but he had no knowledge of this.

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A GAMMA ABSORPTIOMETER FOR LABORATORY ANALYSIS OF THE HEAVY ELEMENTS*

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(*Received* 25 *May* 1959)

Summary—Construction of a simple gamma absorptiometer employing a small ^{241}Am source, for the determination of U or Pu in relatively pure solutions, is described. The instrument yields a recorded voltage directly proportional to absorbance.

THE use of low energy radioactive sources in an absorptiometric technique provides a rapid and sensitive means for the determination of the concentration of heavy elments in solution. The liquids to be tested are inserted in a beam of radiation and the attenuation of the beam is a measure of the sample concentration.

This paper describes an instrument constructed at ORNL for the laboratory analysis of uranium or plutonium in relatively pure solutions.

APPARATUS

Radiation source

Americium-241 is a desirable source of photons for this technique[1] because of its low photon energy—approximately 60 keV—and its long half life—470 years. The relatively low intensities available with this source material are offset by the pronounced sensitivity for heavier elements gained by the use of low photon energies. The source is 10 mg of ^{241}Am as the trifluoride, cast in a plastic disc $\frac{9}{16}$ inch in diameter. This casting is sealed in an aluminium container by pouring a low melting alloy (Wood's alloy) over the source after locating it in the well of the container. The source is exposed to the sample through a 0.012-inch aluminium "window". Details of a procedure for source preparation are reported by Milham.[2]

A brass fitting surrounding the source provides biological shielding and serves to define the beam. Only the portion of the beam that passes through the sample is allowed to strike the detector through an orifice in the lead shield (Fig. 1).

Detector

A thallium-activated sodium iodide scintillation crystal coupled to an RCA 5819 multiplier phototube is the sensing unit. The detector crystal is 0.1 inch thick by 1.5 inches in diameter. This thickness was chosen to discriminate against higher energy background radiation. The low energy photons from the source are effectively absorbed in the crystal while higher energy radiation passes through with little interaction. Protection from the sides is afforded by a lead shield surrounding the crystal. Some stray radiation from this direction would otherwise be absorbed, regardless of its energy, since it would traverse the diameter of the crystal.

The multiplier phototube is taped with electrical insulating tape to insure light-tightness, and is magnetically shielded. Fig. 1 shows the construction of the source-detector assembly. The assembly is cylindrical in cross section, with the source and detector located on the axis. Samples are positioned properly in the beam by placing the cylindrical, flat-bottomed absorption cells in a closely fitting

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* Based on a presentation at the ISA Symposium on Instrumental Methods of Analysis, Houston, Texas, 12–14 May 1958.

† Operated by Union Carbide Corp., for the Atomic Energy Commission.

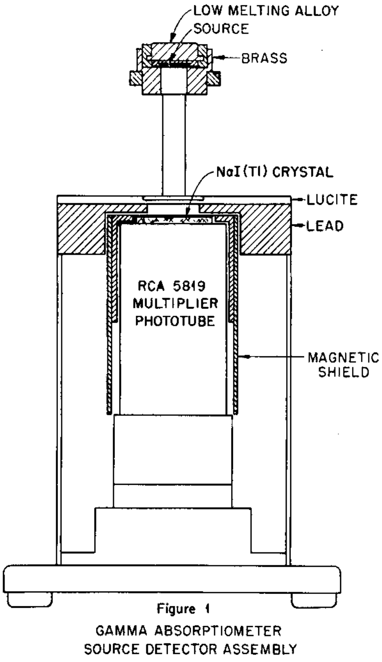

Fig. 1.

depression in the detector housing cap. These cells are 1 inch internal diameter lucite cylinders having ⅛ inch wall and end thickness.

Photometric circuit

The basic circuit employed in this instrument was originally described by Sweet[3] and has been modified by others[4,5] for various uses. The unique property of the circuit is that the anode current from a multiplier phototube is held essentially constant by a feedback system that controls the dynode supply voltage. Sweet has shown that under this condition the voltage is approximately proportional to optical density over a considerable range. This is explained by reference to Fig. 2. A decrease in the light intensity falling on the photocathode, corresponding to an increase in solution density, causes a tendency for the anode current to decrease. A small decrease in current through the 200-M load resistor causes a relatively large voltage signal—in this instance, positive—and so decreases the bias on the cathode follower tube—12AX7. The cathode follower then passes more current, making the potential of its cathode, and that of the grid of the series regulator tube—6BG6, more positive. The lowered resistance of the 6BG6 permits more current to flow, increasing the voltage applied to the multiplier phototube dynodes and counteracting the tendency of the anode current to decrease.

Measuring circuit

The total voltage applied to the dynodes is divided through a series of resistors from which the "range" switch selects fractions giving full scale recorder deflections for various concentration increments. A zero suppression circuit permits selection of the portion of the total instrument range to be covered by these increments. The 500-ohm potentiometer (Note*, Fig. 2) is intended to allow for possible changes in sensitivity with zero setting or by aging of the detector crystal.

Brown recorder

The recorder is a 50-mV, single point Brown Electronik strip chart recorder (type 153) having a pen speed of 12 sec, a chart speed of ⅛ inch per minute, and a high gain amplifier modified to accept high impedance. negative-going signals. The original low impedance transformer input circuit is

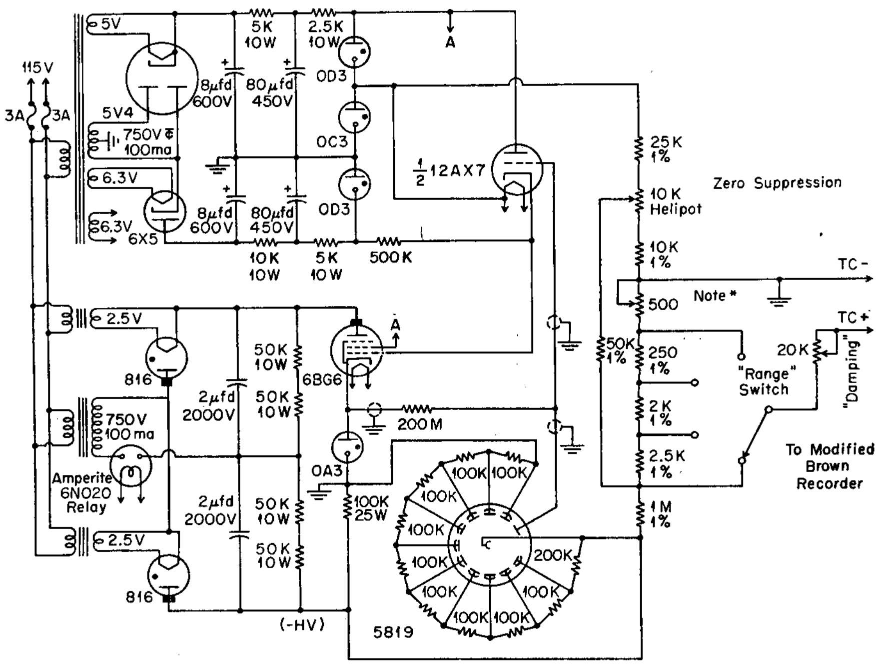

FIG. 2.—Circuit of gamma-absorptiometer, ORNL analytical instrumentation group. Note* Set at $250\,\Omega$

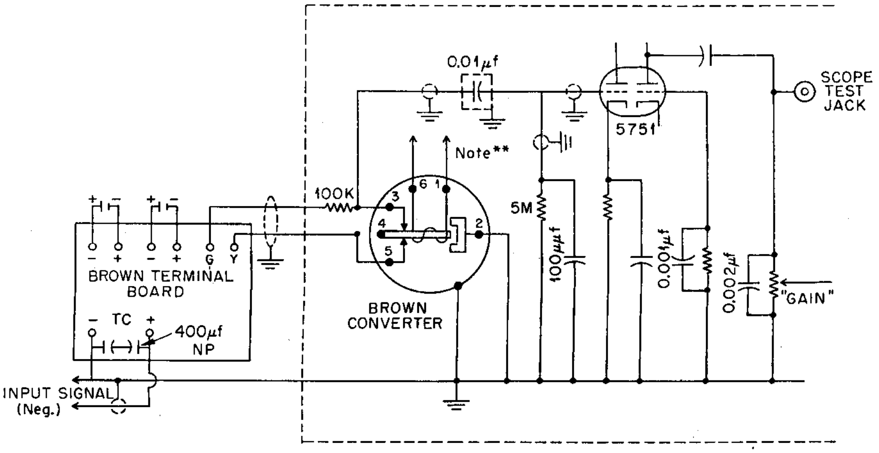

FIG. 3.—Brown recorder modifications for high impedance negative-going signals
Note** Chopper coil polarity is reversed if necessary to get negative feedback. See appendix.

replaced by a high impedance, RC coupling input circuit so that the recorder can be used to record the current through a 5000-ohm resistor. The circuit modifications are shown in Fig. 3. Further information is contained in the appendix.

TEST PROCEDURE

Uranium solutions used in evaluation of the instrument where prepared by dilution of a uranyl nitrate solution that was standardised by potentiometric titration. A sample path length of 4.1 cm was used. A typical series of measurements is shown in Fig. 4.

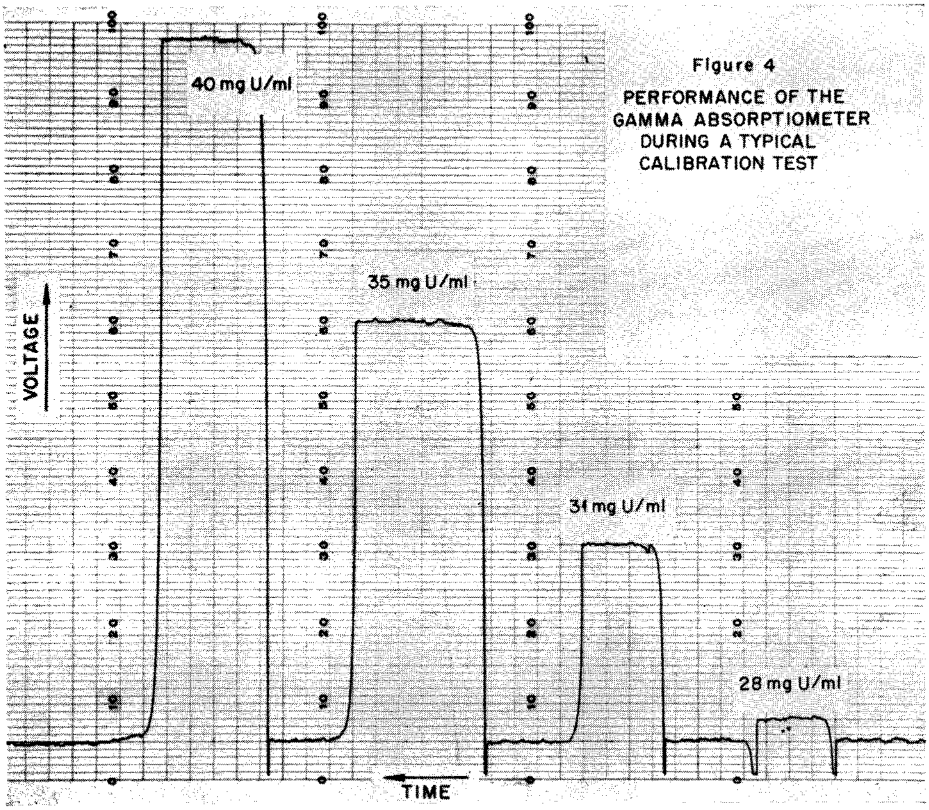

Figure 4

PERFORMANCE OF THE GAMMA ABSORPTIOMETER DURING A TYPICAL CALIBRATION TEST

In order to compensate for both long term drift and short term fluctuations of the dynode voltage, a "background" is obtained by placing a metal absorber of a standard solution in the cell position. This specimen is re-inserted after each sample and the measurement for each material is averaged out over a period of about three minutes. Absorption curves are plotted showing the difference between sample and "background" readings as a function of concentration. These curves are linear and show no change of slope over a period of weeks.

The zero suppression potentiometer is used to set the background absorber reading at a chosen place on the recorder scale each time a given range is used. For example, in Fig. 4, a standard absorber having an absorbance slightly less than that of the 28 g/litre uranium solution was set to 5% on the scale at the beginning of the series.

Contributions to the absorbance by other elements present in the sample can be estimated from a series of measurements made on solutions varying in concentrations of H_2SO_4, HCl, HNO_3, and Fe^{2+} (as sulphate). The relative effects of these materials are illustrated in the curves shown in Fig. 5.

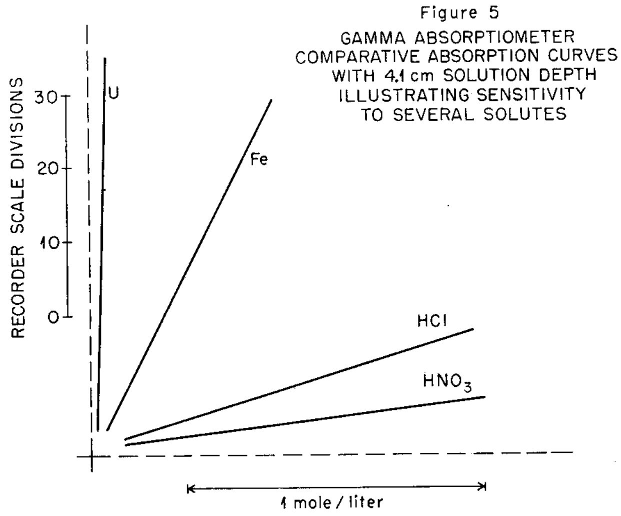

Figure 5
GAMMA ABSORPTIOMETER
COMPARATIVE ABSORPTION CURVES
WITH 4.1 cm SOLUTION DEPTH
ILLUSTRATING SENSITIVITY
TO SEVERAL SOLUTES

From these data it can be shown that an uncertainty of 0.1 mole/litre of HNO_3 would cause an error of 0.06 g U/litre and that Fe, as a typical light element, would contribute an error of 0.2 g U/litre per g Fe/litre.

The solutions for which this instrument is intended will contain Pu in concentrations from 25 to 50 g/litre in various HNO_3 concentrations. In order to analyse such samples, it is planned to analyse two series of standard solutions of different HNO_3 concentrations. The sample concentrations can then be determined by interpolation between the two curves obtained by plotting recorder scale readings vs concentration of Pu.

The reproducibility to be expected from this instrument was obtained from a series of measurements on the absorbance of a 33 g U/litre sample. The standard deviation of 16 observations was 0.55% of recorder scale on the most sensitive range. This corresponds to 0.035 g U/litre in a 4.1-cm absorption cell.

APPENDIX

Brown recorder modifications

1. Remove the two wires leading from the "Run-Standardize" switch to "TC +" and to "G" and replace them with No. 22 shielded Teflon insulated wire. Ground the shields to the recorder chassis.
2. Reverse the polarity of the recorder as follows:
    a. Reverse polarity of standard cell and working cell.
    b. Reverse polarity of chopper coil if required to get negative feedback; wait until the modified amplifier is installed before determining this point.

3. Remove the damping resistor from the terminal board.
4. Remove the input transformer and wire the high impedance circuit as shown.
5. Replace 12AX7 with 5751. Re-label the tube location chart accordingly.
6. Isolate pins 1 and 6 of the Brown converter, by grounded copper shield.
7. Ground the upper, painted shell of the converter to pin 2.
8. Add the scope test jack.
9. Ground all tube socket pin shields.
10. Replace tube shields with Elco low temperature shields.

Acknowledgement—The authors wish to express their appreciation to Dr. D. J. Fisher and Mr. H. C. Jones of the ORNL Analytical Chemistry Division for their advice and assistance.

Zusammenfassung—Die Konstruktion eines einfachen Gammastrahlabsorptiometers unter Verwendung einer kleinen Menge ^{241}Am als Strahlenquelle wird beschrieben. Das Instrument dient zur Bestimmung von Uran oder Plutonium in verhältnismässig reinen Lösungen. Die angezeigte Spannung am Instrument ist der Absorption direkt proportional.

Résumé—On décrit la construction d'un compteur de rayons gamma utilisant une petite source de ^{241}Am, pour le dosage de l'uranium ou du plutonium en solutions relativement pures. L'instrument enregistre une tension directement proportionnelle à l'absorption.

REFERENCES

[1] Americium-241 as a Photon Source for the Gamma Absorptometric Technique, D. G. Miller, *A.E.C. Research and Development Report*, HW-39971 17 Nov., 1955.

[2] The Preparation of An Americium Gamma Source, R. C. Milham, *A.E.C. Research and Development Report*, DP-173 Aug. 1953.

[3] An Improved Photomultiplier Tube Color Densitometer, M. H. Sweet, *Journal of the Society of Motion Picture and Television Engineers*, 1950, **54**, 35-62.

[4] An improved Cuvette Densitometer for Cardiac Output Determination by the Dye-Dilution Method, S. R. Gilford and Others, *Rev. Sci. Instruments*, 1953, **24**, 696-702.

[5] Automatic Derivative Spectrophotometric Titrations, H. V. Malmstadt and C. B. Roberts, *Analyt. Chem.*, 1956, **28**, 1408-12.

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NUCLEATION IN ANALYTICAL CHEMISTRY—II*

NUCLEATION AND PRECIPITATION OF SILVER CHLORIDE FROM HOMOGENEOUS SOLUTION

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(*Received* 17 *July* 1959)

Summary—The nucleation and precipitation of silver chloride from homogeneous solution have been examined. Critical supersaturations of silver chloride were determined; however, they were observed to be qualitatively different from the critical supersaturation of classical nucleation theory, and were interpreted as being dependent on the rates of both nucleation and crystal growth. The precipitation rate is not constant throughout a precipitation from homogeneous solution, but varies considerably during the early portion of the precipitation. Both this early variation in precipitation rate and the number of particles and their size distribution can be controlled to some extent by varying the concentrations of the reactants.

INTRODUCTION

PRECIPITATION is one of the basic and one of the most widely applicable operations of analytical chemistry. Many studies of the precipitation process have shown how the character of a precipitate may be improved by appropriate modifications of the reaction conditions. The purity and crystallinity of the particles are ordinarily improved by decreasing the rate of particle growth. The conditions leading to control of the number and size of the particles, and of their size distribution, are less well known. These properties of the precipitate are determined by the nucleation process, the nature and analytical significance of which have been discussed in a recent review[1]. The present paper describes a study of the nucleation and precipitation of silver chloride from homogeneous solution.

EXPERIMENTAL

Reagents

The chloride-generating reagent selected for the precipitation was allyl chloride, because this compound is easily purified by distillation and it hydrolyzes at a convenient rate in dilute (less than $0.01M$) aqueous solution. Because the suitability of allyl chloride for precipitation depends upon

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* Part I, *Talanta*, 1958, **1**, 334.

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hydrolysis, the kinetics of its hydrolysis were examined. The hydrolysis was followed conductimetrically up to only about 0.1 % reaction, because the later stages of the hydrolysis were not of significance in this work. The conductivity versus time line, at 25°, was found to be

$$10^6 L = (0.203 \pm 0.002)ct,$$

where

L = specific conductance of the solution,
c = initial concentration of allyl chloride in grams/litre,
t = time in minutes.

The hydrolysis rate was not affected by the presence of dissolved potassium chloride or silver nitrate, nor of freshly precipitated silver chloride.

Conductivity water was prepared by passing single-distilled water through an ion-exchange column containing a mixture of the analytical grade Amberlite resins IRA-400(OH) and IR-120(H). Although this treatment yielded a product with a specific conductivity of around 2×10^{-7} reciprocal ohms, it appears that there was some contamination of the water by the resin, as will be discussed later.

Silver nitrate stock solutions were prepared from the Mallinckrodt "Analytical Reagent" grade salt which was used without further purification. These solutions were kept in amber bottles and stored in the dark.

Equipment

The hydrolysis and precipitation reactions were followed conductimetrically. The Wheatstone bridge gave resistance readings reproducible to about 0.1 %. A water bath maintained the temperature of the system constant to within ±0.02°.

Although the conductivity cell, shown in Fig. 1, was designed to permit simultaneous conductimetric and turbidimetric observation of the reaction, conductance measurements only were made in the present research. The cell constant was 0.01400 at 25°, and was taken to be constant over the range from 15° to 35°, because the variation of the cell constant with temperature was calculated to be less than 0.02 % per degree. The bright platinum electrodes were 4-cm discs, separated by about 2 mm. Teflon stopcocks were used so as to avoid contamination by stopcock grease. The lower end of the

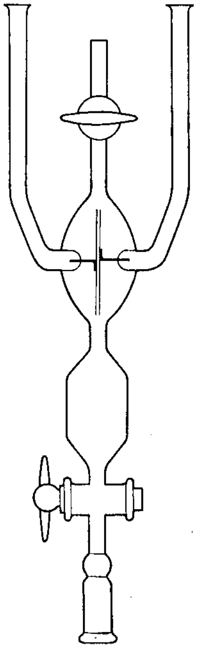

FIG. 1.—Conductivity cell

cell was fitted with a standard taper joint, into which a Teflon filter-support could be set. The arrangement permitted filtration of the reaction mixture immediately before it entered the cell.

Filtration was employed to remove foreign particles which might act as precipitation nuclei. Millipore filters (Millipore Filter Corp., Watertown, Mass.) were used for this purpose. The type HA filters used in this study have a pore size of $0.45\ \mu \pm 0.02\ \mu$.

Procedure

A two-litre resin reaction jar was thoroughly cleaned, placed in the constant temperature bath, swept out with purified nitrogen, and filled with two litres of conductivity water, collected under nitrogen. A suitable amount of stock solution of silver nitrate was added, so as to make the silver concentration about 2.5 to $10 \times 10^{-5}M$, the exact concentration subsequently being determined conductimetrically. An appropriate amount of allyl chloride (about 0.1 to 1 millilitre) was distilled into a hypodermic syringe, and then added to the silver solution with vigorous stirring; a timer was started when the allyl chloride was added. The Millipore filter, in its Teflon support, was connected between the conductivity cell and the mixing jar, and nitrogen pressure applied to the jar to force the reaction mixture through the filter into the cell. After approximately 100 millilitres of solution were rinsed through the cell it was closed off. The conductivity of the mixture was measured at intervals, and the results plotted as conductivity versus time. Upon conclusion of an experiment the cell was rigorously cleaned by consectuive rinsing with concentrated ammonium hydroxide, concentrated nitric acid, alcoholic sodium hydroxide, and then about fifteen times with conductivity water filtered through sintered glass directly into the cell.

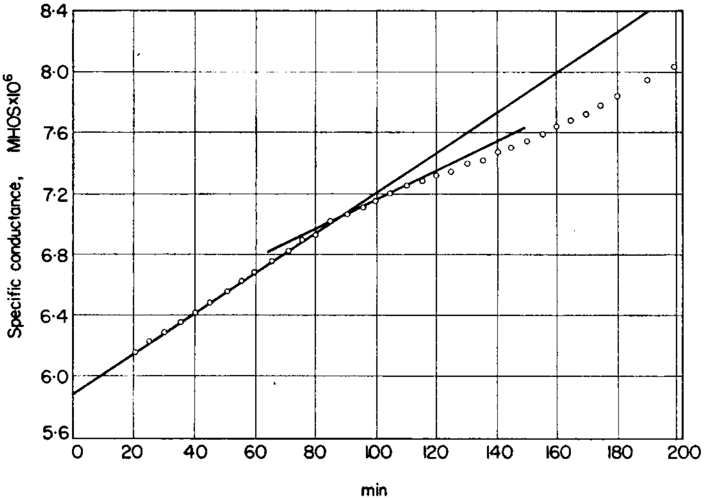

FIG. 2.—Specific conductance of a reacting mixture containing silver nitrate (5.24×10^{-5} M) and allyl chloride (0.28 gram/litre) at 15°.

Kinetic studies had shown that where only hydrolysis of allyl chloride is taking place, the conductivity-time curve was a straight line. This was the case early in an experiment, before nucleation and precipitation began. Precipitation was indicated by a deviation of the observed conductance away from the hydrolysis line, as shown in Fig. 2. The first deviation from the hydrolysis line was taken as the point of "critical supersaturation". Because of the formation of a small amount of the soluble, non-conducting AgCl complex, the conductance of the system at the point of critical supersaturation does not correspond to the concentration of the system. A correction was made for this effect, using the equilibrium constants of Jonte and Martin,[2] and the concentrations of silver and chloride at the point of critical supersaturation were then calculated from the equivalent conductances.[3] In the following discussion, concentrations are expressed either as the ion product, I.P. $= [Ag^+] \times [Cl^-]$, or as the supersaturation ratio, $S = (I.P./K_{sp})^{1/2}$. $[Ag^+]$ and $[Cl^-]$ here refer to the total concentrations, *i.e.* the concentrations of the ions plus the concentration of the complex.

RESULTS

Critical supersaturations of silver chloride

The critical supersaturation, $S_{crit.}$, of silver chloride was examined under various conditions. The first experiments, in which the reacting solution was not filtered, led to a value of $S_{crit.}$ of 2.04, at 25°. When the solution was filtered, using the procedure outlined previously, $S_{crit.}$ dropped to 1.74. This unexpected filtration effect was examined by carrying out the experiments shown in Table I.

TABLE I.—EFFECT OF WATER PURIFICATION AND FILTRATION ON CRITICAL SUPERSATURATION RATIO OF SILVER CHLORIDE AT 25°

Water	Filtration	mean $S_{crit.}$ ± a.d.
distilled	none	1.44 ± 0.02
de-ionized	none	2.04 ± 0.05
de-ionized	Pyrex, grade M	1.87 ± 0.03
de-ionized	Millipore*	1.74 ± 0.02
distilled	Millipore	1.71 ± 0.04

* In two other experiments, about 500 ml of de-ionized water were passed through the filter before using it. This pre-treatment of the filter did not affect the value of $S_{crit.}$; had there been removable nucleating agents present in the filter, this pre-treatment would have separated at least some of them and thus raised the value of $S_{crit.}$.

TABLE II.—EFFECT OF IMPURITY (EOSIN) ON CRITICAL SUPERSATURATION RATIO OF SILVER CHLORIDE AT 25°

Water	Filtration	Impurity*	mean $S_{crit.}$ ± a.d.
distilled	none	none	1.44 ± 0.02
distilled	none	25 μg/litre, added in mixing vessell	1.74 ± 0.02
distilled	none	100 μg/litre, added in mixing vessel	1.73 ± 0.03
de-ionized	Millipore	small indeterminate amount of dye added into conductivity cell after cell is filled with solution	1.96 ± 0.05
de-ionized	Millipore	100 μg/litre dye added into mixing vessel before filtration into cell	1.74 ± 0.09

* 0.1 % solution of eosin in alcohol, filtered through Pyrex frit.

The results indicate that the de-ionizing column introduced some impurity which inhibited nucleation, or its detection, and which could be removed by passage through the Millipore filter. This possible explanation was further tested using eosin, which is known to be strongly adsorbed on silver chloride. The results of these experiments, which are given in Table II, show (*a*) that a readily adsorbed substance may raise the previously observed value of the critical supersaturation, and (*b*) that such a substance may be removed by passage through the Millipore filter, thus lending support to the proposed explanation of the filtration effect, *i.e.*, an impurity introduced by the resin.

Other soluble impurities were added to the reaction mixture in concentrations of around $10^{-5}M$, the same order of magnitude as the silver and chloride concentrations.

TABLE III.—EFFECT OF TEMPERATURE ON THE CRITICAL SUPERSATURATION RATIO OF SILVER CHLORIDE

Temp., °C	$10^{10}K_{sp}$[4]	Number of runs	Avg. S	Standard deviation
15	0.700	13	1.51	0.04
25	1.77	14	1.73	0.05
35	4.20	13	1.85	0.08

TABLE IV.—CRITICAL SUPERSATURATION RATIO OF SILVER CHLORIDE AT 25°

$[Ag^+]$, mole/litre $\times 10^5$	$[Cl^-]_{crit.}$, mole/litre $\times 10^5$	$\frac{[Ag^+]}{[Cl^-]}$	$\frac{d[Ag^+][Cl^-]}{dt}$ mole²/litre² minute $\times 10$	$S_{crit.}$
8.14	0.718	11.3	0.436	1.81
3.99	1.43	2.8	0.553	1.79
8.39	0.668	12.5	0.910	1.78
5.26	1.06	5.0	0.769	1.77
5.85	0.936	6.3	0.593	1.76
5.76	0.938	6.2	0.758	1.75
6.74	0.805	8.4	0.900	1.75
8.32	0.653	13.1	0.837	1.73
8.73	0.602	14.5	1.023	1.72
7.66	0.680	11.3	1.820	1.71
5.36	0.928	5.8	0.594	1.68
6.37	0.772	8.3	0.433	1.67
3.97	1.24	3.2	0.359	1.67
4.77	1.01	4.7	0.750	1.65

The presence of ethanol, allyl alcohol, barium nitrate, dextrose, and carbon tetrachloride at these concentrations had no apparent effect upon the critical supersaturation ratio.

The value of the critical supersaturation ratio was then determined at 15°, 25°, and 35°, using de-ionised water, Millipore filtration, and without added impurities. The results are presented in Table III. The temperature effect was in the opposite direction from that observed by LaMer and Dinegar[5] with barium sulphate. The complete data for the runs at 25° are given in Table IV. The observed critical supersaturation ratio appears independent of the $[Ag^+]/[Cl^-]$ ratio; this does not agree with the findings of Davies and Jones.[6] The rate of increase of silver chloride ion product, $d[Ag^+][Cl^-]/dt$, also appears to be without influence upon the critical supersaturation.

Precipitation of silver chloride from homogeneous solution

The technique of precipitation from homogeneous solution has been employed both as an analytical tool and for co-precipitation studies,[7] because it permits precipitation to occur slowly, under controlled conditions. That is, the precipitation rate is kept small throughout most of the course of the reaction. The present results can be treated to elucidate the characteristics of precipitation from homogeneous solution.

The concentrations of silver and chloride in solution at any time can be obtained from a plot of conductance versus time (*cf.* Fig. 2). The conductance of the entire system at any time, if everything were in solution, is obtained by extrapolation of the initial straight line portion of the plot, and from this one can calculate the total chloride in the system at any time. The difference between this extrapolated conductance and the observed conductance corresponds to the amount of silver chloride precipitated. Because the total amounts of silver and chloride in the system at any time are known, their solution concentrations can be easily calculated.

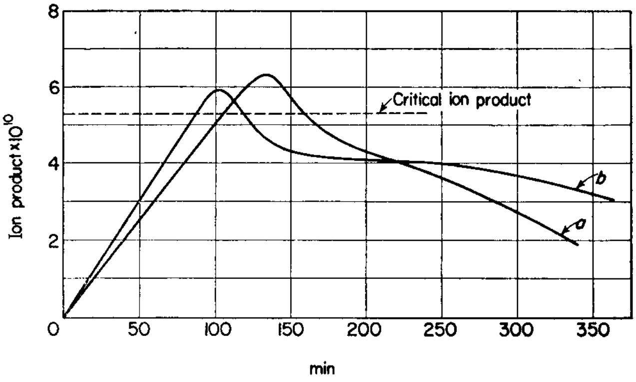

FIG. 3.—Ion product of silver chloride during a precipitation from homogeneous solution.

Fig. 3 represents the ion product, [Ag$^+$] [Cl$^-$], against time for two of the experiments. In run "*a*", the initial concentrations were: silver nitrate, 10.59 $\times$ 10^{-5}M, and allyl chloride, 0.10 grams/litre, while in run "*b*" they were: silver nitrate, 5.11 $\times$ 10^{-5}M, and allyl chloride, 0.25 grams/litre.

Fig. 4 shows a plot of the ion product against the amount of silver chloride precipitated. The ion product initially increased, because chloride ion was being generated and precipitation was not occurring. The curves continued to rise beyond the observed critical ion product. However, as the surface area available for precipitation increased, the ion products decreased. The decrease, rapid at first, became slower as the supersaturation of the system was relieved.

The amount of silver chloride precipitated at any time was known from the calculations for Fig. 3, and thus the rate of precipitation could be computed. Fig. 5 shows the precipitation rates as a function of the amount of silver precipitated. In both cases, the rate rose sharply to a maximum, then decreased, and after the initial supersaturation was relieved somewhat, remained quite constant over the extent of the reaction studied, which was 14% for run "*a*" and 48% for run "*b*". The particular value of precipitation from homogeneous solution as a tool for co-precipitation

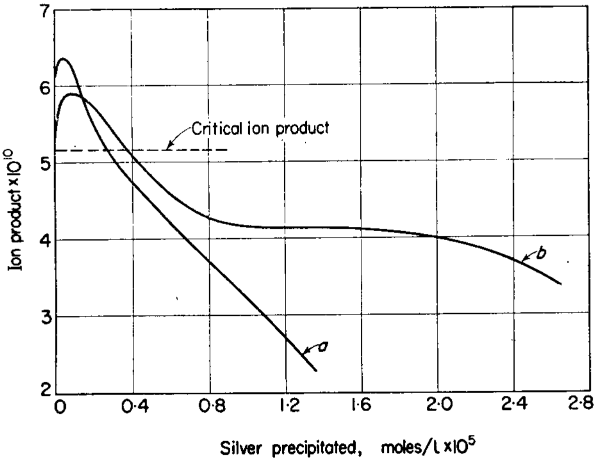

FIG. 4.—Ion product of silver chloride as a function of amount of silver precipitated from homogeneous solution.

studies is dramatically demonstrated by this flat portion of the curve, where precipitation took place at a constant rate.

DISCUSSION

Classical nucleation theory predicts for the formation of relatively large nuclei that the nucleation rate is critically dependent upon concentration; that is, below some well-defined concentration nucleation proceeds so slowly as to be undetectable, while above that concentration the rate becomes so rapid as to be unmeasurable. The critical concentrations of silver chloride observed in the present work are not critical in the sense of the classical theory. This can be seen from Fig. 3, which shows that the ion

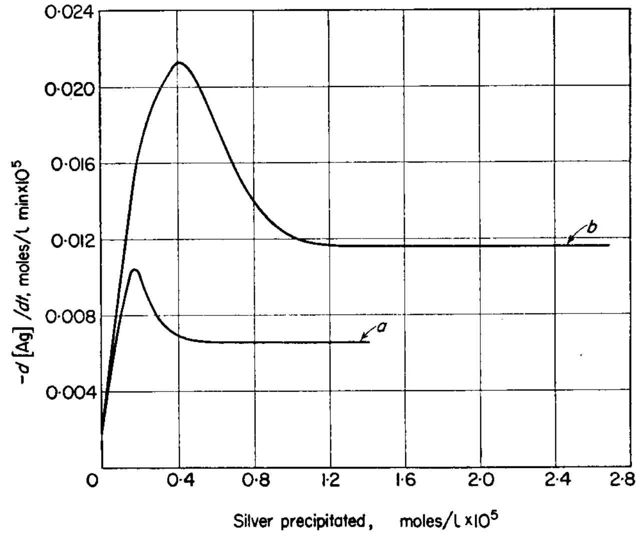

FIG. 5.—Rate of precipitation of silver chloride as a function of amount of silver precipitated from homogeneous solution.

products of the precipitating solutions rise above the observed critical value and remain above it for relatively long periods of time. If the observed critical concentration were truly critical, then concentrations above the critical could exist for only very short times, because the nucleation rate would become extremely large. The relatively long life of the *super-critical* concentrations indicates that nucleation in this system is not drastically concentration dependent. The ability of an impurity (eosin) to increase the value of the critical supersaturation also shows that $S_{\text{crit.}}$ cannot be a function of nucleation rate alone. If the nucleation rate were the sole factor determining the value of $S_{\text{crit.}}$, then it would not be possible for any additive to raise $S_{\text{crit.}}$ above that value required for self-nucleation. The critical supersaturation which is observed must always be that which corresponds to the nucleation process which occurs most readily. Additives which promote nucleation should produce a lower critical supersaturation, while additives which might inhibit nucleation should have no effect on $S_{\text{crit.}}$, because the more rapid nucleation process (*i.e.* the eosin-free nucleus) would still be observed before the slower process (the eosin-containing nucleus). Because the presence of eosin leads to a higher observed critical concentration, and because the increase cannot be attributed to nucleation, processes other than nucleation must be significant in fixing the value of the observed critical concentration. Eosin is known to inhibit the growth of silver chloride particles;[8] the effect of eosin in raising the critical concentration can be explained on this basis.

The results of this research also have some significance for co-precipitation studies, as carried out using the technique of precipitation from homogeneous solution. Such studies have shown that when two compounds precipitate together, their distribution between the solid phase and the solution phase may often be described by the following equation:[7]

$$\ln \frac{\text{(A) initial}}{\text{(A) final}} = \lambda \ln \frac{\text{(B) initial}}{\text{(B) final}},$$

where the brackets refer to solution concentrations and λ is the distribution coefficient. While λ is ordinarily constant for a fixed set of experimental conditions, Hermann[9] and Feibush, Rowley, and Gordon[10] have presented evidence indicating that λ depends upon the rate of precipitation, approaching unity as the rate increases.

The rate of precipitation of silver chloride from homogeneous solution is shown in Fig. 5. Throughout most of the precipitation, the rate was quite constant showing, however, considerable variation during the early portion of the precipitation. In studying the co-precipitation of manganese on basic stannic sulphate, Gordon, Teicher, and Burtt[11] found that the amount of manganese co-precipitated is large during the initial stages of precipitation, and that further co-precipitation is negligible until the tin has been almost completely removed from solution. Assuming that precipitation of basic stannic sulphate is analogous to that of silver chloride, then the large initial co-precipitation can be attributed to the earlier variable and more rapid precipitation rate.

Unless seeded solutions are used, the first portion of a precipitation process must occur at a greater rate than the subsequent portion, for the supersaturation must be high in order to form sufficient nuclei. The early precipitation rate may be controlled by suitable adjustment of the concentrations in the reacting mixture. Because run "*a*" of Fig. 5 initially contained about twice as much silver as run "*b*", the ion product of "*a*" was much more sensitive to chloride ion concentration, so that precipitation of a small amount of silver decreased the ion product of "*a*" much more than that of "*b*", with the precipitation rate decreasing accordingly. However, the influx of chloride ion from the allyl chloride also had a greater effect on "*a*" than "*b*", tending to raise the ion product more. For silver chloride, therefore, the initial variation of precipitation rate is best controlled by working with more concentrated silver and more dilute allyl chloride. In general, the extent of the early rapid precipitation and its attendant high co-precipitation, will depend upon the initial concentration of the ion to be precipitated, the rate of generation of precipitant, the concentration at which the nucleation rate becomes appreciable, and the kinetics of growth of the precipitate.

By proper adjustment of the concentrations in the reacting solution, it should also be possible to influence the size and the size distribution of the particles of precipitate. Fig. 3 shows that the ion product for run "*a*" was above that of "*b*" for about two hours. Because the nucleation rate depends upon the concentration raised to some low power, many more particles were formed in "*a*" than in "*b*". This can be shown from Davies and Jones[12] expression for the precipitation rate of silver chloride:

$$\frac{-d\,\mathrm{AgCl}}{dt} = kS\Delta^2,$$

where

S = available surface area,

Δ = amount of silver chloride to be precipitated, defined by $[\mathrm{Ag}^+ - \Delta]\,[\mathrm{Cl}^- - \Delta] = K_{\mathrm{sp}}$.

Three hours after the start of the runs, the calculated value of kS for run "*a*" was about three times that for run "*b*", although only about one-eighth as much silver chloride had been precipitated. Therefore, many more particles were present in "*a*" than in "*b*".

At the end of the precipitations, the particles of "*a*" should be more uniform in size than those of "*b*" as is suggested by Fig. 3. After 220 minutes, the ion product of "*a*" dropped below "*b*", meaning that new particles were being formed in "*b*" after nucleation had essentially stopped in "*a*"; that is, nucleation occurred over a longer period of time in "*b*". This distinction is emphasised in Fig. 4, which shows that the ion product of "*b*" was higher than "*a*" at all times after 0.12×10^{-5} moles/litre of silver chloride had precipitated. Therefore, run "*a*" nucleated more rapidly than run "*b*" over about 1% of the total precipitation of "*a*", while run "*b*" nucleated more rapidly over about 98% of its total precipitation.

It appears, therefore, that although many more particles formed in run "*a*", they formed within a shorter time span and their growth rate was smaller, so that the final particles should have been more uniform in size. This aspect of nucleation should be studied by other methods in order to draw more definite and quantitative conclusions.

The results of this research have shown that the rate of nucleation is not drastically dependent upon concentration. This suggests that the process of nucleation may be studied by a kinetic method, such as that of Christiansen and Neilsen[13]. During the course of the present research a kinetic method of determining the size of the nucleus was developed. This method, reported in the following paper[14] indicates a small nucleus consisting of a few ion pairs.

Acknowledgement—The authors wish to acknowledge the partial support of the Atomic Energy Commission under Contract AT(11-1)-582.

Zusammenfassung—Keimbildung und Fällung von Silberchlorid aus "homogener Lösung" wurden untersucht. Die kritischen Übersättigungen für Silberchlorid wurden bestimmt. Es wurde gefunden, dass die kritischen Übersättigungen qualitativ von denen nach der klassischen Keimbildungstheorie differieren; dies wurde durch Annahme einer Abhängigkeit von sowohl Keimbildung als auch Wachstum interpretiert. Die Fällungsgeschwindigkeit ist während der Fällung aus homogener Lösung nicht konstant, sondern verändert sich sehr stark in der ersten Phase der Fällung. Sowohl die Änderung der Fällungsgeschwindigkeit am Beginne als auch die Teilchengrösse und die Grössenverteilung der Teilchen können bis zu einem gewissen Grad durch Variieren der Konzentration der Reaktanten beeinflusst werden.

Résumé—Les auteurs ont étudié la formation de germes et la précipitation du chlorure d'argent à partir de solutions homogènes. Ils ont déterminé les sursaturations critiques du chlorure d'argent; cependant, ils ont observé que ces sursaturations étaient différentes qualitativement de la sursaturation critique de la théorie classique de formation de germes et ils les ont interprétées comme dépendant à la fois des vitesses de formation des germes et de croissance des cristaux. La vitesse de précipitation n'est pas constante pendant toute une précipitation à partir d'une solution homogène, mais elle varie considérablement durant la première phase de la précipitation, on peut contrôler jusqu'à un certain point à la fois cette variation initiale de la vitesse de précipitation et le nombre de particules ainsi que leur distribution selon leurs dimensions, en faisant varier les concentrations des corps réagissants.

REFERENCES

[1] D. H. Klein and L. Gordon, *Talanta,* 1958, **1,** 334.
[2] J. H. Jonte and D. S. Martin, *J. Amer. Chem. Soc.*, 1952, **74,** 2052.
[3] *International Critical Tables.* VI, 230, McGraw-Hill, New York, 1929.
[4] J. A. Gledhill and G. Mc P. Malan, *Trans. Farad. Soc.*, 1952, **48,** 258; 1954, **50,** 126.
[5] V. K. LaMer and R. H. Dinegar, *J. Amer. Chem. Soc.*, 1951, **73,** 380.
[6] C. W. Davies and A. L. Jones, *Disc. Farad. Soc.*, 1949, **5,** 103.
[7] L. Gordon, *Rec. Chem. Progr.*, 1956, **17,** 125.
[8] C. W. Davies and G. H. Nancollas, *Trans. Farad. Soc.*, 1955, **51,** 823.
[9] J. A. Hermann, Ph.D. thesis, University of New Mexico, 1955.
[10] A. M. Feibush, Keith Rowley, and L. Gordon, *Analyt. Chem.*, 1958, **30,** 1605.
[11] L. Gordon, H. Teicher, and B. P. Burtt, *ibid.*, 1954, **26,** 992.
[12] C. W. Davies and A. L. Jones, *Trans. Farad. Soc.*, 1955, **51,** 812.
[13] J. A. Christiansen and A. E. Neilsen, *Acta. Chem. Scand.*, 1951, **5,** 673.
[14] D. H. Klein, L. Gordon, and T. H. Walnut, *Talanta,* 1959, **3,** 187.

Talanta, 1959, Vol. 3, pp. 187 to 190. Pergamon Press Ltd. Printed in Northern Ireland

NUCLEATION IN ANALYTICAL CHEMISTRY—III*

THE PRECIPITATION NUCLEUS OF SILVER CHLORIDE

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Summary—Precipitation from homogeneous solution has been employed to study the size of the nucleus of silver chloride. The kinetics of particle formation indicate that this nucleus consists of about five ions. This result supports the findings of the Christiansen-Nielsen nucleation theory.

INTRODUCTION

KINETIC methods for studying the nucleation of slightly soluble salts precipitating from solution have been developed by Christiansen and Nielsen,[1] O'Rourke and Johnson,[2] and Duke and Brown.[3] These workers have found that such nuclei are quite small, consisting of less than ten ions. The methods by which these determinations were made have been criticized on the following points: (*a*) the use of methods of precipitation involving direct mixing of the solutions, which might permit nuclei to form during the mixing process rather than after homogenisation of the solution,[4] (*b*) the failure to remove foreign particles from the reacting solution, thus permitting precipitation to take place on such particles rather than on nuclei formed within the solution,[5] and (*c*), the assumption, in the case of Christiansen and Nielsen, that precipitation is first detected when a constant fraction of the solute has precipitated, whereas it seems more likely that their technique would detect a constant absolute amount of precipitate.[2] The present paper describes a determination of the nucleus size of silver chloride, using a kinetic method which avoids the criticisms of the above methods, (except possibly *b*), but which supports their results.

In a study of the precipitation of silver chloride from homogeneous solution,[6] it was observed that the ion product, $[Ag^+][Cl^-]$, initially rose because chloride ion was being generated and nothing was being removed from the solution. Precipitation was always detected at a fairly well defined "critical" ion product. The observed ion product rose above this value of 5.3×10^{-10} and remained above it for an appreciable length of time. If the observed "critical" concentration were really critical in the sense corresponding to classical nucleation theory, then concentrations above the critical could exist for only a very short time, because the nucleation rate would become extremely great. The fact that super-critical concentrations were obtained for

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extended times indicates that nucleation in this system is not drastically concentration dependent, and that kinetic methods may be used to study the nucleus.

Nucleation is generally considered to take place via a step-wise mechanism, as follows:

$$\begin{gathered} Ag^+ + Cl^- = (AgCl) \\ (AgCl) + Ag^+ = (Ag_2Cl)^+ \\ \vdots \\ (Ag_iCl_{j-1})^{(1-j+1)} + Cl^- \rightarrow (Ag_iCl_j)^{(i-j)} \end{gathered}$$

All steps leading to (Ag_iCl_{j-i}) are steady-state equilibria. (Ag_iCl_{j-i}) is the nucleus, here defined as the smallest cluster for which growth is much more likely to occur than is dissociation.

If all nuclei (or constant fraction of them) grow to observable size, then

$$dN/dt = k[Ag^+]^i[Cl^-]^j, \qquad (1)$$

where N is the number of particles, t is time, and k is a constant. Assuming for simplicity that $i = j$,

$$dN/dt = k\,(I.P.)^n,$$

where I.P. is the ion product, $[Ag^+][Cl^-]$, and n is $\frac{i+j}{2}$. Then

$$N = k \int (I.P.)^n\, dt.$$

This equation then can be used to determine n, which furnishes an indication of the nucleus size.

In order to apply this equation to the case where chloride ion is being generated continuously, it is necessary to make the additional assumption that at all times the concentrations of the various sub-nucleus clusters are near their steady state concentrations, i.e. the steady state in the formation of these clusters must be attained rapidly with respect to the rate of change of the solution concentration.

EXPERIMENTAL

Silver chloride was precipitated from homogeneous solution, with allyl chloride as the chloride generating reagent. The course of precipitation was followed conductimetrically, the reacting solution having been filtered through Millipore filters (pore size $0.45\ \mu \pm 0.02\ \mu$) immediately before being placed in the conductivity cell. The materials, apparatus, and procedures are discussed in detail elsewhere.[6]

Seven precipitations were carried out at 25°. Aliquots of each precipitate suspension were filtered through Millipore filters (pore size $100\ m\mu \pm 8\ m\mu$) at a time approximately five hours after the ion product had reached its maximum value. The number of particles retained on the filter was counted microscopically, using dark field illumination and 100×. This technique did not permit detection of extremely small particles formed late in the precipitation. However, errors from this source were felt to be negligible, because in any one experiment the majority of the particles were formed when the supersaturation was near its maximum value. Therefore, the number of particles observed on a given area of the filter was taken to be proportional to N, the total number of silver chloride particles.

RESULTS AND DISCUSSION

Because the nucleation rate is proportional to the concentration raised to a power, the number of nuclei formed at relatively low supersaturations is negligible compared to the number formed at high supersaturations. Therefore, essentially all particles are produced within a fairly well defined concentration internal. The equation

$dN/dt = k(\text{I.P.})^n$ may therefore be integrated graphically over a closed concentration interval. The limits for the integration were chosen rather arbitrarily. It is quite likely that nucleation took place, perhaps to a significant extent, below the observed critical ion product. If the nucleation rate is dependent on the ion product to some moderately high power, then the exact location of the limits of integration is not important as long as the limits are not set too high. The integration was carried out above the ion product of 3×10^{-10}; subsequent calculations have shown that the results were unchanged by carrying out the integration above an ion product of 4×10^{-10}.

To determine the number of ions in the nucleus, the area under a plot of the ion product, raised to some power x against time was divided by N to give $1/k$. For each value of x the values of $1/k$ were plotted against the corresponding areas under the curve, and also against N. The best straight lines were fitted to the points, using the method of least squares. When the absolute values of the slopes are a minimum, k is a constant and x equals n.

Table I presents the data used in the determination of the nucleus size. No units are given for $\int (\text{I.P.})^x \, dt$ and N, because these were determined only relatively. The results indicate that n is 3, corresponding to a nucleus of 5 ions. Too much precision cannot be attributed to the number 5, for the present method would not seem capable of determining the nucleus size exactly. Errors in determining the ion product as a function of time are increased appreciably when the ion product is raised to a power. Also, the precision in determining N is rather poor, being about 15%. Nevertheless, this method does support the results obtained using other kinetic approaches, namely, that nuclei for the precipitation of salts from solution are quite small.

TABLE I.—KINETIC SIZE DETERMINATION OF THE SILVER CHLORIDE PRECIPITATION NUCLEUS

10^5 Ag, *mole/litre*	Allyl chloride *g/litre*	No. of particles, N	$\frac{\int IP^1 dt^*}{N}$	$\frac{\int IP^2 dt^*}{N}$	$\frac{\int IP^3 dt^*}{N}$	$\frac{\int IP^4 dt^*}{N}$	$\frac{\int IP^5 dt^*}{N}$
4.77	0.32	116.1	0.66	0.80	0.96	1.22	1.53
8.39	0.20	101.7	0.93	0.89	0.87	0.81	0.72
5.26	0.29	85.0	0.76	0.90	0.92	1.01	1.13
6.93	0.16	74.8	1.34	1.28	1.28	1.23	1.13
7.29	0.20	66.5	1.27	1.15	1.07	0.92	0.84
5.36	0.22	52.7	0.93	0.86	0.80	0.67	0.56
8.71	0.14	33.6	1.14	1.11	1.10	1.16	1.11
Slope of plot of $\frac{\int IP^x dt}{N}$ vs. $\int IP^x dt$			+0.0027	+0.00041	+0.0011	+0.0031	+0.0052
Slope of plot of $\frac{\int IP^x dt}{N}$ vs. N			−0.0052	−0.0031	−0.00068	+0.00099	+0.0046

* Expressed in arbitrary units such that the mean value of $\frac{\int IP^x dt}{N} = 1.00$

Acknowledgement—The authors wish to acknowledge the partial support of the Atomic Energy Commission under Contract AT(11-1)-582.

Zusammenfassung—Fällung aus "homogener Lösung" wurde angewendet um die Grösse der Keime von Silberchlorid zu ermitteln. Die Kinetik der Teilchenbildung lässt schliessen, dass die Keime aus etwa fünf Ionen bestehen. Dieses Ergebnis stützt die Resultate der Keimbildungstheorie nach Christiansen-Nielsen.

Résumé—Les auteurs ont utilisé la précipitation à partir de solution homogène pour étudier la grosseur des germes de chlorure d'argent. La cinétique de la formation des particules indique que le germe est constitué d'environ cinq ions. Ce résultat est en accord avec les conclusions de la théorie de formation des germes de Christiansen-Nielsen.

REFERENCES

[1] J. A. Christiansen and A. E. Nielsen, *Acta Chem. Scand.*, 1951, **5,** 673.
[2] J. D. O'Rourke and R. A. Johnson, *Analyt. Chem.*, 1955, **27,** 1699.
[3] F. R. Duke and L. M. Brown, *J. Amer. Chem. Soc.*, 1954, **76,** 1443.
[4] D. Turnbull, *Acta Metallurgica*, 1953, **1,** 684.
[5] A. E. Nielsen, *Acta Chem. Scand.*, 1957, **11,** 1512.
[6] D. H. Klein, L. Gordon, and T. H. Walnut, *Talanta*, 1959, **3,** 177.

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LUMINESCENCE SPECTRA FROM HIGH-FREQUENCY EXCITATION—I

THE SPECTRA OF SOME INORGANIC GASES

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Summary—A high-frequency generator is described which is capable of exciting "Tesla-type" luminescence in inorganic and organic gases and vapours at low pressures. New apparatus and a new method of examining the spectra are described. The results of investigations on air, oxygen, carbon dioxide, sulphur dioxide, nitrogen and argon are presented and discussed.

INTRODUCTION

A HIGH-VOLTAGE discharge in an organic vapour normally decomposes the compound and excites the spectra of carbon and carbon oxides only. Wiedemann and Schmidt[1] were able to produce luminescence, which proved to have continuous emission, in ten particularly stable organic compounds, by passing the electrical discharge from an induction coil through the vapour of the compounds at low pressures. Subsequently Kauffmann[2] produced luminescence in the vapours of a number of carbon compounds, even at ordinary pressures, by applying a high-frequency (Tesla) discharge. He made some attempt, not very successful since it was more or less qualitative, to relate colour of the discharge and constitution of the compound.

In 1923 Stewart and his co-workers[3] published the first results of a series of investigations of the spectra produced by a Tesla discharge in organic vapours, examining the visible and near ultra-violet regions. They examined a fairly complete range of types of organic compound,[4] and to distinguish these spectra from fluorescence spectra and absorption spectra, they coined the name "Tesla-luminescence spectra."

The Tesla discharge used by Stewart and his co-workers was obtained from apparatus of some complexity and massive dimensions. Their first apparatus, for example, consisted of an oil-insulated Tesla transformer having forty coils on the primary and 460 coils on the secondary, and a Leyden jar with a capacity of about 1 litre, in conjunction with a choke-coil off a quarter-kilowatt high-tension transformer. A more powerful apparatus built subsequently contained 330 coils in the secondary and 30 coils in the variable primary of the air insulated high-frequency generator, and four Leyden jars each of about 10-litre capacity; an 18-inch spark coil was employed as source. The lack of detailed information in the literature about their sources, however, makes it impossible to hazard more than a guess about the characteristics of the high-frequency current used by them.

Stewart and his co-workers recorded their spectra photographically using a Hilger Medium Quartz Spectrograph, with no method other than the eye to determine intensities. They found that certain types of compound gave well-defined band spectra, and classified these spectra into the following categories:

1. *Benzene region* spectra, in the range 2500–3150 Å, produced by a phenyl nucleus;

2. *Carbonyl region* spectra in the range 3400–4850 Å, produced by aliphatic aldehydes and ketones;

3. *Blue Band region* spectra in the range 3850–5000 Å, produced by aromatic aldehydes and ketones;

4. *Green Glow region* spectra in the range 4550 Å upwards, produced by a benzene ring substituted by two saturated hydrocarbon radicles or a second non-benzenoid ring;

5. *Condensed Nuclei region* spectra in the range 2900–4900 Å, produced by aromatic condensed ring systems.

They concluded that only compounds containing a benzenoid ring or a carbonyl group were capable of emitting Tesla-luminescence spectra; and Stewart was of the opinion[5] that the diatomic permanent gases, for example, under Tesla excitation, showed only the ordinary spectra which would be produced by high-voltage discharge. Indeed, the original apparatus was used[6] to produce an intense hydrogen continuum in the ultra-violet for the examination of absorption spectra of inorganic crystals, with the advantage that the discharge tube required no internal electrodes and little or no external cooling.

Stewart and his co-workers attempted to calculate relationships between the frequencies of the band heads of the various spectra, and to relate these to structure; but their measurements were too imprecise, with the apparatus then available, to permit of much success. They also recognised the possibility of applying the spectra for analytical purposes, but made no attempt to follow up this line of investigation. A few years ago attention was again drawn[7] to the possibility of applying the spectra analytically, but no work along these lines can be traced in the literature before the present investigations.

In the belief that with modern instrumentation, as applied both to the excitation of the high-frequency discharge and to the recording and measurement of the spectra it should be possible to obtain

1. more precise measurement on which to base an examination of the fundamental nature of the spectra,
2. precise measurements for quantitive analytical purposes as well as for simple identification, and
3. excitation of a greater range of compound types than was obtained by the earlier workers,

we have initiated a series of investigations, both of inorganic and organic compounds, designed to cover these points.

This paper presents the first results obtained in these investigations, and is confined to simple inorganic gases since these have proved more amenable to excitation, and present fewer problems in the recording and measurement of the spectra. Further papers will extend the field to other inorganic compounds and to organic compounds.

EXPERIMENTAL

Apparatus

In developing new apparatus for the production and examination of luminescence spectra excited by high frequency, three separate parts required consideration:

1. The high-frequency or Tesla generator.
2. The sample tube.
3. The instruments for the detection and examination of the spectra.

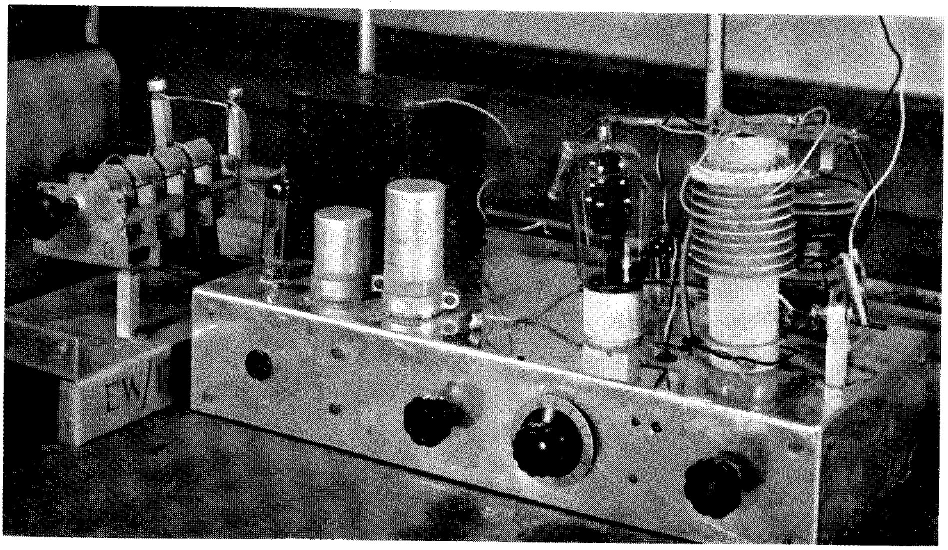

FIG. 1.

1. *The high-frequency generator:* (Fig. 1): The earlier publications provided little help in the construction of a new high-frequency generator. In none of the papers of Stewart and his co-workers was there to be found a statement of the voltage and frequency attainable, or used in obtaining the various spectra; and none of the contemporaries of these workers could recollect if these values were ever known. From a study of the information available it was deduced that a frequency of some 100 kc/s at, perhaps, 10 kV might possibly have been obtained. Using these figures as a guide the apparatus shown in Fig. 1 was developed. This consists of a simple radio-frequency transformer in a self-oscillating circuit at approximately 200 kc/s with an 807 valve. This generator produces a sinusoidal alternating current in the range 5–15 kV.

Two other electrical arrangements gave inferior results to the above circuit: (*i*) variable direct current, 0–15 kV. (*ii*) a pulsed radio-frequency oscillator. The latter was built using an 807 valve and a television line output-transformer as a self-excited oscillator, producing pulses up to 10 kV, approximately 1 μsec wide, in bursts spaced at about 0·1 msec.

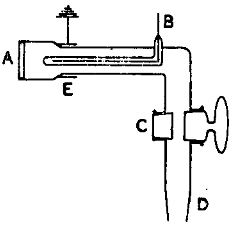

FIG. 2.

2. *The sample tube:* The sample tube in which the vapour or gas was placed for excitation consisted initially of a glass tube 5 cm long and 1 cm in diameter (both dimensions being found by experiment) having at one end a quartz window of diameter 2 cm. Tubes with a body diameter greater than 1 cm did not glow so brightly, presumably because the earth electrode was too remote from the central electrode.

The other end of the sample tube was drawn out, provided with a vacuum tap, and with a ground-glass joint which allowed the tube to be attached to a vacuum train at a convenient point.

The central or inner electrode of the sample tube consisted of a glass-coated tungsten wire, and the external electrode was a piece of metallic foil wrapped round the outside of the tube. The sample tube is shown diagrammatically in Fig. 2.

Notes:

(1) The original sample tubes had straight central electrodes which caused a large portion of the discharge to enter the drawn-out part of the tube, resulting in decreased glow-intensity. The discharge remained opposite the quartz window in sample tubes fitted with the bent central electrode, as shown in Fig. 2.

(2) Some tubes were sealed off before removing them from the vacuum system, but this did not have any advantage. Those with taps fitted retained their low pressures for 3–4 hours, and were very satisfactory.

(3) The quartz window, approximately 1 mm thick, was fixed in position with black wax, and showed no tendency to come away because of heat from the discharge.

(4) The effect of the glass coating on the central electrode was to produce an even discharge without any tendency to sparking, as occurred with uncoated wire.

(5) A sample tube in operation, filled with glowing vapour, is shown in Fig. 3.

3. *Detection of Spectra:* To detect the spectra a Hilger "Uvispek" Spectrophotometer was used. The tube was placed in front of the flame photometer aperture of the spectrophotometer, and the instrument was set as for measurements at this position. The light passing through the spectrophotometer was then examined at different wavelengths in the usual way (see Proceedure below) and the intensities at the different wavelengths recorded on a Honeywell–Brown Pen Recorder.

Notes

(1) Since the intensity of the glow is usually low compared to a normal flame source, it was sometimes necessary to use slit widths of approximately 0·3 mm. If the glow was more intense, the slit was closed to 0·2 mm, thus improving the resolution.

(2) The instrument was set to a high sensitivity, which caused the recorder trace to become slightly erratic at times.

(3) The aperture was screened carefully from external light sources. In addition, it was necessary to wire the hydrogen lamp inside the spectrophotometer in such a way that it could be switched off when not required.

(4) Because of the small size of the high-frequency generator, it was a simple matter, after reducing the pressure in the sample-tube to the required value and admitting the gas or vapour, to arrange the generator and sample-tube in position before the spectrophotometer.

Procedure

A sample-tube was attached to a vacuum train evacuated by a two-stage Hg diffusion pump, backed by a rotary oil pump. The entire system was pumped out to a pressure of less than 10^{-3} mm Hg, as measured by a Pirani gauge, and remained at this pressure for at least half an hour

The filling gas (*i.e.* gas or vapour under examination) was allowed to sweep out the system which was then pumped out again to 10^{-3} mm Hg. The sample-tube was now isolated at 10^{-3} mm pressure and the rest of the system filled with the gas or vapour under examination. On opening the sample-tube to the system the gas or vapour flowed into it.

The pressure in the sample-tube was now reduced. The high-frequency generator was switched on and a note was made of colour changes which occurred at the different pressures. By this means the optimum pressure for the gas or vapour under examination was determined.

The sample-tube was now filled as before, the pressure was reduced to the desired level, and the glow was examined by passing the light through the spectrophotometer. For examination of a spectrum the spectrophotometer was set to "Flame Source" and the recorder was switched on. After allowing approximately 1 hour to warm up, the controls were set to a high sensitivity, keeping the recorder near zero. The slit was set to 0·3 or 0·2 mm, the wavelength drum at 10,000 Å and the generator and sample-tube set up in the recommended way. The generator was now switched on and the optimum glow was obtained by altering the condenser. The slit in the spectrophotometer was opened, the wave-length drum was slowly revolved and the intensity of the glow at each wavelength was recorded on the chart.

A general view of the vacuum train, high-frequency generator, rotary pump and Pirani gauge is shown in Fig. 4.

RESULTS

Air, carbon dioxide, oxygen, sulphur dioxide, nitrogen and argon, have been examined and give reproducible results.

1. *Air*

The spectrum is shown in Fig. 5(*a*). The most intense peak is at 4380 Å. No peaks were observed below 2800 Å or above 6000 Å. Fifteen peaks in all occur in this spectrum.

2. *Oxygen*

The spectrum is shown in Fig. 5(*b*). Nineteen major peaks were present. The spectrum is similar to that of air but is characterised by peaks occurring at 2190 Å and 2300 Å, which were never obtained with air.

3. *Carbon dioxide*

The spectrum, containing seven major peaks, is shown in Fig. 5(*c*). It is completely different from that of air and oxygen. Very slight traces of peaks occur at 5550 Å,

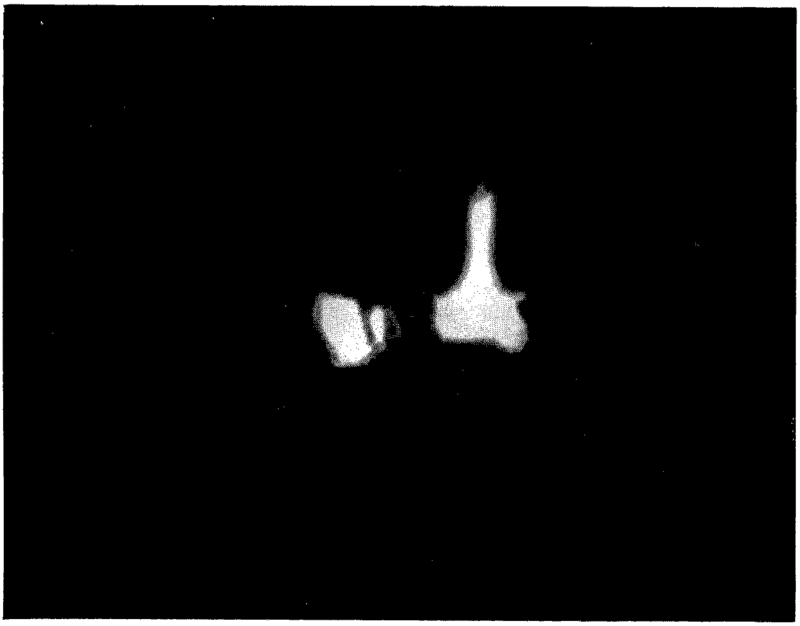

Fig. 3.

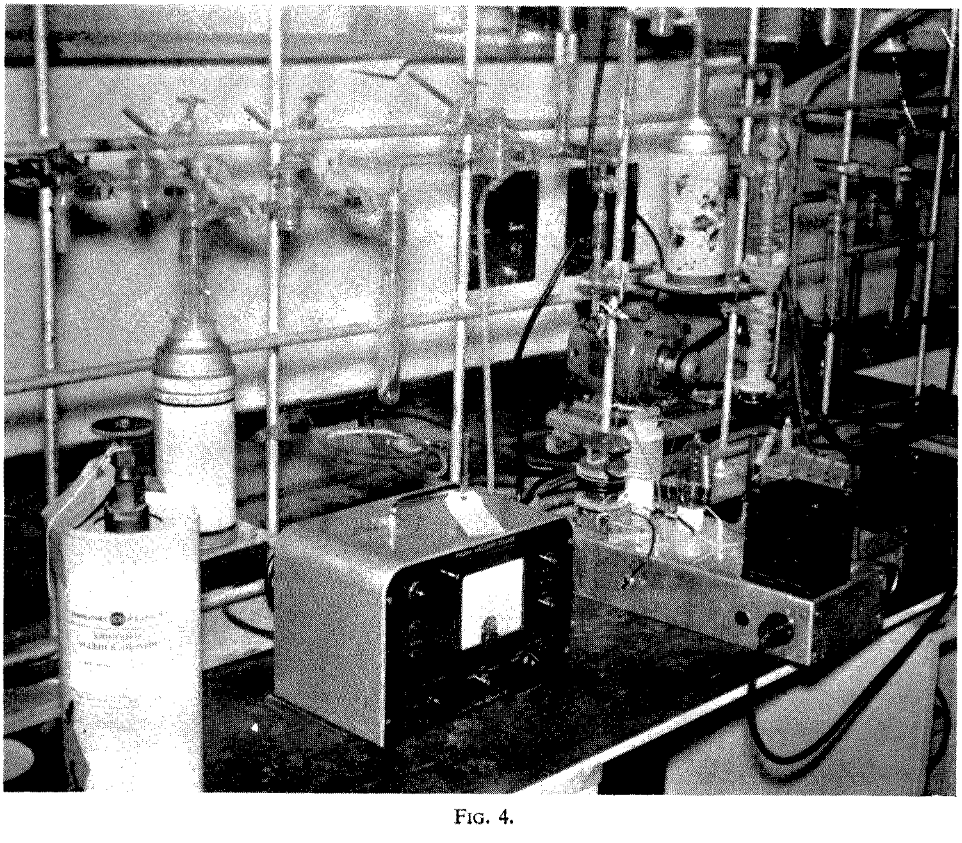

Fig. 4.

5170 Å, 4820 Å etc. These are taken to be due to traces of air or oxygen present in the gas.

4. *Sulphur dioxide*

The spectrum, containing fifteen major peaks, is shown in Fig. 6(*a*). It is similar to that of air or oxygen, but shows a marked difference in having a strong peak at 4270 Å, the strong oxygen peak at 4500 Å being absent.

5. *Nitrogen*

The spectrum, containing ten major peaks, is shown in Fig. 6(*b*). It resembles that of carbon dioxide but shows a difference in the region between 2580 Å and 3900 Å.

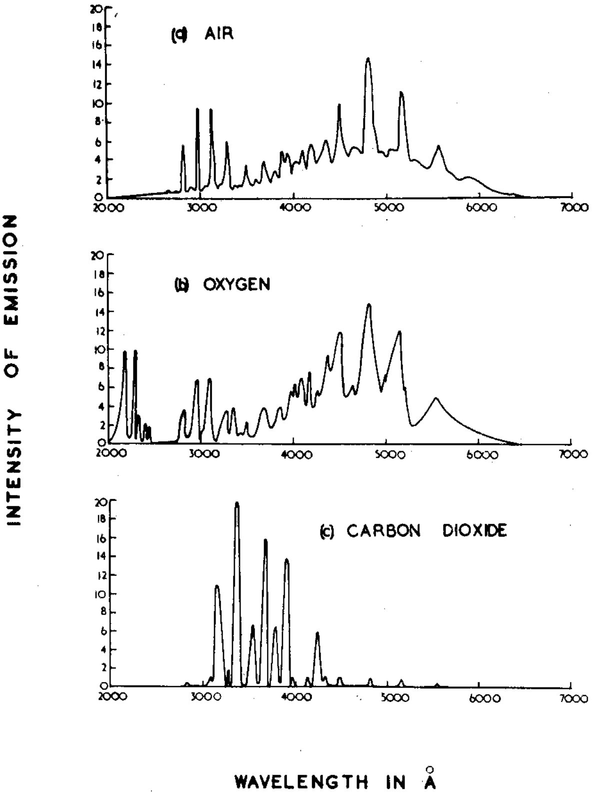

Fig. 5.

6. *Argon*

The spectrum, containing six peaks, is shown in Fig. 6(*c*). It does not resemble any of the others. One characteristic peak occurs at 3085 Å. This did not occur in any other gas examined in the present work.

Detailed results and observations on the above are recorded in the following table.

DISCUSSION

The outstanding characteristic of the results viewed generally is the division of the gases examined into three groups. In one group, comprising air, oxygen and sulphur dioxide, the overall spectra are similar, although distinguishing peaks occur. Nitrogen and carbon dioxide, while showing many common peaks are surprising; bands obtained in spectrographic work associated with high-frequency excitation are generally assumed to be nitrogen bands from air; but in the present work none of the nitrogen bands appear in the air spectrum.

It is believed that the answer to these differences lies in the pressures employed for excitation. The maximum glow of nitrogen was obtained with pressures in the range 1·5–4·0 mm. When operated at pressures below 1·5 mm the luminescence changed to bluish in colour and was then extinguished. For air the maximum glow range was 0·8–1·0 mm Hg, for oxygen, 0·2–2 mm and for sulphur dioxide about 0·1–0·2 mm Hg. In these circumstances, therefore, it would appear that almost all the luminescence spectrum of air is explained by assuming the light emission to result from the oxygen in the air, the nitrogen not showing any luminescence at this pressure.

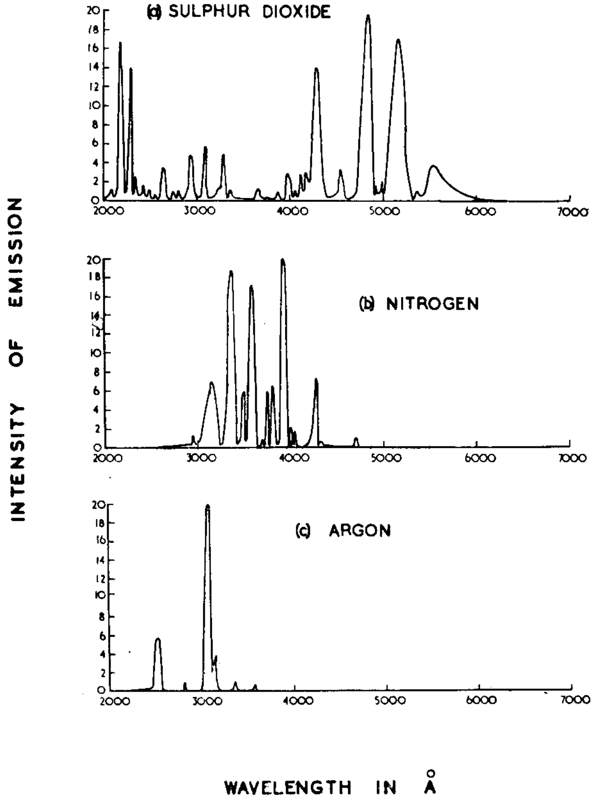

Fig. 6.

It has been pointed out already that sulphur dioxide shows a close similarity to oxygen and air. One portion of the spectrum is common to oxygen and sulphur dioxide but has not been detected in air. This is the portion containing peaks in the far ultra-violet, *viz.* at 2190, 2300, 2325 Å, etc. It may be suggested that the high-frequency excitation of the sulphur dioxide molecule causes dissociation so that the spectrum

TABLE I

Gas	Peaks recorded in spectrum Å	Pressure used, mm Hg	Colour of glow	Remarks
Air	5550	0·8	Blue-violet	Glow bright and very stable.
	5170			
	4830	1·0		
	4500			
	4380			
	4200			
	4120			
	3960			
	3880			
	3700			
	3480			
	3300			
	3120			
	2970			
	2830			
Oxygen	5550	0·2	Blue-pink	Stable glow, maximum at approximately 1 mm.
	5170			
	4820	2·0		
	4500			
	4370			
	4180			
	4110			
	4010			
	3910			
	3880			
	3685			
	3370			
	3290			
	3120			
	2970			
	2830			
	2325			
	2300			
	2190			
Carbon dioxide	4260	0·7	Blue	—
	3910			
	3780	1·5		
	3580			
	3540			
	3370			
	3160			
Sulphur dioxide	5550	0·1	Blue-white	—
	5170			
	4840	0·2		
	4680			

TABLE—I (*contd.*)

Gas	Peaks recorded in spectrum Å	Pressure used, mm Hg	Colour of glow	Remarks
	4270 3950 3290 3120 2970 2820 2480 2445 2325 2300 2190			
Nitrogen	4280 4040 4000 3915 3800 3760 3580 3530 3370 3160	1·5 4·0	Deep purple	Stable over a wide range of pressure.
Argon	3580 3370 3150 3085 2820 2535	0·3 3·0	Pink to green	Pinkish at low pressures; greenish at higher pressures.

obtained is largely that of an oxygen fragment and an SO fragment. In this connection it will be observed that of all the gases studied SO_2 shows luminescence at the lowest pressure, starting about 0·05 mm, but this begins to be quenched above 0·5 mm.

In relation to carbon dioxide and nitrogen it is interesting to record that Keller and Smith, in testing a Tesla-coil source[7] for spectrographic analysis, found that nitrogen bands were always present when they used a carbon dioxide atmosphere. They assumed that this may have been due to air not entirely eliminated from the system, a film of nitrogen adhering to the glass wall, or nitrogen impurity in the carbon dioxide. The present authors are strongly of the opinion that the last reason supplies the answer. That this method of excitation brings out distinctive nitrogen peaks in the carbon dioxide suggests considerable sensitivity.

There is independent support of the suggestion that, in the case of sulphur dioxide, the emission of light is due to radicals produced in the dissociation of the SO_2 molecule. Evidence of dissociation of a molecule during the production of luminescence excited by a high-frequency discharge has already been obtained by the authors in connection with work on organic vapours.[8] It is thought that the emission of the light by the other molecular gases examined may be due not so much to the dissociation of the molecule concerned but to the production of excited states.

The apparatus outlined above is not costly to construct and is capable of wide adaptability. It offers possibilities in the field of analysis and in investigations of inorganic and organic material which, up to the moment, appear to have been overlooked.

Acknowledgement—We would like to express our thanks to Mr. K. Quigg of the Electronics Division of this Department for his assistance and advice in connection with the construction of the Tesla-generator.

Zusammenfassung—Ein Hochfrequenzgenerator wird beschrieben, der imstande ist Teslaluminiscenz in anorganischen und organischen Gasen und Dämpfen, bei niederem Druck zu erregen. Ein neuer Apparat sowie eine neue Methode die Spectren zu untersuchen wird beschrieben. Die Ergebnisse der Untersuchungen an Luft, Sauerstoff, Kohlendioxyd, Schwefeldioxyd, Stickstoff und Argon sind dargelegt und werden diskutiert.

Résumé—Les auteurs décrivent un générateur à haute fréquence qui est capable d'exciter la luminescence "Tesla" dans les vapeurs et les gaz minéraux et organiques à faibles pressions. Ils décrivent un nouvel appareil et une nouvelle méthode d'examen des spectres. Ils présentent et discutent les résultats de recherches sur l'air, l'oxygène, l'anhydride carbonique, l'anhydride sulfureux, l'azote et l'argon.

REFERENCES

[1] E. Wiedemann and G. C. Schmidt, *Ann. Physik*, 1859, **56**, 20.
[2] H. Kauffmann, *Z. phys. Chem.*, 1898, **26**, 719.
[3] W. H. McVicker, J. K. Marsh and A. W. Stewart, *J. Chem. Soc.*, 1923, 642.
[4] A concise account of the investigation, with complete references may be found in A. W. Stewart and C. L. Wilson, *Recent Advances in Physical and Inorganic Chemistry*, 7th Edition, Longmans Green and Co., Ltd., London, 1944, pp. 452–478.
[5] A. W. Stewart, personal communication.
[6] C. L. Wilson, M.Sc. Thesis, The Queen's University, Belfast, 1933.
[7] *Idem*, *Ann. Reports on the Progress of Chemistry*, 1953, **49**, 331: R. E. Keller and L. Smith, *Proc. Iowa Acad. Sci.*, 1950, **57**, 181.
[8] T. Given, R. J. Magee and C. L. Wilson, Work in progress.

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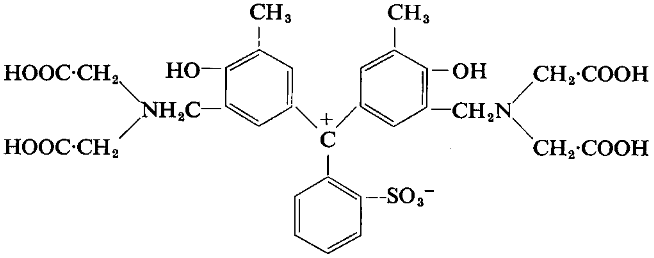
PRELIMINARY COMMUNICATIONS

Contributions to the basic problems of complexometry—II

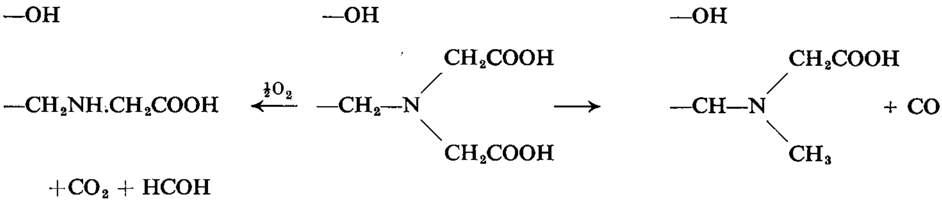
Decomposition of Xylenol Orange in aqueous solutions

(*Received* 3 *October* 1959)

ONE of the more promising metallochromic indicators of the "complexone type" suggested in recent times[1,2] is Xylenol Orange (I). It has already been utilized by a number of authors in various practical applications.



However, the stability of aqueous solutions of Xylenol Orange is limited. Its decomposition is accompanied by slow loss or complete disappearance of its metallochromic properties. This can be well observed in its colour reactions, for example with thorium, bismuth, lead or zinc. In solutions of these cations at suitable pH,[1] one drop of 0·1% to 0·5% Xylenol Orange solution produces an intensely red, eventually red-violet coloration. Aqueous solutions of the indicator more than one month old either do not give these reactions at all or give them only very weakly. Only the reaction with copper—the development of an intense violet-red coloration—is fully maintained. Indeed it is possible, though this is very surprising, to use such "aged solutions" as an excellent indicator for copper, in spite of the fact that fresh Xylenol Orange alone produces with copper robust complexes which react only slowly with EDTA solution. Xylenol Orange thus becomes effectively a specific indicator for copper. The most probable explanation of this is that in aqueous solutions slow decarboxylation of two symmetrically placed carboxyl groups takes place. In this manner a substance with a new complex-forming grouping (III) is developed, which is very similar to the complex-forming grouping of Glycinethymol Blue (IV).[3]



IV Glycinethymol Blue grouping

II Xylenol Orange

III

It is very difficult to achieve artificial aging of Xylenol Orange solutions. Freshly prepared aqueous solutions tolerate boiling without decomposition, and may be evaporated to dryness or heated at 60° for several days. Solutions acidified with glacial acetic acid or hydrochloric acid can also be boiled for a longer time without decomposition. Xylenol Orange decomposes rapidly on boiling with nitric acid or sodium hydroxide. The aqueous solutions are stable to oxidation by atmospheric oxygen. Stronger oxidizing agents (hydrogen peroxide, cerium^{IV} sulphate) decompose the indicator immediately. In the decomposition in this manner all the metallochromic properties disappear, and only the original acid-base properties of the parent indicator—cresol red—are maintained.*

The behaviour of Xylenol Orange with lead dioxide is very interesting as illustrated by the following experiments. Solid lead dioxide was added to an aqueous solution of Xylenol Orange which was slightly acidified with acetic or sulphuric acid and the solution was thoroughly stirred with an electromagnetic stirrer. As in the case of our earlier experiments on the oxidation of EDTA,[4] carbon dioxide and a large quantity of formaldehyde were detected. According to the experimental conditions (quantity and quality of PbO_2, time and intensity of stirring, etc.) the Xylenol Orange solutions lost their metallochromic properties for heavy metals in a short time with the exception of copper, which could still be titrated using the indicator treated in this manner. The quality of the colour changes in the titration of copper (pH 5·5 to 6, hexamethylenetetramine) is, however, not so distinct as in the case of "naturally aged" solutions of Xylenol Orange. With the "artificially aged" indicator the colour change is from red-violet to clear yellow as in the first case. Only solutions carefully buffered to pH 5·2 to 5·4 give a sharp colour change.

This difference in behaviour can be easily explained. In the case of the "natural aging" of solutions only the decarboxylation takes place while the sarcosine derivative (III) develops (formaldehyde was not detected), whereas in the oxidation with lead dioxide the glycine derivative (IV) is produced, which is less suitable for the titration of copper. It would, of course, be necessary to prove this assumption by a chromatographic examination of the two decomposition products of Xylenol Orange, followed by their isolation. The experiments are being continued.

Methylthymol Blue[5] behaves in a similar way. Because of its slight stability in aqueous solutions, it is easily converted to Glycinethymol Blue.[3] This decomposition reaction is also being studied further.

CONCLUSION

On storage aqueous Xylenol Orange solutions are subject to slow decomposition and lose their metallochromic indicator properties. It is probable that during the decomposition a sarcosine derivative is formed, which is a reasonably suitable indicator for the complexometric determination of copper in weakly acidic medium.

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REFERENCES

[1] J. Körbl, R. Přibil and A. Emr, *Coll. Czech. Chem. Comm.*, 1957, **22**, 961.
[2] J. Körbl and R. Přibil, *Chemist-Analyst*, 1956 **46**, 102.
[3] J. Körbl, E. Kraus and R. Přibil, *Coll. Czech. Chem. Comm.*, 1958, **23**, 1219.
[4] R. Přibil and J. Čihalík, unpublished results.
[5] J. Körbl and R. Přibil, *Coll. Czech. Chem. Comm.*, 1958, **23**, 873.

Isomeric complexans:† The dl and meso forms of 2:3-butanediamine-N:N:N′:N′-tetra-acetic acid

(*Received* 19 *October* 1959)

In recent studies on complexans[1] we have isolated two isomers of 2:3 butanediamine-N:N:N′:N′-tetra-acetic acid—2:3 BDTA$^{\alpha}$ and 2:3 BDTA$^{\beta}$, m.ps. 211–2° (decomp.) and 138–151° (decomp.) respectively.

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* Xylenol Orange is prepared by condensation of Cresol Red with formaldehyde and iminodiacetic acid.

† The term "complexan" has been recommended by the Analytical Chemistry Section of the IUPAC to describe polyamino-poly-carboxylic acids.

There were obtained by successive crystallisation from a chloroacetic acid condensation of the unresolved amine, and it is not therefore yet known which is the *meso* and which the *dl* form

By use of the polarographic technique described in a previous communication[2] it has been possible to show that there is a marked difference in the chelating properties of the two isomers. Thus 2:3 BDTA$^{\alpha}$ has virtually the same chelating power as CDTA for copper^{II} and cadmium, whereas that of 2:3 BDTA$^{\beta}$ is considerably weaker and is intermediate between those of CDTA and EDTA.

Values for one of these isomers have already been recorded.[2,3] The purpose of this preliminary communication is to amend the migration rate previously reported for 2:3 BDTA$^{\alpha}$ and to give more complete information on both isomers.

Complexan	M.p.° C	M_{I_1}	$E_{1/2}$ value for Cu chelate, *Volts S.C.E.*	$E_{1/2}$ value for Cu chelate from pherogram, *Volts S.C.E.*	$E_{1/2}$ value of Cd chelate, *Volts S.C.E.*
2:3 BDTA$^{\alpha}$	211–2	4·1	−0·41	−0·33	−0·97
2:3 BDTA$^{\beta}$	138–151	3·8	−0·32	−0·28	−0·87

To the best of our knowledge, this is the first occasion on which isomeric complexans have been reported.

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REFERENCES

[1] R. Belcher, W. Hoyle and T. S. West, Unpublished work; cf. W. Hoyle, Ph.D. Thesis, Birmingham University, 1959

[2] W. Hoyle and T. S. West, *Talanta*, 1959, **2,** 158.

[3] *Idem, ibid*, 1959, **3,** 47.

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SHORT COMMUNICATIONS

The determination of boron in iron and low-alloy steels with dianthrimide: A colorimetric method that does not require preliminary separations

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In recent years boron has been used increasingly in certain types of steel for constructional purposes. It gives improved hardenability and allows economies in the use of other alloying elements. Since the amounts of boron present are usually very low, about 0·001–0·005%, chemical determination has presented some difficulties. There has therefore been a need for a method that is simple but still accurate.

The first stage in the determination of boron in steel is to convert it from the different forms in which it may be present into boric acid. In general this is done by dissolving the steel sample in sulphuric acid and oxidising with hydrogen peroxide. Any boron compounds in the insoluble residue are brought into solution by fusion with sodium carbonate.

Usually the colorimetric determination of boric acid is preceded by some separation process, the extent of which depends on the colour reagent used. The most commonly used reagent, quinalizarin, is highly selective and does not react with any other element normally present in low-alloy steels. Nevertheless the quinalizarin method is often combined with a separation by electrolysis with a mercury cathode. This removes iron, chromium and other elements which would interfere with the determination, the iron by precipitation as the sulphate in the strong sulphuric acid solution in which the determination is made and the chromium by absorption of light at the wavelength of measurement.

A. *Experiments on keeping* Fe^{II} *in solution*

The principal source of interference in the determination of boron in steels low in chromium is the precipitation of iron as sulphate. For boron determinations in steels of this type, Rudolph and Flickinger[1] therefore developed a procedure using quinalizarin without preceding separations in which the ferrous sulphate is allowed to precipitate and settle out before a visual comparison is made. This method was taken as a starting point for the present investigation.

A prerequisite of increased accuracy is the replacement of the visual comparison with standard solutions by a photometric measurement. For this it is necessary to separate the precipitated ferrous sulphate but some difficulty was encountered. The precipitation and the sedimentation are both very slow. Even centrifuging was not sufficiently effective and the strong sulphuric acid solution could not be filtered in a practical way.

It seemed that it might be possible to dilute the solution and thereby keep Fe^{II} in solution at least for the time required to carry out the determination. The acid concentration cannot however be allowed to fall below 90% by weight since this would appreciably impair the sensitivity of the boron determination. These conditions are satisfied by the addition of 25 ml of 96% sulphuric acid to 3 ml of a solution of iron in approximately $2M$ sulphuric acid. It was found that this solution could hold up to 100 mg of Fe^{II} without any risk of the iron being precipitated. The resultant solution was colourless and had no absorption in the 600–650 mμ region.

A method for the determination of boron in low-alloy steels and cast iron based on these results has been in use in this laboratory for several years with satisfactory results. This method offered several advantages, especially in simplicity and speed, over methods used previously. The necessary limitation of the size of the sample and the reduction in the concentration of the acid has however an adverse effect on the determination of the lowest boron concentrations. A considerable improvement was afforded by replacement of quinalizarin by dianthrimide which has a higher sensitivity and more favourable spectral properties.

It was found that up to 100 mg of Fe^{II} could be retained in solution under the same conditions as before, even during the heating necessary for the reaction between boric acid and dianthrimide. No precipitate formed when the reaction solution was heated in a water bath for 2 hours at 100° or for 15 hours in an oven at 80°.

B. *Interferences*

Earlier investigations have shown that there are very few substances that interfere with the reaction between boric acid and dianthrimide. Among them are oxidants such as chromate and nitrate which destroy the reagent. Interference has also been reported due to fluoride, to large amounts of phosphate, and to titanium.

When steel is dissolved in sulphuric acid no oxidising compounds are formed that can interfere with the reaction; they may however be formed when the insoluble residue is fused with carbonate. It is therefore necessary after dissolving the melt to reduce such compounds; sulphurous acid is suitable for this purpose and a slight excess does not interfere with the reaction.

An investigation of possible sources of interference was carried out using solutions, with and without added boron, containing 100 mg of Fe^{II} and varying amounts of the alloying elements that may be present in steel. Tests were made with 10 mg of Ni, 2 mg of Mn, Cu, Cr, Co, 1 mg of Al, V, Ti, Mo, Zr, P and 0·1 mg of Sn and As. No interference from these substances was found provided that corrections were made for the absorption of coloured ions. The quantity of sodium carbonate used for fusion was also without any interfering effect on the determination. The high chromium contents that occur in stainless steels give blank values so large that they reduce the precision of the determination.

Several alloying elements are not completely soluble in diluted sulphuric acid and a considerable amount is then found in the acid-insoluble fraction as well as in the acid-soluble fraction. In some cases the same element may be present with different valency in the two solutions; this is possible with molybdenum and titanium. Analyses of low-alloy steels containing molybdenum showed that this element did not interfere with the determination in either the acid-soluble or the acid-insoluble fractions when the method recommended in section E was used. Unfortunately no corresponding Ti-containing steels were available. Titanium in the acid-soluble part might be present as Ti^{III} but it should be possible to oxidise such a solution with a stream of air followed by sulphurous acid reduction back to Fe^{II} of the iron oxidised at the same time.

C. *Dissolving the sample*

Steel samples for the determination of boron are usually dissolved in sulphuric acid in a flask fitted with a reflux condenser. Experiments on the use of a mixture of sulphuric acid and phosphoric acid showed that the presence of large amounts of phosphoric acid caused a strong decrease in the colour of the boron complex. It was found that it is not necessary to use a reflux condenser. If strong boiling is avoided while the sample is being dissolved a simple pear-shaped glass bulb in the neck of the vessel is just as effective. A series of analyses of a steel sample gave, in both cases, 0·0195% of boron as the mean of four determinations.

When the sample is dissolved in sulphuric acid in a vessel of boron-containing glass there is a risk of dissolving boron out of the glass. It is of course advantageous to use a flask of quartz or boron-free glass but after repeated and prolonged boiling with sulphuric acid even flasks of boron-containing glass can be used. These flasks should be reserved for boron determinations and should only be washed in dilute acid without any added oxidising agent.

The acid-insoluble residue is fused with anhydrous sodium carbonate after ignition in a platinum crucible at a dull red heat. The same results are obtained in this way as when the sodium carbonate is added before ignition, as usually recommended, but it avoids the occasional incomplete ashing of carbonaceous material which may cause the subsequent sulphuric acid solution to be discoloured.

It has long been customary in boron analyses on steel to report the boron contents of the acid-soluble and of the acid-insoluble fractions separately. This presupposes that some boron compounds are always soluble in acid and that others are always insoluble. Analyses of steel samples as described in section F showed large variations in the acid-insoluble fractions from different steels but in every steel there was a certain amount of boron that was insoluble in dilute sulphuric acid. The spread of these values was however greater than that for the total boron content. If the sample was oxidised when it was dissolved a little more of the boron usually went into solution. Kelly[2] made analyses on the same steel samples after solution in hydrochloric acid and oxidation with hydrogen peroxide and in some cases obtained rather large variations in the proportion of acid-soluble to acid-insoluble boron in the same steel. In another investigation,[3] however, treatment with different acids gave roughly the same amount of boron from the same steel.

D. *Modification of the dianthrimide method*

The optimum conditions for the determination of boric acid with dianthrimide as described in an earlier paper[4] were found to be:

Dianthrimide 0·4 mg/ml; *sulphuric acid* 93–95% by weight; *boron* 0·3–1·0 μg/ml; *heating time* at 100°, 1–1·5 h; or at 80°, 4–5 h. In the determination of small amounts of boron in steel without separations, some consideration must be paid to the presence of the iron and the smallness of the boron concentrations. To get the maximum accuracy it is necessary to use the largest amount of sample possible even if the acid concentration has to be reduced to 90% by weight. If the acid concentration is kept in the range 93–95% the weight of sample must be reduced to less than half, thus reducing the possibility of determining the lowest boron contents. It is also advisable to reduce the reagent concentration to less than half. This will of course reduce the sensitivity by 1 or 2 per cent but it will also reduce the reagent absorption by more than a half.

With these modifications it is essential to pay particular attention to certain of the results of the investigation described in the earlier paper.[4] A change in the strength of the concentrated sulphuric acid will affect the analytical result. It is therefore essential to check and if necessary to correct the calibration curve when a new stock solution is taken into use. The small variations in the acid concentration that are produced by varying consumptions of acid when dissolving the acid-soluble and the acid-insoluble parts can be neglected. In the method recommended, two different heating temperatures are suggested. With the modifications suggested here the calibration curves for these two methods will not be identical.

E. *Recommended method*

Solutions required. Dianthrimide reagent solution: Dissolve 150 mg of dianthrimide in 1000 ml of sulphuric acid (approx 96% w/w).

Diluted sulphuric acid (1 + 3).

Sulphurous acid (approx 6%).

Procedure: Take 3 g of sample in an Erlenmeyer flask (100–150 ml) and add 40 ml of diluted sulphuric acid (see note 1). Use a reflux condenser or a simpler corresponding arrangement. Heat to dissolve. Filter through a dense filter paper into a 100-ml volumetric flask. Wash with hot water. Cool to room temperature, dilute to the mark with water and mix. This flask (A) contains the acid-soluble boron. Ignite the filter in a platinum crucible at low temperature. Fuse with 2 g of anhydrous sodium carbonate. Dissolve the melt in 40 ml of diluted sulphuric acid. Add 1 ml of sulphurous acid for the reduction. Filter if necessary. Transfer the solution to a 100-ml volumetric flask, dilute to the mark and mix. This flask (B) contains the acid-insoluble boron.

Transfer 3 ml of solutions A and B to two dry 50-ml Erlenmeyer flasks. Add 25 ml of dianthrimide reagent solution with shaking, then close the flasks with glass stoppers (note 2). For the blanks, transfer 3 ml of solutions A and B to two Erlenmeyer flasks and add 25 ml of sulphuric acid (approx 96% w/w). Heat all four flasks in a boiling water bath for 60 minutes (note 3). Cool to room temperature and measure the absorbance of the solutions against pure concentrated sulphuric acid at 620 mμ in 1 cm or 2 cm cells. Correct for the blanks.

Calibration: Dissolve 0·7621 g boric acid (H_3BO_3 p.a.) in water and dilute to 1000 ml. Take 50 ml of this standard solution and dilute to 1000 ml. This working solution contains 6.667 μg B/ml. Transfer 5–50 ml of this solution by means of a burette to 100-ml volumetric flasks, add 30 ml of diluted sulphuric acid and make up to the marks. These solutions contain 1–10 μg B/3 ml. Take 3 ml from each solution and from a boron-free comparison solution and then proceed according to the description above. Plot a calibration curve or calculate the factor relating the absorbance with the amount of boron present. It is advisable to include with every series of boron determinations a boron-free solution and a standard solution containing, for example, 5 μg boron.

Notes: 1. Alternatively for instance, 50 ml of solution could be prepared from a 1·5-g sample by dissolving in acid and diluting or 10 ml of solution could be prepared from an 0·3-g sample. The quantity of acid should be reduced in proportion to the volume. For occasional boron contents of more than 0·010 % of either acid-soluble or acid-insoluble boron a smaller sample can be weighed out. If the boron content is regularly appreciably higher a smaller aliquot should be taken and a higher reagent concentration used. The calibration curve will of course be different in this case.

2. The dianthrimide reagent should be kept in the dark and protected from moisture. The reagent can suitably be dispensed from an all-glass automatic pipette protected from atmospheric moisture by a drying tube.

3. When the Erlenmeyer flasks are immersed in the water bath the stoppers should be lifted for a moment to release the pressure and allowed to fall back again of their own weight. The colour reaction can also be carried out at a temperature lower than 100°. Heating in an oven at 70° overnight was found quite suitable. The calibration curve will be somewhat steeper the lower the temperature chosen.

4. If only the total boron content is required, dissolve the melt in flask A and then add a few ml of sulphurous acid for reduction. In some cases it may be advisable to add sulphurous acid to the acid-soluble part also. This will counteract any tendency for the iron to oxidise if the solution is kept for a longer time.

5. Check that no boron contamination is introduced from reagent, filter paper or glass vessel. This can be done by making a parallel determination on boron-free carbon steel.

F. *Applications*

This method of analysis has been tested on standard samples from the National Bureau of Standards, USA, the acid-soluble and the acid-insoluble fractions being determined separately. The results are shown in Table I.

TABLE I.—BORON DETERMINATIONS ON NBS STANDARD STEELS

Number and steel type	Certificate value	No. of analyses	Boron sol. in dil. H_2SO_4	Boron insol. in dil. H_2SO_4	Boron total	Stand dev.	Coeff. of variation %
825 Mn–Ni–Cr	0·0006	5	0·0002	0·0005	0·0007	0·00007	10
826 Cr–Mo	0·0011	5	0·0010	<0·0001	0·0010	0·00006	6
151 Cr–Mo	0·0027	11	0·0017	0·0010	0·0027	0·00008	3
828 Mn–Cr	0·0059	6	0·0033	0·0026	0·0059	0·00009	1·5
829 Ni–Cr–B	0·0091	9	0·0041	0·0053	0·0094	0·00016	1·7
830 Ni–Cr–B	0·019	9	0·0103	0·0092	0·0195	0·00017	0·9

Boron values in per cent.

The results show good agreement with the certificate values. The coefficients of variation are relatively low considering the low boron contents. These results compare well with the results of the much more involved procedures that have been reported previously. It should be pointed out that the spread in the values for soluble and insoluble boron is considerably larger than for the total boron.

The results shown here apply to low-alloy steels. The method has also been found to give good precision in analyses on malleable iron but no standard samples with known boron contents were available. In analyses on stainless steel it must be expected that the accuracy will be impaired by the large correction that must be made for chromium. Only a single standard sample of this type was available for testing the method. NBS No. 444 gave by the present method 0·0034 % B; certified value 0·0033 %; this sample contains 20 % Cr, 10 % Ni, 0·2 % Mo, Nb and W and 0·1 % V.

The sensitivity of the method is insufficient for the determination of boron contents below a few ten thousandths of one per cent. In such cases the iron must first be removed, for instance by electrolysis with a mercury cathode, and the solution concentrated. Experiments showed that this could be done without loss of boron by evaporation of a solution in 2*M* sulphuric acid at 100° in a water bath. Analyses of NBS No. 825 in this way gave a value of 0·00062 % B as the mean of 6 determinations with a coefficient of variation of 3 %. Samples containing vanadium could not be analysed in this way since the vanadium is not removed on electrolysis. Even when the solution is reduced with excess sulphurous acid before the evaporation it may subsequently be oxidised to V^V. Vanadate, like chromate, destroys the dianthrimide reagent. The vanadium can however be removed by ion-exchange.[3]

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REFERENCES

[1] G. A. Rudolph and L. C. Flickinger, *Steel*, 1943, **112**, 114.
[2] M. W. Kelly, *Analyt. Chem.*, 1951, **23**, 1335.
[3] B.I.S.R.A., Methods of Analysis Committee, *J. Iron Steel Inst.*, 1958, **189**, 227.
[4] L. Danielsson, *Talanta*, 1959, **3**, 138.

Quantitative spectrochemical determination of minor elements in silicates

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In general, quantitative spectrochemical determination of minor elements in silicates has been based upon separate arcings for the volatile and involatile groups of elements with or without an internal standard.[1,2] The proper selection of suitable internal standard and spectroscopic buffer may eliminate the necessity for the tedious separate arcings. An attempt was made to provide a spectrochemical method for minor elements in silicates, which differ greatly in their volatilization rates from the electrode cavity, (i.e. Pb, Ga, Sn, Cr, V, Co, Ni, and Sc) with a single arcing procedure, by using two internal standards (Sb_2O_3 and metallic Pd).

One part (by weight) of the powdered silicate sample was thoroughly mixed with one part of carbon powder containing 0.8 % Sb_2O_3 and 0·04 % metallic palladium as the internal standards. The mixture was packed into the crater of the lower graphite electrode and excited for 60 sec by an 8-amp, 210-volt continuous a.c. arc supplied from a Pheilsticker-type intermittent a.c. arc source unit with radio-frequency spark. The spectrum was photographed on a process-type plate. For the purpose of plate calibration a self-calibrating method was used with a five-step sector (1 : 2 step ratio). A large Littrow-type spectrograph, Shimadzu QL-170, was used. Natural silicate rocks or minerals were

TABLE I.—ANALYSIS PAIRS AND RANGES OF ANALYSIS

Pair	Range, *ppm*
Ga 2943·637 (4·3)/Sb 2877·915 (5·3)	10 ~ 300
Pb 2833·069 (4·4)/Sb 2877·915 (5·3)	10 ~ 1000
Sn 3175·019 (4·3)/Sb 2877·915 (5·3)	10 ~ 3900
Co 3453·505 (4·0)/Pd 3481·152 (4·8)	5 ~ 300
V 3183·982 (3·9)/Pd 3242·703 (4·6)	10 ~ 1000
Cr 3593·488 (3·4)/Pd 3481·152 (4·8)	5 ~ 500
Ni 3414·765 (3·6)/Pd 3481·152 (4·8)	5 ~ 500
Sc 3613·836 (10·1)/Pd 3242·703 (4·6)	—

The values in parentheses are excitation potentials (eV).

selected as the basis for standards. If necessary, a correction for residual impurity was made. Analysis pairs and analysis ranges are indicated in Table I together with the excitation potentials for the analysis and the internal standard lines.

Following the statistical method of Shaw and Bankier,[3] the precision of the procedure (expressed as a 68% confidence limit and shown in Table II) was evaluated from working curve data and from repeated analyses of arbitrary samples or of the well-known standard rock W1 prepared by the U.S. Geological Survey.

TABLE II.—PRECISION OF THE PROCEDURE

Element	Sample	Values obtained, *ppm*	Values previously reported, *ppm*	Values given by Ahrens, *ppm*
Ga	W 1	$13{\cdot}6\,^{+1{\cdot}2}_{-1{\cdot}1}$	11 ~ 20	14·5
Pb	Feldspar	$177\,^{+17}_{-16}$	—	—
Sn	Gneiss	$48\,^{+11}_{-9}$	—	—
Co	W 1	$55\,^{+10}_{-9}$	20 ~ 55	36
V	W 1	$236\,^{+27}_{-24}$	170 ~ 340	240
Cr	W 1	$139\,^{+20}_{-18}$	100 ~ 150	130
Ni	W 1	$59\,^{+6}_{-5}$	47 ~ 150	90
Sc	W 1	$280\,^{+88}_{-67}$	15 ~ 51	37

If suitable standards are available, the present method may be extended to cover further species of elements including copper. However, the results in Table II indicate that the method failed for scandium. For its successful determination the quantity of carbon buffer should be made at least three times as much as the amount used in the proposed procedure, in order to eliminate a matrix effect.[4] With some modification the logarithmic sector method can be successfully applied without appreciable loss of precision.

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REFERENCES

[1] L. H. Ahrens, *Quantitative spectrochemical analysis of silicates.* Pergamon Press, London, 1954, p. 74.

[2] D. M. Shaw, Trace elements in pelitic rocks, I. *Bull. Geol. Soc. Amer.*, 1954, **65**, 1151.

[3] D. M. Shaw. and J. D. Bankier, Statistical methods applied to geochemistry. *Geochim. et Cosmochim. Acta*, 1954, **5**, 111.

[4] H. Hamaguchi, K. Tomura and R. Kuroda, Quantitative spectroscopic analysis of scandium in silicate rocks, (in Japanese) *J. Chem. Soc. Japan*, 1958, **79**, 504.

Variamine Blue sulphate as redox indicator

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VARIAMINE Blue (4-amino-4′-methoxy-diphenylamine), a redox indicator well established in practice, is usually employed in the form of the hydrochloride,* from which is prepared a 1% aqueous solution or a 1 : 100 solid indicator mixture with sodium chloride or with anhydrous sodium sulphate.[1,2] In such titrations, where the chloride content of the indicator gives some trouble (*e.g.* argentometric titration), chloride-free Variamine Blue acetate solution may be prepared from the hydrochloride by shaking it with benzene and alkali and then with aqueous acetic acid.[3] The preparation of the pure base, soluble in alcohol, is a rather long and expensive operation.[4] Both the hydrochloride and the base are light-sensitive, preparations originally white quickly becoming blue. The indicator solutions are unstable, become blue on standing and a precipitate separates from them. The sulphate provides a chloride-free and stable form of the indicator.

Preparation of sulphate

Dissolve 50 g of technical Variamine Blue B base in 1·5 litre of warm distilled water. Bleach the solution with 5 g of sodium dithionite and 10 g of animal charcoal, then boil the suspension and filter it quickly. Add to the slightly yellow or blue (depending on the pH of the solution), clear, hot filtrate 0·5 litre of sodium sulphate solution, upon which the separation of the sulphate begins immediately. The sodium sulphate solution contains 200 g $Na_2SO_4 . 10 H_2O$ per litre. Cool the solution to room temperature, filter the separated white needle-like crystalline material, wash it with cold water and dry it in vacuum, in a desiccator at room temperature.

The sulphur content (determined by the Grote-Krekeler method) indicates half a molecule of sulphuric acid. Its composition is therefore: 4-amino-4′-methoxy-diphenylamine,$\frac{1}{2}H_2SO_4$. Polarographic examination shows it to be chloride free. Its ash-content is practically zero.

It is very stable, and kept in dark glass it keeps its white colour for months.

Preparations of the indicator

The most stable form of Variamine Blue sulphate for use is the solid indicator mixture made with anhydrous sodium sulphate in a ratio of 1 : 400, using about 200 mg in a titration. This amount dissolves quickly and without residue in the solution to be titrated. For colorimetric use it is naturally

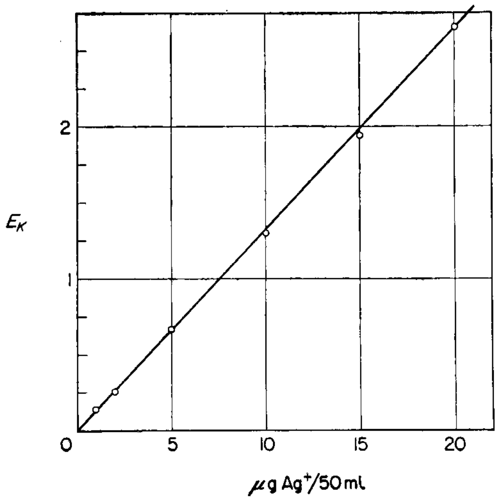

FIG. 1.—Colorimetric determination of silver ion with Variamine Blue sulphate.

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* In the textile industry it is known under the name Variamine Blue B base.

better to use an indicator solution; this may be 0·2% aqueous or 0·4% in 10% acetic acid. The freshly made solution is at the very most pale blue, so that its blank value can be neglected. On standing, this solution, also, naturally becomes blue, and in 4–5 days precipitation takes place.

Some practical applications

The applicability of the indicator was tested for the determination of the ascorbic acid factor and in argentometric chloride determination. The factor of an ascorbic acid solution against potassium iodate was found to be 1·010 with Variamine Blue hydrochloride and 1·009 with Variamine Blue sulphate. The results of argentometric chloride determinations are shown in Table I.

In the colorimetric determination of silver ion, where chloride content would cause some trouble[5], about 0·2% aqueous Variamine Blue sulphate indicator in acetate–acetic acid buffer at pH 3·6 was tested. Fig. 1 shows the extinction curve given.

TABLE I.—ARGENTOMETRIC DETERMINATION OF CHLORIDE WITH VARIAMINE BLUE SULPHATE

0·01N NaCI added, *ml*	0·01N $AgNO_3$ used, *ml*	Δ %
5·00	5·02	+0·40
10·00	10·03	+0·30
15·00	14·98	−0·13
20·06	19·94	−0·60
25·00	24·94	−0·24

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REFERENCES

[1] L. Erdey and E. Bodor, *Z. analyt. Chem.*, 1953, **137**, 410.
[2] L. Erdey, E. Bodor and M. Pápay, *Acta Chim. Hung.*, 1955, **5**, 235.
[3] L. Erdey, I. Buzás and K. Vigh, *Talanta*, 1958, **1**, 377.
[4] L. Erdey, E. Zalay and E. Bodor, *Acta Chim. Hung.*, 1957, **12**, 251.
[5] L. Erdey and F. Szabadváry, *Z. analyt. Chem.*, 1957, **155**, 90.

A new micro method of studying the thermal stability of easily volatile explosives*

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WHEN studying highly brisant explosives, which were very insensitive to shock and impact, and consisted of a solution of chloronitrobenzene (equilibrium mixture of the isomers) in nitric acid, in the molar ratio of chloronitrobenzene : nitric acid : water 1 : 4.6 : 1, it was not found possible to determine the detonation temperature by the usual procedures;[1] on heating, the water and nitric acid volatilized and the isomeric chloronitrobenzenes distilled unchanged at 243°. It therefore became necessary to develop a method for solving the problem, and one which could be used with tiny amounts of the specimen in view of the danger of explosion.

* Translated by Ralph E. Oesper, University of Cincinnati, U.S.A.

Method

The test was conducted in an aluminium block designed for the heating of micro crucibles[2] and provided with a well for a thermometer. Channels were cut into the under side; these were 1.8 mm wide and 2 mm deep. The aluminium block was heated by means of a Teklu burner, and the temperature was read from the thermometer.

The explosive under test was placed in glass capillaries (melting point tubes) whose external diameter ranged from 1 to 1.5 mm. The amounts taken were sufficient to occupy one-fifth of the length of the tube, which was then sealed. The charged tubes were placed in the channels of the block, and heated slowly or rapidly, according to the conditions of the test. Alternatively, the tubes were placed in the channels of a block which had been preheated to the chosen temperature. In this way it became possible to remove tubes at any selected temperature and examine them for changes after they had cooled. In all cases, direct observations were made through a glass shield to avoid injury in case the tubes exploded.

The strength of the tubes was tested by charging the capillaries with nitric acid and heating. It was found that they withstood the vapour pressure of nitric acid up to 330°.

Experimental findings

The mixture described above was tested first. It represents an explosive with an equalized oxygen balance. It explodes violently when detonated with a primer cap.

When heated in the capillary, there resulted above 120° a brown gas (NO_2) as in the case of nitric acid, whose colour deepened with rising temperature. Tubes heated to 200° showed no visible change when cooled; the reactions, such as the formation of nitrogen dioxide, were accordingly reversible. In tubes heated to 210° there was an irrevesible change, in that the contents after cooling consisted of two liquid phases. The heavier (isolated by centrifuging) was green to blue-green. The same behaviour was found also on heating up to 300°. Between 300 and 320° there was a change even in the hot material in that the initial almost black colour (NO_2) gradually faded. After cooling, the contents of the tube consisted entirely of a colourless liquid, which proved to be aqueous hydrochloric acid. When the capillaries were placed in the channels of a block preheated to 330°, no detonation or deflagration was observed. Accordingly, the explosive must have decomposed without detonation:

$$5C_6H_4NO_2Cl + 23HNO_3 \rightarrow 30CO_2 + 19H_2O + 14N_2 + 5HCl$$

For comparison purposes, a study was made of the behaviour of other organic compounds dissolved in highly concentrated nitric nitric acid. A solution of *m*-dinitrobenzene in nitric acid (molar ratio 1 : 4) behaved initially like the chloronitrobenzene-nitric acid studied. Here again, two liquid phases were produced, starting at 210°; however detonation occurred around 290°. Nitric acid solutions of xylene, *p*-dichlorobenzene, pyridine, paraffin, and petroleum were tested at 220 and 300°. The findings are summarized in the following table.

Compound dissolved in or mixed with HNO_3	Behaviour after heating to 220°	Behaviour at temperaures to 300°
Monotrochlorobenzene	2 phases, blue-green	no detonation
m-Dinitrobenzene	2 phase, blue-green	detonation
Xylene*	1 phase, green	detonation
p-Dichlorobenzene	2 phases, blue-green	no detonation
Pyridine	1 phase, light yellow	detonation
Paraffin oil	2 phases, yellow	detonation
Petroleum	combustion	detonation

* Two phases likewise appear in the case of xylene on cooling below 10°.

Discussion

The composition of the green product is not clear as yet; it is noteworthy that it is stable only in closed tubes, *i.e.* under pressure. Possibly, addition compounds of N_2O_3 with organic aromatic nitro compounds are formed.

Of more interest perhaps is the finding that, against all expectation, the system chloronitrobenzene–nitric acid cannot be made to detonate or deflagrate by heating. Since this stability appears only in the instances (see the Table) in which chlorine-containing aromatic compounds were used, it seems logical to assume that the presence of the chlorine atom is essential to this stability. In contrast to all other solutions of organic compounds in highly concentrated nitric acid used for explosive,[3] the mixture monochloronitrobenzene-nitric acid is extraordinarily resistant to shock, impact or bombardment, with no impairment of its ability to be set off by a primer cap.

The following assumption may be advanced to explain the thermal stability and the insensitivity against shock and impact. The reasoning is analogous to the action of anti-knock materials in motor fuels. The relatively heavy and sluggish chlorine atom stops or interrupts some of the reaction chains initiated by temperature or shock. The result is that a continuous reaction is possible only through the initiation of an adequate number of reaction chains, such as is provided by the initial ignition. Consequently, the thermal decomposition, which leads to the same results as the detonation, proceeds slowly and apparently is in accord with the van't Hoff law.

This latter view gives interesting glimpses into the possible use of such solutions as monopropellants.

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REFERENCES

[1] F. Ullmann, *Enzyklopädie der technischen Chemie*, 2nd edition, Vienna, 1929, 720.
[2] F. Feigl, *Spot Tests in Inorganic Analysis*, 5th edition, Amsterdam 1958, p. 35.
[3] J. Marshall, *Dictionary of Explosives*, 1920, p. 90.

Talanta, 1959, Vol. 3, pp. 213 to 215. Pergamon Press Ltd. Printed in Northern Ireland

BOOK REVIEWS

Gaschromatographie. A. I. M. KEULEMANS; übersetzt und bearbeitet von E. CREMER. Verlag Chemie, Weinheim, 1959. DM 24.—xvi + 288 Seiten, 103 Abbildungen und 26 Tabellen.

DIESES 1957 bei der Reinhold Publishing Corporation, New York erschienene Buch liegt nun in ausgezeichneter Ergänzung und Übersetzung in deutscher Sprache vor. Es ist durchaus kein Wagnis, das der Verfasser unternimmt, da er über eine im rasanten Kommen befindliche Methode in buchmässiger Zusammenstellung berichtet. Wohl sind die Methoden der Gaschromatographie noch sehr jung,—über die Gasflüssigkeitschromatographie wurde ja erst von A. J. P. Martin 1952 berichtet—, demnach aber sind die Ergebnisse und der mit dieser Methode erzielte Zeitgewinn so bestechend, dass die Herausgabe einer eingehenden Einführung in dieses Gebiet voll gerechtfertigt erscheint. Das vorliegende Buch ist in acht Hauptkapitel und zwei Anhangskapitel unterteilt.

Kapitel eins erläutert neben einer geschichtlichen Übersicht die allgemeinen Grundlagen der gaschromatographischen Methodik; die von einem Spezialkommitee, welches anlässlich eines vom Institute of Petroleum in London im Juni 1956 veranstalteten Symposiums über Gaschromatographie zusammentrat, vorgeschlagene Nomenklatur wird auch hier benutzt und in diesem Kapitel näher erörtert. Im zweiten Kapitel wird die praktische Anwendungsmöglichkeit der Gasflüssigkeitschromatographie aufgezeigt, im dritten Kapitel die Einzelheiten der möglichen Apparaturen besprochen und auf die verschiedenen Detektoren und ihre Charakteristiken eingegangen. In den Kapiteln vier, fünf und sechs werden die der Gasflüssigkeitschromatographie zu Grunde liegenden Theorien so weit sie heute vertretbar erscheinen, sehr klar und übersichtlich dargelegt. Ein Verzeichnis der verwendeten Symbole (162!) mit ihren genauen Definitionen sind auf den Seiten IX–XII angeführt. Das siebente Kapitel interpretiert die Anwendung dieser Prinzipien bei sehr schwierigen Trennungen und bei ihrer nicht analytischen Verwendung. Das letzte Hauptkapitel (acht) ist endlich der bereits scheinbar überholten Gasfestkörperchromatographie gewidmet, die in letzter Zeit wieder zu gutem Rufe gekommen ist. Im ersten Anhangskapitel wird eine Auswahl von stationären Flüssigkeiten für die Gasflüssigkeitschromatographie angegeben und deren Verwendbarkeit besprochen, das zweite Anhangskapitel, von E. Cremer verfasst, bringt eine vorzügliche Betrachtung über die Gaschromatographie an Adsorptionsschichten unter besonderer Berücksichtigung der auftretenden Grenzschichtphänomene.

Alles in allem liegt hier eine ganz ausgezeichnete, gut ausgefeilte Darstellung über die Gaschromatographie mit instruktiven Abbildungen, sehr brauchbaren Tabellen, ausführlichem Literaturverzeichnis und übersichtlichem Autoren- und Sachverzeichnis vor, die allen Interessenten für dieses Gebiet bestens empfohlen werden kann.

G. WAGNER

Analytical Chemistry in Nuclear Reactor Technology, 1st Conference 1957. U.S. Atomic Energy Commission, Office of Technical Services. Department of Commerce, Washington 25, D.C. Pp. vi + 256. $3.50.

THIS thick paper-bound volume contains 17 of the 21 papers presented at the first conference on analytical chemistry in nuclear reactor technology held at Gatlinburg, Tennessee, U.S.A. in November, 1957. This conference, the first of a projected series, had as theme the analysis of reactor materials; the second conference, which took place in September, 1958, considered analysis in the commissioning and operation of reactors and the third may deal with post-operational analytical problems.

The papers presented aim to describe recent advances in methods for the analysis of some materials of construction of nuclear reactors and for reactor fuels, moderators, coolants and blanket materials.

There are useful review papers on aspects of the analysis of uranium, thorium, zirconium, titanium, beryllium, heavy water and graphite and on the applications of such techniques as neutron activation, X-ray spectroscopy, optical spectroscopy and solvent extraction to problems in the reactor technology field. In only 5 papers have the subsequent discussions been recorded and in three of these the reports are exceptionally brief.

As is unavoidable in conferences of this sort, there is a marked variation in the standards of the papers as now presented; some, for example, are admirably referenced (*e.g.* "Recent Developments in the Analytical Chemistry of Thorium and its Compounds" by C. V. Banks, with 152 references mostly for the years 1955-7 and "The Analytical Chemistry of Beryllium" by E. S. Melick with 78 references) whilst some others have few or no references (*e.g.* "Recent Developments in the Analytical Chemistry of Titanium" by A. L. Gahler where the references are embodied in the text and are for the most part inadequate from the point of view of ready procurement).

C. E. Larson in his reminiscent and sometimes light-hearted introductory paper dealing with the role of analytical chemistry in atomic energy, rightly stresses the importance of the increased participation of the analyst in the discussion and solution of the problems arising both in development and production; this theme is given practical expression by the inclusion in the conference of several papers discussing problems involving both process chemistry and analysis and their frequent interdependence. Whilst appropriately stressing the remarkable developments in instrumental techniques in the course of the war-time atomic energy programme it may be questioned whether "quantitative spectrographic analysis was carried to its present stage of perfection through the development of apparatus for the Manhattan Project"—this does less than justice to the important and independent advances made in the ferrous and non-ferrous metals industries.

The book is clearly printed and well illustrated with nearly 100 diagrams and reproductions from photographs and is undoubtedly a useful reference volume for the increasing numbers of analysts engaged in the expanding field of reactor technology, particularly if one anticipates setting beside it the forthcoming companion volumes covering the second and third conferences.

F. J. WOODMAN

Chemistry of the Co-ordinate Compounds. Vol. I, International Series of Monographs on Inorganic Chemistry. (Papers presented at the Rome Symposium of the International Union of Pure and Applied Chemistry, September, 1957.) Edited by H. TAUBE and A. G. MADDOCK. Pergamon Press, London and New York, Symposium Publications Division, 1958. Pp. 638. £5.

IN the reviewer's opinion it is a mistake to publish volumes of papers presented at symposia. The author who has to write up research work for one of these books is thereby delayed or prevented from publishing it in the proper place, namely one of the standard journals; and it makes the work inaccessible to the many readers whose local libraries cannot afford to buy the (usually expensive) symposium volume. There is, perhaps, a better case for publishing in collected form the review lectures given at symposia, leaving the research communications to appear in due course in the journals. The present volume is a typical symposium publication, containing thirteen reviews and sixty-five research communications. Many papers of both kinds are excellent and interesting, but the result of putting so many diverse items between one pair of covers is a rather indigestible whole, which will probably collect dust on the library shelf at a faster rate than the average for recent books. Most of the papers are in English, with a sprinkling in French, German, and Italian. The book is elegantly turned out but replete with minor errors in the spelling and usages of English.

The book is divided into five sections, each consisting of one or more review papers followed by a number of research communications. There is not space in this review to discuss all the papers individually, but the following selection (which has been made at random without any implication as to merit) will indicate the general character of the book.

Section I, on bonding in complexes, opens with a review by L. E. Sutton of recent developments in the ligand field theory, and is mainly devoted to the spectroscopy of complexes. There is a paper on the vibrational frequencies of water in aquocomplexes. Section II, on stereochemistry, stability constants and reactivity, is distinguished by an amusing account from L. G. Sillén on the problems he has experienced in trying to compile data for the Chemical Society's list of stability constants. Among his several well-taken points is that progress in the study of complex formation in salt solutions has been retarded by the excessive preoccupation of physical chemists with extremely dilute solutions. Section II has a wide scope, including for example papers on the compound P_2NCl_7 and on aromatic metal carbonyls. Section III, on magnetic and structural properties, begins with reviews of nuclear magnetic resonance and electron spin resonance, but contains very little new experimental material on these topics, most of the papers dealing with ordinary magnetic susceptibility measurements and with structural studies by X-ray diffraction. Section IV, perhaps the most interesting to the non-specialist, is about the stabilisation of unusual valence states, and "unusual compounds". It contains valuable reviews by J. Chatt on "Low Valent (*sic*) States" and by W. Klemm on "High Valency States". The progress made recently in this field will surprise anyone not familiar with it. Compounds of the zero oxidation state of transition metals are now very numerous, and even the -1 state of metals is represented in several parts of the Periodic Table. As for the "unusual compounds", the report from C. C. Addison's laboratory on volatile anhydrous copper^{II} nitrate is exceptionally interesting. The fifth and shortest Section, "Catalytically Active Complexes", covers a relatively new field of great potential importance. It begins with a review by G. Natta on stereospecific polymerisations induced by coordinated anionic catalysts.

In spite of the excellence of many of the individual contributions, this volume is too incoherent, too expensive and of too little lasting interest to justify private purchase. Larger scientific libraries should have it.

HENRY HEAL

Talanta, 1959, Vol. 3, p. 216. Pergamon Press Ltd. Printed in Northern Ireland

PAPERS RECEIVED

Contributions to the basic problems of complexometry—II: Decomposition of Xylenol Orange in aqueous solutions. R. PŘIBIL. (3 *October* 1959)

Eine neue Schnellmethode zur Bestimmung von Thorium in Gegenwart von Zirkonium, Eisen, Lanthan, Uran und sonstigen Schwermetallen. R. PŘIBIL und K. BURGER. (3 *October* 1959).

Determination of blood sugar and urine sugar with 3:6-dinitrophthalic acid. TSUTOMU MOMOSE, AKIRA INABA, YOSHIKO MUKAI and MITSUKO WATANABE. (5 *October* 1959).

The determination of silver and thallium in rocks by neutron-activation analysis. D. F. C. MORRIS and R. A. KILLICK. (5 *October* 1959).

Estimation of efficiency for bubbler-type gas absorbers. SEYMOUR CALVERT and WALTER WORKMAN. (6 *October* 1959).

Variamine Blue sulphate as redox indicator. L. ERDEY, E. B.-GERE and E. BÁNYAI. (9 *October* 1959).

Complexometric determination of mercury^{II} and aluminium ions. E. BÁNYAI, E. B.-GERE and L. ERDEY. (9 *October* 1959).

Salting-out chromatography—VI: Effect of the length of the hydrocarbon chain, the eluent salt, and the cross-linking and ionic form of the resin. ARTHUR BREYER and WM. RIEMAN III. (14 *October* 1959).

The indirect complexometric titration of aluminium: A study of the Wänningen-Ringbom method. FOLKE NYDAHL. (16 *October* 1959).

Isomeric complexans: The dl **and meso forms of 2:3-butanediamine-**N:N:N′:N′-tetra-acetic acid. R. BELCHER, W. HOYLE and T. S. WEST. (19 *October* 1959).

Umbellikomplexon und Xanthokomplexon: Ein beitrag zur Kenntnis komplexometrischer Fluoreszensindikatoren. J. H. EGGERS. (25 *October* 1959).

The isolation of platinum metals from partially refined concentrates. H. ZACHARIASEN and F. E. BEAMISH. (28 *October* 1959.)

Analytical applications of 3-acetyl-4-hydroxy coumarin: A. N. BHAT and B. D. JAIN. (29 *October* 1959).

The determination of small amounts of organic sulphur in small samples. JEAN P. DIXON. (11 *November* 1959).

Talanta, 1959, Vol. 3, p. 217. Pergamon Press Ltd. Printed in Northern Ireland

TALANTA MEDAL

The Publishers of TALANTA, Pergamon Press Limited, have generously offered to provide the funds for the institution and award, from time to time, of a TALANTA Medal. This Medal will be awarded for outstanding contributions to analytical chemistry, and will have a value of 100 guineas.

CONDITIONS OF AWARD

1. The TALANTA Medal will be awarded for really outstanding contributions to analytical chemistry made by scientists in any area of research endeavour.

2. Any outstanding paper or papers contributed to TALANTA will automatically be considered for the Medal. Other work may be proposed by any member of the Advisory Board of TALANTA to the Editors for consideration. The award will not be confined to current work, but may be made for work already completed which has since been recognised as outstanding.

3. The Medal will only be awarded on the unanimous recommendation of a committee composed of the Editor-in-Chief, the Regional Editors, and the Chairman of the Advisory Board. In addition, the recommendation must be supported by at least two-thirds of the members of the Advisory Board. Although normally the TALANTA Medal will not be awarded more frequently than once in each year, no attempt will be made to award it at fixed intervals.

International Union of Pure and Applied Chemistry

Analytical Chemistry Section

DURING the XXth Conference of the I.U.P.A.C., which was held in Munich in August, 1959, the Committee of the above Section discussed certain points of confusion in the literature. Recommendations* were made as follows:

1. *Terminology of complexing agents*

Because of the existing confusion regarding terminology in the use of complexing agents as titrants, the committee tentatively recommends the use of the following terms until such time as further action is taken.

(*a*) The group of *polyamino-polycarboxylic acids* which form *anionic* complexes shall be termed **complexans.**

(*b*) Titration processes in which any type of complexing titrant is used shall be termed **complexometric titrations.**

(*c*) Those complexometric titrations which involve titration with a chelating agent shall be termed **chelatometric titrations** and represent a special type of complexometric titration.

2. *Notation of indicators in titrimetric analysis*

Many dyestuffs have been recommended as indicators in chelatometric and redox titrations and a host of trivial names often exists for the same compound. Examples can be found in the literature of a compound having been recommended as a new indicator because it has a different name, when the compound has in fact been in use for years under a different name.

To avoid future confusion, and embarrassment of authors and editors, the Committee recommends that when a dyestuff is proposed as an indicator in any type of titration, *and particularly when it is claimed as new*, the **British Colour Index** or **Schultz Number** be quoted along with the trivial name.

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* These notes are published by permission of the I.U.P.A.C.

NOTES FOR CONTRIBUTORS

1. General

Contributions may deal with any aspect of analytical chemistry, although papers exclusively concerned with limited fields already catered for by specialist journals should normally be directed to those journals, and should only be submitted to TALANTA if their analytical implications as a whole are such as to make their inclusion in a more general background desirable.

Original papers, short communications, preliminary communications and reviews will be published. Suitable books submitted to the Editor-in-Chief will be reviewed.

Since TALANTA is an international journal, contributions are expected to be of a very high standard. Research papers should make a definite contribution to the subject. Special importance will be attached to work dealing with the principles of analytical chemistry in which the experimental material is critically evaluated, and to similar fundamental studies. Reviews in rapidly expanding fields, and reviews of hitherto widely scattered material, will be considered for publication, and should be critical. The Editor will welcome correspondence on matters of interest to analytical chemists.

All papers and short communications submitted for consideration will be refereed in the normal way. Referees will be encouraged to present critical and unbiassed reports which are designed to assist the author in presenting his material in the clearest and most unequivocal way possible. To assist in achieving this completely objective approach, referees will be asked to submit signed reports. At the discretion of the Editor the names of referees may be disclosed if thereby agreement between author and referee is likely to result. Authors should appreciate that the comments of referees are presented in a constructive spirit, and that agreement between the views of author and referee must result in a higher standard of publication.

It is hoped that research and review papers will be published within approximately three to four months of acceptance, and short communications within two months.

Twenty-five free reprints of each paper will be provided (with ten further free copies for each additional author) and additional copies can be supplied at reasonable cost if ordered when proofs are returned. A reprint order form will accompany the proofs.

2. Script Requirements

1. Contributions should be submitted to the Editor-in-Chief, or to the appropriate Regional Editor, and may be written in English, German or French.

2. Scripts should be submitted in duplicate. They must be typewritten and the lines double-spaced. Where possible, research papers should follow the pattern: *Introduction*, *Discussion*, *Conclusion*, *Experimental* (or such of these headings as apply).

3. Summaries will not be required for short or preliminary communications. For other contributions the essential contents of each paper should be briefly recapitulated in a summary at the beginning of the paper. This should be in the language of the paper, but for German or French papers an English version should also be provided wherever possible. Summaries of papers will be printed in all three languages, and authors who are able to provide translations of their summaries are asked to do so.

4. Illustrations should be separated from the typescript of the paper and legends should also be typed on a separate sheet. Line drawings which require redrawing should include all relevant details and clear instructions for the draughtsman. If figures are already well drawn, it may be possible to reproduce them direct from the originals, or from good photoprints, if these can be provided; it is not possible to reproduce from prints with weak lines. Illustrations for reproduction should normally be about twice the final size required. The lettering should be sufficiently large and bold to permit this reduction. The following standard symbols should be used on line drawings, since they are easily available to the printers:

△ △ ⊡ □ ● ○ ◬ ⊙ ⊕ ⊖ ⌽ ⊗

5. Tables should if possible be so constructed as to be intelligible without reference to the text, every table and column being provided with a heading. Units of measure must always be clearly indicated. Unless it is essential to the argument, tables should not list the results of individual experiments, but should summarise results by an accepted method of expression, e.g., standard deviation. The same information should not be reproduced in both tables and figures.

6. References should be indicated in the text by consecutive superior numbers; and the full reference, including title of paper where desired should be given in a list at the end of the paper in the following form:

[1] J. B. Austin and R. H. H. Pierce, *J. Amer. Chem. Soc.*, 1955, **57**, 661.
[2] S. T. Yoffe and A. N. Nesmeyanov, *Handbook of Magnesium-Organic Compounds*. Pergamon Press, London, 2nd Ed., 1956. Vol. 3, p. 214.
[3] A. B. Smith, *The Effect of Radiation on Strengths of Metals*. A.E.R.E., M/R 6329, 1962.
[4] W. Jones, *Brit. Pat.* 654321, 1959.

Footnotes, as distinct from literature references, should be indicated by the following symbols: *, †, ‡, ¶, commencing anew on each page; they should not be included in the numbered reference system.

7. Except in the case of preliminary communications, proofs will be sent to authors for correction when their contribution is first set, but there is rarely time for page proofs also to be sent for checking. This will be done, however, when the amount of alteration makes it advisable.

8. Because of the international character of the Journal, no rigid rules concerning spelling, notation or abbreviation need be observed by authors, but each paper or series of papers should be self-consistent as to symbols and units.

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CONTENTS

Preliminary Communications:

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