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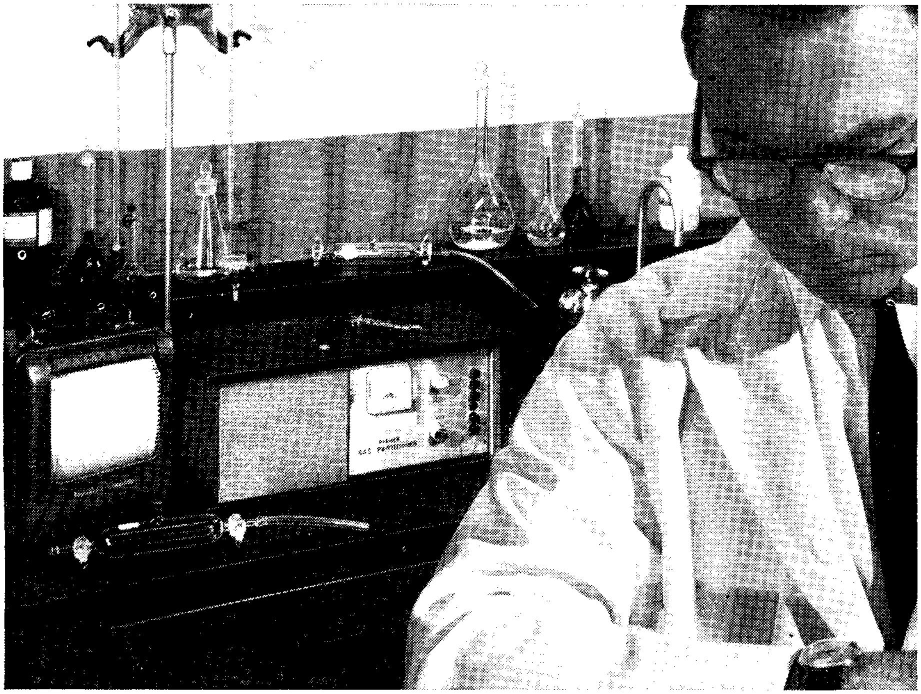

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Heterometry

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Heterometry, a method of analysis devoloped by the author, deals with the quantitative photometric study of chemical reactions in which suspensions are formed. Optical density curves are measured in order to determine the location of the critical points.

This method has attracted the attention of chemists all over the world. Although the development of heterometry covers a period of less than ten years, a great deal of progress has been made and the author has attempted to summarize what has been achieved in this relatively short time.

Much of the book has been devoted to the use of heterometry in the rapid analytical determination of traces of metals, other ions or compounds, in the presence of a large excess of other substances, without any previous separation. The book contains a wealth of original material, generously supplemented with tables and figures, which demonstrate how hitherto unsolved problems can easily be solved by heterometry. Very often a few tenths of a milligram of material is sufficient for a whole investigation. The instrumentation as well as the various aspects of heterometry are thoroughly reviewed so that on the basis of information given chemists will be able to tackle their own problems by heterometry. This method will be of especially great value to all research workers as well as to industrial chemists working in the fields of analytical and microanalytical chemistry, complex chemistry, study of composition and structure of intermediates, lakes, complicated organic nitrogen compounds etc.

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THE ORIGIN OF NUCLEI IN PRECIPITATION REACTIONS

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The purposes of this paper are (a) to present data concerning the origin of nuclei in precipitation reactions and (b) to suggest on the basis of these data and previously published information a mechanism of nucleation which is free of several inconsistencies in other proposed mechanisms.

The classical approach to the physical mechanism of precipitation is based upon the concept of the metastable and labile states of supersaturation[1-3]. As developed and applied to the precipitation of slightly soluble inorganic substances by VON WEIMARN[4] and others, it was concluded that the rate of precipitation and the number of particles are proportional to the degree of supersaturation at the time of precipitation. VON WEIMARN did not clearly distinguish between nucleation and crystal growth, as was promptly emphasized by BANCROFT[5], and many factors other than degree of supersaturation have been found to influence the number of particles. Nevertheless the concept has played a major role in the selection of optimum conditions for analytical precipitation procedures.

Recent approaches to the physical mechanism of nucleation are of two types. One is a theoretical one based upon the work of formation of the nucleus. TURNBULL[6] has developed this concept with particular reference to the nucleation of ionic crystals such as barium sulfate. His conclusions included the following: (a) the rate of nucleation is highly dependent upon the extent of supersaturation, (b) the size of the nucleus is also a function of the degree of supersaturation, and (c) the number of "molecules" or ion pairs is of the order of tens for even the smallest nuclei and likely hundreds for most nuclei.

The other approach to the mechanism of nucleation is based upon the experimental measurement of the induction period, which is the time which elapses between the mixing of reactant solutions and the first detectable appearance of precipitate. CHRISTIANSEN AND NIELSEN[7,8] and others[9-12] have determined the sizes of nuclei from the lengths of the induction periods and obtained, for example, eight ions for barium sulfate, six for silver chromate and nine for calcium fluoride. The experimental methods of measuring the lengths of the induction period may be open to question, but this factor likely would not alter the conclusions that (a) there is a definite critical size of nucleus for each substance, and (b) this critical size is of the order of only a few "molecules" or ion pairs. These two conclusions are contradictory to those of TURNBULL. These two kinetic approaches to nucleation have been reviewed and summarized by KLEIN AND GORDON[13]. It should be emphasized that the TURNBULL approach is a theoretical one with the conclusions not based upon measurements on practical precipitation systems and that the CHRISTIANSEN AND NIELSEN conclusions are based upon laboratory measurements on precipitation reactions. KLEIN, GORDON AND WALNUT[14] reported results of a different type of experiment from which it was also concluded that the nucleus consists of several ions rather than tens or hundreds.

The possibility of induced nucleation, which is nucleation not resulting entirely from random aggregation of a cluster of ions of sufficient size to form a nucleus, has often been encountered in measurements of critical supersaturation. It was found that precipitation from a metastable state could be initiated not only by seed crystals of the substance but also by such varied factors as exposure to air (city air was found to be more effective than country air in one report of 1865 quoted in reference 3), by stirring (copper stirring rod much more effective than platinum and slightly more so than glass[15]), by mechanical shock and by impurities in the reagents[16–18].

The possibility of induced nucleation has also been considered in some of the more recent kinetic studies of nucleation, but generally as a substitute for the usual nucleation process and not as a conceivably necessary part of it. TURNBULL[6] has suggested that induced nucleation may have been involved in the CHRISTIANSEN-NIELSEN experiments[7] on timing the induction period. NIELSEN[18] reported, on the basis of some experiments on barium sulfate in which the containers were cleaned in live steam prior to use, that most and perhaps all of the crystals originated on the walls of the vessel and not from spontaneous nucleation; he did not specifically relate this conclusion to his earlier work on induction periods or to the metastable state. MANSON, CAGLE AND EYRING[19] discussed, in conjunction with a study of the nucleation of ice crystals from supercooled water vapor in the presence of silver iodide seeds, the interconnected roles of induced nucleation and self-nucleation.

Earlier reports from this laboratory have shown that the size and number of precipitated particles may be markedly influenced by the presence of "addition agents"[20] by the age of a solution prior to use[20–22], by the physical form of the reagents[22] and by the time of contact of a reagent solution with an inert electrolyte[22]. Additional experimental data are presented here to show the effect of the past history of the solvent used in preparing a reagent solution and of the nature of the container upon the size and number of precipitated particles.

EXPERIMENTAL METHODS AND DATA

All chemicals were of reagent grade or of comparable purity. Precipitates of barium sulfate were prepared by adding an approximately 0.02 *M* solution of barium chloride at 60° in slight excess to an approximately 0.015 *M* solution of potassium sulfate at 30° and at pH 1. These conditions were chosen empirically to yield precipitates of fairly reproducible physical form. Generally at least six precipitations were performed for each size determination. All six were observed in a light microscope to check uniformity, and particle sizes were measured on at least two of the six by means of an ocular micrometer on the microscope. Some precipitates included fragments which may have broken off of larger dendritic crystals. TAKIYAMA[23] has shown that each large dendrite is a single crystal arising from a single nucleus. Only the larger crystals within each batch were measured in order that the resultant data would clearly show trends in crystal size variation.

Results of a series of experiments using water of varied past histories in preparing the barium chloride solution are shown in Table I. The effect of the age of the barium chloride solution is evident, but this factor has been discussed elsewhere[20–22,24]. Of particular significance now is the fact that the history of the water prior to preparing the solution of one of the reactants exhibits a large effect upon the particle size of the precipitate and thereby upon the number of nuclei which form and persist throughout the precipitation reaction. It hardly seems possible that this factor could influence the extent of a purely spontaneous process of nucleation. It is much more likely that the nucleation is induced, and that the effective number of particles which are induced is fewest with the purest water (D), next fewest with the next purest water (C), and that standing in pyrex (B) removed via adsorption some of the centers for induced nucleation which were initially present in the least pure water (A).

TABLE I

EFFECT OF THE PAST HISTORY OF THE WATER IN THE BARIUM CHLORIDE SOLUTION UPON THE PARTICLE SIZE OF BARIUM SULFATE

Age of $BaCl_2$ solution (h)	*Particle sizes (μ)*			
	Water A	*Water B*	*Water C*	*Water D*
0.5	9	9	9	9
1	11	—	13	13
2	13	—	18	20
4	16	18	23	28
8	16	—	31	40
24	16	45	56	68
48	16	45	68	78

Water A: lab. distilled water. Water B: lab. distilled water after standing 24 h in pyrex prior to dissolving $BaCl_2$. Water C: freshly distilled in all-pyrex system. Water D: freshly prepared (Barnstead) conductivity water.

It was also found that preheating of water for a time, then cooling and dissolving the barium chloride, resulted in much larger particles of the eventual precipitate of barium sulfate than did the use of water that had not received the heat treatment. In Table II are listed data from a series of experiments on preheating the water in various types of containers. Again it appears that nucleation must be induced, not entirely

TABLE II

EFFECT OF TYPE OF CONTAINER DURING PREHEATING OF WATER IN THE BARIUM CHLORIDE SOLUTION UPON THE PARTICLE SIZE OF BARIUM SULFATE

Age of $BaCl_2$ solution (h)	*Particle sizes (μ)*			
	Control (no heating)	*Pyrex*[a]	*soft glass*[a]	*Platinum*[a]
1	11	11	11	11
30	13	42	23	18
85	16	42	28	23
180	18	25	41	28
230	18	18	33	37
330	16	13	23	23
400	13	13	16	13
980	13	9	13	13

[a] Water heated 24 h at 80° prior to dissolving $BaCl_2$.

spontaneous. Preheating the water used in preparing one of the reagent solutions alters the number and/or the effectiveness of the sites upon which nucleation can occur, and the nature of the surfaces of the container is of significance.

DISCUSSION

The data of Tables I and II show that the number of nuclei which form and persist as single crystals throughout a precipitation reaction is considerably influenced by the type of water used in preparing the solution of a reactant and that even the type of container in which that water has been allowed to stand prior to use is significant. These observations are entirely consistent with earlier published information that virtually all circumstances brought to bear upon a precipitation medium can influence the physical characteristics of the precipitate. It is highly doubtful that some of these factors could influence a purely spontaneous nucleation process in which a group of ions of the desired substance cluster together to form a crystal nucleus, but it is conceivable that all of the factors could influence an induced nucleation reaction.

Mechanism of nucleation of ionic precipitates

The following suggestion is now made concerning the mechanism of nucleation of ionic precipitates. Most and very possibly all solutions inevitably contain available sites upon which crystals of a precipitate may be initiated, and these sites cause most and perhaps all nucleation processes in practical analytical precipitation reactions to be induced. Some of these sites are more effective in fulfilling this function than others. The number of available sites and their distribution with respect to effectiveness vary widely with conditions. In order for a crystal to get started, the solution in contact with a solute must be critically supersaturated with respect to that site. Random or statistical fluctuations exist, of course. Each site has a characteristic necessary critical supersaturation value. For a given number and distribution of sites, the number of sites which are used is a direct (but not simple) function of the degree of supersaturation. During subsequent growth of a crystal, the initiating site may be completely entrained within a crystal or the site may become separated from it.

This suggested mechanism of nucleation retains many of the features of other concepts, but it differs in three ways: (a) in considering nucleation sites or induced nucleation to be virtually necessary in practical situations and not merely possible, (b) in considering the overall nucleus to be physically different from that portion of the nucleus containing the lattice ions, and (c) in considering the critical supersaturation value to be a definite one for each available site but to vary widely from one site to another within a single solution. The available sites serve, in effect, as nucleation catalysts in a manner analogous to that described by MANSON, CAGLE AND EYRING[19] for the nucleation of ice crystals on silver iodide seeds.

Origin and function of the available sites

The function of an available site is simply to accumulate ions from the surrounding solution. The mechanism of attraction could be predominantly electrical, although more specific forces of attraction doubtlessly would occur in some cases. Ions of a charge opposite to that on the site would be attracted to it, including some of the eventual lattice types of ions. This "primary adsorbed" group of ions would in turn attract ions of opposite charge and, insofar as the primary group consisted of one type of lattice ion, the "secondary" group would specifically be of the other type of lattice ion. This grouping of lattice ions including the original site upon which it was accumulated is the particle which replaces the nucleus in the sense in which TURNBULL used the term. This is the solid particle which, in subsequent growth, requires work to extend the interface between particle and solution but which is already much larger than the few lattice ions grouped on its surface. Further growth can occur only on one part of the surface of this larger nucleus, but crystal growth frequently occurs selectively at certain points, corners, etc., even on much larger crystals. The grouping of lattice ions on the available site, but not including the site, is the critical nucleus in the sense in which CHRISTIANSEN AND NIELSEN used the term.

The relative effectiveness of a site is determined by the attractiveness which it has for one or the other type of lattice ion. The ideally effective site would be on a crystal of the precipitate itself, on which nucleation as a process distinct from crystal growth is by-passed. Other sites which exhibit specific attraction for one of the desired lattice ions would also be quite effective, such as sites on crystals of another substance containing one ion in common with the desired precipitate or of similar crystalline morphology. However, any surface which exhibits an electrical charge in the environment of the solution could serve as a site of effectiveness sufficient for it to function within the high degrees of supersaturation which may be achieved in the precipitation of slightly soluble substances. The site must be sufficiently large in area to hold a "CHRISTIANSEN-nucleus" of several lattice ions, and the entire solid particle or surface including the available site must be large enough to serve as a "TURNBULL-nucleus".

The sources of available sites are widely varied. They include the surfaces of the container, colloidal contaminants brought in by the solvent, colloidal impurities brought in by the reactants or by some other components of the reactant solutions, residues present from incomplete dissolution of a reagent, and the air.

Nucleation may conceivably occur in a limiting case by a purely spontaneous clustering together of a sufficiently large number of ions of the desired precipitate. However, it is very doubtful that any practical medium of precipitation is sufficiently free of available sites to preclude the possibility of induced nucleation. Surfaces of containers are always in contact with reactant solutions. Some experiments have been conducted in which precipitation occurs within droplets of a spray, but even then the reactant solutions have been in contact with walls of containers prior to the precipitation.

No chemical reagent is of absolute purity, and even a trace of impurity could provide many available sites. For example, consider 0.1 g of a reagent used to form 0.1 g of a precipitate of density 2 and of cubic particles 1 μ on an edge. The precipitate would consist of $5 \cdot 10^{10}$ particles. This number of impurity sites, allowing a cube of the same density and 50 Å on an edge for each site, would weigh $1.25 \cdot 10^{-8}$ g or only about 0.1 p.p.m. of the 0.1 g of reagent. Soluble reagent chemicals meeting A.C.S. purity designations may typically contain up to 50 or 100 p.p.m. of "insoluble matter", far more than enough to provide the nucleation sites. Perhaps the entrainment of available sites during manufacture of the chemicals is a reason for the presence of this impurity within reagent grade-chemicals. In addition, a nucleating site may become separated from a growing crystal and serve to nucleate another crystal in the same reaction. It is interesting to note that even the sulfur, the boiling point of which has been used as one of the defining temperatures on the international temperature scale, has been found to contain sufficient impurity of heavy hydrocarbons to alter[25] the melting point by 0.7°.

Relationship to other factors

If the available sites do play a virtually necessary role in the nucleation of ionic precipitates, other valid experimental facts and principles must be consistent with this concept. Numerous experimentally determined facts have already been attributed to induced nucleation. Space here permits mentioning only a few which have not been specially related to induced nucleation of the type described in this paper.

The irreproducibility of experimental measurements of critical supersaturation values[2,3,5] could result from random fluctuations in conditions, such as past history of the solvent and the containers[18].

The discrepancies concerning whether there is a critical nucleus size or not and whether the nucleus contains several ions or from tens to hundreds of ions[6,7,13] could arise from referring to the two different entities as the nucleus. This suggestion is entirely consistent with the approaches used in the past in getting the contradictory conclusions.

Addition agents[20] can markedly influence the size and number of particles obtained by (a) providing new available sites and/or (b) competing for sites already available to make them less effective. In like manner ionic strength[17] could influence the number and distribution of available sites. The increase in number of particles caused by the presence of a detergent in the precipitation medium[26] could result from nucleation sites provided by micelles of the detergent or from trace impurities.

Use of a solid reagent which dissolves and immediately enters into precipitation reaction in comparison to use of solution reagents[22], not only modifies the extent of supersaturation but also provides many additional sites which would be expected to be of relatively high effectiveness. A freshly dissolved foreign electrolyte[22] results in a different number of particles than the same electrolyte not freshly dissolved because of the sites introduced by that electrolyte, some of which may become adsorbed on or combined with other sites upon standing. The interesting observation[27] that seed crystals which have been aged in a mother liquid are less effective in relieving critical supersaturation than "fresh" seed crystals could result from a coating during aging, perhaps by a hydrolysis product as suggested by the authors, of the surface sites to render them less effective.

The fact that, as the concentration of reactants is increased, the size of particles increase to a maximum and then decrease[4,28] could arise from the interrelated effects of extent of supersaturation attained and the increasing number of sites available at the higher degrees of supersaturation. The fact that, over narrower ranges of concentration, the number of particles is constant[11,29] could arise from equal numbers of sites available within the range of supersaturation reached.

In homogeneous precipitation processes, nucleation is generally not strictly one of homogeneous reaction[30], but it generally does occur under conditions of less supersaturation than in the usual direct mixing of reactants. So only the more effective sites are utilized. It is interesting to note that sulfide precipitates, whether formed directly by hydrogen sulfide or homogeneously by hydrolysis of thioacetamide, contain some sulfur, which could be involved in the induced nucleation. TURKEVICH[31] found a colloidal particle to be involved in the nucleation of colloidal gold.

The effects of stirring and mechanical shock in relieving supersaturation[2,3,15] may result not only from additional sites made available but also from breaking off sites already in use to serve again.

The effects noted in comparing precipitates obtained from fresh and aged solutions of a reactant[20,21,24] could result from introduction of available sites with the dissolving reagent, their subsequent removal by adsorption on the walls of the container or by dissolving or by combination with one another, followed eventually by introduction of still more sites from exposure to the air.

The fact that a solution in an extremely slow homogeneous precipitation process can increase in concentration beyond that at which precipitation begins and can remain thus for many minutes[32] could arise from the use of the most effective sites at the lower concentrations and then some sites of less effectiveness at higher supersaturations.

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SUMMARY

Data have been presented which show that the particle size of a precipitate is influenced by the past history of the water used in preparing a reagent solution. On the basis of these data and previously published information it is proposed that the nucleation process in practical analytical precipitation reactions is one of induced nucleation on sites which are inevitably available. It has been shown that such a mechanism is free of inconsistencies encountered with other proposals concerning the origin of nuclei.

RÉSUMÉ

Il est démontré que la pureté de l'eau utilisée pour la préparation des réactifs a une grande influence sur le nombre de germes de cristallisation et sur la grosseur des grains du précipité formé.

ZUSAMMENFASSUNG

Es wird nachgewiesen, dass die Reinheit des zur Herstellung der Reagenzienlösungen verwendeten Wassers einen grossen Einfluss auf die Zahl der Kristallkeime und Korngrösse des gebildeten Niederschlages ausübt.

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EFFECT OF FORM OF REAGENT ON PARTICLE SIZES OF PRECIPITATES

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The usual method of forming a precipitate in an analytical procedure is to mix solutions of the appropriate reagents. The particle size of the precipitate is influenced by numerous experimental conditions, including in some cases the age of one of the solutions at the time of its use[1-3]. For example, when a solution of freshly dissolved barium chloride is used for the precipitation of barium sulfate, the particles of the precipitate are much smaller than are those formed when the barium chloride solution is allowed to stand at room temperature for several hours prior to use. In research upon this phenomenon it is not possible to use a reagent solution of absolute freshness. However, it is possible to form a precipitate by introducing one reactant as a solid into a solution of the other reactant, so the solid reagent enters in the precipitation as rapidly as it dissolves. The situation is similar to, but obviously not identical with, that of a reagent solution of zero age.

The purposes of the present investigation are (a) to form several precipitates both by use of two solutions and by use of a dissolving solid as one of the reactants and to compare the particle sizes of the resultant precipitates, (b) to observe the relationship of this factor to other conditions of precipitation and (c) to interpret the results with reference to mechanisms of nucleation and crystal growth.

EXPERIMENTAL METHODS

All chemicals were of reagent grade or of comparable chemical purity and were used without further purification. The water used in preparing all solutions was first distilled and then deionized and kept in a polyethylene storage container until used.

Particle sizes were determined directly by microscopic methods employing the light microscope for particles about one micron and larger in average dimension and the electron microscope for particles about five microns and smaller. Both microscopic methods yielded similar results when used on the same precipitate.

In some of the experiments particle sizes of equal mass-concentration suspensions were compared by measuring their optical densities in a Bausch and Lomb Spectronic 20 Colorimeter. The relationship between particle size and light scattering is very complex. But the optical density can be taken as an inverse measure of relative particle size, at least for particles which are appreciably larger than the wavelength of light. This relationship is justified empirically by the data of Table I, in which are listed the optical densities and the size data obtained with a microscope for a series of barium sulfate suspensions. A plot of these data in terms of optical density *vs.* 1/size is a straight line.

TABLE I

DIRECT COMPARISON OF OPTICAL DENSITY OF SUSPENSION WITH PARTICLE SIZE OF PRECIPITATE

Optical density	*Average particle size (μ)*
0.37	17.4
0.42	14.9
0.45	14.1
0.45	13.9
0.47	15.5
0.48	12.2
0.56	10.1
1.08	4.8

The microscopic methods of size determination are advantageous in that they provide actual size numbers and also permit observation of morphology and size distribution if desired. The optical density method of size comparison is advantageous in that it is much quicker and is free from the possible error of segregation of large and small particles during mounting for microscopic observation.

EXPERIMENTAL DATA

Lead sulfate, barium chromate and calcium sulfate were precipitated, first with two reagent solutions and then with one solid reagent plus one solution reagent. When a solid reagent was used, it was in excess so slight variation in weight from one trial to another would not influence the mass of precipitate formed. The volumes and concentrations were such that the molar concentration of precipitate, assuming it to be suspended uniformly, would be constant in all precipitations of each of the three substances. Optical density measurements were made and considered to be inversely related to average particle size. Results of both optical density and microscopic observations of the precipitates are tabulated in Table II. It was also found that addition of two solids, lead nitrate and sodium sulfate, to water resulted in still smaller crystals of lead sulfate, about 1.5 μ in average dimension.

The data of Table II reveal that (a) the crystal sizes of precipitated lead sulfate and calcium sulfate are not significantly influenced by which reagent is in excess and (b) the use of a solid reagent causes a much smaller particle size than does use of two

TABLE II

MEASUREMENTS OF PARTICLES FORMED BY SOLID REAGENT AND BY SOLUTION REAGENTS

Precipitate	*Reagents*	*Optical density*		*Appearance in microscope*
		*Mean**	*S. D. of mean*	
$PbSO_4$	2 ml 0.10 *M* $Pb(NO_3)_2$ 2 ml 0.05 *M* Na_2SO_4	0.61	0.02	rectangular, 30 × 3 μ
$PbSO_4$	2 ml 0.05 *M* $Pb(NO_3)_2$ 2 ml 0.10 *M* Na_2SO_4	0.63	0.01	rectangular, 30 × 4.5 μ
$PbSO_4$	0.05 g $Pb(NO_3)_2$ 4 ml 0.025 *M* Na_2SO_4	0.82	0.03	rectangular, 9 × 3 μ
$PbSO_4$	4 ml 0.025 *M* $Pb(NO_3)_2$ 0.03 g Na_2SO_4	0.87	0.04	rectangular, 18 × 4.5 μ
$BaCrO_4$	2 ml 0.10 *M* $BaCl_2$ 2 ml 0.05 *M* Na_2CrO_4	1.83	0.02	** 1.5 μ
$BaCrO_4$	0.05 g $BaCl_2$ 4 ml 0.025 *M* Na_2CrO_4	1.70	0.02	** 1.5–3 μ
$CaSO_4$	2 ml 2.0 *M* $Ca(NO_3)_2$ 2 ml 1.0 *M* Na_2SO_4	0.33	0.02	rectangular, 9 × 3 μ
$CaSO_4$	2 ml 1.0 *M* $Ca(NO_3)_2$ 2 ml 2.0 *M* Na_2SO_4	0.33	0.01	irregular, 6 μ
$CaSO_4$	0.90 g $Ca(NO_3)_2 \cdot 4\ H_2O$ 4 ml 0.5 *M* Na_2SO_4	0.35	0.01	rectangular, 4.5 × 1.5 μ
$CaSO_4$	4 ml 0.5 *M* $Ca(NO_3)_2$ 0.60 g Na_2SO_4	0.36	0.01	irregular, 3 μ

* Each mean represents at least 5 replicate precipitations, generally 10.
** Apparently spheres, but not clearly resolved.

reagent solutions for lead sulfate and slightly so for calcium sulfate but not for barium chromate.

Several experimental variables were studied in the precipitation of lead sulfate. The following reference conditions were arbitrarily selected: room temperature; solid lead nitrate with particle size of 120–150 μ; solid sodium sulfate with particle size of 60–90 μ; sulfate ion in stoichiometric excess; both solid reagents added with hand swirling to deionized water at neutral pH. Variations from these reference conditions were found to exhibit the effects listed in Table III. It is evident that the smaller size

TABLE III

EFFECTS OF SEVERAL VARIABLES ON PARTICLE SIZE OF LEAD SULFATE PRECIPITATED BY SOLID REAGENTS

Variable	*Effect*
higher temperature	slightly smaller crystals
larger particle size of reagents	much larger crystals
smaller particle size of reagents	much smaller crystals
no stirring	no difference
vigorous stirring	same size, but crystals more perfect
stirring by bubbling air	same size, but crystals more perfect
change in volume of water	no difference
1 : 1 ethanol–water medium	slightly smaller crystals
low pH	no difference
other reagent in excess	no difference

resulting from use of solid reagents is very real and is not dependent upon some chance interaction of other conditions. Apart from the use of larger particles of the solid reagents, none of these variations in conditions removed or even decreased the effect of the use of the solid reagents.

Effect of particle size of the solid reagent

Additional experiments were performed on barium, calcium and lead sulfates to obtain further information on the effect of the particle size of a solid reagent upon the particle size of the precipitate. A barium sulfate precipitated by mixing solutions of barium nitrate and sodium sulfate consisted of dendritic crystals with overall sizes of about 22–30 μ. When one large crystal of barium nitrate was added directly to the sulfate solution, the crystals of precipitated barium sulfate were still somewhat dendritic but were only about 12 μ. When the barium nitrate was added as a finely divided substance, the precipitated particles were of similar morphology but only about 1.5 μ.

Calcium sulfate was precipitated, both with large crystals of calcium nitrate and with finely divided crystals, each added to a sulfate solution. The crystals precipitated by the latter were only one-third as large as the former, although there was much variation of size within each.

Barium and lead sulfates were precipitated with solid sodium sulfate of several different particle sizes. The most finely divided sodium sulfate which could be obtained by hand-grinding was about 6 μ. To obtain even smaller particles for this experiment, a solution of sodium sulfate was passed through an atomizer ("Vaponefrin Nebulizer") operated continuously by compressed air, and the tiny droplets were evaporated by heat and their residues collected. The intention was to force evaporation of each tiny droplet of the solution to leave one or more tiny crystals of sodium sulfate as the residue from each droplet. No difficulty was experienced in evaporating the droplets readily, but the efficiency of collecting the tiny crystals from the air was never over 20% in the several methods tried. The particles of sodium sulfate which were thus obtained ranged down to one-tenth μ as determined by examination in the electron microscope. These particles were used as solid reagents in the precipitation of barium and lead sulfates, and the resulting precipitates consisted of smaller crystals than those obtained either by use of larger particles of solid reagent or of solution reagents.

It is concluded that the use of a solid reagent in place of one of the solution reagents results in a precipitate of smaller crystals and that the effect is enhanced as the particle size of the solid reagent is decreased.

Some other precipitates

Six other precipitates were formed, both by means of two solutions and by means of one solid reagent plus one solution reagent in order to establish further how general the effects are. All precipitates in this series were observed in the electron microscope. In five of them, calcium fluoride, lead fluoride, nickel dimethylglyoxime, strontium sulfate and silver chromate, it was found (a) that the use of a solid reagent results in particles from one-third to one-tenth of the size obtained when both reagents were used as solutions and (b) that the effect is enhanced by finely grinding the solid reagent prior to use. Therefore these two conclusions appear to be very definite and quite general. Data on the sixth precipitate, silver chloride, were inconclusive, although this precipitate probably fits into the general pattern as well.

Effect of the presence of a freshly dissolved inert electrolyte

As an aid in interpreting the results of the preceding experiments in terms of nucleation and crystal growth, a series of experiments was conducted to determine whether or not the presence of a recently dissolved inert electrolyte (one which is not a direct reactant in the precipitation process) would exert any influence on the particle size of the precipitate. Four precipitates were selected for study, strontium sulfate, lead fluoride, lead chromate and barium sulfate. Two inert electrolytes, sodium nitrate and potassium nitrate, were each used with each of the four precipitates. The major reactants were used as solutions throughout. All precipitations were run at least in triplicate, and optical density measurements were made for comparison of particle sizes. In all four precipitation reactions and with each of the two inert electrolytes, the presence of a recently (0.5 to 1.0 min) dissolved inert electrolyte influenced the particle size, and in every case the influence was different in magnitude and/or in direction to the effect of the same inert electrolyte which had been in solution for a longer period of time. It is concluded (a) that the presence of a freshly dissolved inert electrolyte at the time that a precipitation process occurs very markedly influences the particle size of the precipitate and (b) that this influence can not be attributed solely to the presence of the ions of that inert electrolyte.

DISCUSSION

The fact that use of a solid reagent results in smaller particles of a precipitate than does use of solution reagents signifies that the solid reagent somehow enhances nucleation at the expense of crystal growth. It is now of interest to consider possible reasons for this enhanced nucleation.

According to classical VON WEIMARN concepts, the rate of nucleation and thereby the number of particles is a function of the degree of supersaturation at the time the particles form. If this be the determinative factor in the present situation, the degree of supersaturation would be greater when a solid reagent is used than when all reagents are in the form of solutions. However, such may not be the case. Considering first the overall bulk of the precipitation medium, the supersaturation must be less with a solid reagent, because the reagent ions are used up in forming the precipitate as rapidly (or nearly so) as they enter the solution from dissolution of the solid reagent.

Considering second not the overall bulk of the precipitation medium but only the immediate environment as the added reagent meets the other reagent (where the drops "hit" in using solutions and the surfaces of the dissolving particles in using a solid), it is more difficult to compare the extents of supersaturation in the two cases. Three factors conceivably could influence the temporary, localized degrees of supersaturation. (Let X represent the solid reagent and Y the solution of the same reagent, each added to a solution of the other requisite reagent.) (a) X is more concentrated than Y, tending to make greater supersaturation with X than with Y. (b) Y is added all quite abruptly by pouring in, whether dropwise or not, while X is effectively added only at its dissolution rate, tending to make greater supersaturation with Y than with X. (c) The area of contact with X is the surface area of the particles which, except when only a few large crystals are used, is greater than the area of contact where two liquids hit each other; thus the area (and volume) of supersaturation is spread out more in X than in Y, tending to make greater supersaturation with Y. These factors are interrelated, especially (a) and (b). If factor (a) were predominant, the rate of stirring would be expected to influence the number of nuclei formed, but the data of Table III indicate that this is not the case. From these considerations it may be tentatively concluded, but is not proved, that even the localized extent of supersaturation with a solid reagent is no greater than that with solution reagents. If this be true, the larger number of crystals resulting from use of a solid reagent can not be accounted for by a consideration of the relative degrees of supersaturation in the two cases.

Of more direct significance in this connection are the results of the experiments with inert electrolytes. The extent to which a solution is supersaturated with respect to barium sulfate, for example, can not be influenced by whether some sodium nitrate also present has been there for one minute or for an hour.

The presence of the solid phase must directly enhance nucleation, possibly by providing additional surfaces upon which nucleation can get started. This mechanism is discussed in a broader context in another paper from this laboratory[4].

CONCLUSIONS

1. A precipitate formed by mixing one solid reagent with one solution reagent consists of particles which are much smaller than are those formed when solutions of the two reagents are mixed. The phenomenon occurs in the precipitation of lead sulfate, calcium sulfate, barium sulfate, strontium sulfate, calcium fluoride, lead fluoride, nickel dimethylglyoxime and silver chromate, so it is quite general.
2. The effect is enhanced as the particle size of the solid reagent is decreased.
3. The presence of a freshly dissolved inert electrolyte at the time two solutions are mixed to form a precipitate influences the particle size of a precipitate, and this effect can not be attributed solely to the presence of the ions of that inert electrolyte.
4. The effects can probably not be attributed to the degrees of supersaturation existing at the time that the precipitate is formed.
5. The presence of the solid phase must directly enhance nucleation. Combining these results with those reported earlier on the aging of solutions, it appears that the presence or the recent presence of a solid phase, whether of one of the main reactants or not, enhances nucleation by providing sites upon which the formation of nuclei may be induced.

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SUMMARY

The particle size of an ionic precipitate is much smaller when one of the reactants is introduced as a solid rather than as a solution. The effect is enhanced as the particle size of the solid reagent is decreased. The presence of a freshly dissolved inert electrolyte also influences the particle size of a precipitate. The affects are not attributable merely to the degree of supersaturation but rather to the provision by the freshly dissolved material of sites upon which nucleation can be induced.

RÉSUMÉ

L'auteur a étudié l'effet, sur la grosseur des particules d'un précipité, de la forme sous laquelle le réactif est utilisé (à l'état solide, ou en solution). Il a examiné également l'influence d'un électrolyte neutre.

ZUSAMMENFASSUNG

Der Einfluss der Form (fest oder gelöst) eines Fällungsmittels auf die Korngrösse eines gebildeten Niederschlages wurde untersucht. Zugabe eines neutralen Salzes kurz vor der Fällung beeinflusst ebenfalls die Korngrösse des Niederschlages.

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Anal. Chim. Acta, 22 (1960) 508–514

DETERMINATION OF NIOBIUM AND TANTALUM WITH CINNAMYL HYDROXAMIC ACID AND N-CINNAMOYL-N-PHENYLHYDROXYLAMINE

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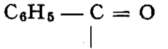
We have shown that N-benzoyl-N-phenylhydroxylamine[1] is a suitable reagent for the separation of niobium and tantalum, and for the direct gravimetric determination of niobium[2]. Further investigations have been carried out to discover if other reagents with similar atomic groupings could be equally useful. Organic derivatives of hydroxamic acids are structurally related to N-benzoyl-N-phenylhydroxylamine and may be regarded as derived from hydroxylamine, NH_2OH, by the replacement of one or both of the hydrogen atoms linked to nitrogen.

$$\begin{array}{l} C_6H_5 - \overset{\displaystyle C = O}{} \\ \qquad\quad | \\ C_6H_5 - N - OH \end{array}$$

N-benzoyl-N-phenylhydroxylamine



$$\begin{array}{l} C_6H_5 - C = O \\ \qquad\qquad | \\ H \; - N - OH \end{array}$$

Benzohydroxamic acid

Of the organic hydroxamic acids prepared, benzohydroxamic acid and phenylacetylhydroxamic acid formed no precipitate with niobium or tantalum in tartrate solution, even when it was made ammoniacal. Salicylhydroxamic acid formed insoluble complexes with both niobium and tantalum, but the reaction was not strictly quantitative when the solution contained oxalate, tartrate or citrate. Cinnamylhydroxamic

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acid, however, quantitatively precipitated both niobium and tantalum under different pH conditions. When oxalate or tartrate was present, both niobium and tantalum could be precipitated from solutions of acidity anywhere between 5% by volume of sulphuric acid and a maximum pH of 6.5; with citrate, precipitation was satisfactory up to pH 2.0 for tantalum and 2.8 for niobium. At acidities above 5% of sulphuric acid or at pH above 6.5 the complexes became more soluble. Though cinnamylhydroxamic acid failed to give a clean separation of niobium and tantalum from each other, these metals could be separated from other elements in presence of EDTA, and niobium could be determined by direct weighing of the stable complex $NbO(C_9H_8NO_2)_3$, which decomposed only at 225°. The tantalum precipitate, however, had to be ignited to the pentoxide before the final weighing.

Of the derivatives of phenylhydroxylamines, N-phenylacetyl-N-phenylhydroxylamine gave only incomplete precipitation of niobium and tantalum on prolonged digestion with oxalate or tartrate solutions.

N-cinnamoyl-N-phenylhydroxylamine, however, behaved like N-benzoyl-N-phenylhydroxylamine and precipitated niobium under the same conditions. With the N-cinnamoyl reagent the pH range for complete precipitation extended up to a maximum of 7.5. The niobium complex was not very stable to EDTA and had to be ignited to the oxide because it was always associated with the sparingly soluble reagent. With tantalum, N-cinnamoyl-N-phenylhydroxylamine required an oxalate or tartrate medium containing 2.5 to 10% by volume of sulphuric acid; with less acid the tantalum complex was colloidal.

Although N-cinnamoyl-N-phenylhydroxylamine does not permit the separation, by a simple pH adjustment, of the earth acid elements from each other, it allows the separation of niobium and tantalum from a large number of ions, *e.g.* Zn^{+2}, Mn^{+2}, Ni^{+2}, Co^{+2}, Mg^{+2}, Be^{+2}, Cu^{+2}, Hg^{+2}, Cd^{+2}, As^{+3}, Bi^{+3}, Al^{+3}, Cr^{+3}, UO_2^{+2}, Th^{+4}, Ce^{+4}, PO_4^{-3} and AsO_4^{-3}.

Details of the investigation of cinnamylhydroxamic acid and N-cinnamoyl-N-phenylhydroxylamine as reagents for the precipitation and separation of niobium and tantalum from each other and from other elements are given below.

EXPERIMENTAL

The chemicals and standard solutions used were the same as reported earlier[1,2]. Standard oxalate, citrate and tartrate solutions of niobium and tantalum were prepared[1-3] from specpure (Johnson and Matthey) Nb_2O_5 and Ta_2O_5. A Cambridge pH indicator was used for all pH measurements.

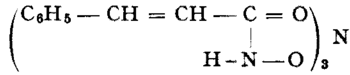
Cinnamylhydroxamic acid (m.p. 110–111°) was prepared according to the method of THIELE AND PICKARD[4]; a 1% freshly prepared aqueous solution was used as the precipitant.

A 2.5% alcoholic solution of N-cinnamoyl-N-phenylhydroxylamine, prepared according to the following procedure, was also used as a precipitant. To a cold solution of phenylhydroxylamine (30 g) in water (1200 ml) was added dropwise over a period of 90 min, a solution of cinnamoyl chloride (53 g) in ether (75 ml). The mixture was stirred vigorously by a mechanical stirrer and kept faintly alkaline throughout by occasional additions of sodium bicarbonate. Stirring was continued for a further 45 min. The mono-derivative was then separated and recrystallised from alcohol in the same way as for N-benzoyl-N-phenylhydroxylamine. The pale green crystals melted at 158–160°. Analysis showed that the formulae of the N-phenylacetyl-N-phenylhydroxylamine and N-cinnamoyl-N-phenylhydroxylamine were, respectively, $C_{14}H_{13}NO_2$ (% calc.: C, 73.99; H, 5.77; N, 6.16; % found: C, 74.01, 74.03; H, 5.78, 5.77; N, 6.14, 6.12), and $C_{15}H_{13}NO_2$ (% calc.: C, 75.29; H, 5.48; N, 5.85; % found: C, 75.20, 75.36; H, 5.43, 5.46; N, 5.81, 5.82).

Composition of cinnamylhydroxamic acid complex

The yellow niobium and the white tantalum complexes were isolated by the procedure given below for their estimation and dried at 110°. The percentage of the element in the respective complexes was determined by igniting a known amount of the dried complex and weighing as the pentoxide. The nitrogen contents were determined by Kjeldahl's method. The niobium complex was found to have the composition $NbO(C_9H_8NO_2)_3$ (% Nb calc.: 15.60; %N calc.: 7.09; %Nb found: 15.27, 15.56; % N found: 7.02, 7.05).

Structurally the complex may be represented as follows:



$$\left(\begin{array}{l} C_6H_5-CH=CH-C=O \\ \qquad\qquad\qquad\quad\ \ | \\ \qquad\qquad\qquad H-N-O \end{array}\right)_3 Nb=O$$

The thermolysis curve (Fig. 1) showed that the niobium complex could be easily dried at 110°; it is stable up to 225° and at higher temperatures decomposes slowly to pentoxide; thermolysis of the tantalum complex proved the absence of any definite composition. The niobium complex can therefore be directly weighed as $NbO(C_9H_8NO_2)_3$, but the tantalum complex must be ignited to the weighable pentoxide.

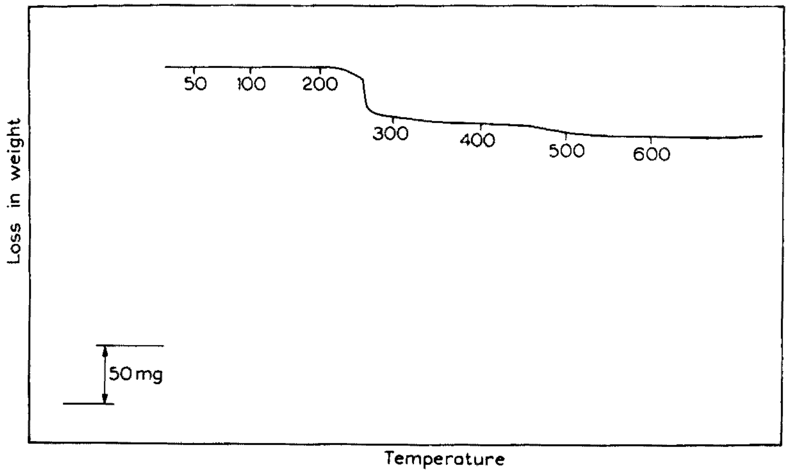


Fig. 1. Thermolysis curve.

Effect of pH and the determination of niobium and tantalum

(*a*) *With cinnamylhydroxamic acid*

An aliquot of the standard solution of niobium or tantalum was diluted to about 150 ml and the pH was adjusted with dilute sulphuric acid, ammonium acetate or ammonia. The solution was heated nearly to boiling, and an aqueous solution of the reagent was added with stirring till a slight turbidity appeared (25 ml of 1% solution was sufficient for every 10 mg of the pentoxide). The beaker was then placed on a boiling water bath for 30 to 60 min for the complete coagulation of the precipitate. The solution was then cooled to room temperature (30°) and the precipitate was filtered through a sintered glass No. 4 crucible, washed thoroughly with warm water (40°), dried at 110° and weighed. The weight of the complex multiplied by 0.2231 gave the weight of Nb_2O_5.

For tantalum, a few ml of a suspension of ashless paper pulp was added before the coagulation of the precipitate; after filtration through a quantitative filter paper the precipitate was washed with warm water containing 1% ammonium nitrate and 0.2% reagent. The precipitate was then dried, ignited and weighed as Ta_2O_5.

In presence of oxalate and tartrate, niobium and tantalum were quantitatively precipitated from solutions containing 5% (v/v) sulphuric acid or up to a pH of 6.5. For complete precipitation in presence of citrate, the acidity could be as high as 5% sulphuric acid but the pH had to be less than 2.0 for tantalum or 2.8 for niobium. Higher acidities or higher pH gave low results owing to incomplete precipitation (Table I).

TABLE I

pH	*Nb_2O_5 taken mg*	*Wt. of complex mg*	*Nb_2O_5 found mg*
*[a]	15.0	48.7	10.86
**[a]	15.0	66.3	14.80
1.5[a]	15.0	66.8	14.9
4.0[a]	15.0	67.0	15.0
5.4[a]	15.0	67.0	15.0
6.5[a]	15.0	66.5	14.8
7.3[a]	15.0	56.2	12.54
1.2[b]	15.0	66.3	14.80
2.8[b]	15.0	66.5	14.80
3.2[b]	15.0	64.0	14.30

pH	*mg Ta_2O_5*	
	taken	*found*
*[a]	13.8	9.4
**[a]	13.8	13.8
1.3[a]	13.8	13.7
4.2[a]	13.8	13.6
6.4[a]	13.8	13.8
8.6[a]	13.8	8.2
0.8[b]	13.8	13.7
2.0[b]	13.8	13.8
2.6[b]	13.8	12.7

* 10% (v/v) H_2SO_4
** 5% (v/v) H_2SO_4
[a] oxalate or tartrate solution
[b] citrate solution

(*b*) *With N-cinnamoyl-N-phenylhydroxylamine*

An aliquot of the standard oxalate or tartrate solution of niobium or tantalum was diluted to about 250 ml, and dilute sulphuric acid or ammonia was added to adjust the pH to the desired value. The solution was heated nearly to boiling and niobium or tantalum was precipitated by following the procedure given under (*a*) (7.5 ml of 2.5% reagent solution was sufficient for every 10 mg of the pentoxide). The precipitate was finally ignited and weighed as the pentoxide. When the pH of the solution was less than 2.0, precipitation was done at room temperature (25–30°) to prevent the formation of a gummy precipitate.

The precipitation of niobium was quantitative from 10% (v/v) sulphuric acid solutions and from solutions of pH up to 7.5; for tantalum the acidity should be between 2.5 and 10% (v/v) sulphuric acid. At lower acidity the tantalum precipitate is colloidal. The results are given in Table II.

TABLE II

mg Nb_2O_5		pH	mg Ta_2O_5		pH
taken	found		taken	found	
18.3	18.3	*	13.4	13.4	*
18.3	18.3	**	13.4	13.3	**
18.3	18.3	0.5	13.4	13.3	***
18.3	18.2	3.2	13.4	11.0	0.6
18.3	18.2	5.1			
18.3	18.2	6.9			
18.3	18.3	7.5			
18.3	16.0	8.0			

* 10% (v/v) H_2SO_4
** 5% (v/v) H_2SO_4
*** 2.5% (v/v) H_2SO_4

Effect of various ions

(*a*) *With cinnamylhydroxamic acid*

Preliminary experiments showed that in presence of EDTA neither niobium nor tantalum was precipitated below pH 5.0. An aliquot of the standard oxalate or tartrate solution of niobium or tantalum was therefore mixed with a few ml of the solution of the ion whose effect was to be studied; the solution was diluted to 200 ml, and treated with sufficient EDTA to mask the ions, and the pH was adjusted by ammonium acetate to above 5.0. The niobium or tantalum was then precipitated, washed and weighed as described above. The results are given in Table III.

TABLE III

Ion	Added mg	mg Nb_2O_5		mg Ta_2O_5	
		taken	found	taken	found
Fe^{+3}	100.0	12.3	12.1	10.6	10.6
Al^{+3}	100.0	12.3	12.0	10.6	10.5
Cr^{+3}	100.0	12.3	12.3	10.6	10.8
Zn^{+2}	100.0	12.3	12.4	10.6	10.4
Mn^{+2}					
Ni^{+2}					
Co^{+2}					
Be^{+2}	100.0	12.3	12.4	10.6	10.6
Mg^{+2}					
Th^{+4}	120.0	12.3	12.5	10.6	10.6
UO_2^{+2}	120.0	12.3	12.2	10.6	10.7
Ce^{+4}	100.0	12.3	12.1	10.6	10.3
Cu^{+2}	100.0	14.6	14.5	15.0	15.2
Cd^{+2}	100.0				
Bi^{+3}	100.0				
Hg^{+2}	100.0				
As^{+3}	100.0	14.6	14.2	15.0	14.7
Sb^{+3}	100.0				
Sn^{+2}	100.0				
AsO_4^{-3}	100.0	14.6	14.7	15.0	15.0
WO_4^{-2}	100.0				
PO_4^{-3}	100.0				

(*b*) *With N-cinnamoyl-N-phenylhydroxylamine*

The effect of various ions was studied by the method described above with 10% (v/v) sulphuric acid. The results (Table IV) show that only Ti^{+4}, Zr^{+4}, VO_3^- MoO_4^{-2}, WO_4^{-2}, Fe^{+3}, Sn^{+2} and Sb^{+3} interfere.

TABLE IV

Ions	*Added mg*	*mg Nb_2O_5*		*mg Ta_2O_5*	
		taken	*found*	*taken*	*found*
UO_2^{+2}	200.0	16.0	16.0	11.0	11.1
Be^{+2}	100.0	16.0	16.1	11.0	11.1
Mg^{+2}	100.0				
Cu^{+2}	100.0	16.0	16.2	12.4	12.5
Cd^{+2}	100.0				
Hg^{+2}	100.0				
Zn^{+2}	100.0	15.2	15.2	12.4	12.4
Mn^{+2}	100.0				
Ni^{+2}	100.0				
Co^{+2}	100.0				
Al^{+3}	100.0	16.0	16.1	11.0	11.1
Cr^{+3}	100.0				
Bi^{+3}	100.0	15.0	15.1	12.4	12.5
As^{+3}	100.0				
Th^{+4}	250.0	16.0	16.0	11.0	11.0
Ce^{+4}	200.0	16.0	16.2	11.0	11.2
PO_4^{-3}	250.0	15.2	15.2	12.4	12.5
AsO_4^{-3}	240.0	15.2	15.3	12.4	12.6

SUMMARY

The determination and separation (from other ions) of niobium and tantalum by means of cinnamylhydroxamic acid and N-cinnamoyl-N-phenylhydroxylamine are described. Cinnamylhydroxamic acid permits the separation of both elements above pH 5.0 (titanium, zirconium and molybdenum interfere) and the niobium complex can be weighed after drying at 110°. With N-cinnamoyl-N-phenylhydroxylamine, the optimum conditions are slightly different; titanium, zirconium, vanadate, molybdate, tungstate, iron, tin and antimony contaminate these precipitates.

RÉSUMÉ

Une méthode est proposée pour le dosage du niobium et du tantale, et leur séparation d'avec d'autres ions. On utilise comme réactifs l'acide cinnamylhydroxamique et la N-cinnamoyl-N-phénylhydroxylamine.

ZUSAMMENFASSUNG

Es wird eine Methode beschrieben zur Abtrennung und Bestimmung von Niob und Tantal mit Hilfe der Cinnamylhydroxamsäure und des N-cinnamoyl-N-phenylhydroxylamins.

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DOSAGE COMPLEXOMÉTRIQUE DE BROMURES ET D'IODURES EN PRÉSENCE L'UN DE L'AUTRE

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La méthode que nous décrivons est basée sur celle de BEKK[1], selon laquelle les deux halogènes sont précipités simultanément par addition d'un excès de nitrate d'argent. Ce précipité servira pour le dosage complexométrique.

On répète la même opération et le précipité de bromure et d'iodure d'argent est traité à chaud par un oxydant (mélange chromique). L'iodure est transformé en iodate alors que le bromure est décomposé en brome et libéré sous forme gazeuse. L'iodate d'argent est ensuite réduit en iodure au moyen d'une solution de sulfite de sodium. L'iodure d'argent est filtré, lavé et sert au dosage complexométrique.

La différence des lectures des deux titrages avec le complexon, permet de calculer les quantités de bromures et d'iodures présents. Les halogénures d'argent sont dissous dans une solution ammoniacale de tétracyanure de nickel suivant la technique de FLASCHKA ET HUDITZ[2,3]. Les réactions se passent comme suit:

$$2AgX + [Ni(CN)_4]^{-2} \rightarrow 2[Ag(CN)_2]^- + Ni^{+2} + 2X^-$$

Le nickel déplacé est dosé par voie complexométrique et l'halogène est ainsi déterminé indirectement.

Réactifs

Solutions de nitrate d'argent à 5% et à 0.1%; solution d'acide nitrique à 1%; solution de complexon III 0.1*M*; solution saturée de murexide (aqueuse); solution ammoniacale de tétracyanure de nickel 0.1 *M*, obtenue par titrage précis d'une solution de sulfate de nickel 0.1 *M* avec une solution de KCN 1 *M* après addition d'ammoniaque, le titrage est terminé lorsque l'indicateur (murexide) vire du jaune au violet; bichromate de potassium (pro analisi); acide sulfurique concentré (pro analisi); solution concentrée de sulfite de sodium.

Mode opératoire

Les bromures et les iodures en solution sont précipités par la méthode usuelle en utilisant une solution de nitrate d'argent à 5%. Le précipité est filtré sur laine de verre et lavé deux fois avec une solution de nitrate d'argent à 0.1%, puis deux ou trois fois avec de l'acide nitrique à 1%. On répète la précipitation pour le dosage des iodures seuls.

Le premier précipité est conservé pour le dosage complexométrique des bromures et des iodures. Le second est traité (laine de verre et précipité) dans un bécher par une solution de 4 g de bichromate de potassium dans 60 ml d'acide sulfurique concentré, à 95°, et laissé sur le bain-marie pendant une demi-heure. Les iodures sont transformés en iodates alors que les bromures sont décomposés et le brome mis en liberté. Après digestion au bain-marie, on fait passer un courant d'air dans la solution pour chasser tout le brome.

Le contenu du bécher est dilué à 400 ml environ. On filtre et on lave bien le filtre avec de l'eau. On ajoute au filtrat, goutte à goutte, une solution concentrée de sulfite de sodium, en agitant constamment, jusqu'à ce qu'une faible odeur d'anhydride sulfureux persiste après un repos de 10 min. L'iodure d'argent se forme et précipite. On recueille le précipité d'iodure d'argent sur la laine de verre et on lave deux fois avec la solution de nitrate d'argent à 0.1%, puis deux à trois fois avec celle de l'acide nitrique à 1%.

Le précipité d'iodure d'argent est transféré (avec la laine de verre) dans un bécher contenant la solution ammoniacale de tétracyanure de nickel. On chauffe doucement en agitant le contenu du bécher jusqu'à dissolution complète du précipité. On ajoute quelques gouttes d'indicateur et l'on titre le nickel libéré avec la solution de complexon jusqu'à ce que la solution vire au violet. On note le nombre de ml de complexon utilisés.

Le précipité de AgI + AgBr est traité de la même façon et la lecture de la burette notée. On mesure la différence des deux lectures pour connaître la quantité de complexon nécessaire pour le dosage du brome. Les teneurs en mg d'iode et de brome, sont obtenues en multipliant le nombre de ml de complexon III par 25.38 et 15.98, respectivement.

CONCLUSION

Les résultats obtenus avec différentes proportions de bromures et iodures sont satisfaisants. La méthode complexométrique s'est montrée sensiblement plus rapide que la méthode gravimétrique. La méthode décrite sert également pour les microdosages. On utilise dans ce cas une solution de complexon III 0.001 M et les facteurs pour l'iode et le brome sont respectivement 0.254 mg et 0.160 mg par ml de réactif.

RÉSUMÉ

La méthode décrite est basée sur celle de Bekk. Dans une première opération, les bromures et les iodures sont précipités à l'aide de nitrate d'argent. Après une seconde précipitation, le bromure et l'iodure d'argent sont oxydés. Le bromure se décompose et le brome se dégage, alors que l'iodure se transforme en iodate. L'iodate est réduit au moyen de sulfite de sodium en iodure d'argent qui précipite. Les précipités des deux opérations sont dissous dans une solution ammoniacale de tétracyanure de nickel. L'argent forme un complexe avec le cyanure et libère le nickel qui est dosé par voie complexométrique. Ainsi les bromures et les iodures sont déterminés indirectement. La méthode donne des résultats très satisfaisants et est assez rapide. Elle peut être utilisée pour les microdosages de bromures et d'iodures.

SUMMARY

Bromides and iodides are determined simultaneously by precipitation as silver halide. In another aliquot, silver halides are oxidized, bromine being liberated; the iodate formed is then reduced to iodide which precipitates. The silver precipitates are treated with ammoniacal tetracyano nickelate and displaced nickel is determined complexometrically. Bromide is determined by difference.

ZUSAMMENFASSUNG

Es wird eine komplexometrische Methode zur Bestimmung von Bromid und Jodid im Gemisch beschrieben. Nach Fällung mit Silbernitrat wird die Summe von Silberbromid und -jodid komplexometrisch bestimmt. Eine zweite Fällung der beiden Halogenide wird mit Bichromat-Schwefelsäure oxydiert. Nach Vertreibung des Broms wird das Jodat reduziert, wobei Silberjodid

ausfällt. Der abgetrennte Silberjodidniederschlag wird nach Zugabe von Tetracyanonickelat mit Komplexonlösung titriert. Der Bromidgehalt wird aus der Differenz der beiden Titrationen errechnet.

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DOSAGE INDIRECT DU POTASSIUM PAR COMPLEXOMÉTRIE

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Les méthodes gravimétriques pour le dosage du potassium sont relativement longues et délicates. Les sels de potassium doivent être soigneusement séchés et déshydratés avant d'être pesés. Ces deux opérations exigent des soins spéciaux et peuvent durer des heures jusqu'à poids constant. D'autre part, les sels de potassium étant beaucoup plus volatils que les sels correspondants de sodium, il y a toujours le risque de provoquer une volatilisation partielle par un chauffage prolongé.

Ces difficultés[1] nous ont fait recourir à une méthode volumétrique pour le dosage du potassium sous forme de perchlorate.

Le principe réside dans la transformation du perchlorate en chlorure de potassium[2,3] et précipitation du chlorure par le nitrate d'argent. On applique ensuite la méthode complexométrique[4,5] pour le dosage des halogènes, basée sur la mise en liberté de l'ion nickel lorsqu'on ajoute un sel d'argent à une solution de tétracyanure de nickel

$$2AgCl + [Ni(CN)_4]^{-2} \rightarrow 2[Ag(CN)_2]^- + Ni^{+2} + 2Cl^-$$

Le nickel libéré est titré à l'aide du complexon III.

Réactifs

Chlorure d'ammonium (pro analisi); solution de nitrate d'argent à 5%; solution de nitrate d'argent à 0.1%; solution d'acide nitrique à 1%; solution de complexon III 0.1 *M*; solution de murexide, saturée dans l'eau; solution ammoniacale de tétracyanure de nickel 0.1 *M*, préparée par titrage précis d'une solution de sulfate de nickel 0.1 *M* avec une solution de cyanure de potassium *M*, après addition d'ammoniaque (le titrage est terminé lorsque l'indicateur (murexide) vire du jaune au violet).

Mode opératoire

Le précipité de perchlorate de potassium est séché rapidement en le lavant avec un peu d'éther et ensuite enlevé soigneusement du filtre Gooch* et introduit dans une capsule de platine. On ajoute 2 à 3 g (environ 5 fois le poids du précipité) de chlorure

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* Pour de petites quantités de potassium, il pourrait être avantageux d'effectuer la précipitation de $KClO_4$ dans un tube à centrifuger.

d'ammonium et on mélange le tout intimement. On recouvre le mélange avec une couche de chlorure d'ammonium et l'on chauffe doucement pendant une à deux heures après avoir couvert la capsule avec un verre de montre.

Au cas où l'on utilise une capsule en porcelaine, il faut ajouter au mélange 1 ml d'acide chloroplatinique. On doit veiller à ce que la température du mélange soit en-dessous du point de fusion du chlorure résiduel (sinon on risque d'attaquer les parois de la capsule de platine). On ajoute encore du chlorure d'ammonium et l'on chauffe doucement pendant une demi-heure. On laisse refroidir et on dissout les chlorures dans de l'eau distillée contenue dans un bécher. On ajoute de l'acide nitrique, puis on précipite à l'aide de nitrate d'argent à 5%. On porte le contenu du bécher à l'ébullition pendant 5 min en prenant soin de couvrir le bécher avec un verre de montre.

On refroidit la solution et l'on filtre sur un gooch. Le précipité est lavé avec une solution de nitrate d'argent à 0.1% et ensuite avec l'acide nitrique à 1%. Le filtre est introduit dans un bécher contenant la solution ammoniacale de tétracyanure de nickel. On chauffe doucement en agitant jusqu'à dissolution complète du précipité. On ajoute quelques gouttes d'indicateur et l'on titre le nickel libéré avec la solution de complexon III, jusqu'à ce que la couleur de la solution vire au violet. Pour connaître la quantité de potassium en mg, il faut multiplier le nombre de ml de complexon 0.1 M par 7.820 et pour obtenir K_2O par 9.420.

RÉSULTATS ET CONCLUSIONS

Les résultats obtenus par la méthode que nous venons de décrire sont très satisfaisants. Au premier abord, la technique adoptée paraît compliquée et très longue. En effet, il s'agit de traiter deux précipités et avoir recours à une voie indirecte pour déterminer la teneur en potassium. Toutefois, l'expérience nous a montré que la méthode gravimétrique est tout aussi longue et plus délicate. Les écarts maxima sont de l'ordre de 1% sur les valeurs obtenues par gravimétrie.

RÉSUMÉ

Une méthode indirecte par voie complexométrique est décrite pour le dosage du potassium. Le précipité de perchlorate de potassium obtenu par la technique habituelle, est chauffé avec du chlorure d'ammonium pour réduire le perchlorate en chlorure. Le chlorure est dissous dans l'eau et précipité sous forme de chlorure d'argent. Ce précipité est ensuite dissous dans le tétracyanure de nickel. L'argent déplace le nickel et ce dernier est dosé par voie complexométrique.

SUMMARY

An indirect complexometric method for the determination of potassium is described. Potassium is precipitated as perchlorate, which is reduced to chloride. Silver chloride is treated with tetracyano nickelate, nickel being titrated chelatometrically.

ZUSAMMENFASSUNG

Beschreibung einer indirekten komplexometrischen Bestimmung von Kalium. Dieses wird als Kaliumperchlorat gefällt, zu Chlorid reduziert und als Silberchlorid in Gegenwart von Tetracyanonickelat mit Komplexonlösung titriert. Der Umrechnungsfaktor für Kalium wird angegeben.

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COMPLEXOMETRIC AND ARGENTOMETRIC TITRATIONS USING CHEMILUMINESCENT INDICATORS

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We have already described[1,2] some new analytical applications of the chemiluminescent indicators siloxene and luminol (aminophthalic acid hydrazide) which were recommended by KENNY AND KURTZ[3]. We have shown that lophine (2,4,5-triphenylimidasole)[4] and lucigenin (dimethyl-diacrydilium-dinitrate)[5,6] are also suitable indicators for some titrations; the end-points are again based on the appearance or disappearance of chemiluminescent light. Lucigenin seems to be especially suitable owing to its adaptability and reversibility.

There is an essential difference between the mechanism of chemiluminescence of lucigenin and luminol. Both indicators emit light in alkaline media. However, luminol emits the light with various oxidizing agents provided that catalysts are present, whereas, lucigenin emits only with hydrogen peroxide.

We established that in the chemiluminescent mechanism of luminol the hydroxyl free radicals which are formed by the interaction of the catalyst play an important role. Lucigenin needs no free radicals for chemiluminesce. Thus luminol seems to be suitable for the detection of hydroxyl free radicals.

To investigate this problem we first studied the mechanism of decomposition of hydrogen peroxide in alkaline media[7]; we found that the decomposition in the presence of metal hydroxides proceeds mainly by a chain reaction through hydroxyl free radicals according to the Haber-Weiss mechanism[8]. Hence, in a hydrogen peroxide solution containing a catalyst hydroxyl free radicals are formed in almost all cases.

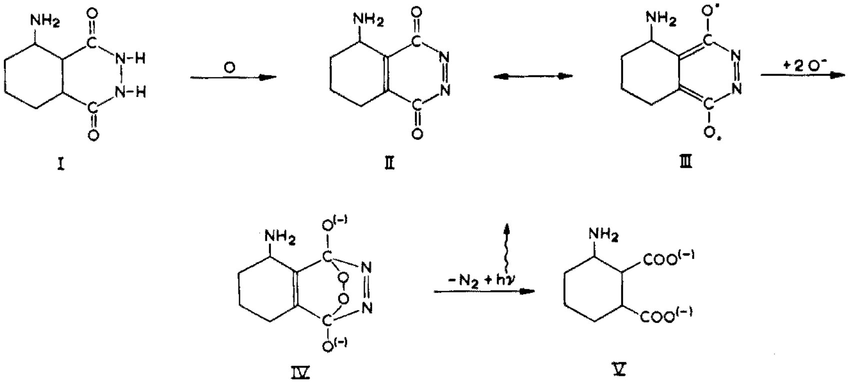

Fig. 1. Chemiluminescent mechanism of luminol.

In a strongly alkaline, catalyst-free media, the kinetics of the autodecomposition of hydrogen peroxide are quite different. In this case perhydroxyl ions, formed by the dissociation of hydrogen peroxide, react with the undissociated hydrogen peroxide molecules forming an unstable complex, which decomposes on collision with the wall of the vessel or with a molecule which can take up the energy. We found that lucigenin takes up this energy from the unstable perhydroxyl complex and thus catalyses the decomposition of hydrogen peroxide. The transferred energy is then emitted by the lucigenin molecule as chemiluminescent light, which has the same spectral composition, as its fluorescent light. Lucigenin is regenerated at the same time.

With this decomposition mechanism of hydrogen peroxide in relation to our previous investigations, we consider that the chemiluminescent mechanism of *luminol* is as shown in Fig. 1.

The chemiluminescent reaction starts with the oxidation of aminophthalic acid hydrazide (I) to the red coloured quinone (II). The mesomer partner of this quinone, the biradical (III), reacts with hydroxyl or oxygen free radicals, which are produced by the oxidizing agents, forming the transannular peroxide (IV). This unstable product loses nitrogen and emits light with simultaneous spin compensation. The end-product of the reaction is aminophthalic acid (V). The reaction is irreversible, because nitrogen splits off more easily than oxygen in the decomposition of the transannular peroxide (IV). The chemiluminescent reaction is thus started in the case of luminol by hydroxyl or oxygen free radicals.

With regard to the chemiluminescent mechanism of *lucigenin*, a blue light is emitted as well as a green luminescent light when a catalyst, *e.g.* heavy metal ions, is present. This blue light is spectrally the same as the fluorescent light of methylacridone, which is the oxidized product of lucigenin; it disappears quickly and the

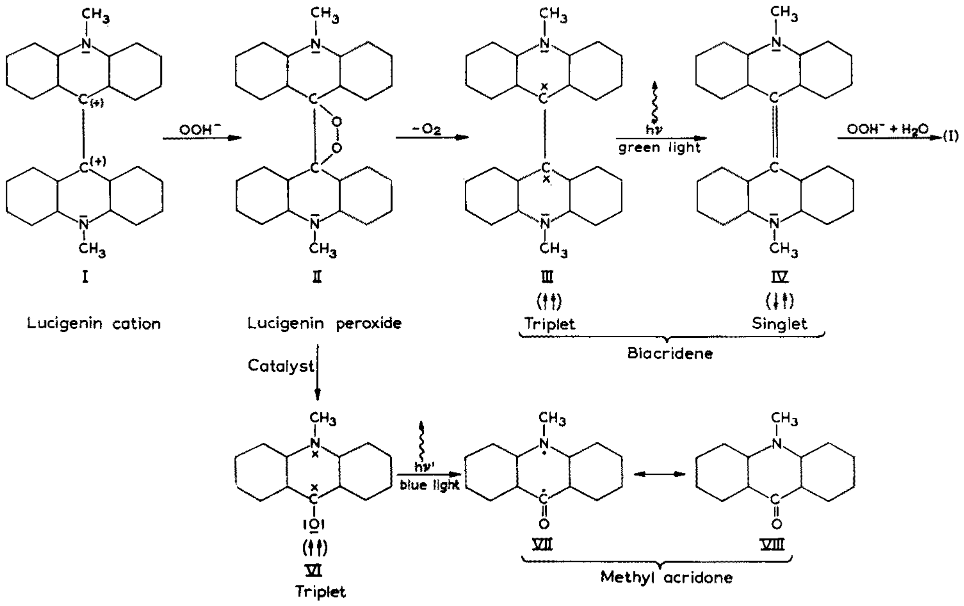

Fig. 2. Chemiluminescent mechanism of lucigenin.

reaction is irreversible. Lucigenin thus emits a green light in alkaline media without catalysts for a long time, and the emittance can be reproduced by further additions of hydrogen peroxide; but in the presence of a catalyst the molecule splits into two parts, the blue chemiluminescent light appears and the reaction becomes irreversible.

We established by polarographic methods that lucigenin forms with hydrogen peroxide a loose complex which takes up four electrons on reduction.

We therefore suggest the mechanism shown in Fig. 2 for the chemiluminescence of lucigenin. The lucigenin cation (I) forms lucigenin peroxide (II) with perhydroxyl ions. This molecule loses oxygen at a relatively low activation energy (20–25 cal.) and forms an excited molecule, the biacridene (III), which has a triplet electron system. This emits a green light by spin compensation. The biacridene (IV) is oxidized by a new perhydroxyl ion to the lucigenin cation (I), and the cycle is then repeated. According to this mechanism lucigenin may be regarded as a catalyst for peroxide decomposition, transforming the energy of the reaction into light, while regenerating itself. The fact that lucigenin emits light very steadily for a long time until the hydrogen peroxide is consumed can thus be explained. Water plays an important part in the last reaction step. We established that in carbon tetrachloride containing pyridine or in benzene, neither lucigenin nor the biacridene emits light with water-free hydrogen peroxide. When water is added to these systems chemiluminescence occurs immediately. This makes it possible to determine the water content of organic solvents by a photometric method.

In the presence of catalysts an irreversible reaction also occurs. The catalyst decomposes the lucigenin peroxide and the methylacridone (VI) is formed in an excited state. This emits a blue chemiluminescent light by spin compensation. The methylacridone, in the ground state, is an inactive end-product.

It is possible to use chemiluminescent indicators for the complexometric determination of copper(II). The sodium salt of EDTA stabilizes the hydrogen peroxide solution, because it forms complexes with the copper(II) (and other heavy metal ions) which catalyse the decomposition. In an alkaline solution containing the copper(II)–EDTA luminol shows no chemiluminescence because there are no hydroxyl free radicals present. Lucigenin however emits light steadily, because it does not require hydroxide free radicals for chemiluminesce. When an ammoniacal copper(II) solution is titrated in the presence of luminol with an EDTA solution containing 0.01% hydrogen peroxide, the mixture emits light until an excess of copper(II) is present. At the equivalence point the light disappears. If the titration is carried out in the presence of lucigenin, there are short flashes of light before the equivalence point is reached but steady chemiluminescence appears only when all the copper has been titrated and hydrogen peroxide no longer decomposes.

EXPERIMENTAL

Stock solutions. 0.01 *M* Copper(II) sulphate solution: 2.4969 g of pro analysi $CuSO_4 \cdot 5H_2O$ was dissolved in 1 l of water. Its copper content was checked by electrogravimetric measurements.

0.01 *M* lead nitrate solution: To 3.3123 g of pro analysi $Pb(NO_3)_2$ 1 ml of 2 *N* nitric acid was added, and the mixture was made up with water to 1 l. Its lead content was checked gravimetrically as lead sulphate.

0.01 *M* mercury(II) nitrate solution: 1.2 g of yellow mercuric oxide was dissolved in 5 ml of 1 : 1 nitric acid, and the mixture was made up with water to 1 l. The mercury content was determined by Volhard's method.

0.1 *N* silver nitrate solution: 16.9888 g of pro analysi $AgNO_3$ was dissolved in 1 l of water.

0.1 *N* potassium iodide solution: 16.6014 g of KI was dissolved in 1 l of water; the iodide content was measured argentometrically in the presence of Variamine Blue indicator[9].

Standard solution. 0.02 *M* EDTA solution: 3.8 g of Na_2-EDTA was dissolved in water and diluted to 0.5 l. It was standardized against standard magnesium sulphate solution. 0.01 *M* solution was prepared by dilution of this solution. The 0.01 *M* solution containing hydrogen peroxide which was required for titrations of copper(II) was mixed per litre with 20.0 ml of 3% hydrogen peroxide before dilution. The normality of this solution decreased by 0.5% weekly.

Indicators. 1) 0.5% lucigenin: 1.0 g of lucigenin was dissolved with slight heating in 200 ml of water. 2) 0.01% luminol: 0.1 g of luminol was dissolved in a mixture of 500 ml of water and 5 ml of 1 *N* sodium hydroxide, and, after complete dissolution, the mixture was diluted to 1 l.

PROCEDURES

1. *Determination of copper(II)*

Add to the test solution 20 ml of 4 *N* ammonium hydroxide and 1 ml of 0.5% lucigenin or 3 ml of 0.01% of luminol solution. Heat to 90°. Titrate with 0.01 *M* EDTA containing hydrogen peroxide in the dark. The end-point is indicated by the occurrence of a steady chemiluminescent light in the case of lucigenin or by the disappearance of the light in the case of luminol.

TABLE I

DETERMINATION OF COPPER(II)

0.01 *M* $CuSO_4$ taken ml	0.01 *M* EDTA used ml (mean of 3 titrations)	Difference ml	Difference %
In presence of lucigenin			
5.00	5.02	+0.02	+0.4
9.96	10.01	+0.05	+0.5
20.00	20.01	+0.01	+0.13
50.04	49.97	—0.07	—0.15
In presence of luminol			
5.00	5.02	+0.02	+0.4
9.96	9.96	±0.0	±0.0
20.00	20.03	+0.03	+0.15
50.04	49.90	—0.14	—0.3

The reproducibility of the method is shown in Table I. The standard deviations, calculated from 12 parallel titrations of 20 ml of 0.01 *M* cupric sulphate, were ± 0.028 ml (± 0.14%) when lucigenin was used, and ± 0.032 ml (± 0.16%) when luminol was used.

Notes

Luminol gives an indicator error of + 0.06 ml (the data in Table I have been corrected). It is advantageous that the determination can be carried out even in the presence of silver ions. Strong oxidizing agents and ions which form stable complexes with EDTA, naturally interfere.

Micro-scale determinations. Place the solution containing 6–720 μg of copper in a 5-ml titration vessel, add 1.0 ml of 4 *N* ammonium hydroxide and 0.5 ml of luminol indicator, heat to boiling and titrate with a suitable 0.01 or 0.001 *M* EDTA solution containing hydrogen peroxide from a micro buret in a dark room until chemiluminescence disappears. The accuracy of the micromethod is shown in Table II.

TABLE II

MICRO-DETERMINATION OF COPPER(II)

0.01 M $CuSO_4$ taken ml	*0.01 M EDTA used ml (mean of 3 titrations)*	*Cu calculated μg*	*Cu found μg*	*Difference*	
				μg	*%*
0.100	0.099	63.5	62.4	— 1.1	— 1.7
0.200	0.197	127.1	125.2	— 1.9	— 1.5
0.500	0.495	317.7	314.6	— 3.1	— 1.0
1.000	0.980	635.4	622.3	—13.1	— 2.1

0.001 M $CuSO_4$ taken ml	*0.001 M EDTA used ml (mean of 3 titrations)*	*Cu calculated μg*	*Cu found μg*	*Difference*	
				μg	*%*
0.100	0.115	6.4	7.3	+ 0.9	+15.0
0.200	0.203	12.7	12.9	+ 0.2	+ 1.6
0.500	0.499	31.8	31.7	— 0.1	— 0.2
1.000	0.992	63.5	63.0	— 0.5	— 0.8

2. *Determination of EDTA*

The first procedure can be carried out in the reverse direction. To the *ca.* 0.01 *M* EDTA solution add 20 ml of 4 *N* ammonium hydroxide, 1 ml of 3% hydrogen peroxide and 3 ml of luminol or 1 ml of lucigenin indicator. Heat the solution to 90° and titrate in the dark with a standard copper(II) sulphate solution. The end-point is indicated in the case of lucigenin by the disappearance of the light; with luminol a green light appears. The method, as is shown by the data in Table III, is suitable for the standardization of EDTA solutions. The standard deviations, calculated from 12 parallel titrations of 20 ml of 0.01 *N* EDTA, were ± 0.026 ml (± 0.13%) when lucigenin was used. The difference between the mean and true values was —0.1%. With luminol these deviations were ± 0.034 ml (± 0.17%) and —0.2% respectively.

TABLE III

DETERMINATION OF EDTA

0.01 M EDTA taken ml	*0.01 M $CuSO_4$ used ml (mean of 3 titrations)*	*Difference*	
		ml	*%*
In presence of lucigenin			
5.00	5.02	+0.02	+0.4
9.96	9.93	—0.03	—0.3
20.00	19.99	—0.01	—0.05
50.04	49.93	—0.11	—0.2
In presence of luminol			
5.00	4.96	—0.04	—0.8
9.96	9.97	+0.01	+0.1
20.00	19.96	—0.04	—0.2
50.04	49.97	—0.07	—0.14

3. *Determination of lead and mercury(II) ions*

The titration of EDTA with a copper(II) solution makes possible the determination of ions which form a stable complex with EDTA in ammoniacal media; excess of EDTA can be back-titrated in the presence of luminol or lucigenin with a standard copper(II) sulphate solution.

Procedure

To the *ca.* 0.01 *M* lead or mercury(II) nitrate solution add a known excess of standard 0.01 *M* EDTA. Heat the solution to boiling, add 20 ml of 4 *N* ammonium hydroxide, 1 ml of 3% hydrogen peroxide and finally 3 ml of luminol or 1 ml of lucigenin indicator. Titrate the mixture in the dark with a standard copper(II) sulphate solution. At the equivalence point the solution containing lucigenin ceases to light, while in the presence of luminol the dark solution begins to emit chemiluminescence.

TABLE IV

DETERMINATION OF LEAD

0.01 M $Pb(NO_3)_2$ taken ml	*0.01 M EDTA added in excess ml*	*0.01 M $CuSO_4$ used ml (mean of titrations)*	*0.01 M $Pb(NO_3)_2$ found ml*	*Difference*	
				ml	%
In presence of lucigenin					
5.00	25.00	20.02	5.02	+0.02	+0.4
9.96	30.00	20.00	9.96	±0.0	±0.0
20.00	40.00	19.96	19.96	—0.04	—0.2
30.00	50.00	20.02	30.02	+0.02	+0.1
In presence of luminol					
5.00	25.00	20.00	5.00	±0.0	±0.0
9.96	30.00	20.04	10.00	+0.04	+0.4
20.00	40.00	20.00	20.00	±0.0	±0.0
30.00	50.00	20.04	30.04	+0.04	+0.1

TABLE V

DETERMINATION OF MERCURY(II) IN PRESENCE OF LUMINOL

0.01 M $Hg(NO_3)_2$ taken ml	*0.01 M EDTA added ml*	*0.01 M $CuSO_4$ used ml (mean of 3 titrations)*	*0.01 M $Hg(NO_3)_2$ found ml*	*Difference*	
				ml	%
5.06	20.00	14.95	5.05	—0.01	—0.2
10.11	30.00	19.85	10.15	+0.04	+0.4
20.23	49.90	29.58	20.32	+0.09	+0.5
30.34	49.90	19.63	30.27	—0.07	—0.2

Table IV shows the results of determinations of lead with lucigenin or luminol indicator, while Table V gives mercury(II) determinations with luminol. Precision and accuracy data computed from 12 titrations of 20 ml of 0.01 *M* solutions are as follows. The standard deviation of the determination of lead was ± 0.05 ml (± 0.25%) the difference between the mean and true value being —0.1%. The corresponding data for mercury(II) determinations were ± 00.4 ml (± 0.21%) and —0.05% respectively.

4. *Argentometric determination of iodide ions*

Lucigenin can be used as a chemiluminescent indicator for argentometric titrations of iodide ions. It is absorbed in an ammoniacal media on the surface of the negative

TABLE VI

DETERMINATION OF IODIDE

0.1 N KI taken ml	*0.1 N $AgNO_3$ used ml (mean of 3 titrations)*	*Difference*	
		ml	%
5.00	5.03	+0.03	+0.6
9.96	9.94	—0.02	—0.2
20.00	20.02	+0.02	+0.1
50.04	50.09	+0.05	+0.1

TABLE VII

MICRO-DETERMINATION OF IODIDE

0.1 N KI taken ml	*0.1 N $AgNO_3$ used ml (mean of 3 titrations)*	*mg I^-*		*Difference*	
		calculated	*found*	*mg*	%
0.100	0.112	1.27	1.41	+0.14	+12
0.200	0.207	2.54	2.61	+0.7	+ 3.5
0.500	0.503	6.35	6.39	+0.04	+ 0.6
1.000	0.993	12.69	12.60	—0.09	— 0.7

TABLE VIII

INTERFERENCE OF FOREIGN IONS IN THE TITRATION OF IODIDE

(In all cases 20.00 ml of 0.1 *N* KI was taken)

Foreign ion	*0.1 N $AgNO_3$ used ml (mean of 3 titrations)*	*Difference*		*Remarks*
		ml	%	
Cl^-	20.03	+0.03	+ 0.15	Clear end-point
Br^-	20.12	+0.12	+ 0.6	
CN^-	30.09	+10.09	+50.5	Solution emits light till 11.10 ml of $AgNO_3$ is consumed, but becomes dark when AgI is precipitated. At the end-point it looks like an I^- solution when CN^- ions are not present
SCN^-	26.80	+6.80	+34.0	Light disappears slowly when $AgNO_3$ is added. At the end-point a very slight light can be seen
$C_2O_4^{-2}$	20.07	+0.07	+ 0.3	Clear end-point
PO_4^{-3}	20.43	+0.43	+ 2.15	Clear end-point
$[Fe(CN)_6]^{-4}$	20.68	+0.68	+ 3.4	Light is less at the end-point than it is when only I^- ions are present
$[Fe(CN)_6]^{-3}$				No light since $Fe(CN)_6^{-3}$ oxidizes H_2O_2
CrO_4^{-2}	23.33	+3.33	+16.6	A very little light appears at the end-point

charged silver iodide precipitate and thus does not emit light even in the presence of hydrogen peroxide; when the charge on the surface of the precipitate is changed, lucigenin is desorbed and the solution suddenly luminesces.

Procedure

To the solution to be examined add 10 ml of 4 *N* ammonium hydroxide, 1 ml of lucigenin indicator and 1 ml of 0.3% hydrogen peroxide. Titrate the mixture in a dark room until chemiluminescent light appears suddenly and steadily.

Note

Tables VI and VII show that the method is suitable for macro and micro determinations of iodide. It is advantageous that the titration can be carried out even in the presence of chloride and bromide ions, the silver salts of which are soluble in ammonium hydroxide. When cyanide and iodide ions are present, they are titrated together. Thiocyanates and complex-forming ions interfere. The results of titrations carried out in the presence of other ions are shown in Table VIII. The standard deviation of the method, calculated from 12 titrations of 20 ml of 0.1 *M* potassium iodide, was ± 0.032 ml (± 0.16%); these was no difference between the mean and true value.

Chemiluminescent indicators are very useful when the solution to be examined is turbid, opaque or dark and the usual dye-indicators cannot be used.

SUMMARY

Lucigenin and luminol are suitable chemiluminescent indicators for complexometric and argentometric titrations. The mechanisms of chemiluminescence of these indicators are quite different. Methods are given for the determination of copper(II), lead and mercury(II) ions and for the standardization of EDTA solutions. Lucigenin is suitable as an adsorption indicator for the argentometric determination of iodide ions, even in the presence of chloride and bromide.

RÉSUMÉ

La lucigénine et le luminole sont proposés comme indicateurs pour les titrages complexométriques et argentométriques. Des méthodes ont été établies pour le dosage du cuivre, du plomb et du mercure ainsi que pour l'étalonnage de solution de complexon(III). La lucigénine peut être utilisée comme indicateur d'adsorption pour le dosage argentométrique des iodures, même en présence de chlorures et de bromures.

ZUSAMMENFASSUNG

Lucigenin und Luminol eignen sich als chemiluminescente Indikatoren bei komplexometrischen und argentometrischen Titrationen. Es werden Methoden beschrieben zur Bestimmung von Kupfer, Blei und Quecksilber sowie zur Einstellung von Komplexon(III) Lösungen. Lucigenin kann ferner als Adsorptionsindikator bei der Titration von Jodid, auch in Gegenwart von Chlorid und Bromid, verwendet werden.

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THE HETEROMETRIC DETERMINATION OF PLATINUM, PALLADIUM AND GOLD BY TITRATION WITH PHENANTHROLINE

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INTRODUCTION

The reactions of platinum, palladium and gold chlorides with phenanthroline in chloride or thiocyanate solution have already been studied heterometrically[1]. The various compounds obtained have been discussed.

The present report deals with the actual determinations of the metals singly and in mixtures. We have already shown that the sensitivity of the phenanthroline-noble metal reaction is lower than that with other specific and complex nitrogen compounds. (A study with papaverine will be presented later). However, the sensitivity is often not the decisive criterion of the importance of a heterometric reaction. Thus, phenanthroline presents a series of heterometric reactions and compounds which can be applied successfully for the precise, direct determination of all the metals present in mixtures without any previous separations whatsoever.

The importance of the proposed methods is that two or three noble metals in an alloy (or in a solution of chlorides) can be determined from the critical points of one titration curve only, *i.e.* two noble metals, forming different insoluble compounds can both be determined accurately from the same heterometric curve.

The simultaneous determination of platinum and palladium or gold and palladium required only 2 mg of alloy; the determination of gold and platinum required at least double this amount. Generally the third noble metal present could be determined from the difference. The determination of all three metals in an alloy or in a soluble mixture of chlorides was possible in several ways by two separate heterometric titrations. A titration lasted about 10–15 min at 20°. In almost all cases studied, the second end-point (↓↓) agreed exactly with the theoretical sum of the amounts of metals determined. Some errors occurred at the last analytical intersection point (↓) (first end-point), but these could be avoided by practise.

EXPERIMENTAL

The same reagents and working conditions were used as in previous reports[2,3].

RESULTS

Table I describes a series of heterometric titrations of mixtures, chiefly of two metals, with phenanthroline. The course of a few titrations is also shown in Fig. 1. Before the different methods for the determination of the metals are indicated, the working principles and the results are discussed.

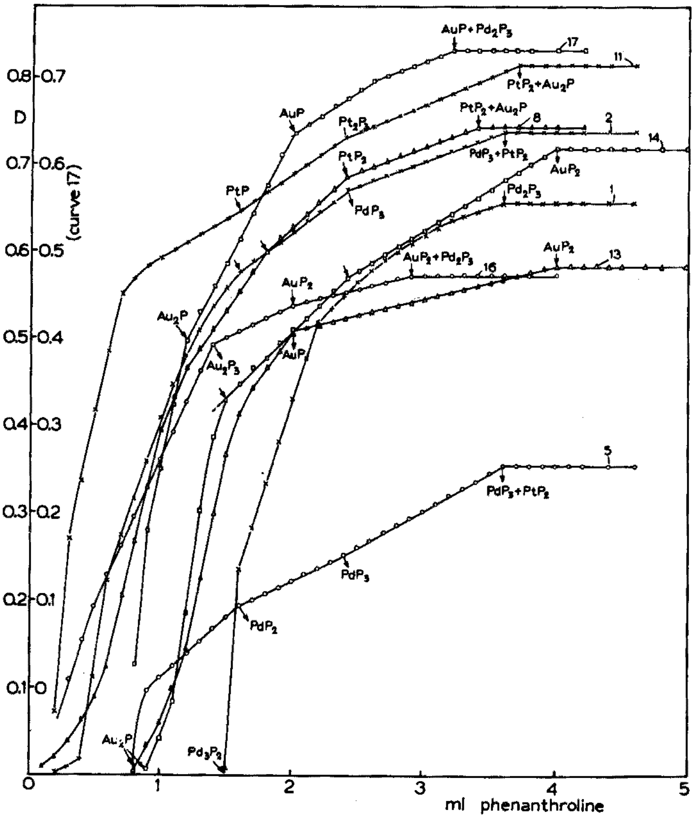

Fig. 1. Titrations of mixtures of platinum, palladium and gold halides with phenanthroline.

In the case of platinum, it is possible to keep the platinum dissolved or to determine the platinum simultaneously with one of the two other noble metals present. Probably any quantity of platinum could remain dissolved in chloride solution at pH 1–7, or in thiocyanate solution at about pH 7. Palladium and gold were both precipitated either in chloride or thiocyanate solutions at pH 1–7. Therefore, if both are present, they can only be determined from two different critical points of the titration curve. The platinum was precipitated from acid thiocyanate solution only, thus the insoluble platinum thiocyanate compound could also be determined from an intersection point of the same curve.

In all the cases given, only those metal-phenanthroline compounds which functioned as *final* compounds (↓↓) were of analytical value if the single metal analysed was titrated under the same working conditions.

The presence of chloride in large excess seemed to have no influence on the results. The influence of the concentration of the thiocyanate varied. Generally (especially

TABLE I

General composition: *a* ml reagents + (10 — *a*) ml H

Expt. No.	*Composition*	*%/mg metal* *Pt*	 *Pd*	 *Au*	*Molarity of P*
1	3 ml 0.004 *M* H_2PtCl_6 + 3 ml 0.004 *M* $PdCl_2$ + 1 ml *M* HNO_3 + 2 ml *M* NaCl	64.7% 2.3427	35.3% 1.2804		0.005
2	3 ml 0.002 *M* H_2PtCl_6 + 4 ml 0.002 *M* $PdCl_2$ + 1 ml *M* HNO_3 + 1 ml 0.25 *M* KCNS	57.8% 1.1714	42.2% 0.8536		0.01
3	3 ml 0.002 *M* H_2PtCl_6 + 4 ml 0.002 *M* $PdCl_2$ + 1 ml *M* HNO_3 + 2 ml 0.25 *M* KCNS	57.8% 1.1714	42.2% 0.8536		0.01
4	3 ml 0.002 *M* H_2PtCl_6 + 4 ml 0.002 *M* $PdCl_2$ + 1 ml 3 *M* HNO_3 + 2 ml 0.25 *M* KCNS	57.8% 1.1714	42.2% 0.8536		0.01
5	3 ml 0.002 *M* H_2PtCl_6 + 4 ml 0.002 *M* $PdCl_2$ + 1 ml *M* HNO_3 + 2 ml *M* KCNS	57.8% 1.1714	42.2% 0.8536		0.01
6	3 ml 0.004 *M* H_2PtCl_6 + 4 ml 0.005 *M* $HAuCl_4$ + 1 ml *M* HNO_3	37.3% 2.3427		62.7% 3.9440	0.005
7	3 ml 0.004 *M* H_2PtCl_6 + 4 ml 0.005 *M* $HAuCl_4$ + 1 ml 3 *M* HNO_3	37.3% 2.3427		62.7% 3.9440	0.005
8	3 ml 0.004 *M* H_2PtCl_6 + 4 ml 0.005 *M* $HAuCl_4$ + 1 ml *M* HNO_3 + 1 ml 0.25 *M* KCNS	37.3% 2.3427		62.7% 3.9440	0.01
9	3 ml 0.004 *M* H_2PtCl_6 + 5 ml 0.005 *M* $HAuCl_4$ + 1 ml *M* HNO_3 + 1 ml 0.25 *M* KCNS	32.2% 2.3427		67.8% 4.9300	0.01
10	3 ml 0.004 *M* H_2PtCl_6 + 4 ml 0.005 *M* $HAuCl_4$ + 1 ml *M* HNO_3 + 2 ml 0.5 *M* KCNS	37.3% 2.3427		62.7% 3.9440	0.01
11	4 ml 0.004 *M* H_2PtCl_6 + 2 ml 0.005 *M* $HAuCl_4$ + 1 ml *M* HNO_3 + 2 ml 0.5 *M* KCNS	61.3% 3.1236		38.7% 1.9720	0.01
12	3 ml 0.004 *M* H_2PtCl_6 + 4 ml 0.005 *M* $HAuCl_4$ + 1 ml *M* Na-acetate + 1 ml 0.25 *M* KCNS	37.3% 2.3427		62.7% 3.9440	0.01
13	3 ml 0.004 *M* H_2PtCl_6 + 4 ml 0.005 *M* $HAuCl_4$ + 1 ml *M* Na-acetate + 1 ml 0.25 *M* KCNS	37.3% 2.3427		62.7% 3.9440	0.01
14	3 ml 0.004 *M* H_2PtCl_6 + 4 ml 0.005 *M* $HAuCl_4$ + 1 ml *M* Na-acetate + 1.5 ml 0.5 *M* KCNS	37.3% 2.3427		62.7% 3.9440	0.01
15	3 ml 0.004 *M* H_2PtCl_6 + 4 ml 0.005 *M* $HAuCl_4$ + 1 ml *M* Na-acetate + 1.5 ml *M* KCNS	37.3% 2.3427		62.7% 3.9440	0.01
16	3 ml 0.002 *M* $PdCl_2$ + 4 ml 0.0025 *M* $HAuCl_4$ + 1 ml *M* Na-acetate + 2 ml 0.25 *M* KCNS		24.5% 0.6402	75.5% 1.9720	0.01
17	3 ml 0.004 *M* H_2PtCl_6 + 2 ml 0.004 *M* $PdCl_2$ + 4 ml 0.005 *M* $HAuCl_4$ + 1 ml *M* HNO_3	32.8% 2.3427	12% 0.8536	55.2% 3.9440	0.01
18	3 ml 0.004 *M* $PdCl_2$ + 4 ml 0.0025 *M* $HAuCl_4$ + 1 ml *M* Na-acetate + 1 ml 0.5 *M* KCNS		39.3% 1.2804	60.7% 1.9720	0.01
19	4 ml 0.004 *M* $PdCl_2$ + 3 ml 0.0025 *M* $HAuCl_4$ + 1 ml *M* Na-acetate + 1 ml 0.5 *M* KCNS		53.5% 1.7072	46.5% 1.4790	0.01
20	3 ml 0.005 *M* H_2PtCl_6 + 3 ml 0.004 *M* $PdCl_2$ + 3 ml 0.005 *M* $HAuCl_4$ + 1 ml *M* HNO_3	40.8% 2.9284	18.0% 1.2804	41.2% 2.9580	0.01
21	3 ml 0.005 *M* H_2PtCl_6 + 3 ml 0.004 *M* $PdCl_2$ + 3 ml 0.0025 *M* $HAuCl_4$ + 1 ml *M* Na-acet. + 1 ml 0.5 *M* KCNS	51.4% 2.9284	22.5% 1.2804	26.1% 1.4790	0.01

x = Corning yellow filter (3484); c = contact point; h = horizontal maximum density line; i = inter

TABLE I

ml *M* *b* phenanthroline (= *P*) T = 20°

	Found			*End-point*				*Titration time in min*
	Initial ppt.	*Intermediates*						
D	*compound formed*	*ml of P used*	*Compounds obtained*	*at ml P*	*Compounds obtained*	*Optical density value*	*% error*	
	$Pd_3P_2\uparrow$			i 3.60 h	$Pd_2P_3\downarrow\downarrow$	0.66	0.0	12
		c 1.6; 2.4	$PdP_2\downarrow \rightarrow PdP_3\downarrow\downarrow$	i 3.60 h	$PdP_3\downarrow\downarrow + PtP_2\downarrow\downarrow$	0.74	0.0	15
		2.5	$PdP_3\downarrow\downarrow$	i 3.60 h	$PdP_3\downarrow\downarrow + PtP_2\downarrow\downarrow$	0.50	0.0	12
		c 2.0 (?)	$PdP_3\downarrow\downarrow$ (?)	i 3.60 h	$PdP_3\downarrow\downarrow + PtP_2\downarrow\downarrow$	0.52	0.0	15
	$PdP\uparrow$	1.6; 2.4	$PdP_2\downarrow \rightarrow PdP_3\downarrow\downarrow$	i 3.60 h	$PdP_3\downarrow\downarrow + PtP_2\downarrow\downarrow$	0.36	0.0	14
	$Au_4P\uparrow$	2.5	$Au_3P_2\downarrow$	i 4.00 h	$AuP\downarrow\downarrow$	0.49	0.0	13
	$\sim Au_4P\uparrow$	c ~1.9; 2.6	$Au_2P\downarrow \rightarrow Au_3P_2\downarrow$	i 4.00 h	$AuP\downarrow\downarrow$	0.41	0.0	14
		1.8; 2.4	$Pt_2P_3\downarrow \rightarrow PtP_2\downarrow\downarrow$	i 3.40 h	$PtP_2\downarrow\downarrow + Au_2P\downarrow\downarrow$	0.75	0.0	12
		c 1.0; 1.75; 2.4	$\sim PtP\downarrow \rightarrow Pt_2P_3\downarrow \rightarrow PtP_2\downarrow\downarrow$	i 3.70 h	$PtP_2\downarrow\downarrow + Au_2P\downarrow\downarrow$	0.76	0.0	11
		c 1.9	$Pt_2P_3\downarrow$	i 3.40 h	$PtP_2\downarrow\downarrow + Au_2P\downarrow\downarrow$	0.76	0.0	12
		1.6; 2.4	$PtP\downarrow \rightarrow Pt_2P_3\downarrow$	i 3.70 h	$PtP_2\downarrow\downarrow + Au_2P\downarrow\downarrow$	0.82	0.0	12
	$Au_2P\uparrow$	2.0; ~2.9	$AuP\downarrow \rightarrow Au_2P_3\downarrow$	i 4.00 h	$AuP_2\downarrow\downarrow$	0.46	0.0	12
	$Au_2P\uparrow$	2.0	$AuP\downarrow$	i 4.00 h	$AuP_2\downarrow\downarrow$	x0.59	0.0	11
	$Au_2P\uparrow$	c 1.5; 2.40	$Au_4P_3\downarrow \rightarrow Au_4P_5\downarrow$	i 4.00 h	$AuP_2\downarrow\downarrow$	0.72	0.0	12
				i 4.00 h	$AuP_2\downarrow\downarrow$	0.32	0.0	17
		1.4; 2.0	$Au_2P_3\downarrow \rightarrow AuP_2\downarrow\downarrow$	i 2.90 h	$AuP_2\downarrow\downarrow + Pd_2P_3\downarrow\downarrow$	0.57	0.0	14
	$Au_2P\uparrow$	1.2; 2.0	$Au_2P\downarrow\uparrow \rightarrow AuP\downarrow\downarrow$	i 3.20 h	$AuP\downarrow\downarrow + Pd_2P_3\downarrow\downarrow$	0.74	0.0	13
		1.44; 2.01	$Au_2P_3\downarrow \rightarrow AuP_2\downarrow\downarrow$	i 3.80 h	$AuP_2\downarrow\downarrow + Pd_2P_3\downarrow\downarrow$	0.93	0.0	13
		1.0; 1.47	$Au_2P_3\downarrow \rightarrow AuP_2\downarrow\downarrow$	i 3.90 h	$AuP_2\downarrow\downarrow + Pd_2P_3\downarrow\downarrow$	0.91	0.0	14
		1.54; 2.02	$AuP\downarrow\downarrow$	i 3.30 h	$AuP\downarrow\downarrow + Pd_2P_3\downarrow\downarrow$	0.78	0.0	13
		1.1; 1.50	$Au_2P_3\downarrow \rightarrow AuP_2\downarrow\downarrow$	i 3.30 h	$AuP_2\downarrow\downarrow + Pd_2P_3\downarrow\downarrow$	0.84	0.0	13

loint.

at about pH 1) there was an optimum concentration of thiocyanate in each case. An excess of thiocyanate decreased the maximum optical density values, although the composition of the final compound usually remained unchanged. Large amounts of acid also had an adverse effect on the determination. Thus the best results for platinum and palladium (Expts. 2–5, Table I) were obtained with a minimum quantity of thiocyanate, although below a certain level of thiocyanate the results become uncertain. In the determination of platinum and gold (Expts. 8–11) the first end-point (PtP_2) was reliable only if a minimum amount of thiocyanate was used. In the presence of an excess of thiocyanate a different platinum compound was found (Pt_2P_3). In all these cases the maximum optical density value remained the same (Expts. 8–10). In acetate solutions (Expts. 12–15), the platinum always remained dissolved. The final gold compound was always of the same composition (AuP_2), but the intermediates traced were different if more thiocyanate was used. The optimum quantity of thiocyanate seemed to be somewhat larger than usual in these experiments (Expt. 14). The ratio of the metals in the test solution could also influence the result; we did not examine this further.

TABLE II

pH	*R^-*	*Metals present*	*Metals determined as*	*Approx. mg metal analyzed*
1	Cl^-	Pt, Pd	Pd_2P_3	3.5
1	CNS^-	Pt, Pd	PdP_3 (1), PtP_2 (2)	2
1	Cl^-	Pt, Au	AuP	6
1	CNS^-	Pt, Au	PtP_2 (1), Au_2P (2)	5–6
7	CNS^-	Pt, Au	AuP_2	6
7	CNS^-	Pd, Au	AuP_2 (1), Pd_2P_3 (2)	2.5
1	Cl^-	Pt, Pd, Au	AuP (1), Pd_2P_3 (2)	6–7

Table II summarizes the final compounds obtained. The numbers in brackets show the order of formation of the compounds; this depended on the composition of the test solution. Thus in mixtures of platinum and palladium in thiocyanate solution at about pH 1, the palladium was precipitated first; in mixtures of platinum and gold (under the same conditions), the platinum came first, while in mixtures of gold and palladium in all cases the gold precipitated first. For the determination of a single metal, approximately 1 mg of palladium, 1–2.5 mg of platinum and 2–4 mg of gold were necessary.

METHODS

General remarks

In all the following methods, the error at the first maximum optical density point was always approximately equal to zero. The last intermediate intersection point (↓) was always obtained from the intersection of the two adjacent lines (branches) of the titration curve.

1. *Determination of platinum*

About 3–4 mg of platinum as chloroplatinic acid in 10 ml aqueous solution, containing 1 ml of *M* HNO_3 and 1–2 ml of 0.5 *M* KCNS, are titrated with aqueous

0.01 *M* phenanthroline. The end-point appears at the first maximum optical density point, coinciding with the quantitative formation of Pt_1P_2.

2. *Determination of platinum and palladium*

About 2 mg of the metals, as chlorides, in 10 ml of solution containing 1 ml of *M* HNO_3 and 1 ml of 0.25 *M* KCNS are titrated with aqueous 0.01 *M* phenanthroline. Two critical points are obtained. The first point, which is the last intermediate intersection point, appears when Pd_1P_3 is quantitatively precipitated. The second point coincides with the first maximum optical density point, giving exactly the sum of Pd_1P_3 and Pt_1P_2.

3. *Determination of palladium*

About 1 mg of palladium as chloride in 10 ml of aqueous solution containing 1 ml of *M* HNO_3 and 1 ml of *M* NaCl, is titrated with aqueous 0.005 *M* phenanthroline. The first optical maximum density point coincides exactly with the quantitative formation of Pd_2P_3. The titration can also be carried out at *ca.* pH 7, using 1 ml of *M* Na-acetate instead of the acid. The solution may then contain 1 ml of *M* KCNS instead of the NaCl.

4. *Determination of palladium in platinum*

The procedure is the same as in 3, with chloride solutions.

5. *Determination of gold in platinum*

About 4 mg of gold, as gold chloride, in 10 ml of aqueous solution, containing 1 ml *M* of Na-acetate and 2–3 ml of 0.25 *M* KCNS, are titrated with aqueous 0.01 *M* phenanthroline. The first optical maximum density point coincides exactly with the quantitative precipitation of Au_1P_2.

The same titration can be carried out in acid solution, by replacing the Na-acetate and the KCNS by 1 ml *M* HNO_3. The titrant is then 0.005 *M* phenanthroline. The end-point appears at the quantitative formation of Au_1P_1. The former method is preferable.

6. *Determination of palladium and gold*

About 3 mg of the metals, as chlorides, in 10 ml of aqueous solution, containing 1 ml of *M* Na-acetate and 2 ml of 0.25 *M* KCNS, are titrated with aqueous 0.01 *M* phenanthroline. Two critical points are obtained; the first point (*i.e.* the last intermediate point) coincides with the quantitative formation of Au_1P_2. The second point (*i.e.* the first maximum optical density point) coincides exactly with the quantitative formation of the sum of Au_1P_2 and Pd_2P_3.

7. *Determination of platinum and gold*

About 5 mg of the metals, as chlorides, in 10 ml of aqueous solution, containing 1 ml of *M* HNO_3 and 1 ml of 0.25 *M* KCNS, are titrated with aqueous 0.01 *M* phenanthroline. Two critical points are obtained. The first point (the last intermediate point) coincides with the quantitative formation of Pt_1P_2. The second point (the first maximum optical density point) coincides exactly with the quantitative formation of the sum of Pt_1P_2 and Au_2P_1.

8. *Determination of phenanthroline*

About 4 mg of phenanthroline in 10 ml aqueous solution, containing 1 ml of *M* Na-acetate are titrated with a 0.004 *M* solution of palladium chloride. The end-point, at the first maximum optical density point, coincides with the quantitative formation of Pd_2P_3.

The test solution may contain some sodium chloride. The analysis can also be carried out at about pH 1 in nitric acid solution, but the former method is preferable.

SUMMARY

Platinum(IV), palladium(II) and gold(III), as chlorides, were determined directly in thiocyanate or chloride solutions by heterometric titration with phenanthroline at pH values of 1–7. Two or even three metals could be determined precisely from the critical points of one or two heterometric titration curves. Several methods are presented.

RÉSUMÉ

Plusieurs méthodes sont proposées pour le dosage du platine, du palladium et de l'or, en présence les uns des autres. On procède par titrage hétérométrique en utilisant la phénanthroline comme réactif.

ZUSAMMENFASSUNG

Durch heterometrische Titration mit Phenanthrolin können Platin, Palladium und Gold nebeneinander bestimmt werden.

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THE ACCURATE DETERMINATION OF COBALT

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INTRODUCTION

Primary standards

The analytical chemistry of cobalt has been reviewed recently[1]. A literature survey reveals the use of a wide range of substances as primary standards (Table I) some of which have been critically discussed by YARDLEY[2].

$CoSO_4$. The important question here is whether ignition of the hydrated sulphate to

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the anhydrous form can be carried out without thermal decomposition of the latter. This affects not only the use of $CoSO_4$ as a primary standard but also the analytical method based on finally weighing the cobalt in this form. The extensive literature on the thermal decomposition of $CoSO_4$, much of which is reported in Mellor[3], gives values ranging from 440° to 900° for the temperature at which decomposition starts.

TABLE I

COBALT PRIMARY STANDARDS

- $CoSO_4$
- $CoSO_4 \cdot 7H_2O$
- $CoCl_2$
- $CoCl_2 \cdot 6H_2O$
- $Co(NO_3)_2 \cdot 6H_2O$
- $CoSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$
- $K_3[Co(CN)_6]$
- $[Co(NH_3)_4CO_3]NO_3$
- $[Co(NH_3)_5Cl]Cl_2$
- J. M. Cobalt sponge 99.9% pure[a]
- J. M. Cobalt sheet[a]
- Electrolytic cobalt
- Metallic cobalt (Hydrogen reduced)

[a] Johnson Matthey & Co. Ltd., London.

Willard and Hall[4] found 550° as the upper limit for ignition without decomposition, although later Willard and Fowler[5] prepared the anhydrous sulphate by heating to constant weight at 500°–650°. Yardley[2] in assessing the value of $CoSO_4$ as a primary standard found that ignition at 400°–550° always produced a product either containing a trace of water, or deficient in SO_3. In a thermogravimetric study of cobalt sulphate Duval[5] concluded that dissociation took place over the whole range 350°–820°. Recently, by means of thermogravimetric and differential thermal analysis Ostroff and Sanderson[6] have reported the relative decomposition temperature as 708°.

$CoSO_4 \cdot 7H_2O$. For accurate work it is questionable whether this substance can be dried without partial decomposition taking place, a difficulty often met in hydrated compounds. Duval[5] states that the original substance contains 8.5 molecules of water of crystallisation.

$CoCl_2$ *and* $CoCl_2 \cdot 6H_2O$. The hexahydrate is sufficiently efflorescent to make its use inadvisable. The anhydrous form is easily made but is too hygroscopic for weighing with certainty.

$Co(NO_3)_2 \cdot 6H_2O$. This is subject to the same disadvantage as the hydrated sulphate.

$[Co(NH_3)_4CO_3]NO_3$; $[Co(NH_3)_5Cl]Cl_2$; $K_3[Co(CN)_6]$. These complexes have many favourable features as primary standards, *e.g.* they may be easily recrystallised and dried. The pyrosulphate fusion required before preparing the standard solution presents no difficulty.

J.M. 99.99% sponge. The product is described as 99.99% pure, excluding gas content, and this has encouraged some recent workers to use it as a primary standard. The manufacturers state that the sponge contains a little unreduced oxide. Clearly, its value will depend on how much is present and the extent to which oxidation takes place on storing it. Cobalt sheet and wire are also available.

Electrolytic cobalt. This has been used as primary standard in many cases. It will be shown in a following paper that electrolytic cobalt is invariably impure, the degree of impurity depending on the procedure used in its preparation.

Metallic cobalt. By this is meant finely divided hydrogen reduced metal similar to the sponge. At lower temperatures the reduction yields a black pyrophoric powder. Metallic cobalt has the same potential defects as the sponge.

Many investigators, for the purpose of assessing particular methods, have standardised cobalt stock solutions of arbitrary strength by using other methods of cobalt analysis. Table II lists the methods which have been used for this purpose.

TABLE II

Electrolytic
Sulphate
α-Nitroso-β-naphthol reduction to metallic cobalt
Anthranilate
Phosphate
EDTA
Ferricyanide
Oxidation by H_2O_2 followed by iodometric procedure

Where a particular method has been used, knowledge of the exact procedure would be required to assess its value, as many methods give erroneous results unless used carefully. The phosphate method provides a striking example of this. KOLTHOFF AND WATERS[7] standardised a cobalt nitrate solution using the method although DUFTY[8] had established that presence of nitrate ion interferes giving low results.

Methods of cobalt analysis have been critically examined and it will be shown* that most of the recommended methods contain unsatisfactory features and are unsuitable for the accurate determination of cobalt.

To summarise, many methods have been used to prepare standard cobalt solutions for assessing methods of analysis. Many involve substances or procedures invalidated by previous work. This, coupled with the fact that primary standards have been ignored by many workers means that apart from relatively few cases where care has been taken, it is doubtful whether great importance can be attached to the degree of accuracy claimed in much of the cobalt analytical literature.

The aim of the present work is to compare, using a reproducible method under strictly controlled conditions, a number of cobalt primary standards, some of which have not hitherto been used for this purpose. In order to standardise conditions as much as possible, quantities of the standard containing about 100 mg of cobalt were taken for each analysis. To compare the actual cobalt content of each standard with the stoichiometric amount it was necessary to employ a precise method of analysis. A form of the phosphate method was eventually used. Owing to the slight solubility

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* Parts II and III of this paper.

of $CoNH_4PO_4 \cdot H_2O$, determination of residual cobalt in the filtrate was carried out by means of the Nitroso-R-salt method.

Standard examined

$CoSO_4$; J. M. 99.99% cobalt sponge; $CoSO_4 \cdot K_2SO_4 \cdot 6H_2O$; J. M. spectrographically standardised cobalt wire; $[Co(NH_3)_5Cl]\ Cl_2$; $K_3[Co(CN)_6]$; $[Co(NH_3)_6]Cl_3$.

EXPERIMENTAL

Weighing. A calibrated set of Baird and Tatlock Series I nickel–chrome alloy weights was used to calibrate all other weights used.

Volumetric glassware. Volumetric flasks and pipettes were calibrated by the usual methods.

pH measurements. These were carried out using a Cambridge meter with glass and saturated calomel electrodes. The instrument was standardised using $M/20$ potassium hydrogen phthalate (pH 4.00) and a sodium phosphate–potassium phosphate buffer solution (pH 6.81 at 18°).

Chemicals. Unless otherwise stated, all chemicals used were of 'AnalaR' quality.

Preparation of standards

$CoSO_4$. The hydrated compound was re-crystallised three times from almost boiling water. The dried crystals were ground up and ignited in an electric furnace at various temperatures between 500° and 550°. The anhydrous sulphate was stored over phosphorus pentoxide.

$K_3[Co(CN)_6]$. The method of preparation was identical with that used by YARDLEY[2].

$CoSO_4 \cdot K_2SO_4 \cdot 6H_2O$. Equimolecular amounts of cobalt sulphate and potassium sulphate were mixed and the disulphate re-crystallised three times from hot water. The crystals were washed with a little water and acetone, ground up and dried in vacuo.

$[Co(NH_3)_6]Cl_3$. The ordinary grade material was recrystallised three times from hot water, the crystals being filtered off after cooling in a refrigerator. They were washed with 60% alcohol and dried in vacuo.

$[Co(NH_3)_5Cl]Cl_2$. This was prepared by the method of WILLARD AND HALL[4].

Preparation of stock solutions

Amounts of the various standards were taken such that their solutions contained approximately 100 mg cobalt per 50 ml.

For the complexes, pyrosulphate fusion was necessary. This was done in a long necked 500-ml thick walled bolt head flask heated in a thermomantle. Possible loss by splashing was thus prevented. After heating to dryness twice using 20 ml conc. sulphuric acid for each 5 g complex, the residue in each case was dissolved in water and made up to one litre. The cobalt sponge and wire were first dissolved in nitric acid and then taken to dryness twice with sulphuric acid.

Analytical methods

Phosphate method I: This method is based partly on the analogous method for zinc[9].

To a neutral cobalt solution containing approximately 100 mg cobalt, 5 g ammonium chloride and 10 ml 2 N sodium acetate were added. The total volume was adjusted to 120 ml. The solution was heated on a water bath; when hot, 12 ml 10% ammonium phosphate was slowly added, and the solution stirred occasionally until the precipitate turned violet. The beaker was now removed and left to stand for one hour. The precipitate was filtered (X4 sintered crucible) washed with 1% ammonium phosphate solution which had been adjusted to pH 7.0 and finally with 5 ml 50% alcohol. After drying for about 15 min at 110° it was ignited for one hour at 730° to convert to $Co_2P_2O_7$.

Filtrate analysis: The filtrate and washings from the phosphate method were made up to 500 ml. To 25 ml diluted to 40 ml and containing one drop phenolphthalein, 1:50 HCl was added until colourless and then a few ml in excess. The solution was boiled gently for a few min, 4 ml 50% sodium acetate solution was added, and after further boiling, 4 ml 0.2% nitroso-R-salt solution was introduced. When the colour had developed fully (about 2 min boiling), 2 ml conc. nitric acid was added, the solution boiled for one more minute, and then cooled rapidly. It was made up to 100 ml in a volumetric flask, and the optical density measured using a 4-cm cell, No. 605 Ilford yellow-green filter (peak transmission 545 mμ) and a blank treated similarly.

Notes: (i) A calibration curve was used for which $[Co(NH_3)_5Cl]Cl_2$ had been used as primary standard. (ii) the reported failure of Beer's law at low cobalt concentrations[10] was not encountered probably owing to the procedure used. (iii) in order to ensure that no interference was caused by ammonium or phosphate ions under the analytical conditions, tests were carried out on dilute cobalt solutions of known strength containing these ions. Neither was found to interfere.

In a second series another form of the phosphate method based on a procedure recommended by SCHOELLER[11] was used.

Phosphate method II: To a neutral cobalt solution containing approximately 100 mg cobalt 10 ml conc. HCl and 10 ml 10% ammonium phosphate solution was added. The total volume was adjusted to 150 ml. After heating on a water bath until hot, sufficient 1:1 ammonia was added to cause the precipitate formed to partly dissolve (25 ml approx.). The precipitate was left to stand 1–2 hours, filtered through an X4 sintered crucible, washed with 1% ammonium phosphate solution followed by a little 50% alcohol, and dried at 110°. It was then ignited at 730° and weighed as the pyrophosphate. The filtrate cobalt was estimated as in the previous method.

Both phosphate methods were tested carefully on arbitrary cobalt solutions and were found to give very consistent results.

RESULTS

Reproducibility of phosphate method

Typical batch of six analyses using phosphate method I: found resp.: 104.6, 104.7, 104.6, 104.6, 104.6 and 104.7 mg Co.

DISCUSSION

Although the two phosphate methods give different results for a particular standard, a similar pattern of results is obtained for a series of different standards. In each case $[Co(NH_3)_5Cl]Cl_2$, $[Co(NH_3)_6]Cl_3$ and $K_3[Co(CN)_6]$ give very similar results, the difference being of the same order as the experimental error for the method. The cobalt wire gives slightly higher results, the mixed sulphate much higher, and the sponge lower results.

It was been pointed out that both the phosphate methods of analysis are precise although method I gives high results in relation to II. A comparison of the mean relative error, therefore, indicates whether the actual cobalt content of a particular standard in relation to the stoichiometric amount, is high or low, in comparison with another standard. For example, in Series I, if $[Co(NH_3)_6]Cl_3$ is assumed to have the exact stoichiometric composition, then in relation to it, cobalt sponge I will have a cobalt content of 99.75%. Comparison of standards in this way does not depend on the absolute accuracy of a method but only on its precision; if slightly high or low in an absolute sense, the relative error would remain constant.

TABLE III

ANALYSIS OF STANDARDS

(Series I: phosphate method I used)

Standard		*Cobalt*[a] *taken mg*	*Total cobalt found mg*	*% difference*
$CoSO_4 \cdot K_2SO_4 \cdot 6H_2O$	A[b]	97.8	98.5	+0.7
	A	97.8	98.6	+0.8
	B	100.0	101.0	+1.0
	B	100.0	100.9	+0.9
	C	99.6	100.6	+1.0
	C	99.6	100.7	+1.1
$[Co(NH_3)_5Cl]Cl_2$	A	100.1	100.8	+0.7
	A	100.1	100.6	+0.6
	B	99.9	100.5	+0.6
	B	99.9	100.4	+0.5
	C	100.4	100.9	+0.5
	C	100.4	100.8	+0.4
	C	100.4	100.9	+0.5
J. M. sponge I	A	101.0	101.2	+0.2
(as sulphate)	A	101.0	101.2	+0.2
$[Co(NH_3)_6]Cl_3$	A	100.1	100.5	+0.4
	A	100.1	100.6	+0.5
$K_3[Co(CN)_6]$	A	100.2	100.9	+0.7
	A	100.2	100.8	+0.6
	B	100.2	100.7	+0.5
	B	100.2	100.7	+0.5
$CoSO_4$[c]	A	100.1	100.4	+0.3
	A	100.1	100.3	+0.2
	B	99.0	100.0	+1.0
	B	99.0	100.0	+1.0
	C	100.2	100.3	+0.1
	C	100.2	100.3	+0.1

[a] Based on stoichiometric formula of standard.

[b] A, B etc. refer to independent batches of the particular standard.

[c] $CoSO_4$ A, B, and C were prepared from the anhydrous sulphate ignited at 500°, 530°, and 550° respectively.

In relation to the complexes which have the least objectionable features as primary standard, the cobalt sponge would appear to contain unreduced oxide. It is stated to contain an unspecified amount of this, but it is not included in the 99.99% purity value quoted for the product, a figure derived on the basis of spectrographic analysis.

TABLE IV

ANALYSIS OF STANDARDS

(Series II: phosphate method II used)

Standard		*Cobalt taken mg*	*Total cobalt found mg*	*% difference*
$[Co(NH_3)_5Cl]Cl_2$	A	100.2	100.4	+0.2
	A	100.2	100.2	0
	B	100.5	100.8	+0.3
	B	100.5	100.6	+0.1
	C	100.4	100.7	+0.3
	C	100.4	100.7	+0.3
	D	100.2	100.3	+0.1
	D	100.2	100.4	+0.2
J. M. sponge II	A	100.9	100.4	—0.5
(as sulphate)	A	100.9	100.5	—0.4
	B	100.1	99.5	—0.6
	B	100.1	99.6	—0.5
J. M. wire	A	100.2	100.6	+0.4
(as sulphate)	A	100.2	100.6	+0.4
	B	100.2	100.4	+0.2
	B	100.2	100.4	+0.2
$K_3[Co(CN)_6]$	B	76.9	77.0	+0.1
	B	76.9	77.0	+0.1
	C	72.3	72.5	+0.2
	C	72.3	72.4	+0.1
$CoSO_4$	D	100.6	101.1	+0.5
	D	100.6	101.2	+0.6

Co sponge II was not the same batch used in Series I.
$CoSO_4$ D was prepared from anhydrous $CoSO_4$ ignited at 530°.
For sponge and wire, A and B refer to different solutions made from the same sample.

A comparison of Series I and II indicates that in relation to the complexes, cobalt sponge I differs slightly in purity from sponge II. In relation to the sponge, the wire has a higher cobalt content. It is probable that in the process of manufacturing the wire from sponge, the oxide content is reduced.

The relatively high result obtained for the mixed sulphate would result if there were a deficiency in water of hydration as a result of drying, a potential source of error in all hydrated salts used for this purpose.

$CoSO_4$ gives erratic results, which suggests that slight decomposition occurs at the temperatures used and confirms previous doubts as to its value as a primary standard.

The complexes have many qualities that make them suitable for use as primary standards, *e.g.* absence of hydrated water and high molecular weight. In view of this and their mutual agreement and position relative to the other standards examined in the present work, it is recommended that they should be used as primary standards in cobalt analysis. The results indicate that their actual composition agrees closely with the theoretical composition. Of the three, the pentammine complex is the easiest to prepare and purify. It has been used for all further work in this series.

TABLE V

SUMMARY OF RESULTS

	Standard	*Mean relative error for phosphate method used %*
Series I	$[Co(NH_3)_5Cl]Cl_2$	+0.54
	$[Co(NH_3)_6]Cl_3$	+0.45
	$K_3[Co(CN)_6]$	+0.57
	Co sponge I	+0.20
	$CoSO_4 \cdot K_2SO_4 \cdot 6H_2O$	+0.92
	$CoSO_4$	+0.45 (but results erratic)
Series II	$[Co(NH_3)_5Cl]Cl_2$	+0.19
	$K_3[Co(CN)_6]$	+0.17
	Co sponge II	−0.50
	Co wire	+0.30
	$CoSO_4$	+0.55

TABLE VI

To indicate the amount of filtrate cobalt, two typical results are given in full.

Standard being examined	*Co taken mg*	*Phospate method used*	*Co found as $Co_2P_2O_7$ mg*	*Filtrate Co by N-R-S mg*	*Total Co mg*
$[Co(NH_3)_6]Cl_3$	100.1	I	100.1	0.4	100.5
$[Co(NH_3)_5Cl]Cl_2$	100.4	II	99.0	1.7	100.7

The cobalt sponge, although admirable, no doubt, for many purposes, cannot be recommended for use as a standard. The cobalt wire examined was evidently a very pure specimen. The only disadvantages in using it as a standard is that weighing errors would have the maximum effect.

It is not suggested that only the complexes recommended are suitable as cobalt primary standards. Probably many other compounds such as carbonatotetrammine cobaltic nitrate would give similar results. However, very few compounds other than those considered have been used for the purpose, and the standards mostly used have been those indicated as unsuitable in the present work. It is desirable that all papers on cobalt analysis should state clearly the standard used or the method used to standardise the stock solution, and in the latter case, for reasons given earlier, full details should be given.

SUMMARY

A number of primary standards for use in cobalt analysis have been compared under controlled conditions using the phosphate method of analysis. $[Co(NH_3)_6]Cl_3$, $[Co(NH_3)_5Cl]Cl_2$, and $K_3[Co(CN)_6]$ are recommended in preference to others which have hitherto been used for the purpose.

RÉSUMÉ

Les auteurs ont examiné plusieurs composés en vue de leur utilisation comme étalon pour l'analyse du cobalt. $[Co(NH_3)_6]Cl_3$, $[Co(NH_3)_5Cl]Cl_2$ et $K_3[Co(CN)_6]$ sont recommandés.

ZUSAMMENFASSUNG

Als Testsubstanzen für Kobaltbestimmungen werden folgende Verbindungen vorgeschlagen: $[Co(NH_3)_6]Cl_3$, $[Co(NH_3)_5Cl]Cl_2$ und $K_3[Co(CN)_6]$.

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RAPID ESTIMATIONS OF ZONE CONTENT IN PAPER CHROMATOGRAPHS

VI. R.Lf. METHOD

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In a previous paper the writer described an electro-static discharge method[1] whereby rapid approximate zone content estimations can be made. Since that was published he has carried out similar estimations by means of his rectified low-frequency apparatus described in this journal[2]. This alternative method has several advantages:

1. An ordinary micro-ammeter is employed in place of the delicate reflecting galvanometer used in the other method.

2. No "keys" are required[1].

3. As soon as a sample of solution has been drawn up into the conductimetric tube the micro-ammeter deflection *remains at a constant reading* until the tube is emptied

and the solution is returned to its original container, and the needle then returns to zero.

Preliminary procedure

The mode of proceeding is similar to that required for the "static discharge method". First a $N/500$ solution of the required solute is prepared and a graph is plotted "Solution concentration *vs.* μA". Fig. 1 is a sample graph.

Commencing with a carefully dispensed solution which in this case was an aqueous solution of nickel chloride, a series of dilutions were made by additions of two ml between each reading down to $N/3000$ and after that volumes of 10 ml were added till the graph was completed.

Approximate determination of zone content

Having located the zone or spot, that section of the chromatograph is excised and the content of the zone is dissolved in a measured volume of the solvent. It is best to commence with a small volume in case the spot is very small or is only a poor conductor. Should this solution prove to be too conductive the volume 'X' must be increased by a suitable amount which will bring the meter reading within the range of its scale.

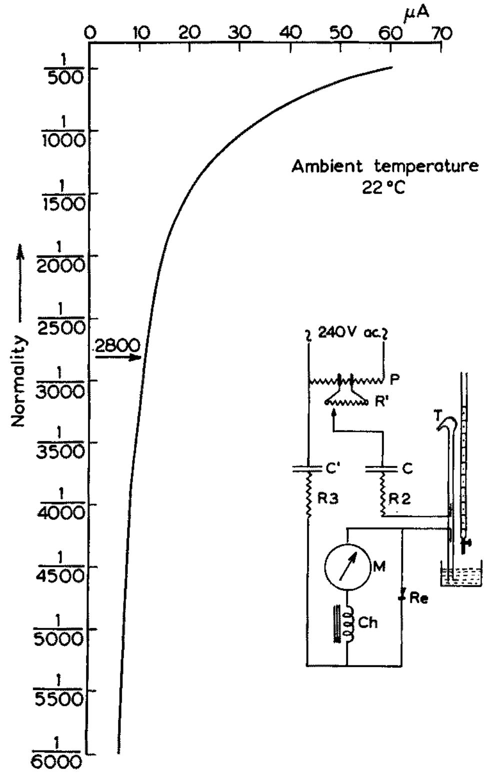

Fig. 1. This graph plotted on squared paper shows a series of nickel chloride concentrations plotted against current in μA. The arrow indicates the position of the sample spot on the graph. The inset on this figure shows the ac. R.Lf. circuit employed.

A sample of the solution is drawn up into the conductimetric tube T and the first reading is plotted. In the example which follows this reading was 60 μA. Fig. 1* gives a diagram of the electrical circuit.

Procedure

The approximate zone content is found by $N \cdot x/c$ when N = mol. wt. in g per l; c = concentration of solution and x = volume of the solvent in which the zone is dissolved.

Example

A reading of 10.1 μA was obtained for a solution made by dissolving a nickel chloride spot in 10 ml of distilled water $129.6/2800 \times 10$. Therefore the spot contained approximately 0.46 mg. The same circuit provides also a reliable method for dispensing and matching solution concentrations.

Comparison of the utility of the Electro-static discharge and the Rectified Low-frequency methods

The static discharge circuit is more sensitive towards the zero end of the scale and it undoubtedly provides the better method by which to estimate the relative purities of samples of water, also for the detection of an impurity, as for example, when it is required to ascertain the cleanliness of a conductimetric tube. Operation at near the zero end of the galvo.-scale is comfortably slow and precise readings are easily obtained. However as conductivity of the solution increases the speed of the galvo swing accelerates and it becomes more difficult to take readings.

When the R.Lf. circuit is employed there is no difficulty at all in taking readings, as the needle of the micro-ammeter remains stationary for as long as the conductimetric tube is full, however this method is less sensitive when near the zero end of its scale.

SUMMARY

The employment of BLAKE's "Rectified Low-frequency" circuit for plotting graphs for rapid determinations of the content of chromatograph zones is described. Comparison is made between this and his "Electro-static discharge" method. It is seen from graphs that either method may be used over the range required. The R.Lf. circuit presents several advantages for this work in general, but when the solute content is less than one part in 10.000 as is the case when samples of distilled water are to be compared the Static discharge method is by far the better.

RÉSUMÉ

L'appareil de BLAKE ("Rectified Low-frequency") est décrit en vue de son utilisation pour la détermination rapide des concentrations des zones chromatographiques. On compare avec la méthode de décharge électrostatique. Pour de très faibles concentrations, cette dernière donne de meilleurs résultats.

ZUSAMMENFASSUNG

Es wird die Anwendung von BLAKE's "Rectified Low-frequency" Apparat zur raschen Konzentrationsbestimmung in chromatographischen Zonen beschrieben und mit seiner "Electro-static Discharge" Methode vergleichen. Bei sehr kleinen Konzentrationen gibt die letztere Methode bessere Werte.

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* For constructional details of Fig. 1. see Ref. 1.

SPECTROPHOTOMETRIC STUDIES ON THE NATURE OF IRON COMPLEXES WITH PYRIDINE- AND QUINOLINE-CARBOXYLIC ACIDS

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SKRAUP[1] observed that pyridine- and quinoline-carboxylic acids, with a carboxyl group in the α-position to the heterocyclic nitrogen atom produce intense yellow or red colours with ferrous iron; methods for the determination of iron with quinaldinic[2,3], picolinic[4] and benzoquinaldinic[5] acids have been based on this reaction.

MAJUMDAR AND SEN[3-5] found that in solution the metal ion and the organic acid, in the absence of potassium cyanide, formed a 1 : 2 complex. However, SHINRA *et al.*[6] suggested the formation of a 1 : 3 complex between the metal and picolinic or quinaldinic acid, while RAY AND BANERJEE[7] found a ratio of 1 : 2 for quinaldinic acid and 1 : 3 for picolinic acid. These workers obtained dissociation constants for the complexes of the order of $3.63 \cdot 10^{-6}$ and $5.07 \cdot 10^{-12}$ respectively, whereas WENGER *et al.*[8] found a value of $2.6 \cdot 10^{-8}$ for ferrous quinaldinate, and MAJUMDAR AND SEN[4] a value of $4.23 \cdot 10^{-5}$ for ferrous picolinate.

These discrepancies necessitated a critical investigation of the composition and dissociation constants of the complexes formed in solution by ferrous ion with pyridine and quinoline carboxylic acids in the presence or absence of potassium cyanide.

EXPERIMENTAL

Apparatus and solutions

A Hilger Uvispek spectrophotometer was employed for optical density measurements at room temperature (25°) with 1-cm quartz cells. Corrections were made for any slight differences in the transmittancies of the cells.

A Cambridge pH meter was used for all pH determinations.

Iron solution: A standard solution was prepared by dissolving ferric nitrate, A.R., B.D.H., in twice distilled water. It was standardized and weaker solutions were prepared by dilution.

Reagent solution: α-Picolinic acid[13] (m.p. 130–132°), quinaldinic acid[14] (m.p. 155–157°) and quinolinic acid[15] (m.p. 192–194°) were prepared. A 1% solution of each was used.

Other solutions used were a 1.5 *M* (approx. 10%) solution of potassium cyanide, a 1% solution of hydroxylamine hydrochloride, sodium acetate–acetic acid and ammonium acetate–acetic buffers of pH 5.9.

Colour reactions and absorption maximum regions

The orange-yellow complex formed by ferrous ion with picolinic or quinolinic acid[12] either in presence of potassium cyanide (pH 9.0) or in presence of a large excess of the reagent (pH 5.9) showed maximum absorption at 440 mμ. The pink-red complex of iron and quinaldinic acid in the absence of potassium cyanide at pH 5.9 gave the absorption maximum at 480 mμ though the optical density remained constant up to 500 mμ; the complex formed in the presence of potassium cyanide had the maximum absorption at 515 mμ with no change in absorption values up to 520 mμ. In Fig. 1, curves Ia, Ib and Ic represent the optical density values in presence of potassium cyanide of the coloured complexes formed with 8 p.p.m. of iron; curves IIa, IIb and IIc present the values obtained at pH 5.9 in absence of potassium cyanide with 12 p.p.m. of iron.

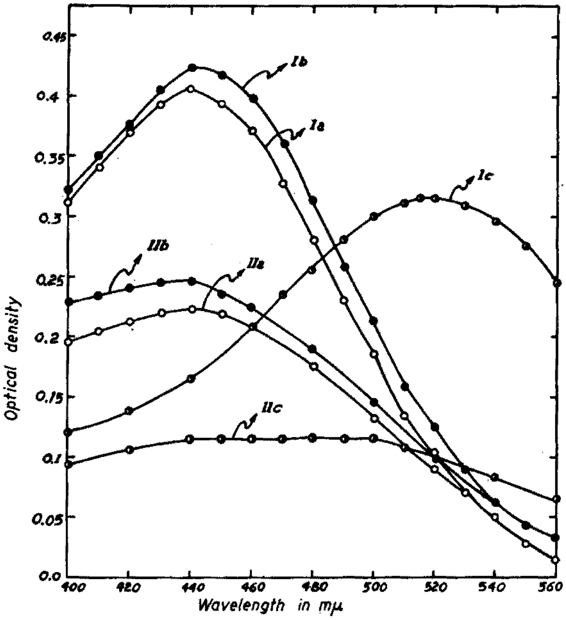

Fig. 1. Spectral transmittancy curves: Ia, IIa – picolinic acid complex; Ib, IIb – quinolinic acid complex; Ic, IIc – quinaldinic acid complex.

Composition of the complexes

The composition of the complexes in solution was determined by JOB[9] and molar ratio[10] methods.

For Job's method, equimolar solutions of iron and reagent were taken in different quantities (total 10 ml) in 25-ml flasks. The iron solution was mixed with 1 ml of hydroxylamine hydrochloride, and the necessary amount of reagent, 1 ml of potassium cyanide and water to make up the volume were added. Curves A, B and C (Fig. 2) represent the picolinic, quinaldinic and quinolinic acid complex systems respectively.

In the absence of potassium cyanide, a large excess of reagent was required for maximum colour development. With equimolar solutions the reagent concentration was small and the optical density of the coloured complexes formed without cyanide was slightly higher at 420 mμ than at 440 mμ in the case of picolinic and quinolinic acids. The absorption maximum always occurred at 480 mμ with quinaldinic acid. The compositions of the picolinic and quinolinic acid complexes were determined both at 420 mμ and at 440 mμ and that of quinaldinic acid at 480 mμ by following the procedure given above except that 8 ml of the buffer pH 5.9 solution were added instead of 1 ml of the potassium cyanide solution. (Sodium acetate–acetic acid buffer was used in the picolinic and quinolinic acid systems while ammonium acetate–acetic acid buffer was more suitable for the quinaldinic acid complex; the former buffer formed a precipitate in the latter system.) Curves D, E and F (Fig. 2) represent respectively the picolinic, quinaldinic and quinolinic acid systems formed without cyanide. From the curves it can easily be inferred that in presence of potassium cyanide, the metal forms a 1 : 1 complex with these acids, whereas without cyanide the ratio is always 1 : 2.

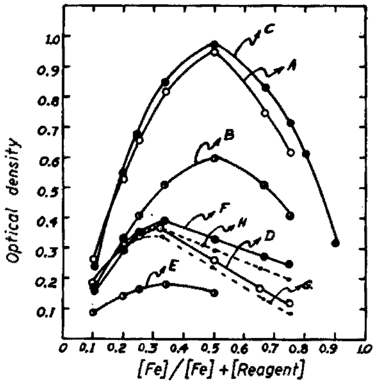

Fig. 2. Job's method of continuous variation: A – Fe = picolinic acid = 2.5 · 10^{-3} M at 440 mμ; B – Fe = quinaldinic acid = 2.5 · 10^{-3} M at 515 mμ; C – Fe = quinolinic acid = 2.66 · 10^{-3} M at 440 mμ; D and F – Fe = picolinic and quinolinic acids respectively = 5 · 10^{-3} M at 420 mμ; E – Fe = quinaldinic acid = 5 · 10^{-3} M at 480 mμ; G and H – Fe = picolinic and quinolinic acids respectively = 5 · 10^{-3} M at 440 mμ.

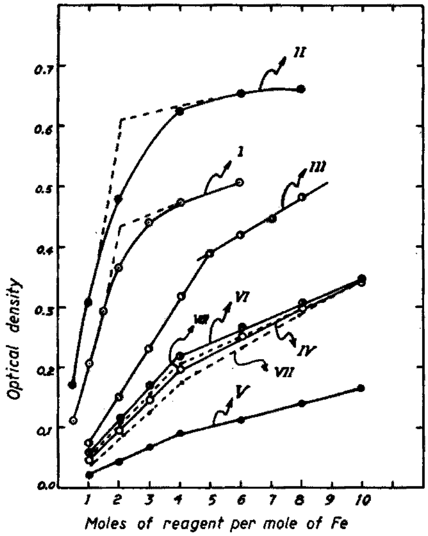

Fig. 3. Molar ratio method: I – 2 ml of 2.5 · 10^{-3} M Fe and 2.5 · 10^{-3} M picolinic acid at 440 mμ; II – 2 ml of 5 · 10^{-3} M Fe and 5 · 10^{-3} M quinaldinic acid at 515 mμ; III – 1 ml of 5.32 · 10^{-3} M Fe and 1.064 · 10^{-3} M quinolinic acid at 440 mμ; IV and VI – 2 ml of 5 · 10^{-3} M Fe and 5 · 10^{-3} M picolinic and quinolinic acids respectively at 420 mμ; V – 2 ml of 5 · 10^{-3} M Fe and 5 · 10^{-3} M quinaldinic acid at 480 mμ; VII and VIII – 2 ml of 5 · 10^{-3} M Fe and 5 · 10^{-3} M picolinic and quinolinic acids respectively at 440 mμ.

For the molar ratio method, the optical density values of the solutions were obtained by adding varying amounts of the organic acids and a fixed amount of potassium cyanide to a constant amount of iron; the values are shown in Fig. 3. The breaks in curves I, II and III indicate that for all the complexes the metal and the reagent were in a ratio of 1 : 1.

The data for the curves IV, V and VI (Fig. 3) were obtained by adding different amounts of the reagents (5 · 10^{-3} M) to 2 ml of an iron solution of the same molarity and by adjusting the pH to 5.9, without adding cyanide. The curves IV and VI show the absorption at 420 mμ and curve V that at 480 mμ. The breaks indicate a metal to reagent ratio of 1 : 2. Even when the measurements for the picolinic and quinolinic acid complexes were made at 440 mμ, after the addition of potassium nitrate to increase the ionic strength, the metal to reagent ratio of 1 : 2 remained unchanged. Curves G and H (Fig. 2) by Job's method, and VII and VIII (Fig. 3) by the molar ratio method, support this statement.

It is thus conclusively shown that in the absence of potassium cyanide, iron in solution is associated with pyridine and quinoline carboxylic acids in a ratio of 1 : 2 and that in presence of cyanide the ratio is 1 : 1. The formulae of the complexes may be suggested as:

Reagent	*with potassium cyanide*	*without potassium cyanide*
Quinolinic	$K_4[Fe(C_7H_3NO_4)(CN)_4]$	$Na_2[Fe(C_7H_3NO_4)_2(H_2O)_2]$
α-Picolinic acid	$K_3[Fe(C_6H_4NO_2)(CN)_4]$	$Fe(C_6H_4NO_2)_2(H_2O)_2$
Quinaldinic acid	$K_3[Fe(C_{10}H_6NO_2)(CN)_4]$	$Fe(C_{10}H_6NO_2)_2(H_2O)_2$

Instability constants of the complexes

The instability constant K of the complexes, formed in the presence or absence of potassium cyanide, was calculated by the following equations[11],

$$\alpha = \frac{Em - Es}{Em} \quad \text{and} \quad K = \frac{\alpha C(n\alpha C)^n}{C(1\text{-}\alpha)}$$

where α, Em, Es, C and n have their usual significances. The results are given in Table I.

TABLE I

Complex with	*Instability constant, K*	
	with potassium cyanide	*without potassium cyanide*
α-Picolinic acid	$2.51 \cdot 10^{-5}$	$1.53 \cdot 10^{-8}$
Quinaldinic acid	$7.51 \cdot 10^{-6}$	$2.02 \cdot 10^{-8}$
Quinolinic acid	$2.73 \cdot 10^{-5}$	$1.72 \cdot 10^{-9}$

MAJUMDAR AND SEN[4] found a higher value ($4.23 \cdot 10^{-5}$) for ferrous picolinate possibly because they used solutions of low pH. The instability constant found for ferrous-quinaldinate agrees fairly well with the values of WENGER *et al.*[8] ($2.6 \cdot 10^{-8}$). Increase of ionic strength by the addition of potassium nitrate had no effect on the final result.

SUMMARY

The compositions of the ferrous iron complexes with α-picolinic, quinaldinic and quinolinic acids have been reinvestigated. In presence of potassium cyanide, iron combines with these reagents in a ratio of 1 : 1; at pH 5.9, in absence of cyanide, the metal to reagent ratio is 1 : 2. The instability constants of the complexes are given.

RÉSUMÉ

Les auteurs ont effectué une étude spectrophotométrique sur la composition des complexes ferreux des acides α-picolique, quinaldique et quinoléique.

ZUSAMMENFASSUNG

Es wird eine spektrophotometrische Untersuchung über die Zusammensetzung der Eisen(II)-Komplexe von α-Picolin-, Chinaldin- und Chinolinsäure beschrieben.

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THERMOLYSIS OF SULPHIDES PRECIPITATED BY SODIUM SULPHIDE

II. SULPHIDES OF SELENIUM, TELLURIUM, GOLD, PLATINUM, RUTHENIUM, LEAD, BISMUTH, CADMIUM, SILVER, PALLADIUM AND INDIUM

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The thermolysis of several sulphides precipitated by sodium sulphide has already been studied[1]. The present investigation deals with the thermolysis of the remaining sulphides. $Ir_2S_3 \cdot 10H_2O$ has been studied by DUVAL *et al.*[2].

EXPERIMENTAL

The reagents and methods for the preparation of the precipitates were as reported in earlier papers. The precipitates taken for thermolysis were in exactly the same condition as those used in the gravimetric determinations just before weighing.

A standard Stanton thermobalance was used. The rate of heating was $5.3 \pm 0.2°$ per min. Palladium sulphide required a maximum temperature above 800°; to obtain automatically a linear rate of heating the high and low switches were preset at 3 and 1 respectively. The thermograms shown were obtained by plotting different points of the original graph on the X and Y axes.

Selenium disulphide

Oven-dried selenium disulphide[3] started to volatilize at 210° and had volatilized completely at 520°. (Fig. 1).

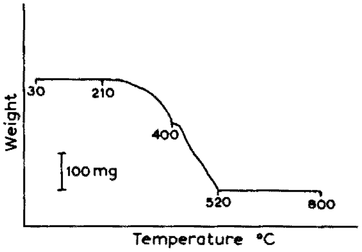

Fig. 1. Thermal decomposition curve of selenium sulphide (SeS_2) precipitated by sodium sulphide reagent.

Tellurium disulphide

Oven-dried tellurium disulphide[3] lost weight from 180° to 370°. From 370° to 410° the horizontal corresponded to metallic tellurium. From 410° to 620° a gain in weight showed the formation of TeO_2. The horizontal after 620° corresponded to TeO_2. (Fig. 2).

Tellurium trisulphide

The oven-dried precipitate[4] lost weight from 180° to 380°. From 380° to 430° the horizontal corresponded to metallic tellurium. From 430° the weight increased and TeO_2 was formed completely at 630°. The horizontal from 630° to 800° showed TeO_2. (Fig. 2).

Gold sulphide

Oven-dried gold sulphide[5] gave a horizontal up to 220°; it then started to lose weight and was completely converted to the metal at 280°. (Fig. 2).

Platinum sulphide

An air-dried sample of the pentahydrate[6] lost water and sulphur from 50° to 310°. From 310° the horizontal found corresponded to the metal. (Fig. 3).

The trihydrate[7] behaved in exactly the same way.

Ruthenium sulphide ($Ru_2S_3 \cdot 2H_2O$)

The air-dried precipitate[6] lost weight from 60° to 180°. The horizontal found at 180° to 240° did not correspond to the anhydrous form. From 240° to 340° there was a continuous gain in weight; the horizontal found from 340° to 410° did not correspond to any definite compound. After 410° the precipitate lost weight and was completely converted to the metal at 500°. (Fig. 3).

Lead sulphide

The air-dried precipitate[8] gave a horizontal up to 110°, after which it continuously gained weight. The gain became very small after 500°. (Fig. 4).

Bismuth sulphide

The oven-dried precipitate[8] gave a horizontal up to 160°; no other horizontal corresponded to any definite composition. (Fig. 4).

Cadmium sulphide

The oven-dried precipitate[8] lost 3–4% in weight from 50 to 140°, after which there was no further loss up to 300°. Above 300° it gained weight without any horizontal. (Fig. 4).

Silver sulphide

The air-dried precipitate[9] gave a near horizontal up to 570°; the gain in weight of about 1% may be due to impurities. From 570° to 710° the weight decreased and then increased continuously up to 800°. (Fig. 5).

Palladium sulphide ($PdS \cdot 2H_2O$)

The air-dried precipitate[6] lost weight from 50° to 420°. From 420° to 430° the weight increased and then decreased from 450° to 460°. From 460° to 800° it increased smoothly. Between 800° and 840° the horizontal found corresponded to PdO. From 840° to 890° the weight decreased and the metal was formed. (Fig. 5).

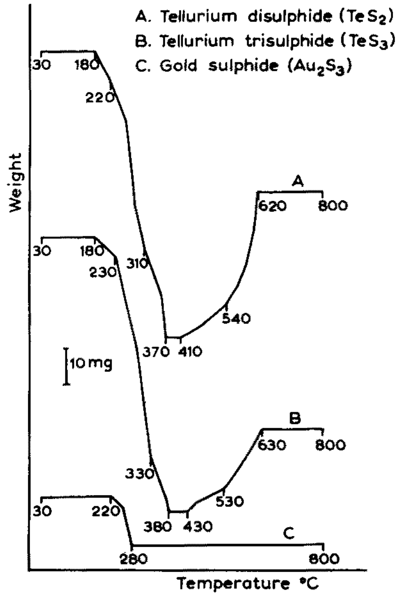

Fig. 2. Thermal decomposition curves of sulphides precipitated by sodium sulphide reagent.

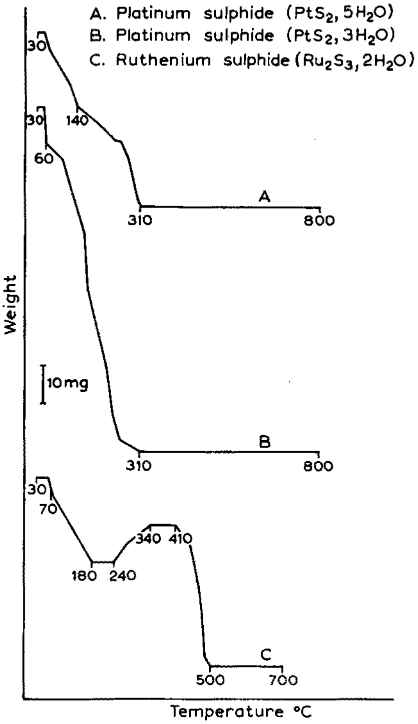

Fig. 3. Thermal decomposition curves of sulphides precipitated by sodium sulphide reagent.

Indium sulphide

The oven-dried precipitate[8] lost about 3% in weight from 50° to 100° after which it remained constant up to 340°. Above 340° the weight decreased continuously. (Fig. 5).

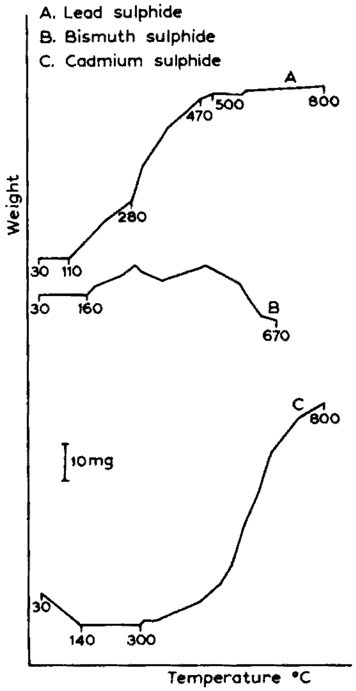

Fig. 4. Thermal decomposition curves of sulphides precipitated by sodium sulphide reagent.

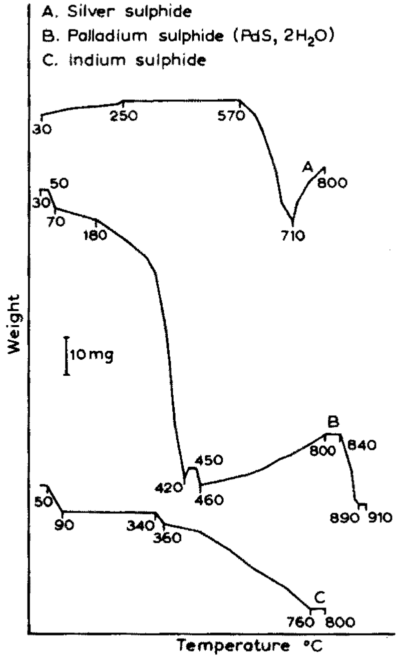

Fig. 5. Thermal decomposition curves of sulphide precipitated by sodium sulphide reagent.

In the case of SeS_2, the volatilization began at 210° and ended at 520°. TeS_2 and TeS_3 were finally converted to TeO_2 which was stable up to 800°. Au_2S_3, $PtS_2 \cdot 5H_2O$, PtS_2, $3H_2O$, $Ru_2S_3 \cdot 2H_2O$, and $PdS \cdot 2H_2O$ were finally converted into the metals. PbS, Bi_2S_3, CdS and In_2S_3 did not give horizontals corresponding to any definite formula at higher temperatures. The error in the weight of gold is greater than in any other case (see Table 1).

Notes:

a. Ruthenium sulphide spurts during heating and should be heated carefully in the partly covered crucible.

b. Bismuth sulphide is precipitated by sodium sulphide and ammonium acetate.

c. Indium sulphide is soluble in sodium sulphide and is precipitated by ammonium sulphide; it is included here for completeness.

d. The thermolysis of cadmium sulphide shows that the precipitate should be dried at a temperature above 140°. If the lower temperature, 105°–115°, previously recommended is used, the factor is not quite correct. In fact, the amount of cadmium sulphide found from a given weight of the sulphate is 3–4% higher than the theoreti-

TABLE I

TeS_2 taken (mg)	Te calculated (mg) (370°–410°)	Te from graph (mg) (370°–410°)	TeO_2 calculated (mg) (620°–800°)	TeO_2 from graph (mg) (620°–800°)
229	152	153	191	191
159	106	107	132	132
TeS_3 taken (mg)	Te calculated (mg) (380°–430°)	Te from graph (mg) (380°–430°)	TeO_2 calculated (mg) (630°–800°)	TeO_2 from graph (mg) (630°–800°)
175	100	101	125	123
176	100	101	125	119
	Au_2S_3 taken (mg)	Au calculated (mg) (280°–800°)	Au from graph (mg) (280°–800°)	
	104	84	91	
	96	77	85	
	Platinum sulphide taken (mg)	Pt calculated (mg) (310°–800°)	Pt from graph (mg) (310°–800°)	
$PtS_2 \cdot 5H_2O$	111	64	64	
$PtS_2 \cdot 3H_2O$	238	148	145	
$Ru_2S_3 \cdot 2H_2O$ taken (mg)	Weight from graph (180°–240°)	Weight from graph (340°–410°)	Ru calculated (mg) (500°–700°)	Ru from graph (mg) (500°–700°)
130	107	117	78	79
103	87	95	62	60
$PdS \cdot 2H_2O$ taken (mg)	PdO calculated (mg) (800°–840°)	PdO from graph (mg) (800°–840°)	Pd calculated (mg) (890°–910°)	Pd from graph (mg) (890°–910°)
246	172	180	150	160
254	178	184	155	163

cal value. It is therefore necessary to use the conversion factor 0.75191 instead of 0.77840 to calculate the amount of cadmium metal.

SUMMARY

Thermolysis of selenium, tellurium, gold, platinum, ruthenium, lead, bismuth, cadmium, silver, palladium or indium sulphide precipitated by sodium sulphide has been studied. The methods used for drying and weighing these sulphides are reliable, except in the case of cadmium where an empirical factor is needed.

RÉSUMÉ

Une étude a été effectuée sur la thermolyse de sulfures précipités par le sulfure de sodium. Les conditions de séchage et de pesée des sulfures de sélénium, de tellure, d'or, de platine et de ruthénium conviennent très bien à leur dosage gravimétrique.

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über das thermolytische Verhalten von Sulfiden. Es wird gezeigt, dass die üblichen Methoden der Trocknung und Wägung der Sulfiden von Selen, Tellur, Gold, Platin, Ruthenium, Blei, Wismut, Silber, Palladium und Indium zuverlässig sind.

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OXIDATIONS WITH POTASSIUM PERMANGANATE IN PRESENCE OF FLUORIDE

II. POTENTIOMETRIC TITRATION OF MERCURY(I) AND THE REDOX POTENTIAL OF THE Mn^{+7}/Mn^{+3} SYSTEM

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The direct titration of mercury(I) in sulphuric acid medium in the presence of fluoride[1] provides a useful determination; and back-titration of permanganate with mercurous solution can be applied for the determination of manganese in steels containing chromium and vanadium[2]. However, the visual procedure is only successful in the titration of dilute solutions; otherwise the pink colour of trivalent manganese interferes seriously. RAO *et al.*[3] have also studied the oxidation of mercury(I) in hydrochloric acid medium with permanganate but they preferred iodine monochloride as catalyst.

We have now studied the potentiometric titration of mercury(I) with permanganate and the reverse titration in order to discover whether the method is satisfactory for more concentrated solutions.

EXPERIMENTAL

Potentiometric equipment

The titration device was similar to that previously described[4]; a potassium nitrate salt bridge was used.

Preparation and standardization of solutions

The potassium permanganate solutions were prepared by a method similar to that of STAMM[5] and standardized by sodium oxalate[6]. The solutions used were 0.1958 *N*, 0.0482 *N* and 0.0241 *N*, based on a valency change of 5. However, for the present calculations the normalities should be multiplied by 0.8.

Mercurous solutions were prepared as before[1] and standardized by titration with potassium permanganate. The solutions prepared were 0.1024 *N*, 0.0512 *N* and 0.0256 *N*.

Other solutions: 9 *N* sulphuric acid, 2% NaF, and 0.25 *N* $CuSO_4$.

RESULTS AND DISCUSSION

I. Titration of mercury(I) with potassium permanganate

The reaction of mercurous solution with potassium permanganate proceeded more or less rapidly at the beginning of the titration but as the end-point was approached the reaction became rather sluggish needing about 5 min to attain equilibrium. A systematic study of the different factors affecting the accuracy of results was made.

TABLE I

Titration of 10 ml 0.1024 *N* $Hg_2(NO_3)_2$ (205.5 mg Hg_2^{+2}) with 0.1958 *N* $KMnO_4$ using varying quantities of 9 *N* H_2SO_4 in presence of 50 ml 2% NaF.

Volume of H_2SO_4 *ml*	*Volume of $KMnO_4$ consumed* *ml*	*Theoretical end-point* *ml*	*Error* %	*Max. inflection mV/0.02 ml*
1.0	5.89	6.54	9.94	80
2.5	6.54	6.54	0.00	192
5.0	6.52	6.54	0.31	156
10.0	6.54	6.54	0.00	146
15.0	6.63	6.54	1.38	163
20.0	6.70	6.54	2.45	111

The effect of acidity

The results shown in Table I indicate that the concentration of sulphuric acid could vary from 0.36 *N* to 1.29 *N*, without greatly affecting the values. However, at concentrations of 1.8 *N* and 2.25 *N* larger errors were obtained. The end-points appeared later than the equivalence points, which was ascribed to a slight production of quadrivalent manganese (a faint brown turbidity).

TABLE II

Titration of 5 ml 0.0512 *N* $Hg_2(NO_3)_2$ with 0.0481 *N* $KMnO_4$ in presence of 50 ml 2% NaF

Volume of 9 N H_2SO_4 *ml*	*Time of exposure to atmospheric oxygen before titration* *min*	*Volume of 9 N H_2SO_4* *ml*	*Volume of $KMnO_4$ consumed* *ml*	*Theoretical end-point* *ml*	*Error* %
—	5	5	6.67	6.65	0.30
—	30	5	6.67	6.65	0.30
1	5	4	6.65	6.65	0.00
1	20	4	6.68	6.65	0.45
1	60	4	6.67	6.65	0.30

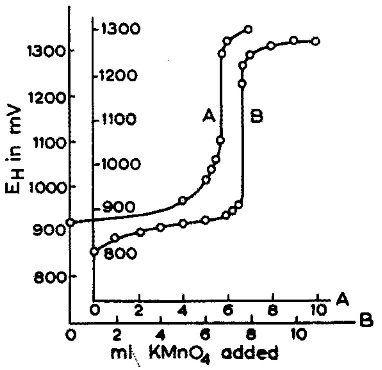

Fig. 1. Titration of 10 ml 0.1024 *N* $Hg_2(NO_3)_2$ in 50 ml 2% NaF and different volumes of 9 *N* H_2SO_4 with 0.1958 *N* $KMnO_4$. A. 20 ml H_2SO_4, B. 2.5 ml H_2SO_4.

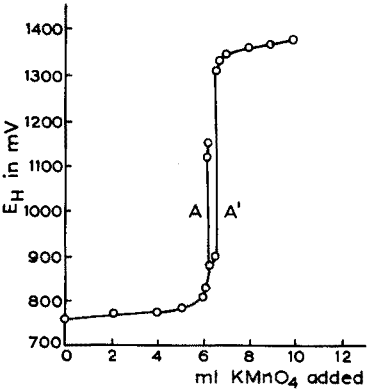

Fig. 2. Titration of 10 ml 0.0512 *N* $Hg_2(NO_3)_2$ in 50 ml 2% NaF. A. in presence of 1 ml 9 *N* H_2SO_4, A'. after end-point of A, 4 ml 5 *N* H_2SO_4 were added and the titration continued.

When the sulphuric acid concentration was less than 0.15 *N*, the end-points appeared much too early. This error cannot be due to atmospheric oxidation of mercury(I) in alkaline solutions, for mercurous fluoride mixtures could be left in contact with the atmosphere for one hour while stirring without the titre being affected. However when the solution was brought to the correct acidity and titrated further with permanganate, a drop in potential was observed and when the titration was completed the second end-point was found to agree with the theoretical value (*cf.* Fig. 2 and Table II). The titration curves obtained at different sulphuric acid concentrations (Fig. 1) indicate that the inflection at the end-point decreases with rise of acidity.

The effect of sodium fluoride

The results shown in Table III and Fig. 3 indicate that the fluoride concentration could vary from 0.07 *M* to 0.42 *M*, the amount of sulphuric acid remaining constant without appreciable errors. At the lower fluoride concentration, the reaction was slow near the end-point taking about 8 min to attain equilibrium. At higher fluoride concentrations the reaction was more rapid. There was no exact relation between the fluoride concentration and the size of the inflection at the end-point.

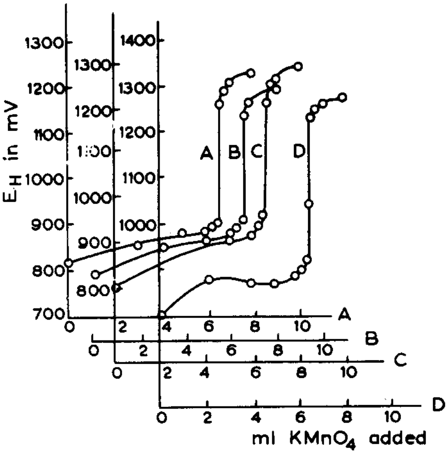

Fig. 3. Titration of 10 ml 0.1024 *N* $Hg_2(NO_3)_2$ with 0.1958 *N* $KMnO_4$ in presence of 5 ml 9 *N* H_2SO_4 A. 75 ml 2% NaF, B. 100 ml 2% NaF, C. 50 ml 1% NaF, D. 50 ml 2% NaF.

TABLE III

Titration of 10 ml 0.1024 *N* $Hg_2(NO_3)_2$ with 0.1958 *N* $KMnO_4$ in presence of varying quantities of 2% NaF and 5 ml 9 *N* H_2SO_4

Volume of NaF ml	*Volume of H_2O added ml*	*Volume of $KMnO_4$ consumed ml*	*Theoretical end-point ml*	*Error %*	*Max. inflection mV/0.02 ml*
10	40	6.53	6.54	0.15	80
50	—	6.52	6.54	0.31	156
70	—	6.54	6.54	0.00	136
100	—	6.52	6.54	0.31	92

The effect of mercurous concentration

The results given in Table IV indicate that when the amounts of fluoride and sulphuric acid remained constant, the method could be used to determine from 25 to 616 mg of mercury. The potentiometric method was therefore satisfactory for higher concentrations of mercury(I) than the visual method. The inflection at the end-point decreased with increasing mercury concentration (Fig. 4). It is noteworthy that mercury gave a turbidity with sulphuric acid which became more evident with increasing mercurous concentration.

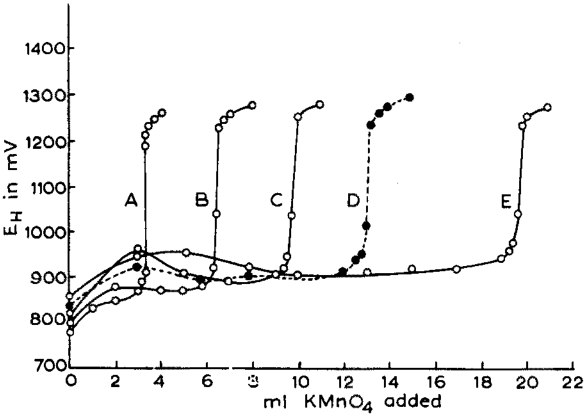

Fig. 4. Titration of different volumes of 0.1024 N $Hg_2(NO_3)_2$ in 50 ml 2% NaF and 5 ml 9 N H_2SO_4 with 0.1958 N $KMnO_4$. A. 5 ml, B. 10 ml, C. 15 ml, D. 20 ml, E. 30 ml.

TABLE IV

Titration of $Hg_2(NO_3)_2$ with $KMnO_4$ in presence of 5 ml 9 N H_2SO_4 and 50 ml 2% NaF

Mercury (I) titrated ml	*Vol. of $KMnO_4$ consumed ml*	*Theoretical end-point ml*	*Error %*	*Max. inflection mV/0.02 ml*
Titration of 0.01024 N $Hg_2(NO_3)_2$ with 0.1958 N $KMnO_4$				
10	6.52 [a]	6.54	0.31	156
10	6.50 [b]	6.54	0.62	106
10	6.49 [c]	6.54	0.93	103
15	9.82	9.81	0.1	90
30	19.62	19.62	0.00	84
Titration of 0.0512 N $Hg_2(NO_3)_2$ with 0.04814 N $KMnO_4$				
5	6.68	6.65	0.45	126
Titration of 0.0256 N $Hg_2(NO_3)_2$ with 0.02407 N $KMnO_4$				
10	13.21	13.3	0.68	128

[a] at 25°, [b] at 40°, [c] at 55°

The effect of temperature

Table IV indicates that accurate results could be obtained by carrying out titrations at ordinary temperature (25°) under the optimum conditions *i.e.* 1 N sulphuric acid and 0.4 M sodium fluoride. The error increased to 0.93 % at 55°. The end-point appeared before the theoretical value probably owing to the decomposition of some permanganate at higher temperatures or to the increased ability of mercury(I) to reduce manganese(VII) to the manganous state. However, a rise of temperature increased the reaction rate enormously and it is preferable to carry out the titration at 40°.

The effect of copper ion on the reaction

The results obtained under varying conditions of acidity, fluoride and copper(II) concentrations were the same as in the absence of copper. Copper(II) was especially important when more concentrated solutions were titrated, for it enhanced the reaction and its blue colour masked the pinkish colour of the manganic fluoride complex, so that as much as 273.3 mg of mercury could be determined by a visual titration. The amount of copper sulphate which should be present increased as the amount of mercury(I) increased. The ratio of copper(II) to mercury(I) should lie between 1:1 and 3:1. However, because some permanganate is consumed before the appearance of the violet colour characterising the end-point, a blank must be determined. The amount of permanganate required for the blank is higher, the higher the concentration of the copper sulphate. A further advantage of copper(II) is that in its presence the titration curves are smoother (*cf.* Fig. 5).

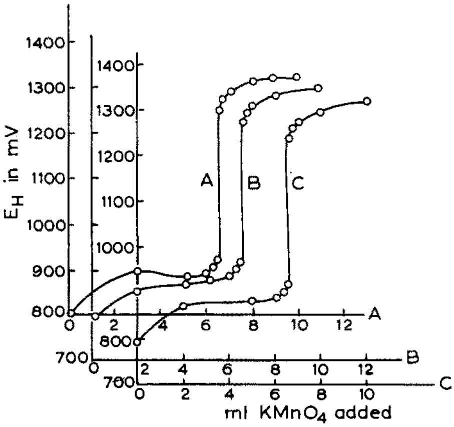

Fig. 5. Titration of 10 ml 0.1024 N $Hg_2(NO_3)_2$ in 50 ml 2% NaF and 9 N H_2SO_4 with 0.1958 N $KMnO_4$. A. in absence of $CuSO_4$, B. in presence of 5 ml 0.25 M $CuSO_4$, C. in presence of 10 ml 0.25 M $CuSO_4$.

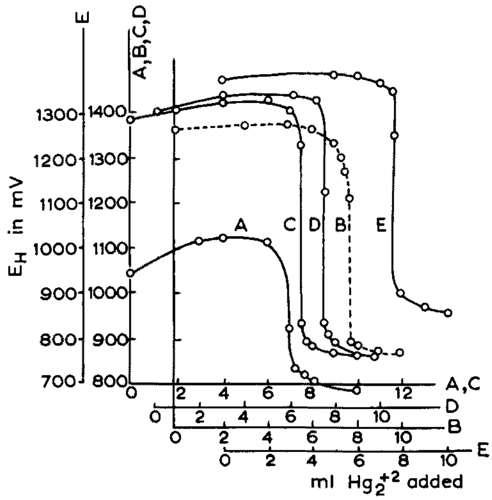

Fig. 6. Titration of 5 ml 0.1958 N $KMnO_4$ in 50 ml 2% NaF and different volumes of 9 N H_2SO_4 with 0.1024 N $Hg_2(NO_3)_2$. A. in absence of H_2SO_4, B. 4 ml H_2SO_4, C. 5 ml H_2SO_4, D. 10 ml H_2SO_4, E. 5 ml H_2SO_4 and 5 ml 0.25 M $CuSO_4$.

II. Titration of potassium permanganate with mercury(I)

The effect of acidity

The titration curves of permanganate with mercurous solution at different acidities are shown in Fig. 6. The curves are characterised by sharp inflections which do not vary in regular manner with acidity.

In the absence of sulphuric acid, the end-point was attained earlier than the theoretical value (Table V); this was due to the formation of a brown turbidity of manganese dioxide. When the solutions were 0.24 *N*, 0.38 *N* and 0.61 *N* in sulphuric acid and contained 50 ml of 2% fluoride, the end-points coincided with the theoretical values. In 0.75 and 1.38 *N* sulphuric acid, the end-points appeared too early because of partial decomposition of potassium permanganate which increased with the rise of acidity.

Note

That early end-points were not due to partial production of manganese dioxide was confirmed as follows:

5 ml of 0.1958 *N* permanganate were titrated with 0.1024 *N* mercurous nitrate in the presence of 0.75 *N* sulphuric acid; the end-point appeared at 7.57 ml. The volume of mercurous nitrate added was then completed to 10 ml and the excess was titrated with permanganate, when 1.59 ml were used.

The total volume of $KMnO_4$ = 6.59 ml
the total volume of Hg_2^{+2} = 10 ml
theoretically 10 ml of Hg_2^{+2} = 6.54 ml $KMnO_4$

If, however, the early end-point was due to the production of manganese dioxide, then the end-point corresponding to the titration of excess mercury(I) should be attained after the addition of 1.54 ml; for the dioxide would react with the mercury added and give manganese(III). In presence of 1.38 *N* acid the volume of permanganate consumed by the excess mercury(I) was 1.68 ml instead of 1.59 in the presence of 0.75 *N* acid. Accordingly the end-point appeared later by an amount equivalent to the permanganate decomposed.

TABLE V

Titration of 5 ml 0.1958 *N* $KMnO_4$ (10.75 mg Mn) with 0.1024 *N* $Hg_2(NO_3)_2$ using varying quantities of 9 *N* H_2SO_4 in presence of 50 ml 2% NaF

Volume of 9 N H_2SO_4 ml	*Volume of $Hg_2(NO_3)_2$ ml*	*Theoretical end-point ml*	*Error %*	*Max. inflection mV/0.02 ml*
—	7.0	7.65	8.5	194
1	7.56	7.65	1.18	234
1.5	7.63	7.65	0.25	213
4	7.62	7.65	0.39	208
5	7.55	7.65	1.31	255
5	7.65	7.65	0.00	257 [a]
10	7.4	7.65	3.27	199
10	7.59	7.65	0.79	393 [a]

[a] in presence of 5 ml 0.25 *M* $CuSO_4$

The errors obtained at high acidities decreased in the presence of copper(II) because the reaction was then enhanced and the tendency to autodecomposition was minimized.

Effect of sodium fluoride

The curves in Fig. 7 and the data in Table VI show that good results were obtained at concentrations of sodium fluoride of 0.12 *M* to 0.42 *M*. However, with 0.05 *M*–0.02 *M* fluoride and an acidity of 0.23 *N* sulphuric acid, the end-points appeared very late owing to the tendency of potassium permanganate to yield bivalent manganese in the presence of less sodium fluoride. This is confirmed by carrying out the following experiment:

5 ml of 0.1958 *N* permanganate were mixed with 10 ml of 2% sodium fluoride, 40 ml of water and 2.5 ml of 9 *N* sulphuric acid. The solution was titrated with 0.1024 *N* mercurous solution and the end-point appeared after 9.35 ml had been added. The volume of mercury(I) solution was completed to 10 ml and the excess was then titrated with permanganate. The end-point appeared after the addition of 0.5 ml.

The total volume of mercurous solution = 10 ml
the total volume of $KMnO_4$ = 5.5 ml
volume of $KMnO_4 \equiv$ to mercurous = 6.54 ml

The smallness of the volume of permanganate consumed compared to the mercurous present indicates the formation of manganese(II), since the latter is not oxidised by permanganate in acid medium. The solution under these conditions is quite clear and colourless due to the absence of manganese(III).

Increasing the fluoride concentration decreases the magnitude of the inflection at the end-point (Fig. 7).

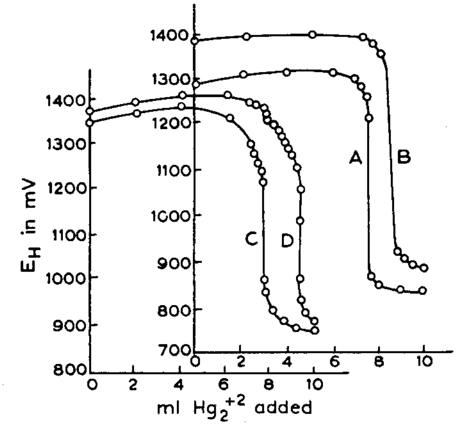

Fig. 7. Titration of 5 ml 0.1958 *N* $KMnO_4$ in varying volumes of 2% NaF and 2.5 ml 9 *N* H_2SO_4 with 0.1024 *N* $Hg_2(NO_3)_2$. A. 75 ml NaF and completed to 100 ml with H_2O, B. 5 ml NaF and completed to 100 ml with H_2O, C. 25 ml NaF and completed to 100 ml with H_2O, D. 10 ml NaF and completed to 100 ml with H_2O.

TABLE VI

Titration of 5 ml 0.1958 *N* $KMnO_4$ with 0.1024 *N* $Hg_2(NO_3)_2$ using varying quantities of 2% NaF in presence of 2.5 ml 9 *N* H_2SO_4

Volume of NaF used ml	*Volume of H_2O added ml*	*Volume of $Hg_2(NO_3)_2$ consumed ml*	*Theoretical end-point ml*	*Error %*	*Max. inflection mV/0.02 ml*
75	17.5	7.61	7.65	0.52	216
50	—	7.64	7.65	0.13	138
25	67.5	7.69	7.65	0.52	155
10	82.5	9.35 colourless	7.65	22.22	89

Effect of permanganate concentration

Amounts of manganese ranging from 1.3 mg up to 32 mg could be determined with reasonable accuracy (Table VII). The inflections at the end-points (Fig. 8) were sharp and generally increased as the permanganate concentration increased.

TABLE VII

Titration of $KMnO_4$ with $Hg_2(NO_3)_2$ in presence of 2.5 ml 9 *N* H_2SO_4 and 50 ml 2% NaF

$KMnO_4$ *ml*	*Titrated Mn* *mg*	*Vol. of $Hg_2(NO_3)_2$ consumed* *ml*	*Theoretical end-point* *ml*	*Error* *%*	*Max. inflection* *mV*
Titration of 0.1958 N $KMnO_4$ with 0.1024 N $Hg_2(NO_3)_2$					
5 [a]	10.755	7.64	7.65	0.13	138
5 [b]	10.755	7.65	7.65	0.00	199
5 [c]	10.755	7.58	7.65	0.93	210
15	32.265	23.04	22.95	0.39	171
Titration of 0.04814 N $KMnO_4$ with 0.0512 N $Hg_2(NO_3)_2$					
10	5.293	7.56	7.52	0.53	162
Titration of 0.02407 N $KMnO_4$ with 0.0256 N $Hg_2(NO_3)_2$					
10	2.647	7.55	7.52	0.4	238

[a] at 25°; [b] at 40°; [c] at 55°.

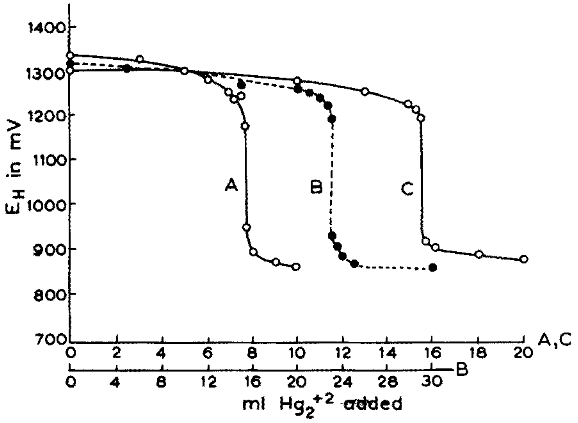

Fig. 8. Titration of different volumes of 0.1958 *N* $KMnO_4$ in 50 ml 2% NaF and 2.5 ml 9 *N* H_2SO_4 by 0.1024 *N* $Hg_2(NO_3)_2$, A. 5 ml $KMnO_4$, B. 15 ml $KMnO_4$, C. 10 ml $KMnO_4$.

Effect of temperature

The results in Table VII show that a rise of temperature caused some decomposition of potassium permanganate; early end-points were obtained at 55°. Accurate results, as in the reverse titration, could be obtained at ordinary temperatures or at 40°.

The redox potentials of the Mn^{+7}/Mn^{+3} system

The redox potentials of the Mn^{+7}/Mn^{+2} and the Mn^{+7}/Mn^{+4} system have been measured or calculated from free energy data. However, a value for the Mn^{+7}/Mn^{+3} couple is not known. This value can be found from the titration curves of perman-

TABLE VIII

Normality of H_2SO_4	—	0.24	0.39	0.75	1.38
Formal potential of the Mn^{+7}/Mn^{+3} system (V)	1.120	1.220	1.310	1.360	1.420
Normality of NaF	0.02	0.05	0.12	0.36	0.42
Formal potential of the Mn^{+7}/Mn^{+3} system (V)	1.400	1.410	1.390	1.310	1.310
Normality of H_2SO_4	—	0.15	0.36	0.69	2.25
Formal potential of the Hg^{+2}/Hg_2^{+2} system (V)	0.73	0.77	0.860	0.870	0.93
Normality of NaF	0.07	0.18	0.37	0.42	
Formal potential of the Hg^{+2}/Hg_2^{+2} system (V)	0.980	0.880	0.860	0.850	

ganate with the mercurous solution in the presence of fluoride. Trivalent manganese is kept in solution; the potential set by a bright platinum electrode when 50% of the permanganate has been reduced represents the formal redox potential of the system. The values shown in Table VIII indicate that the redox potential of the Mn^{+7}/Mn^{+3} increases with rise of acidity and decreases with increase of fluoride concentration.

From the titration curves of mercurous solutions with potassium permanganate, the formal redox potential of the mercuric/mercurous couple can be evaluated. From the data shown in Table VIII it is apparent that the redox potential again increases with rise of acidity and decreases with increase of fluoride concentration. (These points will be investigated later).

SUMMARY

Mercury(I) can be titrated potentiometrically with permanganate in the presence of fluoride and sulphuric acid. The optimum conditions are 2.5–10 ml of 9 *N* acid and 10–100 ml of 2% sodium fluoride at a temperature of 25–40°. Larger amounts can be determined than in the visual method, although copper (II) is a suitable indicator screen in the titration of fairly large amounts. The reverse titration is also satisfactory; the optimum conditions are 1.5–4 ml of 9 *N* acid and 25–75 ml of 2% fluoride at 25–40°. The formal redox potential of the Mn^{+7}/Mn^{+3} couple is 1.4 V, in presence of 1.38 *N* H_2SO_4 and 0.12 *N* NaF.

RÉSUMÉ

Les auteurs proposent un titrage potentiométrique du mercure(I) au moyen de permanganate, en présence de fluorure et d'acide sulfurique. Inversément le permanganate a pu être titré aussi, avec succès, par une solution de mercure(I).

ZUSAMMENFASSUNG

Zur Bestimmung von Quecksilber(I) wird die potentiometrisch Titration mit Permanganat in Gegenwart von Fluorid und Schwefelsäure empfohlen. Umgekehrt lässt sich auch Permanganat mit Quecksilber(I) nach dieser Methode bestimmen.

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THE RAPID ANALYSIS OF SILICA IN REFRACTORIES AND MINERALS

AN IMPROVED METHOD OF SAMPLE PREPARATION

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INTRODUCTION

Rapid semi-micro photometric procedures for the determination of silica in refractories and minerals are well established. A simple method for the dissolution of siliceous materials prior to colorimetric estimation of silica is required.

The following methods of sample preparation have been reported. RILEY[1] fused the sample with sodium hydroxide in a silver crucible at 800 – 850°. SHAPIRO AND BRANNOCK[2] and ARCHER *et al.*[3], fused the sample with sodium hydroxide in a nickel crucible and leached the fusion overnight with water. The range of materials decomposed was limited and the time required for water-leaching excessive. The contamination by nickel and silver salts was undesirable and the crucibles were appreciably attacked and difficult to clean.

HARPHAM[4] recommended sodium peroxide fusions for certain minerals resistant to decomposition by other methods. Finely powdered materials (240-B.S. sieve) were completely decomposed when sintered for 7 min at 480° ± 10° in an electric muffle furnace. Either acidification or 50–100 ml of cold water, completely and rapidly dissolved the cake. The sintering was effected in platinum crucibles without any attack on the platinum, or in iron or nickel vessels with insignificant attack on the metal. It was also reported that many substances were decomposed at 200° with even less attack on the vessels. Extremely resistant minerals were decomposed by fusion with sodium peroxide at the lowest possible temperature using iron, nickel or platinum crucibles. PETRETIE[5] recommended the use of zirconium crucibles because they were extremely resistant to sodium peroxide fusions. Sodium peroxide treatment was considered to be most satisfactory because a wide range of materials were decomposed and water extraction was rapid.

Procedures for the estimation of silicon are described in the literature. These methods are based on the measurement of the yellow colour of silicomolybdic acid or on the blue colour of reduced silicomolybdic acid. KNUDSON, JUDAY AND MELOCHE[6] showed that in sulphuric acid medium, maximum colour development of silicomolybdate occurred at a pH of 1.6 – 2.0. The silicomolybdate formation was shown to be complete within 5 min and phosphate was the main interfering ion. KAHLER[7] used sodium sulphite as a reducing agent for silicomolybdate. LINDSAY AND BIELENBERG[8] used 1-amino-2-naphthol-4-sulphonic acid together with sulphite as reducing agent.

BUNTING[9] stated that the blue reduction colour was stable for several days when tartaric acid was used to prevent iron and phosphate interference and 1-amino-2-naphthol-4-sulphonic acid together with sulphite was used as the reducing agent.

EXPERIMENTAL AND DISCUSSION

A wide range of materials such as coal ash, slags, clays, ores, and refractories were readily decomposed by sintering with sodium peroxide in a platinum crucible. When sintering with sodium peroxide the average platinum loss was 0.5 mg, compared with 1–2 mg for a normal sodium carbonate fusion. The crucible was easily cleaned and the sintered mixture dissolved readily in water.

The concentration of sulphuric acid was controlled in order to obtain the maximum colour development and highest stability of the molybdenum blue reduction compound. The blue colour was stable for at least two days.

It was found that undecomposed peroxide interfered in the determination of silicon. The interference when using 0.075 mg silicon and 6.5 ml of 0.5% v/v sulphuric acid per 100 ml of assay is shown in Table I.

TABLE I

INTERFERENCE OF PEROXIDE

mg Na_2O_2	0.0	0.2	0.4	0.6	0.8	1.0	4.0	8.0	16.0[a]
Absorbance	0.572	0.573	0.574	0.574	0.573	0.574	0.536	0.434	0.281

[a] 16 mg of Na_2O_2 corresponds to 1.5 g of undecomposed peroxide in the original sample.

The peroxide interference appeared to be caused by the formation of a complex with ammonium molybdate. This interference could not be eliminated by increased ammonium molybdate addition. The peroxide interference was eliminated by the addition of potassium permanganate to the warm solution and the subsequent removal of the excess with dropwise additions of 1 volume hydrogen peroxide. The interference study shows that 1 mg of sodium peroxide can be tolerated, and in the suggested procedure one drop excess of hydrogen peroxide is equivalent to only 0.035 mg of sodium peroxide.

Aliquots taken from this preparation are also suitable for the determination of Al_2O_3, TiO_2 and Fe_2O_3 using the procedures of ARCHER *et al.*[3]

APPARATUS AND REAGENTS

Apparatus

Muffle furnace capable of maintaining a temperature of 500° ± 5°. *Polyethylene* ware should be used wherever possible. *Volumetric flasks*[10] should be reserved for this work only and treated as described to prevent silicon contamination. Clean overnight in chromic–sulphuric acid, rinse, and then fill overnight with 1 : 1 sulphuric–nitric acid which will render them insoluble. Rinse with distilled water. When not in use the flasks should be left filled with distilled water.

Reagents

Sodium peroxide, powdered AnalaR; 25% v/v sulphuric acid A.R.; 5% v/v sulphuric acid A.R.; 3.6% w/v potassium permanganate A.R. solution; 0.3% w/v hydrogen peroxide A.R. (1 volume); 1.5% w/v ammonium molybdate solution, dissolve 15.0 g of ammonium molybdate A.R. in 250 ml of water, add 200 ml of 5% sulphuric acid and dilute to 1000 ml with water; 8% w/v tartaric acid A.R. solution; reducing solution, dissolve 0.70 g of sodium sulphite A.R. in 20 ml of water, add 0.15 g of 1-amino-2-naphthol-4-sulphonic acid and stir until dissolved, dissolve 9.0 g of sodium metabisulphite A.R. in 180 ml of water and mix both solutions. Fresh reducer should be prepared each week.

RECOMMENDED PROCEDURE

Weigh 50 mg of finely ground sample (240 B.S. sieve) into a platinum crucible and mix with 1.0 g of powdered sodium peroxide using a platinum wire. Cover the mixture with a layer of 0.5 g of sodium peroxide and place in a muffle furnace at 500° and sinter for ten minutes. The temperature should not be allowed to exceed 500° because of accelerating attack on the platinum by molten sodium peroxide at higher temperatures.

Allow the crucible to cool, cover with a lid and half-fill with water. After the reaction has ceased and the crucible is cool, add 5.0 ml of 25% sulphuric acid. Add the contents of the crucible to a 200-ml plastic bottle containing 25.0 ml of 5% sulphuric acid and 15 ml of water. Leach the crucible with 15.0 ml of hot 5% sulphuric acid, scrub with a rubber policeman, and add the washings to the bottle.

Warm the bottle to 90° on a water bath and add 3.6% potassium permanganate solution dropwise until the solution is pink. Excess peroxide will be destroyed. Just decolourize the solution with the dropwise addition of 1 volume hydrogen peroxide solution. Cool and dilute to 1 litre. Store in a polyethylene bottle.

Transfer 2 × 10-ml aliquots to 100-ml volumetric flasks. A calibration series may be prepared by adding standard silicon solution to 10-ml aliquots of a blank which has been carried through the procedure.

Add 50 ml of water to standards, assays and blanks.

Assays

Add 5 ml of 1.5% ammonium molybdate solution, swirling during the addition. Allow to stand 10 min. Add 5 ml of 8% tartaric acid solution, mix and add 2.0 ml of reducing solution immediately. Mix and dilute to volume at once. Allow to stand 1 h for colour development.

Blanks

Add 5 ml of 8% tartaric acid, mix. Add 2.0 ml of reducing solution and mix. Add 5 ml of 1.5% ammonium molybdate solution, mix, dilute to volume and allow to stand 1 h.

Read the absorption at a wavelength of 813 mμ using a 10-ml aliquot and a 2-cm cell, samples containing 8–34% silicon obey Beer's law.

ACKNOWLEDGEMENT

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SUMMARY

A method of dissolution of siliceous material has been proposed, together with a method for the subsequent colorimetric estimation of silica as the molybdenum blue reduction compound. The finely ground samples are sintered at 500° with powdered sodium peroxide in platinum crucibles, the mixture extracted with water, and acidified. Excess peroxide is removed by oxidation with potassium permanganate. Silica is determined by reduction of yellow silicomolybdic acid with 1-amino-2-naphthol-4-sulphonic acid to the blue reduction compound. Phosphates and iron are masked with tartaric acid. The sample solution may also be used for the colorimetric determination of alumina, ferric oxide, and titania.

RÉSUMÉ

Une méthode rapide est proposée pour le dosage de la silice dans des substances réfractaires et dans des minerais. L'attaque se fait par fusion au peroxyde de sodium; la silice est finalement dosée colorimétriquement, après réduction de l'acide molybdique en bleu de molybdène, au moyen de l'acide amino-1-naphthol-2-sulfonique-4.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur raschen Bestimmung von Silizium in Mineralien und keramischen Massen. Nach Aufschluss der Substanz durch Erhitzen mit Natriumperoxyd auf 500° im Platintiegel wird das Silizium kolorimetrisch bestimmt.

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THE POLAROGRAPHIC DETERMINATION OF HEXAVALENT URANIUM IN THE PRESENCE OF EXCESS FERRIC IRON

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FURMAN AND HAIGHT[1] have reported that uranyl ions give a wave at —0.5 V (*vs.* S.C.E.) in 0.01 *M* sodium fluoride and at —1.10 V in 1.0 *M* sodium fluoride. They also state that while ferric ions give a wave at —0.58 V in 0.01 *M* sodium fluoride, no wave due to iron is found when using the stronger supporting electrolyte.

WEST, DEAN AND BREDA[2] have shown that sodium fluoride forms a complex with ferric iron which is so stable that the reduction potential is shifted to values more negative than the discharge potential of the sodium ions in the supporting electrolyte. Their observation is supported by VERDIER *et al.*[3,4] and by recent work in these laboratories[5]. On the other hand various workers[6–10] have reported waves due to the reduction of ferric ions in fluoride media. Unfortunately, in most cases, the exact experimental conditions are not stated, and it is therefore difficult to compare the results

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of the various authors. As is shown later, pH, for example, has a large effect on the reduction of uranyl ions, and it is therefore a pity that much published work is rendered of little value to others by the lack of essential details. A review of published work has recently been compiled by one of the authors[5].

This investigation was undertaken in order to determine whether the use of sodium fluoride as a supporting electrolyte would enable the rapid, quantitative estimation of hexavalent uranium in the presence of excess iron, with the aim of extension to the analysis of the "pregnant liquors" of the uranium mining industry, where uranyl ions must be determined in the presence of an approximately 200 fold excess of iron.

EXPERIMENTAL

Reagents

All reagents were tested to determine their polarographic purity. The sodium fluoride used was found to contain a small amount of lead (0.002%) which was not removed as the wave due to this impurity was only observed at high sensitivities; (20 mm/μA or higher, waveheight 0.02 μA) and, moreover, did not interfere with the determination of uranium.

In all cases, the uranium solutions were prepared by dilution of an exactly $1 \cdot 10^{-2}$ *M* solution of uranyl nitrate, standardised by the gravimetric procedure of precipitation as ammonium diuranate and ignition to U_3O_8.

Apparatus

All curves were recorded using a Cambridge pen-recording polarograph. The cells used were of the Cambridge 2-ml type, carrying an S.C.E., separated from the solution by means of an agar bridge, as a reference electrode.

pH measurements were made with a Beckman model H-2 meter with a Beckman glass electrode as indicator and an S.C.E. as reference.

Procedure

Polarograms were recorded at 25.0 ± 0.05°.

Oxygen was removed from the test solution by bubbling nitrogen for 10 min before recording. The capillary used had a mean drop-time of 3.64 sec/drop at zero applied potential and an *m* value of 0.001854 g/sec. 0.004% gelatin was used as a maximum suppressor.

Unless otherwise stated, the pH of the test solutions was 6.5 or greater, and the supporting electrolyte was 0.75 *M* sodium fluoride. To obtain these conditions solutions of iron and uranium of pH between 2.5 and 3.0 were diluted ten times with 0.8333 *M* sodium fluoride. If the original pH is below the limit stated above, the pH after addition of the fluoride solution is less than 6.5.

The reduction of uranyl ions alone in sodium fluoride

Although FURMAN AND HAIGHT[1] report only one wave for uranyl ions in 0.01 and 1.0 *M* sodium fluoride, it was found that, provided the pH of the test solution was 6.5 or greater, uranyl ions in 0.1, 0.25, 0.5 and 0.75 *M* sodium fluoride gave rise to two waves before the discharge potential of sodium ions. The waves tend to coalesce and the diffusion current plateau of the first wave ($E_{\frac{1}{2}}$ close to —0.65 V) is hardly developed. The second wave ($E_{\frac{1}{2}}$ close to —0.95 V), which is approximately twice the height of the first, has a well defined diffusion current plateau. These waves both correspond to an irreversible reduction process at the dropping mercury electrode, and the voltage span covering the two waves is —0.5 to —1.2 V. The half-wave potential of the first wave becomes slightly less negative with decreasing uranyl ion concentration, particularly below a concentration of 10^{-4} M, whereas that of the second wave remains constant. In all cases, and unlike ferric iron waves at low fluoride concentrations[5], the combined height of the two waves was time independent, remaining constant for periods of 12 hours.

As it is not possible to measure accurately the start of the second wave, any quantitative method for determination of uranyl ions must be based on the measurement of the sum of the diffusion currents of both waves. All wave-heights reported are therefore measured at —1.4 V and are the combined wave-heights of the two uranyl waves.

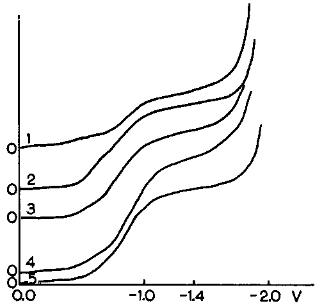

Fig. 1. Typical UO_2^{+2} curves. Curve 1. 10^{-4} M UO_2^{+2} in 0.75 M NaF, Sens. 1/10, Curve 2. 10^{-3} M UO_2^{+2} in 0.25 M NaF, Sens. 1/50, Curve 3. 10^{-3} M UO_2^{+2} in 0.75 M NaF, Sens. 1/50, Curve 4. $6 \cdot 10^{-4}$ M UO_2^{+2} in 0.75 M NaF, Sens. 1/20, Curve 5. $5 \cdot 10^{-3}$ M UO_2^{+2} in 0.75 M NaF, Sens. 1/200.

The behaviour of various concentrations of uranyl ions in 0.1, 0.25, 0.5 and 0.75 M sodium fluoride was studied. In all cases the pH of the test solution was greater than 6.5 and the measured wave-height decreased regularly with decreasing uranyl ion concentration between $5 \cdot 10^{-3} M$ and 10^{-5} M. The optimum range was found to be 10^{-4} to 10^{-3} M over which lineality existed. Concentrations of uranyl ion below $5 \cdot 10^{-5}$ M gave wave heights of less than 0.1 μA which were not considered analytically useful.

Typical polarograms are shown in Fig. 1, while Fig. 2 shows the relation between

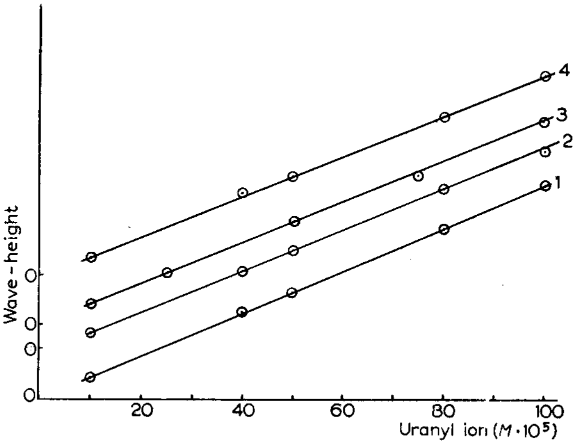

Fig. 2. Variation of wave-height with uranyl ion concentration. The zero wave-height of each curve is marked on the ordinate. Curve 1. 0.10 M NaF; 2. 0.25 M NaF; 3. 0.50 M NaF; 4. 0.75 M NaF.

wave-height and concentration of uranyl ion in the range 10^{-4} to 10^{-3} *M* for the various concentrations of supporting electrolyte used.

Effect of pH

Polarograms of 10^{-3} *M* uranyl nitrate in 0.5 and 0.75 *M* sodium fluoride, with various amounts of added hydrochloric acid, were recorded to observe the effect of pH on the curves. An effective buffering action was observed in this pH variation and was pronounced below a pH value of 5, as would be expected from the formation of the weak undissociated acid, hydrogen fluoride. The uranyl waves were found to be pH independent only when the pH of the test solution was 6.5 or higher. Since the reduction of hexavalent uranium involves hydrogen ions, it would be expected that any lowering of the pH would cause marked changes in the uranyl waves. From typical curves shown in Fig. 3, the great influence of pH on (*a*) the number of waves formed, (*b*) the half-wave potentials of these waves, and (*c*) the wave-heights for a given concentration of uranyl ion, may be seen. Although the wave-heights are greater, the adverse effects of acid solutions of sodium fluoride on the glass of the dropping mercury electrode, and the necessity for very accurate control of pH when this less than 6.5, made it desirable to work in neutral solution. All subsequent curves were thus recorded on solutions of pH in the range 6.5 to 7.8.

Since the large increase in wave-height of solutions having pH between 6.5 and 6.0 was also observed in uranyl acetate solutions acidified with hydrochloric acid, it does not seem that this increase in wave-height can be due to the well known effect[11] of nitrate ions on uranium waves.

Complexing of iron(III) by sodium fluoride

Recent studies in these laboratories[5] have shown that the use of 0.45 *M* sodium fluoride as a supporting electrolyte removes waves due to ferric iron up to a concentration of $2 \cdot 10^{-3}$ *M*. It was also shown that the efficient removal of these waves depended mainly on a high fluoride to ferric ion ratio. It was, therefore, decided to investigate the use of 0.75 *M* sodium fluoride as a supporting electrolyte, since weaker concentrations would not only prove less effective in complexing ferric ions, but would also have a less pronounced neutralising effect on acid solutions.

Efficient complexing of ferric ions by sodium fluoride does not occur unless the pH of the iron solution is between 2 and 3 before addition of the fluoride[4,5]. The amount of ferric ion which can be complexed by a particular sodium fluoride solution is thus limited by the pH of that solution (and therefore by the ionic concentration of the solution) as well as by the ratio of fluoride to ferric ions.

Using 0.75 *M* sodium fluoride as a supporting electrolyte it was found that waves due to ferric iron were not present up to a concentration of $5 \cdot 10^{-2}$ *M*.

Determination of uranium in the presence of excess ferric iron

Polarograms of 10^{-4} *M* uranyl nitrate and various concentrations of ferric iron in 0.75 *M* sodium fluoride were recorded. Table I shows the results obtained for the determination of uranium in these samples. In this series no acid was added to the solutions, so that it can be seen that simple polarography of uranyl and ferric ion mixtures in 0.75 *M* sodium fluoride allows the determination or uranium in the presence of up to a 400 times excess of ferric iron.

The precipitate of the complex fluoroferrate which forms on adding fluoride ions to ferric ions need not be filtered off before recording the polarogram as it has been shown[5] not to affect the result.

TABLE I

DETERMINATION OF UO_2^{+2} IN PRESENCE OF Fe^{+3}

Conc. UO_2^{+2} *taken (M)*	*Conc.* Fe^{+3} *(M)*	*Conc.* UO_2^{+2} *found (M)*	*Remarks*
$1 \cdot 10^{-4}$	—	$1 \cdot 10^{-4}$	
$1 \cdot 10^{-4}$	$1 \cdot 10^{-2}$	$1.03 \cdot 10^{-4}$	
$1 \cdot 10^{-4}$	$2 \cdot 10^{-2}$	$0.98 \cdot 10^{-4}$	
$1 \cdot 10^{-4}$	$3 \cdot 10^{-2}$	$0.98 \cdot 10^{-4}$	
$1 \cdot 10^{-4}$	$4 \cdot 10^{-2}$	$1.02 \cdot 10^{-4}$	
$1 \cdot 10^{-4}$	$5 \cdot 10^{-2}$	$1.14 \cdot 10^{-4}$	pH of test solution 6.3
$1 \cdot 10^{-4}$	$6 \cdot 10^{-2}$	$1.18 \cdot 10^{-4}$	pH of test solution 6.2
$1 \cdot 10^{-4}$	$7 \cdot 10^{-2}$	$1.64 \cdot 10^{-4}$	pH of test solution 6.1

Determination of uranium in the presence of acid and excess ferric iron

Since efficient complexing of ferric ions occurs between pH 2.0 and 3.0, any excess hydrogen ion present in the samples must necessarily be removed before addition of the supporting electrolyte. In order that the pH of all test solutions need not be strictly controlled to a constant value, this pH range must be narrowed to 2.5 to 3.0 in the procedure used. Under these conditions, addition of the sodium fluoride not only complexes the iron but also gives a final pH of 6.5 or greater.

Attempts at pH correction, by addition of hydroxyl ions at various stages in the preparation of the test solution, and by the use of buffer solutions, were not satisfactory. It was found that the elimination of pH effects, in samples containing added acid, was most conveniently achieved by evaporation of the solution to dryness before addition of the sodium fluoride supporting electrolyte. If the acidity is not due to either nitric or hydrochloric acid, it is recommended that the elements be precipitated as hydroxides, washed with water and then dissolved in the minimum amount of 20% nitric acid before evaporation to dryness. Baking on a hot plate of surface temperature about 140° for 2–4 min when dry, not only ensures complete volatilisation of any acid, but also removes some of the iron by decomposition of ferric nitrate to the insoluble oxide. Decomposition of the uranyl salt does not occur in this short time. Longer baking, however, results in some loss of uranyl ion by decomposition and a subsequent decrease in the height of the uranyl wave. Table II shows results obtained for various mixtures. The standard deviation of the method is 2.0%.

Interferences

Apart from the presence of molybdenum and vanadium, the effect of which has already been reported[1], the effect of the presence of Ti^{+3}, Mn^{+2}, Cu^{+2} and Pb^{+2} was studied. Fig. 4 shows polarograms of uranyl mixtures containing these ions.

TABLE II

DETERMINATION OF UO_2^{+2} IN PRESENCE OF EXCESS Fe^{+3} AND H^+

Conc. of UO_2^{+2} taken (M)	*In presence of*	*Conc. of UO_2^{+2} found (M)*	*Diff. %*
$1 \cdot 10^{-4}$	$4 \cdot 10^{-2}$ *M* Fe^{+3} 2 *N* HCl	$0.975 \cdot 10^{-4}$	—2.5
$1 \cdot 10^{-4}$	$4 \cdot 10^{-2}$ *M* Fe^{+3} 4 *N* H_2SO_4	$0.981 \cdot 10^{-4}$	—1.9
$1 \cdot 10^{-4}$	$4 \cdot 10^{-2}$ *M* Fe^{+3} 1 *N* HNO_3	$0.985 \cdot 10^{-4}$	—1.5
[a] $1 \cdot 10^{-3}$	$4 \cdot 10^{-1}$ *M* Fe^{+3} 2 *N* HCl	$0.982 \cdot 10^{-3}$	—1.8

[a] Solutions diluted ten times before evaporation to dryness.

Only titanium ($E_{\frac{1}{2}}$ —1.22 V) gives a wave within the voltage span of the uranium waves. The half-wave potential of Mn^{+2} (—1.54 V) is sufficiently negative to enable the tolerance of at least a 400 times excess in the presence of 10^{-4} *M* uranyl ion. Cupric ions are reduced at approximately —0.3 V so that their presence provides no difficulty unless they occur in excess. Lead should be previously largely removed as the sulphate if a precipitate of lead fluoride is to be avoided on addition of the supporting electrolyte. This is probably unimportant if the concentration of lead is of the order of 10^{-3} *M*, since the small reduction in concentration of the supporting electrolyte has been shown to make no difference to the wave-height of the uranyl wave, and since the lead fluoride may be removed from the test solution by filtration.

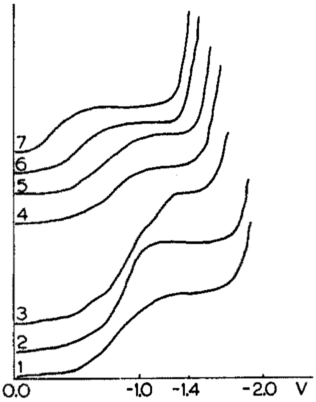

Fig. 3. Effect of pH on UO_2^{+2} curves: All curves on 10^{-3} *M* UO_2^{+2} in 0.5 *M* NaF; pH varied using HCl. Curves 1 – 3, Sens. 1/50; 4 – 7, Sens. 1/100. Curves 1 – 7 pH's of resp. 7.5, 6.4, 5.1, 4.3, 3.5, 2.3 and 1.4.

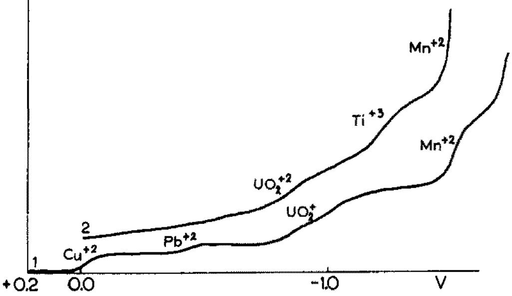

Fig. 4. 1. Polarogram of 10^{-4} *M* UO_2^{+2} in 0.75 *M* NaF in the presence of $5 \cdot 10^{-4}$ *M* Ti^{+3} and 10^{-3} *M* Mn^{+2}. Sensitivity 1/20. 2. Polarogram of a mixture of 10^{-3} *M* UO_2^{+2}, 10^{-3} *M* Cu^{+2}, 10^{-3} *M* Mn^{+2}, 10^{-3} *M* Pb^{+2} made up in 0.75 *M* NaF and filtered before recording. Sensitivity 1/100.

CONCLUSIONS

1. The rapid polarographic determination of hexavalent uranium, within the concentration range 10^{-3} to 10^{-4} M, and in the presence of up to 400 times excess of ferric iron and even larger amounts of free acid, is possible using 0.75 M sodium fluoride as a supporting electrolyte.

2. The presence of Cu^{+2}, Pb^{+2}, Mn^{+2} does not interfere with the procedure if they occur in amounts stated above. The presence of Ti^{+3}, or other interfering elements, would, however, necessitate prior separation, thus robbing the method of its simplicity and rapidity.

3. When using a dropping mercury electrode it is best to work in neutral fluoride solution (pH 6.5 or greater).

4. The standard deviation of the method is 2.0% so that determinations can be made with 95% confidence to an accuracy of 4.0%.

5. The method should prove applicable to the determination of uranyl ions in the "pregnant liquors" of the uranium mining industry. An investigation into this possibility is being undertaken and it is hoped to publish results shortly.

ACKNOWLEDGEMENTS

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SUMMARY

It is shown that concentrations of uranyl ions varying from 10^{-4} M to 10^{-3} M may be rapidly determined polarographically, to an accuracy of 4% (95% confidence), in the presence of concentrations of ferric iron up to four hundred times in excess of the uranyl ion concentration. The determination is insensitive to the concentration of the 0.75 M sodium fluoride used as a supporting electrolyte, and to time; but is not valid if the pH of the test solution is below 6.5. The ions Cu^{+2}, Pb^{+2} and Mn^{+2} are shown not to interfere, while Ti^{+3} must be removed.

RÉSUMÉ

Les auteurs ont examiné et mis au point une méthode de dosage polarographique de l'uranium(VI) en présence d'un excès de fer(III). On peut ainsi doser des teneurs en ions UO_2^{+2} de 10^{-3} à 10^{-4} M, en présence de fer(III) en très fortes concentrations, jusqu'à 400 fois celle de l'uranyle.

ZUSAMMENFASSUNG

Es wird eine Methode beschrieben zur polarographischen Bestimmung von Uran(VI) in Gegenwart eines Überschusses an Eisen(III), der das 400 fache der vorhandenen Menge Uran betragen kann. Der Einfluss von Fremdionen wird erwähnt.

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CONTROLLED POTENTIAL COULOMETRIC DETERMINATION OF TIN

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Although tin has been determined several times by controlled potential gravimetric procedures[1,2] a coulometric determination has not been previously reported. The known polarography of tin indicates that coulometric analysis should be feasible in halide media. Reduction of tin(IV) takes place stepwise, to the metal, on a mercury cathode, and coulometric analysis at both reduction stages was undertaken.

EXPERIMENTAL TECHNIQUE

Apparatus

The electrolysis cell (100-ml capacity and with mercury cathode of 16.7 cm^2 area) was the same as that described by LINGANE[3]. Tall-form electrolysis beakers were employed when gold cathodes were used. A constant speed mechanical stirrer was used, with stirring blades adjusted to keep the mercury-solution interface in rapid but smooth motion. Oxygen was excluded by passing a stream of nitrogen through the solution, prior to, and during electrolysis.

The anode was a platinum electrode (1 cm^2) isolated from the test solution by enclosure in a glass tube with a sintered glass bottom. The anolyte (2 *M* sulfuric acid) was maintained at a higher level than the solution in the cathode chamber.

A potentiostat[3] was used to maintain automatically the potential of the cathode at a constant value in reference to a saturated calomel electrode. The quantity of electricity consumed was measured with a hydrogen–nitrogen gas coulometer[4]. A more convenient coulometer which may be employed is the d.c. motor integrator[5]. Current measurements were made with a calibrated multi-ammeter in series with the cathode.

Procedure

The supporting electrolyte (3 *M* sodium bromide, 0.3 *N* hydrochloric acid) alone was placed in the cell, dissolved air was removed with purified nitrogen and the solution was subjected to a preliminary electrolysis with the potential of the cathode at —0.80 V *vs.* S.C.E., to remove traces of reducible impurities. This pre-electrolysis was continued until a small, constant, residual current was observed. The potentiostat was then set to maintain the potential of the cathode at the value used in the determination (—0.40 V *vs.* S.C.E. for reduction of tin(IV) to tin(II), —0.70 V *vs.* S.C.E. for reduction of tin(II) to the metal), the sample solution was added, and the

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electrolysis was allowed to proceed under automatic control until the current decreased to a constant, minimal value. The total quantity of electricity passed, the electrolysis duration, and the final current were noted.

Correction for the quantity of electricity associated with the background current was applied by assuming the final electrolysis current was constant throughout the electrolysis.

When a tin amalgam electrode was used, a similar procedure was followed, except that the tin solution, entirely in the stannic form, was stirred with the amalgam several minutes before electrolysis to reduce the tin(IV) to tin(II). The results were calculated as in the previous case, taking into account that twice as much tin was electrolyzed as was introduced. Tin amalgam was prepared by shaking an excess of pure granulated tin (20 to 40 mesh) with mercury, under dilute hydrochloric acid, until a saturated amalgam was obtained.

RESULTS AND DISCUSSION

The investigation of the electrogeneration of stannous tin as a coulometric titrant[6] showed that reduction of stannic tin takes place with 100% current efficiency at a gold electrode in solutions containing a high concentration of bromide ion. This generation of tin(II) for coulometric titration was performed with a large and constant stannic tin concentration (0.2 *M*) at a small electrode. Controlled potential reduction of tin(IV) involves much smaller tin concentrations (0.03 *M*) and relatively large electrodes. These conditions have the effect of increasing the residual current relative to the stannic ion reduction current, causing the reduction to proceed at decreased current efficiency, and necessitating large residual current corrections. In Table I are shown some typical results for the reduction of stannic to stannous tin at gold electrodes.

The current decay during controlled potential electrolysis usually follows the expression[3]:

$$i = i_0 \; 10^{-kt} \qquad (1)$$

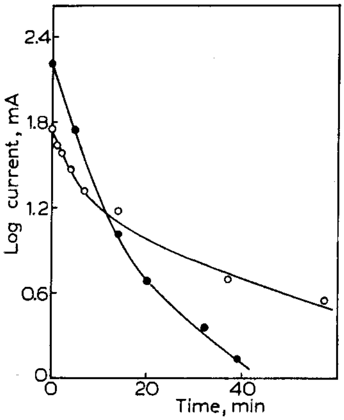

Fig. 1. Typical log current–time curves for the controlled potential electrolysis of tin(IV) at a gold electrode (*ca.* 72 cm²) in 3 *M* sodium bromide and 0.4 *N* hydrochloric acid. About 55.9 mg of stannic tin was reduced at a potential of —0.40 V *vs.* S.C.E.

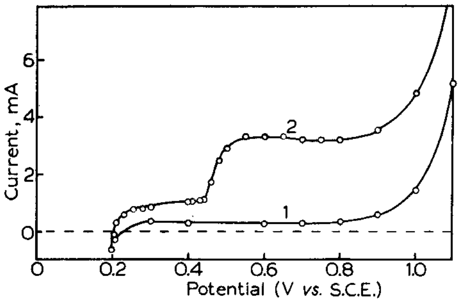

Fig. 2. Current–potential curves for the reduction of tin(IV) on a stirred mercury pool (*ca.* 16.7 cm²). (1) 3.2 *M* sodium bromide and 0.2 *N* hydrochloric acid alone. (2) supporting electrolyte containing 0.002 *M* stannic chloride.

where i is the current at time t, i_0 is the initial current, and k is a constant, whose magnitude depends upon the stirring rate, electrode area, solution volume and temperature. Typical log current *vs.* time curves for the reduction of tin(IV) at a gold cathode are shown in Fig. 1. The initial slope of these curves was used to calculate the k values quoted in Table I. From this k, predicted by the initial slope, (0.061 min^{-1}), the reaction would be predicted to be 99.9% complete in about 50 min. It is evident that the electrolysis does not follow equation (1) however, since the curves deviate significantly from linearity. The decrease of slope of the curves, which occurs after more than 80% of the reduction is complete, is primarily responsible for the long electrolysis durations.

TABLE I

COULOMETRIC DETERMINATION OF TIN ON GOLD ELECTRODES

The solution was 2–3 *M* in sodium bromide and 0.3–0.6 *N* in hydrochloric acid. Control potential —0.40 V *vs.* S.C.E. (55.91 mg Sn taken)

Trial	*Volume (ml)*	*Initial current (mA)*	*Final residual current (mA)*	*Electrolysis duration (h)*	*Amount Sn found (mg)*	*k (in min^{-1}) $\times 10^2$*
1[a]	60	11	0.4[c]	13.8	56.18	0.2
2[a]	25	18	0.8[c]	12.1	60.06	0.4
3[b]	100	165	2.2	2	64.33	7.8
4[b]	100	80	0.5	8.3	54.06	6.1
5[b]	100	145	0.3	12	55.84	7.2
6[b]	115	56	1.0	8	54.71	6.3
7[b]	83	22	1.0	9	48.24	4.6
				mean = 56.20 ± 3.71		
				% error = 0.5%		

[a] 14.7 cm^2 flat gold electrode.

[b] 72 cm^2 gold-plated platinum gauze, cylindrical, electrode.

[c] Background current corrections made on the basis of the *pre*-electrolysis residual current (0.064 mA). Correction on the basis of postelectrolysis current would yield very low results.

Deviation of log current *vs.* time curves from linearity has been shown[7] to be caused by kinetic complications of the electrode reactions, such as secondary or competing chemical reactions. The curvature of the curves in this case might be caused by some constant reoxidation of stannous ion at the gold electrode (an example of case IIc, Ref.[7]), which would also give rise to a larger residual current during and following the electrolysis than before it[8]. Correction by assuming a constant background current, equal to the post-electrolysis current, would lead to overcorrection for the background current, and negative errors. Assumption of constant background current equal to pre-electrolysis current causes undercorrection and positive errors.

Another possible kinetic complication might be the presence of two tin complexes in sluggish equilibrium with each other; the reduction at the given electrode potential proceeding through only one of the forms. After most of the easily reducible form has reacted, the rate of the electrode reaction will be governed by the slow, equilibration, step. This would lead to a decrease in the slope of the log current–time curves and anomalously long and varying electrolysis durations.

Therefore, although a coulometric determination of tin based upon the reduction of stannic to stannous tin at a gold electrode is possible, the results obtained are neither very precise, nor very accurate. A large degree of uncertainty is introduced by the background current corrections, which often amounted to 20% of the total coulombs consumed, because of the long electrolysis durations.

Electrolysis of tin(IV) on a mercury cathode offers the advantages of lower residual currents, shorter electrolysis durations by the use of smaller solution volumes and efficient stirring, and the possibility of carrying out a second reduction step, that of stannous ion to tin (amalgam). A current–potential curve for the reduction of tin(IV) at a large mercury pool electrode is shown in Fig. 2. This curve is quite similar to polarograms of tin(IV) taken with a d.m.e.[9]. Since mercury reduces stannic tin in a bromide medium, the first wave corresponds to the reduction of a mercury species (*e.g.* $HgBr_4^{-2}$) rather than tin(IV).

Electrolysis of tin(IV) solutions on a mercury cathode were performed by electrolysis at both —0.40 and —0.70 V *vs.* S.C.E., and typical results of this two-step reduction are shown in Table II. Although the first reduction step is 2.4% incomplete, the second reduction, to tin amalgam, is complete and accurate. The stannic tin is reduced directly by the mercury and the first electrolysis at least partially involves reduction of a mercury species. Apparently some mercury species (*e.g.* Hg_2Br_2) is present which remains unreduced, even at a potential of —0.70 V *vs.* S.C.E. The second reduction step, stannous ion to tin amalgam, is rapid and quantitative, and therefore has greater analytical applicability.

TABLE II

COULOMETRIC DETERMINATION OF TIN ON MERCURY CATHODE

The solution was 3 *M* in sodium bromide and 0.3 *N* in hydrochloric acid, with a volume of 30 ml (46.02 mg tin taken)

Control potential (V vs. S.C.E.)	*Initial current (mA)*	*Residual current (mA)*	*Electrolysis duration (h)*	*Amount Sn found (mg)*
—0.40	50	0.25	3.5	45.15
—0.70	205	0.35	2.1	46.09
—0.40	88	0.25	2.5	45.31
—0.70	240	0.35	2.0	46.33
—0.40	74	0.35	2.5	44.29
—0.70	190	0.55	2.5	45.85

mean = step 1: 44.92 ± 0.42
% error = —2.4%
step 2: 46.09 ± 0.24
% error = +0.15%

To eliminate the time-consuming primary reduction step, a tin–amalgam cathode was employed. An investigation in this laboratory has shown[10] that tin–amalgam completely reduces tin(IV) to tin(II), producing an equivalent quantity of tin(II), in a bromide medium. Of course in the presence of other substances which are reduced by tin–amalgam, a mercury cathode must be used. Typical results in Table III demonstrate that 20 to 50 mg of tin in a volume of 30 ml can be determined with an average

TABLE III

COULOMETRIC DETERMINATION OF TIN ON TIN–AMALGAM CATHODE

Electrode potential = —0.70 V *vs.* S.C.E.
The solution was 3.3 *M* sodium bromide and 0.2 *N* hydrochloric acid, with a volume of 30 ml

Initial current (mA)	*Residual current (mA)*	*Electrolysis duration (hours)*	*Amount Sn taken (mg)*	*Amount Sn found (mg)*
300	0.08	3.5	23.01	23.31
190	0.15	2.3	23.01	23.16
210	0.15	2.2	23.01	22.71
			mean = 23.06 ± 0.23, error = 0.21%	
465	0.30	1.0	53.57	54.49
465	0.35	1.0	53.57	53.67
430	0.70	2.0	53.57	52.98
			mean = 53.71 ± 0.52, error = 0.26%	

error of somewhat less than 0.3%, with an electrolysis duration of about 2 hours, with this method. The results show an average deviation of about 1%, mainly because of the uncertainty in the background current corrections.

CONCLUSION

Since tin(IV) is reduced to stannous tin at potentials of —0.3 to —0.4 V *vs.* S.C.E., it will interfere during the controlled potential determination of copper and antimony, unless it is complexed (*e.g.* with tartrate[1]). The reduction of tin(II) at potentials of —0.50 to —0.70 V *vs.* S.C.E. proceeds with 100% current efficiency at a mercury cathode, and may be determined coulometrically in the absence of metals not reduced at these potentials. Pre-reduction at —0.40 V will eliminate interference of copper, antimony and bismuth in this determination. Lead, which is reduced at about —0.50 V, will interfere. Finally, by electrolysis at —0.60 to —0.70 V *vs.* S.C.E., tin may be removed prior to the determination of such metals as nickel and zinc.

ACKNOWLEDGEMENT

The author is grateful to Dr. JAMES J. LINGANE for helpful discussions and suggestions during the course of this work. Appreciation is expressed to the National Science Foundation for a fellowship held by the author.

SUMMARY

The controlled potential coulometric determination of tin in a bromide medium is described. Although the reduction of tin(IV) to tin(II) suffers from complications, and is analytically unsuitable, reduction of stannous tin at a mercury, or tin–amalgam electrode forms the basis of a successful analytical method.

RÉSUMÉ

Une méthode coulométrique, à potentiel contrôlé, est décrite pour le dosage de l'étain, en milieu bromhydrique. La réduction de l'étain(II) à une électrode de mercure ou d'étain amalgamé est tout à fait satisfaisante.

ZUSAMMENFASSUNG

Beschreibung einer coulometrischen Methode mit kontrolliertem Potential zur Bestimmung von Zinn in bromwasserstoffsaurer Lösung. Als Grundlage der Methode dient die Reduktion von Zinn(II) an einer Quecksilber- oder Zinnamalgam Elektrode.

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CARBON PASTE ELECTRODES

APPLICATION TO ANODIC VOLTAMMETRY

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The use of carbon pastes (carbon or graphite intimately mixed with an organic liquid) as substitutes for noble metal electrodes offers several distinct advantages in solid electrode voltammetry. Preliminary reports have dealt with the properties of such electrodes[1,2]. The present study is a critical evaluation of the potentialities of this new electrode system with particular emphasis on its application to routine analysis using standard techniques of anodic voltammetry. Throughout this study an attempt was made to keep the experimental procedures simple while still retaining the best possible analytical results.

Experimental conditions

Polarograms were run by conventional voltage scan techniques using a Leeds and Northrup Model E Electrochemograph. All results were obtained with a stationary electrode configuration in a quiet solution. Typical peak-type polarograms were obtained for which the measurement of peak current (i_p) and half peak potential ($E_{p/2}$) were conventional in all respects.

Half-peak potentials have no special significance but they are preferred for characterization of a given electrode process especially in those cases where the electrode reaction is markedly irreversible. In such cases the peak polarogram is considerably rounded and a precise evaluation of the peak or maximum potential is difficult. However, the measurement of the peak current is rarely impaired and thus the half-peak potential can be located with considerable precision. An open 50-ml beaker was used as the polarographic cell.

Buffer solutions and background electrolytes were prepared from c.p. chemicals in all cases. The Britton and Robinson buffer solutions were prepared according to the directions given by MULLER[3]. For some of the work, the ionic strength was "swamped" by the addition of 0.2 M Na_2SO_4.

The organic electroactive compounds were either Eastman white label or purified samples kindly supplied through the courtesy of Mr. JOHN TINKER, E. I. du Pont de Nemours and Company. Since many of the amines are susceptible to air oxidation their stock solutions were made from air free water. The solutions were not deaerated prior to or during the run.

Preparation of carbon pastes

Carbon rods have been investigated for some time. To eliminate large residual currents observed with these electrodes it is necessary to impregnate them with wax[4,5]. It was reasoned that a thick paste of carbon with a water immiscible, non-electroactive liquid might function as well as a wax-impregnated rod.

An ideal pasting liquid would be one which was completely water immiscible, of very low volatility and which contained no electroactive impurities. Among the liquids investigated (from which successful electrodes can be prepared in all cases) were carbon tetrachloride, bromoform, benzene, mixed trimethylbenzenes, ethylnaphthalene, bromonaphthalene and Nujol. The last two named liquids seem to present the best compromise of the desired characteristics. Electrodes prepared from these pastes are described in detail. It should be pointed out that probably any non-electroactive liquid will function as the pasting material. A liquid of low volatility is to be preferred in order that the electrode may be used for long periods without evaporation changing the surface character. If the electrode is to be used for aqueous solutions, the liquid must be highly immiscible with water.

Several varieties of carbon and graphite were evaluated. Nuchar, Norite and vegetable charcoal were found to be too gritty to give smooth pastes. Acheson Grade 38 powdered graphite and spectroscopic graphite (United Carbon Products were ideally suited. Acetylene black, 50% compressed ("Shawinigan Black") commonly employed as a battery mix was also found to be very satisfactory. All of the data reported here were with Acheson Grade 38 graphite.

Pastes were prepared in the simplest possible manner by hand mixing measured quantities of carbon and organic liquid. A typical mixture contained 6 g of powdered graphite and 4 ml of bromonaphthalene. This paste was moderately thick and ideally suited for pool electrodes.

The construction details of the electrode proper are shown in Fig. 1. The Teflon plug was machined to a well configuration about 1/4" deep and 1/4" in diameter. The dimensions are in no way critical and can be altered to suit sensitivity requirements. A fine bore hole through the back of the Teflon plug admits a platinum wire electrical contact. Other materials could probably be used in place of Teflon but it is particularly useful in that it is wetted by few materials and easy to clean. A standard taper glass joint surrounds the electrical connection and insulates it from contact with the solution. The paste was tamped into the well until flush with the edges. Excess paste was removed by smoothing with a spatula. Any paste remaining on the rim can be easily wiped off with Kleenex or similar material. A remarkably smooth carbon paste surface is obtained with this simple procedure. Bromonaphthalene pastes form exceptionally smooth surfaces and are very easy to handle. Nujol pastes are somewhat sticky and a bit more difficult to work with. They have, however, some distinct advantages as discussed later.

The electrode was used in an inverted pool configuration, *i.e.*, with the Teflon plug dipping down *ca.* 1–2 cm below the level of the solution. Fig. 2 shows an overall picture of the electrode.

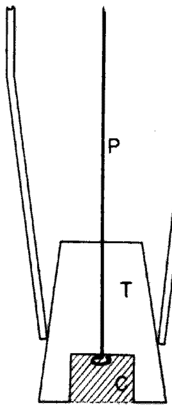

Fig. 1. Carbon paste electrode holder. T. Teflon plug with well 1/4 inch diameter, 3/16 inch deep. C. Carbon paste, P. Platinum wire, G. Glass tube.

Fig. 2. Carbon paste electrode.

Using the terminology carbon paste electrode, the natural abbreviation would be CPE. However, this may be somewhat confusing in that the rotating platinum electrode has long been abbreviated RPE. To avoid this difficulty, it was decided to adopt the term CE (carbon electrode) followed by the type of pasting liquid. Thus, the bromonaphthalene paste electrode will be abbreviated here and any subsequent publications as CE–BnP (Carbon Electrode – Bromonaphthalene Paste). Similarly, the Nujol paste electrode is designated CE–NjP.

RESULTS AND DISCUSSION

(a) Anodic range of the CE–BnP

TABLE I

ANODIC RANGE OF THE CARBON PASTE ELECTRODE IN VARIOUS BACKGROUND MEDIA

Media	*Potential when $i_r = 2$ μA (V vs. SCE)*
1 *M* KCl	1.10
0.1 *M* KCl–HCl, pH 2.5	1.08
1 *N* HCl	1.02
0.1 *M* NaAc–HAc	1.27
1 *M* Na_2SO_4	1.28
0.2 *N* H_2SO_4	1.30
B.R.B.[a] + 0.2 *M* Na_2SO_4, pH 2.4	1.30
B.R.B. + 0.2 *M* Na_2SO_4, pH 4.8	1.30
0.2 *N* NaOH	0.87

[a] Britton and Robinson buffer.

Table I shows the useful anodic range of the CE–BnP in a variety of supporting electrolytes. The useful range was arbitrarily set at that potential *vs.* SCE at which the residual current exceeded 2 μA. One of the most desirable characteristics of carbon paste electrodes is the extreme low level and flatness of the residual current over the entire useful potential range. For instance in the Britton and Robinson buffer solution (pH *ca.* 2.5, 0.2 *M* in sodium sulfate), the residual current at +0.10 V *vs.* SCE is about 0.02 μA and has only increased to 0.1 μA at +1.0 V *vs.* SCE with the CE–NjP. This same residual current behavior is found in almost all supporting electrolytes and with all types of pastes. Since the important parameter for analytical usage of solid electrodes is the ratio of faradaic current to residual current, carbon paste electrodes show considerable promise in this respect. The residual currents encountered are much lower than those at noble metal electrodes where oxide formation and history effects are prevalent.

The anodic limits of most of the pastes examined are similar and in general equal or superior to those of platinum. The CE–NjP has a slightly greater anodic range than that of the CE–BnP listed in Table I for Britton and Robinson buffer. Due to the excellent residual current level, the entire anodic range is available for study.

(b) Pretreatment of electrodes

Starting with a fresh paste electrode, no pretreatment whatsoever is needed. In general, after a polarographic run, the electrode is simply washed with a stream of distilled water. In some cases, for instance where reproducibility data is desired on the same solution, it is only necessary to stir the solution to sweep away oxidation products before beginning the next run. On the other hand, the oxidation of some compounds like naphthols and aromatic thiols seems to form films on the electrode surface (this is common behavior for the electro-oxidation of these materials at solid electrodes). In these cases it may be wiser to build a fresh electrode for each run, although cathodic treatment at *ca.* —0.4 V prior to the next run seemed helpful in obtaining reproducibility in some cases.

(c) Temperature effects

Since carbon pastes represent a new form of solid electrode it seemed desirable to check the temperature coefficient of limiting currents. Fig. 3 shows the linear varia-

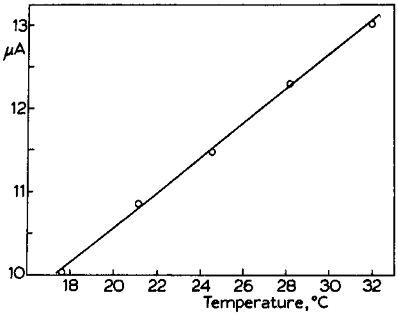

Fig. 3. Variation of peak current with temperature for 10^{-3} *M* $K_4Fe(CN)_6$ in 1 *M* KCl.

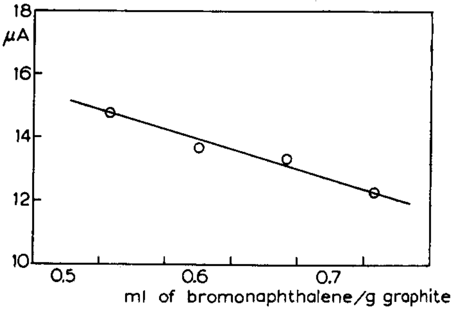

Fig. 4. Variation of peak current with paste composition for 10^{-3} *M* $K_4Fe(CN)_6$ in 1 *M* KCl.

tion of peak current with temperature over the temperature range of 18–32°. In the terminology of previously reported data, this represents a temperature coefficient of about 2% per degree.

(d) Effects of variation in paste composition

The peak current is proportional to the surface area of the electrode. As the ratio of organic liquid to carbon increases, the peak current decreases. This is seen in Fig. 4 for bromonaphthalene paste. These currents are for the oxidation of 10^{-3} M ferrocyanide in a background of 1 M KCl. Each point represents an average current for three individual pastes with the indicated composition. Clearly the more "dry" paste is advantageous in terms of sensitivity. In addition, such pastes are somewhat easier to handle.

Attempts were made to dilute the carbon content of the paste without changing the fluidity characteristics by substituting filler material for the carbon. All of the materials tried, celite, barium sulfate, alumina, and starch were unsatisfactory since they separated from the paste proper immediately upon immersion in the liquid. Thus, it was not possible to evaluate the dependence of peak current on the available carbon content. On the other hand, the electrochemical area obtained from linear diffusion studies on ferrocyanide oxidation was found to be approximately the same as the measured geometrical area.

(e) Reproducibility and storage of electrodes

Since carbon paste electrodes can be prepared with such ease (a fresh electrode can be made in 2–5 min), it is possible to use new electrodes for each run or to arrange a suitable storage technique for one electrode. The reproducibility of each of these techniques was examined.

Normally a paste is prepared in a large batch. Freshly packed electrodes were prepared on 9 consecutive days from the same batch of bromonaphthalene paste and the peak current for the oxidation of $5 \cdot 10^{-4}$ M N,N-dimethyl-*p*-phenylenediamine (DPP) was checked on each electrode. Table II shows that peak currents (i_p) can be reproduced to about 6%. It is rather surprising that the surface areas are thus reproducible.

TABLE II

REPRODUCIBILITY OF THE CARBON PASTE ELECTRODE AREA ON FRESHLY PREPARED ELECTRODES

Peak height (μA)	*$E_{p/2}$ vs. SCE (V)*
14.4	0.455
16.6	0.426
17.2	0.427
15.4	0.433
16.2	0.430
15.0	0.437
14.4	0.441
16.2	0.439
14.8	0.444

Average 15.6, average deviation 5.7%.

TABLE III

PEAK CURRENT (μA)

Day	*CE–BnP*	*CE–NjP*
1	12.27	16.34
2	12.24	16.82
3	12.20	17.00
4	11.92	16.68
6	12.20	17.02
7	11.80	16.66
8	11.50	16.16
9	11.70	
14	12.30	
15	11.87	
17	12.05	
18	11.90	
21	11.55	
22	11.80	
Average	11.95	16.67
Average deviation	0.22	0.24
% Average deviation	1.84	1.44

Two storage techniques were investigated: *(a)* the electrode was kept in a sealed atmosphere of bromonaphthalene vapor, and *(b)* kept under distilled water when not in use. Storage in an open beaker under distilled water turned out to be much more reproducible and convenient. Table III shows the reproducibility of i_p for a CE–BnP stored for 22 days and a CE–NjP for 8 days. Two different electrode reactions were used; oxidation of $1 \cdot 10^{-3}$ *M* ferrocyanide in 1 *M* KCl for the CE–BnP, and oxidation of $5 \cdot 10^{-4}$ *M* *o*-dianisidine in pH 2.5 buffer for the CE–NjP. It is readily seen that long range reproducibility is a little less than ± 2%. The short time reproducibility of carbon paste electrodes is much better than this value. Using a standard comparison polarogram run concurrent with an "unknown", reproducibility of about ± 0.5% is attainable. For instance, Fig. 5 shows three successive polarograms for the oxidation of *o*-dianisidine in buffered medium. This is an actual chart recording and it can be seen that the three polarograms are almost superimposable over the entire voltage span. In general successive polarograms seem to have a short time reproducibility of about ± 0.2%.

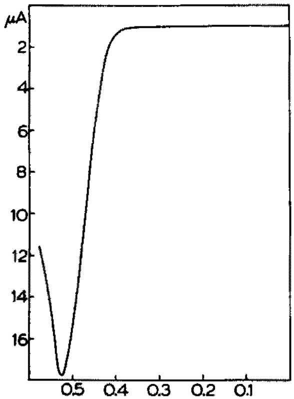

Fig. 5. Successive reproducibility of CE–BnP for oxidations of *o*-dianisidine.

TABLE IV

Constancy of i_p/C *versus* concentration for DPP in 0.1 M KCl–HCl at pH of about 2.5

Concentration *($M \cdot 10^5$)*	*Peak current* *(μA)*	i_p/C *(μA)*
1.0	0.316	3.16
2.0	0.663	3.31
4.0	1.30	3.25
6.0	1.96	3.27
8.0	2.58	3.23
10.0	3.25	3.25
14.0	4.48	3.20
20.0	6.30	3.25
		Dev. 1.2%

Constancy of i_p/C *versus* concentration for oxidation of $FeSO_4$ in 1 N HCl

Concentration *($M \cdot 10^4$)*	*Peak current* *(μA)*	i_p/C *(μA)*
1.0	1.35	1.35
2.0	2.75	1.38
3.0	3.99	1.33
4.0	5.35	1.36
5.0	6.50	1.30
6.0	7.53	1.26
10.0	12.8	1.28
		Dev. 2.8%

TABLE V

SURVEY OF OXIDATIONS AT CARBON PASTE ELECTRODES

Electroactive species	*Background*	*Type electrode*	$E_{p/2}$ *(V vs. SCE)*	
A. Inorganic				
1. $Fe(CN)_6^{-4}$	BRB[a]	CE–BnP	(+)0.21	
2. Fe^{+2}	1 N HCl	CE–BnP	0.75	
3. I^-	BRB[a]	CE–NjP	0.49	
4. I^-	1 N H_2SO_4	CE–NjP	0.44	
5. Tl^+	1 N NaOH	CE–NjP	0.32	
6. NO_2^-	BRB[a]	CE–NjP	0.89	
B. Organic				
1. 1-Naphthylamine	BRB pH 5.1	CE–BnP	(+)0.53	
2. 1-Naphthol	BRB[a]	CE–BnP	0.63	
3. 1-Amino-7-naphthol	BRB[a]	CE–BnP	0.45	
4. 5-Amino-2-naphthalene sulfonic acid (1-6 Cleves acid)	BRB[a]	CE–BnP	0.52	
5. 7-Anilino-1-naphthol 3-sulfonic acid (phenyl gamma acid)	BRB[a]	CE–BnP	0.50	
6. Aminoazobenzene	BRB pH 4.1	CE–BnP	0.74	
7. 3,4-Diamino toluene	BRB pH 4.4	CE–BnP	0.28	
8. 2,4-Diamino toluene	BRB[a]	CE–BnP	0.71	
9. *p*-hydroxydiphenylamine	BRB pH 4.4	CE–BnP	0.22	
10. *p*-ethoxydiphenylamine	BRB pH 2.6	CE–BnP	0.63	
11. *o*-Dianisidine	BRB[a]	CE–BnP	0.46	
	BRB[a]	CE–NjP	0.46	
12. Dimethylaniline	BRB[a]	CE–BnP	0.68	(1st wave)
			0.92	(2nd wave)
13. *o*-Tolidine	HCl–KCl pH 2.5	CE–BnP	0.51	
14. N,N-dimethyl-*p*-phenylenediamine (DPP)	HCl–KCl pH 2.5	CE–BnP	0.45	

[a] Britton-Robinson buffer solution A containing 0.2 N Na_2SO_4, pH 2.4.

Table IV shows the constancy of i_p/C *vs.* concentration for the oxidation of typical organic and inorganic species at the CE–BnP. These results are quite good and compare very favorably with previous stationary solid electrode data. Nujol pastes (and, for that matter, pastes of all other liquids examined) show essentially the same results.

Table V summarizes the spectrum of anodic oxidations examined at carbon paste electrodes. In general, half-peak potentials at carbon paste electrodes are comparable but not always identical with those obtained at platinum electrodes. The half-peak potentials of many of the organic compounds listed in Table V agree within ± 5 – 10 mV of the corresponding values at platinum. In the case of inorganic oxidations, somewhat greater differences exist in some cases. It has also been found that the half-peak potentials of inorganic compounds vary in some cases with the particular carbon used. This problem is of great interest and will be discussed in detail later. From the practical analysis viewpoint, using Acheson Grade 38 graphite a series of highly reproducible and self-consistent $E_{p/2}$'s can be obtained.

ACKNOWLEDGEMENT

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SUMMARY

The use of carbon paste electrodes (carbon of graphite intimately mixed with an organic liquid) as substitutes for noble metal electrodes is described. This method offers several distinct advantages in solid electrode voltammetry and can be applied to routine analysis using standard techniques of anodic voltammetry.

RÉSUMÉ

Les auteurs proposent l'emploi d'électrodes de carbone (charbon ou graphite intimement mélangé à un liquide organique) pouvant être substituées aux électrodes de métaux nobles; elles présentent plusieurs avantages et elles peuvent être appliquées à la voltammétrie anodique.

ZUSAMMENFASSUNG

Elektroden aus Edelmetallen können vorteilhaft durch solche aus einer Graphitpaste ersetzt werden. Ihre Anwendungsmöglichkeit bei der anodischen Voltammetrie wird beschrieben.

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Short Communications

A preheating, automatic, self-flushing still

In titrimetric investigations at high precision[1,2] a primary requirement was a source of grease-free distilled water of very low halogen and sulphur content. The primary objectives in the original design were therefore a still and dispenser completely free from lubricated joints or taps, without rubber connections or bungs, and a means of eliminating vapour and spray entrainment. The quality of output proved to be surprisingly high, particularly in respect to nitrogen content, and after incorporation of filtration and dust protection the product also proved to be and to remain sterile. This led to the development of the still, referred to in a recent communication[1], which combines the following advantages.

(1) The economy of a preheated feed, which reaches the heater at boiling point. *(2)* The convenience of safe automatic working. *(3)* The high quality of product produced by all glass/quartz construction, a high reflux ratio, the virtual elimination of entrainment, and the long vapour path. *(4)* The economy of space and the facility of mounting (one clamp at either end) by placing the still high up on a wall out of the way. *(5)* Automatic cleaning, any sludge or deposit formed being carried away through the overflow. *(6)* Security of operation. If water supply pressure drops, although the distillate temperature will rise, the still continues to operate in safety so long as any water continues to flow. Should the supply cease entirely, the top fusible link will

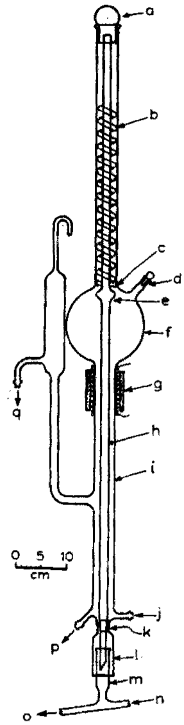

Fig. 1. Diagram of the preheating, automatic, self-flushing still. a. Deflector dome. b. Spiral of 7 mm borosilicate. c. 3-point spacer fused to inner tube. d. Inlet for chemical cleaning B-14 joint. e. Spray baffle. f. Boiling chamber (1-litre bulb). g. 800–1000 Watt nichrome ribbon heater. h. 15-mm thin wall borosilicate or quartz. i. 40-mm thick wall borosilicate. j. Cold feed. k. B 14 borosilicate socket, quartz or borosilicate cone sealed with Apiezon wax. l. Sheath. m. Collector. n. From other stills. o. To quartz filter and storage. p. Flushing (normally closed). q. Overflow.

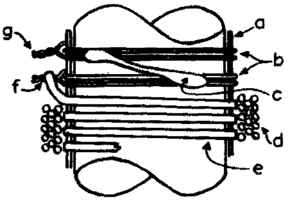

Fig. 2. Detail of heater arrangement (half size). a. Mica. b. 14 s.w.g. copper binding posts. c. 2.5-cm fusible link of 14 s.w.g. 60/40 cored solder. d. Asbestos lagging. e. 800–1000 Watt nichrome ribbon element. f. Silver solder. g. Mains connection.

blow just before the water level falls to heater level, thus preventing damage to heater element or glass.

Construction

The construction is illustrated in Figs. 1 and 2. The heater is wound from nichrome ribbon in a single layer on mica. Each end is silver soldered to a binding post made from two turns of 14 s.w.g. copper wire with the ends twisted together not too tightly. This in turn is connected through a 2.5-cm fusible link made of 14 s.w.g. 60/40 lead/tin resin-cored solder wire to a second binding post. The mains leads are connected to the outer pair of binding posts. If asbestos tape or string is used to cover the winding, it should be heated to remove dressing and moisture before the element is operated, else the upper link tends to blow in the evolved steam. The upper link should not be covered with asbestos. The overflow height should be so adjusted that the water level when cold lies between the top of the heater and the bottom of the boiling chamber, and the length of the overflow chamber should be adequate to permit flushing of the whole boiling chamber when the overflow is closed. The deflector dome at the top should be a fairly loose fit and be lightly seated by grinding. This constitutes a safety valve in case of sudden excessive bumping. When the still surfaces are very clean, "bumping", or explosive boiling, is liable to occur. It is important to cut off all delivery tubes at an acute angle to avoid liquid locks. The unit is vented to atmosphere only at the bottom of the inner tube where the distillate drips into the collector which is sheathed to prevent access of dust or heavy fumes. The inner tube is interchangeable: borosilicate gives excellent quality water and, if thin wall tubing is used, good heat transfer; quartz gives an even better, boron-free distillate, but heat transfer is less efficient. For ease of removal, the joint is lightly sealed with Apiezon wax which can be released by warming, but, being at the coldest part of the unit, does not contaminate the feed. The collector manifold (a battery of stills is actually in use) carries the distillate to an encapsulated porosity 3 sintered quartz filter, thence to a 20-litre borosilicate storage bottle. Supplies are dispensed from a fully protected all-glass syphon arrangement. It is convenient to arrange the plumbing so that overflow and flushing outlets join through a Y-piece, the flushing outlet normally being closed with a screw clip. A screw clip on the combined outlet permits flushing of the boiling chamber.

Cleaning

Sludge, humus, loose and siliceous and ferruginous deposits are normally carried away in the overflow, but hard scale builds up gradually. This is removed by disconnecting the collector manifold, charging the still with 800 ml of hot 5 – 10% potassium acid sulphate through the side arm on the boiling chamber, and boiling for 10 min. This is followed by thorough flushing with water and steaming out with feed and overflow closed and the boiling chamber half filled. If the deposit is highly siliceous, preliminary boiling with 800 ml of hot 5% caustic soda loosens the deposit ready for the acid treatment.

Performance

One still in operation for six years has produced some 5000 l without breakdown other than once blowing off the deflector dome and twice blowing a fusible link. The cost of running is approximately 1.2 pence (1.4 cents) per l, and the distillation rate is 800–1000 ml per hour per still. The quality may be judged from the figures below. The distillate naturally contains carbon dioxide, and so is not suitable for conductivity work. However, by allowing partial steam off at the top by inserting a very fine nylon hair in the dome seating, and cutting down the cold feed so that the distillate is delivered at above 65° into carbon dioxide free containers, very little carbon dioxide is dissolved in the distillate, and the dissolved solids from the glass show only a slight increase.

TABLE I

Analysis of feed p.p.m.		*Analysis of distillate p.p.m.*	
Chloride	13	Chloride	< 0.001
Nitrate	1.2	Sulphate	< 0.001
Temporary hardness	26–52	Total nitrogen	< 0.0001
Permanent hardness	30–34	Total solids	
Saline ammonia	0.024	(borosilicate inner tube)	0.002
Albuminoid ammonia	0.024–0.048	(quartz inner tube)	0.0001
Total solids	100–130		
Suspended solids	2–5		

Washington Singer Laboratories,
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J. R. B. SUTTON

[1] E. BISHOP, *Anal. Chim. Acta*, 20 (1959) 315.
[2] E. Bishop, *Anal. Chim. Acta*, 20 (1959) 405.

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Low pressure method for carbon analysis in steels: a note

The low pressure method for the analysis of less than 0.1% of carbon in steels is well-established[1]. As described recently by COOK AND SPEIGHT[2], it is both simple and reliable.

However, when an apparatus similar to that of COOK AND SPEIGHT was set up in our laboratories, some difficulty in its operation was observed: when the multiple coil trap for freezing out carbon dioxide was immersed in liquid air—which is the coolant used here—oxygen from the gas stream condensed in it. The temperature of the liquid air was about —188.5°, at which temperature oxygen has a saturated vapour pressure of about 405 mm[3]. Owing to this lowering of pressure and the condensation of oxygen, it was difficult to maintain a steady outflow of the gas from the trap and prevent a back suction of atmospheric air. Moreover, the liquefied oxygen in the multiple coil trap tended to rise with the gas stream, especially during evacuation, resulting in quick evaporation at the exposed parts followed by a localised increase of pressure; this involved the risk of damage to the apparatus.

It was, therefore, necessary to design a trap which when used with liquid air as the coolant would be free from these difficulties.

After some trials the trap shown in Fig. 1, which is similar to that described by WELLS[4], was constructed for use with liquid air as the coolant. The inlet end of the trap was fused to a vacuum tested stopcock S_1 and the exit end to a similar three-way stopcock (S_2). One lead of S_2 served as the gas outlet through the moisture absorbers, while the other was connected by means of an interchangeable ground glass joint to the calibrated carbon dioxide pressure measuring unit. The rest of the apparatus followed the established pattern[2].

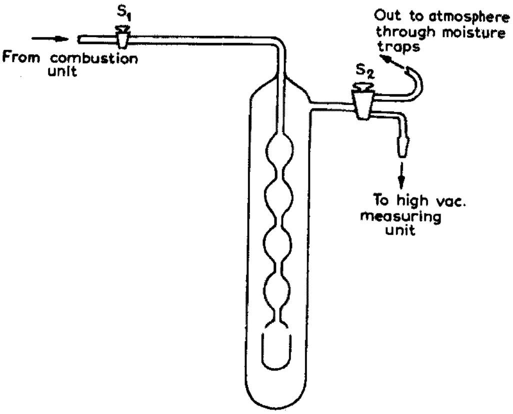

Fig. 1. Modified trap for CO_2 condensation.

Since oxygen started condensing in the trap when the latter was immersed in liquid air, the procedure had to be modified as follows.

After the initial flushing out of the combustion system with purified oxygen, stopcocks S_1 and S_2 were closed and the trap was immersed in liquid air. Oxygen gas continued to bubble out of the safety mercury bubbler included in the gas line, keeping the system up to stopcock S_1 under a positive pressure of about 5 cm of mercury. When the trap had attained the temperature of liquid air, the oxygen flow rate was increased to the desired value and the sample introduced for combustion. Stopcock S_1 was then manipulated so as to maintain a constant flow of gas past the sample boat into the trap. During this period, the system remained under a slight negative pressure of 1–1.5 cm of mercury, the mercury bubbler indicating the internal pressure. A second liquid air flask was raised under the calibrated measuring coil, stopcock S_1 was closed after the usual combustion period, and S_2 was opened gently to connect the trap with the evacuating pumps through the measuring unit. Pumping out condensed oxygen from the trap and returning the measuring unit to its original evacuated state required 4–5 minutes. Frozen carbon dioxide was then transferred from the trap to the coil in the usual way and its pressure was measured.

The time of analysis was slightly longer, but the use of liquid air instead of liquid oxygen as the coolant caused no difficulty.

Thanks are due to the Chief Chemist, and to the Management of Tata Iron & Steel Co. for permission to publish this work.

Research & Control Labs.,
Tata Iron & Steel Co.,
Jamshedpur (India)

V. Ramakrishna*

1 Methods of Analysis Committee Report, *J. Iron Steel Inst. London*, 183 (1956) 287.
2 R. M. Cook and G. E. Speight, *Analyst*, 81 (1956) 144.
3 *International Critical Tables*, vol. III (1928) 203.
4 J. E. Wells, *J. Iron Steel Inst. London*, 166 (1950) 113.

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ERRATA

Anal. Chim. Acta, 20 (1959) 406, under *Vacuum weighing correction*, the equations should read:

$$W_{s_1} - W_{s_1} \times d_a/d_1 = W_{s_2} - W_{s_2} \times d_a/d_2$$

$$\therefore W_{s_1}/W_{s_2} = \frac{d_2 - d_a}{d_1 - d_a} \times \frac{d_1}{d_2}$$

The error incurred by ignoring vacuum correction will be:

$$\frac{1 - W_{s_1}/W_{s_2}}{1} = \frac{d_a(d_1 - d_2)}{d_2(d_1 - d_a)} \approx \frac{d_a(d_1 - d_2)}{d_1 d_2} \approx d_a(d_1 - d_2)$$

Following paragraph, line 4, should read: . . . . . the error incurred is 2.42 (instead of 2.44) in 10^6, ...
lines 7 and 8 should read: . . . . . the error is still only 10.9 in 10^6, or 0.00109%.

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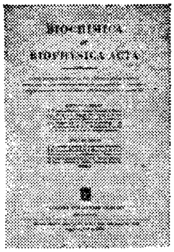

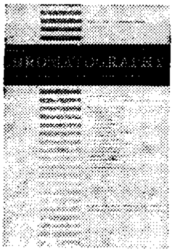

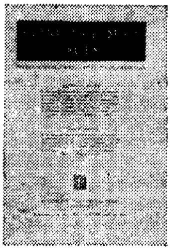

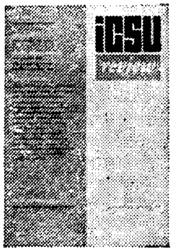

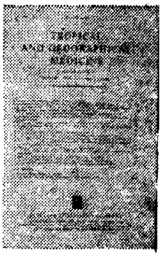

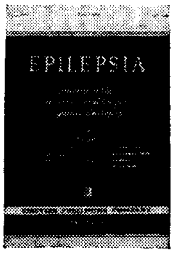

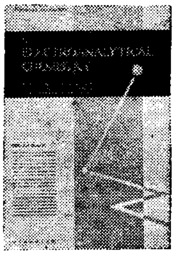

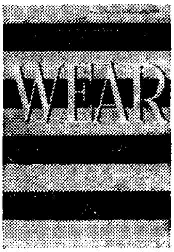

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