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## THE DETERMINATION OF COPPER WITH TRIETHYLENETETRAMINE USING A METALFLUORECHROMIC INDICATOR

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(Received 3 October 1958)

**Summary**—Triethylenetetramine (trien) has been applied as a selective titrant for the determination of copper without separations or masking of many elements normally found in brasses and bronzes.

The application of a metalfluorechromic indicator has made possible the use of trien for the determination of macro amounts of copper without resort to an instrumental end-point detection method.

Calcein W serves as a selective indicator for copper in the presence of many elements normally found in brasses and bronzes.

THE wide application of ethylenediaminetetra-acetic acid (EDTA) and nitrilotriacetic acid in chelometric titrations has not been extended to include polyamines. In contrast to the voluminous literature applying EDTA to inorganic analytical problems only two papers have appeared using triethylenetetramine as a chelometric reagent.<sup>1,2</sup>

In order to be useful as a titrimetric reagent in a chelometric titration, a polyamine must form a complex with a metal ion sufficiently stable to provide a sharp end-point in a titration. In general, this necessitates the formation of a stable 1 : 1 complex between the metal ion and the chelating agent ( $pK > 8$ ). The actual stability constant is not as important as the apparent stability constant as has been adequately demonstrated by Schwarzenbach.<sup>3</sup> Theoretical titration curves have been calculated for triethylenetetramine and copper<sup>4</sup> as well as a theoretical treatment of the titration of pure copper solutions.<sup>5</sup>

The actual stability constants of several polyamines have been accumulated.<sup>6</sup> Of these, three appear promising as titrimetric reagents: 2:2':2''-triaminotriethylamine, triethylenetetramine, and N:N':N'':N'-tetrakis-(2-aminoethyl)-ethylenediamine. Fortunately the selection of a suitable polyamine for a volumetric titration can be made with a few relatively simple calculations.

The polyamines may be treated as polybasic acids; as such the acidity constants may be expressed mathematically as follows:

$$\begin{aligned} K_1 &= \frac{[H_4B^{+4}]}{[H^+][H_3B^{+3}]} & K_3 &= \frac{[H_2B^{+2}]}{[H^+][HB^+]} \\ K_2 &= \frac{[H_3B^{+3}]}{[H^+][H_2B^{+2}]} & K_4 &= \frac{[HB^+]}{[H^+][B]} \end{aligned}$$

for example for triethylenetetramine. The concentration of the polyamine present in solution is equal to the sum of the ionic species of the polyamine

$$C = [B] + [HB^+] + [H_2B^{+2}] + [H_3B^{+3}] + [H_4B^{+4}] \quad (1)$$

where  $C$  is the total concentration of triethylaminetetramine not bound to the metal

and the members on the right hand side of equation (1) are the various ionized species of the polyamine. The expressions for the four ionization constants may be rearranged so as to place the undissociated species in each expression on the left side of the equation and, by substitution, from the preceding equation (2 to 5) each species is expressed in terms of the completely ionized form (designated as B).

$$[\text{HB}^+] = [\text{H}^+]K_4[\text{B}] \quad (2)$$

$$[\text{H}_2\text{B}^{+2}] = [\text{H}^+]K_3[\text{HB}^+] = [\text{H}^+]^2K_4K_3[\text{B}] \quad (3)$$

$$[\text{H}_3\text{B}^{+3}] = [\text{H}^+]K_2[\text{H}_2\text{B}^{+2}] = [\text{H}^+]^3K_4K_3K_2[\text{B}] \quad (4)$$

$$[\text{H}_4\text{B}^{+4}] = [\text{H}^+]K_1[\text{H}_3\text{B}^{+3}] = [\text{H}^+]^4K_4K_3K_2K_1[\text{B}] \quad (5)$$

The equivalent values for the various ionized species from equations (2) to (5) may be substituted into equation (1).

$$C = [\text{B}] + [\text{H}^+]K_4[\text{B}] + [\text{H}^+]^2K_4K_3[\text{B}] + [\text{H}^+]^3K_4K_3K_2[\text{B}] + [\text{H}^+]^4K_4K_3K_2K_1[\text{B}] \quad (6)$$

Equation (6) may be rearranged in a manner more convenient for the calculation of apparent stability constants of metal-triethylenetetramine complexes.

$$[\text{B}] = \frac{[\text{C}]}{1 + [\text{H}^+]K_4 + [\text{H}^+]^2K_4K_3 + [\text{H}^+]^3K_4K_3K_2 + [\text{H}^+]^4K_4K_3K_2K_1} = \frac{[\text{C}]}{\alpha_H} \quad (7)$$

The term designated by  $\alpha_H$  has been derived in a more generalized manner and applied to theoretical considerations of chelometric titrations with ethylenediaminetetra-acetic acid and nitrilotriacetic acid by Schwarzenbach.<sup>3</sup>

The actual stability constant for the reaction between a metal ion and polyamine may be expressed as follows:

$$K = \frac{[\text{MB}]}{[\text{M}][\text{B}]} \quad (8)$$

where [M] is the concentration of metal ion not complexed with the polyamine and [B] is concentration of the free polyamine. Substitution of the value for [B] from equation (7) into equation (8) gives the expression for the apparent stability constant  $K_a$ .

$$K_a = \frac{K}{\alpha_H} = \frac{[\text{MB}]}{[\text{M}][\text{C}]} \quad (9)$$

Equation (9) is useful to compare the apparent stability of several polyamine complexes. The  $\alpha_H$  term, derived above for triethylenetetramine, may be derived for other polyamines and a first approximation may be obtained concerning their relative merits as titrants. For example Fig. 1 shows the variation with pH of  $\log \alpha_H$  for triethylenetetramine, 2:2':2''-triaminotriethylamine, and N:N':N'':N'-tetrakis-(2-aminoethyl)-ethylenediamine (hereafter referred to as trien, tren, and penten respectively).<sup>4</sup> The application of this mathematical treatment of the effect of pH on the apparent stability of the complexes of copper with polyamines is more obvious if the logarithm of the apparent stability constant is plotted as a function of pH (Fig. 2). The curves in Fig. 2 were obtained by subtracting  $\log \alpha_H$  from  $\log K_{Cu}$ . It is obvious from Fig. 2 that at a low pH trien is the most effective complexing agent for copper.

The minimum value of the apparent stability constant which will allow a successful

titration must be determined in a somewhat arbitrary manner. A rigorous treatment of this value must include the concentration of the metal being titrated, the presence of auxiliary complex formers (for example, buffers), the tolerable titration error, etc., and is beyond the scope of this article.

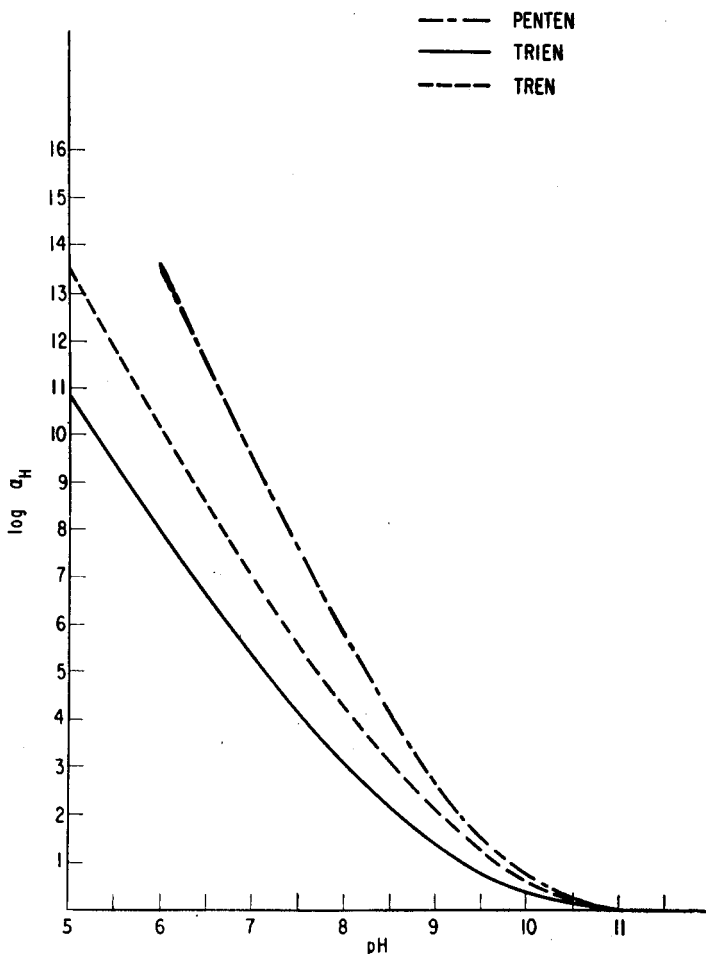


FIG. 1.  $\log \alpha_H$  vs. pH for three polyamines.

An additional criterion which must be considered, however, is the availability of the reagent. Triethylenetetramine (trien) is available commercially (although impure) whereas tren and penten must be prepared in the laboratory by somewhat laborious procedures.

The mathematical treatment presented above indicated that tren and penten have no advantages over the trien for the determination of copper. On this basis triethylenetetramine was selected as a suitable titrant. It should be mentioned, however, that the larger apparent stability of the penten copper complex at a high pH could prove advantageous for microtitrations.

Previous investigations of the use of trien to titrate copper<sup>1,2</sup> have recommended instrumental methods for detecting the end-point. The titration of copper using

murexide as an indicator is limited to less than 0.05 millimoles of copper because of the intense blue colour of the copper-polyamine complex.<sup>2</sup> The introduction of metalfluorechromic indicators has eliminated many of the difficulties previously encountered in chelometric titrations in which the colour of the metal-EDTA complex interfered with the colour change at the end point.

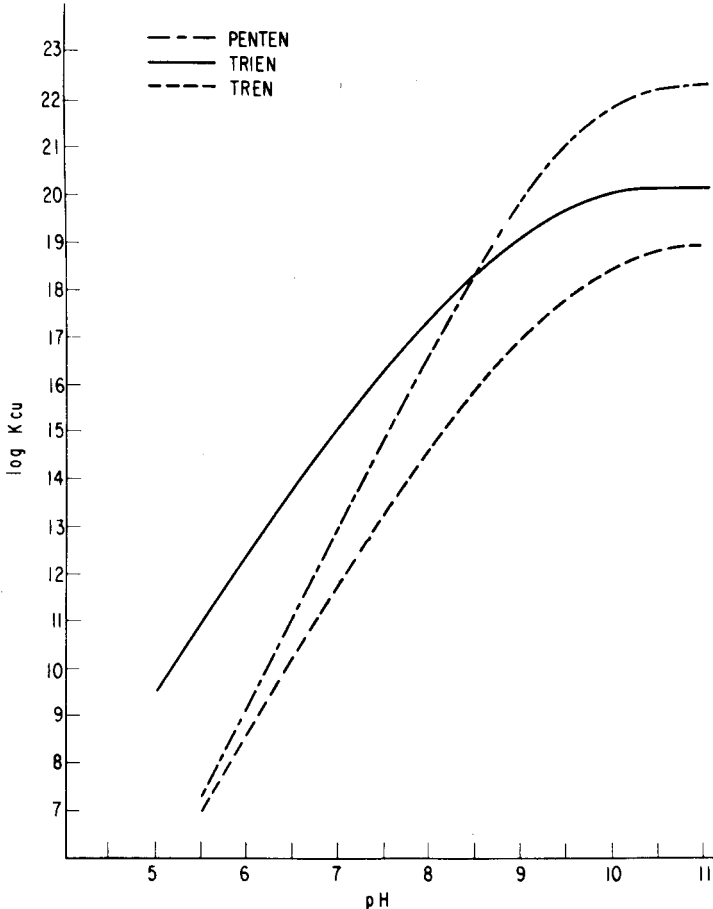


FIG. 2. Logarithm of the apparent stability constant of the copper-polyamine complex *vs.* pH for three polyamines.

The successful application of calcein as a metalfluorechromic indicator for back titrations of EDTA with a copper solution<sup>7</sup> suggested that a similar technique would provide a suitable indicator for the titration of copper with triethylenetetramine. A copper solution was prepared and standardized with EDTA. Aliquots were taken to contain from one to sixty mg of copper and were titrated with triethylenetetramine using calcein W as an indicator under ultraviolet light. The end-point is characterized by the appearance of the green fluorescence of the free indicator. Dropwise addition of the titrant near the end-point produces a fluorescence where the drop enters the solution. This fluorescence with the local excess of titrant disappears with stirring in the same manner as with conventional indicators. At the end-point a single drop of

titrant produces a brilliant fluorescence throughout the solution. The results obtained by titrating pure copper solutions with trien using calcein W as an indicator under ultraviolet illumination are presented in Table I.

It is apparent from the stability constants that some metals form more stable complexes with trien than others.<sup>6</sup> This fact introduces the possibility of titrating

TABLE I. TITRATION OF PURE COPPER SOLUTIONS WITH TRIEN

<i>mg</i> Cu present	<i>mg</i> Cu found	pH
19.06	19.10	7
19.06	19.06	7
19.06	19.08	7
19.06	19.06	7
38.12	38.03	7
38.12	38.11	7
38.12	38.05	7
38.12	38.17	7
57.18	57.10	7
57.18	57.19	7
76.24	76.06	7
76.24	76.18	7
19.06	19.11	9.5
19.06	19.09	9.5
19.06	19.05	9.5
19.06	19.05	9.5

copper in the presence of elements which do not form particularly stable ammine complexes such as calcium, magnesium, manganese, etc. The possibility of performing such titrations is more apparent from a plot of the apparent stability constant *vs.* pH (Fig. 3). Copper has been determined in an aluminum alloy by titrating with trien using a spectrophotometric end-point.<sup>1</sup> An examination of Fig. 3 indicates that the determination of copper with trien should be possible in the presence of other elements with a suitable end-point detection method. Although spectrophotometric and potentiometric methods are possible, it is more desirable for routine analysis to use a visual indicator.

An investigation was initiated into the possibility of using calcein W as an indicator for the determination of copper with trien in the presence of manganese and zinc. Preliminary investigations revealed that manganese and zinc do not quench the fluorescence of calcein W in a solution buffered to a pH of 7 with ammonium acetate. The magnitude of the apparent stability constant (Fig. 3) of the copper complex compared to those of manganese and zinc suggest that copper (in the presence of manganese or zinc) will be essentially completely titrated with trien before an appreciable amount of trien-manganese or trien-zinc complex is formed.

Solutions of manganese and zinc were prepared and added to measured aliquots of the standard copper solution. The solution was adjusted to a pH of 7 by the addition of solid ammonium acetate, one drop of calcein W solution was added and the solution

titrated with trien under ultraviolet illumination to the appearance of the green fluorescence of the free indicator. The results of these titrations are shown in Table II.

The determination of copper in the presence of zinc and manganese suggests the feasibility of developing a procedure for the rapid determination of copper in brasses

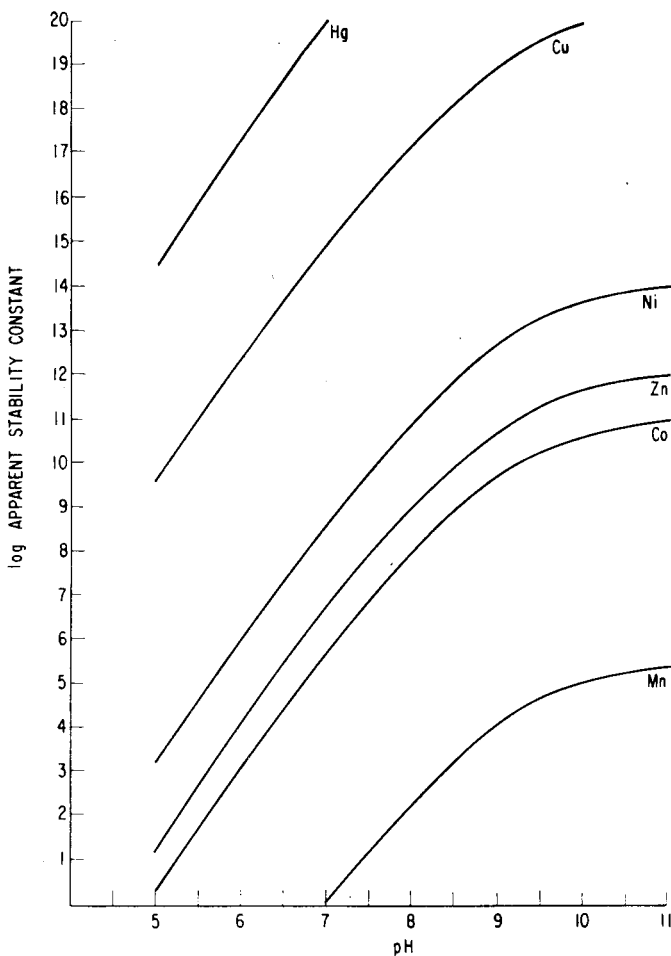


FIG. 3. Logarithm of the apparent stability constant of several metal-trien complexes *vs.* pH.

and bronzes. In order to verify such a procedure a National Bureau of Standards sample (No. 164) was selected and copper determined using the procedure given below.

#### Procedure

Dissolve a 0.5-g sample in 3 ml of water, 1 ml of nitric acid and 10 drops of hydrochloric acid. After dissolution transfer the sample solution to a 100-ml volumetric flask and dilute to volume with water. Add 100 ml of water, 3 g of ammonium acetate and 5 drops of calcein to a 10-ml aliquot in a 250-ml beaker. Titrate the copper with a standard trien solution which has been adjusted to a pH of 7 (pH paper) before standardization. The end-point is characterized by the appearance of the green fluorescence of the free indicator. The values in Table II designated sample number 164 and 52c were determined by the procedure described above.



## DISCUSSION

The titrations of the standard copper solutions and the brass sample were conducted using ultraviolet lamps as the sole source of illumination. An apparatus designed for fluorescent titrations has been previously described.<sup>7</sup>

An interesting development in the application of metalfluorechromic indicators to chelometric titrations is found in the fact that several of the titrations presented in

TABLE II. TITRATION OF COPPER IN PRESENCE OF OTHER ELEMENTS WITH TRIEN

Sample No.	mg Cu present	mg Cu found	Second element present mg
1	19.06	19.07	10 Mn
2	19.06	19.00	10 Mn
3	19.06	18.95	10 Mn
4	19.06	18.97	10 Mn
5	19.06	19.07	10 Mn
6	19.06	19.01	10 Mn
7	19.06	19.03	10 Zn
8	19.06	18.99	10 Zn
9	19.06	19.03	10 Zn
10	19.06	18.97	10 Zn
164-1	32.42	32.37	NBS Bronze No. 164*
164-2	32.42	32.42	NBS Bronze No. 164*
164-3	32.42	32.42	NBS Bronze No. 164*
164-4	32.42	32.37	NBS Bronze No. 164*
164-5	32.06	32.16	NBS Bronze No. 164*
164-6	32.06	31.92	NBS Bronze No. 164*
164-7	32.06	32.11	NBS Bronze No. 164*
52c-1	41.89	41.75	NBS Bronze No. 52c*
52c-2	41.89	41.75	NBS Bronze No. 52c*
52c-3	41.89	41.78	NBS Bronze No. 52c*

\* 52c 89.25 Cu, 7.85 Sn, 2.12 Zn, 0.76 Ni, 0.011 Pb, 0.004 Fe

\* 164 63.76 Cu, 21.89 Zn, 6.21 Al, 4.68 Mn, 2.52 Fe, 0.63 Sn, 0.22 Pb, 0.046 Ni

Tables I and II were performed by an individual who is colour blind (blue-green). Thus, in addition to eliminating interferences from highly coloured complexes, metalfluorechromic indicators may be used in instances where the operator is unable to detect the colour changes of conventional indicators.

It should be noted that the procedure for the determination of copper in brasses and bronzes is dependent on the fact that the indicator is not blocked by elements present in the sample. The procedure will not work at a pH of 9 since the fluorescence of calcein W is quenched by other elements at this pH. A more exhaustive study is in progress to determine the properties of calcein W as an indicator for elements other than copper.

Commercial trien should be purified before it is used as a titrant. A procedure for its purification by precipitating the sulphate has been described.<sup>2</sup>

Calcein W is preferable to calcein for fluorescent titrations. Both are a condensation product of fluorescein, formaldehyde and iminodiacetic acid, but calcein W

is not contaminated with unreacted fluorescein. Fluorescein gives a fluorescence which is not quenched by copper and the residual fluorescence causes some difficulty when the procedure is applied to a brass such as NBS 164 or 52c.

**Zusammenfassung**—Es wurde die Anwendung von Triäthylentetramin (Trien) zum Titrieren von Kupfer beschrieben. Ein Metallfluorochromatischer Indikator, Calcein W, wurde angewandt. Die Bestandteile der Kupferlegierungen (Bronze und Messinge) üben keine Wirkung auf die Bestimmung aus.

**Résumé**—Les auteurs ont utilisé la triéthylène triamine (trien), comme réactif titrant sélectif pour le dosage du cuivre sans séparation ou dissimulation des nombreux éléments présents normalement dans les laitons et les bronzes.

L'application d'un indicateur "metallofluorochromique" a rendu possible l'utilisation de la "trien" pour le dosage de très grandes quantités de cuivre sans recourir à une méthode instrumentale pour la détermination du point équivalent.

La "calceine W" sert comme indicateur sélectif pour le cuivre en présence des nombreux éléments que l'on trouve normalement dans les bronzes et les laitons.

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# WET OXIDATION OF ORGANIC MATTER EMPLOYING MIXED PERCHLORIC AND SULPHURIC ACIDS AT CONTROLLED TEMPERATURES AND GRADED HIGH POTENTIALS

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(Received 27 October 1958)

**Summary**—The oxidation potential of perchloric acid at the boiling point is a function of temperature and concentration. At ordinary temperature no oxidation potential is provided in the concentration range 0 to 73.6%. At its boiling temperature 50% perchloric acid fails to oxidize  $\text{Fe}^{\text{II}}$  except very slowly. At 72.5% acidity, (the azeotropic concentration), the boiling acid, ( $203^\circ$ ), is a strong oxidant. For example  $\text{Cr}^{\text{III}}$  is easily oxidized to  $\text{CrO}_3$ . Between concentrations of 50% to 72.5%, the boiling acid provides oxidation potentials of continuously mounting values. By control of suitable desired concentrations through boiling under reflux, many practical procedures may be devised for the controlled wet oxidations of organic compositions.

For higher oxidation potentials, higher concentrations of perchloric acid are required. By the addition of concentrated sulphuric acid in various ratios by volume to 70% perchloric acid, effective concentrations of the latter may be provided up to and including 100%. Again by control of the particular concentrations of the mixed acids selected, through boiling under reflux, extremely high graded oxidation potentials, under static control, may be provided.

The use of sulphuric acid in such applications serves the additional important function of tempering the reaction and controlling reaction rates. The addition of 1 to 2 mg of vanadium as reaction catalyst serves the same purpose. Vanadium also favorably influences the reaction kinetics while shortening the oxidation period required.

Procedures making use of these reaction variables are herein experimentally demonstrated. The wet oxidation of such samples as coal, ion-exchange resins, alkaloids, synthetic fabric materials, rubber, heterocyclic ring nitrogen compounds and other materials serve as examples. No hazardous reactions were encountered in this work.

## INTRODUCTION

THE preparation of macro-weight samples of natural and artificially prepared organic compositions for the determination of metallic and non-metallic elements, either principal constituents or trace-element ingredients, involves the oxidation of the organic matter as a preliminary operation. Two general type procedures are employed: dry ashing, or wet ashing. The use of perchloric acid, or its mixtures with nitric or sulphuric acid, has in great measure replaced dry ashing procedures and also the use of other reactants for wet ashing techniques.

For the wet ashing methods requiring the application of the highest available oxidation potential, the use of mixed perchloric and sulphuric acids is required. The present work deals with this general problem. The variable factors governing the magnitude of the oxidation potential attainable, and illustrative procedures in the wet oxidation of organic compositions most resistant to oxidation are provided.

## PREVIOUS APPLICATIONS

The mixed oxidants, nitric and perchloric acids have been extensively applied in wet oxidation procedures.<sup>1</sup> The fields of application have been foods, feeds, biological

materials, leather, paper and paper pulp, wine, fuels, powdered dry milk and buttermilk, as well as blood and blood fibrin<sup>2</sup> and other materials.

The use of perchloric acid alone at graded oxidation potentials and controlled temperatures, has been applied to compositions essentially of cellulose, proteins, and sugars.<sup>3</sup>

The application of mixed perchloric and sulphuric acids in the wet oxidation of animal feeds and faeces has been extensively employed as described by Bolin and Stamberg.<sup>4</sup> Molybdenum was added as reaction catalyst. This process has been adapted to the determination of Eden's Indicator Method for evaluation of "digestive coefficient" using chromic oxide as indicator and is widely used in animal feeding experiments.

An extensive accumulation of literature references is found by examination of these publications. Techniques in the use of dry ashing procedures, applied almost exclusively in the field of millimicrogram trace-element determinations, has been described by Thiers.<sup>5</sup>

### BASIC REACTION CHARACTERISTICS

By the use of mixed perchloric and sulphuric acids at elevated temperatures, the effective concentration of perchloric acid made available is conveniently altered. The concentration range made available is from 70% to 100%. By addition of sulphuric acid, the rate of oxidation of organic matter is tempered by its dilution effect. The dehydration of 70% perchloric, as by addition of concentrated sulphuric acid, accounts for the increase in effective perchloric acid concentration.

By proper selection of the governing proportions of concentrated sulphuric and 70% perchloric acid, and by providing means to maintain the original concentration of reaction ingredients, a wide range of available oxidation potentials is made readily available. By the addition of pre-determined portions of water to the mixed oxidants, and with suitable control in maintenance of the original reactants, potentials from moderate to maximum values may be rigidly established.

By the use of vanadium in milligram amounts, the time interval required for a given wet ashing oxidation is markedly shortened. Provision for ready alteration of reactant concentrations during a given digestion adds to the versatility of the process and widens its scope.

### APPARATUS DESIGN

The Bethge digestion apparatus<sup>6</sup> is admirably designed to control reaction conditions. A line drawing is shown in Figure 1.

A Rogers ring burner<sup>7</sup> and plain Nichrome wire gauze upon which the Bethge digestion flask is mounted, serves to provide a readily controlled heat supply. The reaction flask may be 125-, 250- or 500-ml volume with a 24/40  $\text{\textcircled{S}}$  ground joint opening. The reaction flask, only, requires a clamp support. The air-cooled condenser provided with  $\text{\textcircled{S}}$  ground joints at top and bottom as shown has a three-way lower stopcock terminal. Through its setting, provision is made for either the return or retention of flask distillate. The water-cooled condenser is held firmly in place at the ball and socket union with the air-condenser by a standard clamp.

At the completion of a reaction of wet oxidation, the apparatus is conveniently disassembled and both the water-condenser and air-condenser placed on the side. A suitable sturdy screw pinch-clamp is provided over the tubing connecting the Rogers ring burner to the gas supply. By its use the heat may be discontinued more conveniently between reactions or during reaction. The setting of the gas supply is adjusted at the base of the burner with micro-control. Provision is made for regulation in

the height of the reaction flask on the wire gauze support above the ring burner gas flame. No lubricant other than perchloric acid is required for all glass joints.

It is not a prerequisite, but a sensible precaution, to provide a shield of 6-mm Lucite 30 to 40 cm square mounted on suitable metal supports to place between the operator and the reaction flask. The reaction flask should be provided with a thermometer-well and 250° thermometer. By its use control of reaction rates and designation and detection of exothermic reaction stages may be accurately noted.

A stop-watch is appropriate for tabulation of reaction intervals and temperatures. With reactants added to the flask, the water and air-condenser are mounted in place with the stopcock set to return

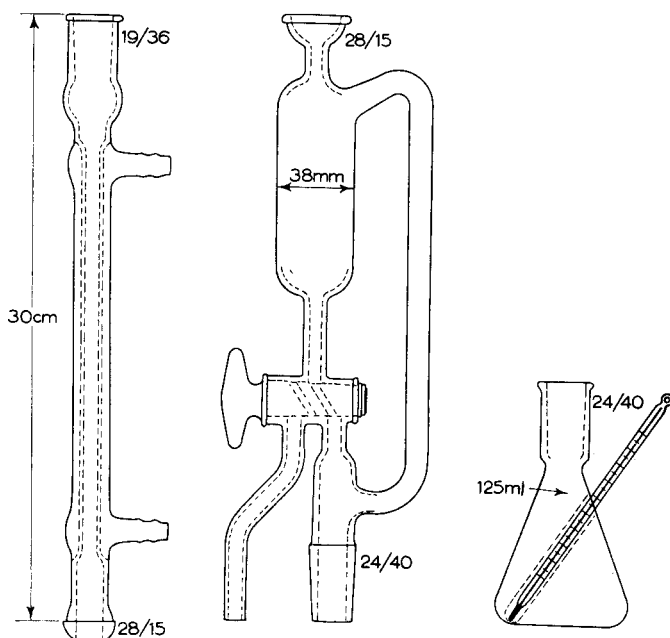


FIG. 1.

reflux to the digestion flask. By this means the reaction oxidant may be maintained for the entire period of reaction practically unaltered in composition. If desired the air-condenser stopcock may be altered. This results from the distillation of aqueous perchloric acid, with corresponding alteration of the effective ratio of sulphuric to perchloric acids in the reacting oxidants.

During the progress of a given digestion reactants may be added through the water-condenser. Reaction catalyst may be added by this process at any time interval during a given digestion.

#### MIXED PERCHLORIC AND SULPHURIC ACIDS AS OXIDANTS

For the lower magnitude oxidation potentials, concentrated sulphuric (96.3%) and perchloric (69.6%) acids, with added water, in various proportions are applicable. The boiling point of a series of such mixtures is given by reference to the data shown in Figure 2. The higher the boiling point the greater the potential provided.

For various mixtures of the same concentrated acids without added water, the effective concentrations of perchloric acid produced upon boiling are shown in the data of Figure 3. For these data, a 0.5- to 1-ml volume of distillate from the boiling mixed acids was collected and the concentration of perchloric acid determined. The boiling point, with some little decomposition, was between 212° and 216°. The formation of chlorine and oxides of chlorine as degradation products of perchloric acid was noted.

By examination of the data of Figure 3, it is seen that the effective concentration of perchloric acid provided is up to and including the anhydrous strength.

From the data of Figures 2 and 3 it is thus obvious that provision is made for establishing, and maintaining, controlled oxidation potentials covering a wide range of stepwise increasing magnitude.

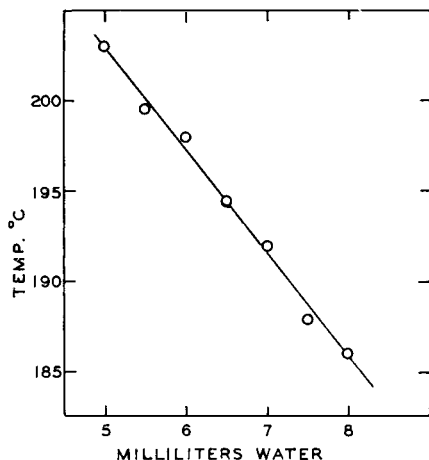


FIG. 2.

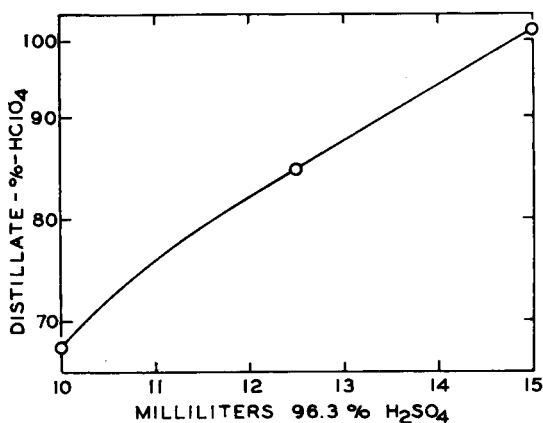


FIG. 3.

#### PREVIOUS APPLICATIONS OF PERCHLORIC-SULPHURIC ACIDS IN THE DESTRUCTION OF ORGANIC MATTER

The early use of hot concentrated sulphuric acid in the destruction of organic matter, with the use of perchloric acid additions as accelerator, were employed by Gauduchon-Truchot in a *Contribution to the Study of the Kjeldahl Process Employing Perchloric Acid*.<sup>9</sup> The boiling solution of concentrated sulphuric acid, and the decomposition products of the organic material, were treated dropwise by the addition of perchloric acid avoiding excess beyond the minimum required to finally decolorize the reaction mixture. By such procedure the determination of amino-nitrogen in the wet ashed solution was successfully applied.

This procedure was again investigated by M. Oosting<sup>8</sup> as a wet ashing process. The organic composition was heated in contact with concentrated sulphuric acid and then oxidized by the dropwise addition of perchloric acid. Added perchloric acid was left in contact with the organic matter until consumed before additional dropwise addition of oxidant. Chromium as potassium dichromate, vanadium as ammonium vanadate and selenium dioxide in 5-mg amounts were used as catalysts. Vanadium was found to be the most effective of the three.

No reference has been found in which the use of sulphuric-perchloric acid mixtures were employed in wet ashing processes at controlled and graded high oxidation potentials.

#### THE OXIDATION OF DARCO DECOLORIZING CARBON AND COCONUT CHARCOAL

A sample of 1 g of coconut charcoal (2-3-mm particle size) was placed in a 125-ml Bethge apparatus flask and 4 to 5 mg of ammonium vanadate added. Fifteen ml of a mixture of equal parts by volume of 96.3% sulphuric acid and 69.6% perchloric acid was employed as oxidant. The reflux air- and water-cooled condenser parts of the digestion apparatus were set in place and the heat applied. At 4 minutes the reaction temperature was 209° and the reaction mixture still orange in colour due to the pervanadic acid formed. The particles of carbon were not being oxidized at this temperature. At 5 minutes and 213° the carbon particles began to disintegrate and the solution resulting began to oxidize as indicated by the reduction of the pervanadic acid and the black colour of the reacting solution. At 12 minutes the reaction mixture was yellow in tint and at 15 minutes the reaction was complete and the colour orange due to reoxidized vanadium, indicating the complete destruction of organic matter. There was no acid insoluble residue.

The same reaction conditions in the oxidation of Darco decolorizing carbon (Atlas Powder Co., in one-gram samples) required only 9 minutes digestion for complete oxidation. The Darco oxidation was accompanied by 30 to 35 mm of foam formation and the oxidation was productive of considerable white fumes emitted by the water condenser. The foam quickly subsided and no insoluble matter was evident in the cold, diluted, wet ash residue.

#### THE WET OXIDATION OF COAL, ANTHRACITE, OR BITUMINOUS, OF HIGH AND LOW VOLATILE COMBUSTIBLE MATTER

The determination of arsenic in coal has formerly been carried out following wet oxidation using mixed nitric and sulphuric acids. This procedure is time-consuming, and is complicated by troublesome foam production. The presence of complex heterocyclic ring nitrogen compounds requires a more effective oxidant. The wet oxidation of coal employing mixed perchloric and sulphuric acids overcomes these three limitations.

For such wet oxidation of coal a two-stage reaction is involved. First the volatile combustible matter (the V.C.M. of the proximate analysis of coal) is oxidized. The required oxidation potential is not excessive for this stage of the reaction. The second stage of the oxidation demands a much higher oxidation potential. Foam formation accompanies the first stage but not the second stage. The first stage is markedly exothermic and must be temperature controlled. The second stage is carried out at higher temperature and vanadium is added as catalyst.

The procedure found best suited for the wet oxidation of coal is as follows:

The Bethge digestion reaction with 125-ml reaction flask is suited to the oxidation of one gram samples.

The first stage reaction employs 2.5 ml of 96.3% sulphuric acid and 7.5 ml of 69.6% perchloric acid. No vanadium catalyst is present.

The gas flame is lit and in less than 2 minutes the temperature is 80 to 85°. At this point the heat is cut off by closing the screw-clamp of the gas supply tube, and the exothermic reaction resulting carries the reaction temperature to 180 to 185°. The foam formation at this stage is from a small amount, approximately 15 mm for anthracite coal, to 50 mm for bituminous high V.C.M. type coal. After a 5-minute time interval for reaction the temperature begins to drop slowly. A 5-ml portion of sulphuric acid in which 5 to 6 mg of ammonium vanadate is dissolved, is then added through the water-condenser

and the heat again applied. The completion of the digestion follows in 15 to 20 minutes for anthracite, 13 to 14 minutes for Pocahontas coal, and 9 to 10 minutes with high volatile Orient (Southern Illinois) coal.

A feature of the wet oxidation reaction with equal parts by volume of sulphuric and perchloric acids (effective perchloric acid concentration 100%) is the formation of decomposition products which during the early stage of oxidation issue as white fumes out of the top of the water-condenser. These are due to the dissociation of 100% perchloric acid into chlorine, oxides of chlorine and oxygen. No indication of an oily reflux of decomposition products from the coal is noted by examination of the inside walls of the air-condenser. This indicates no loss of volatile combustible matter through the water-condenser.

#### WET OXIDATION OF COAL AS A SINGLE STAGE REACTION

The oxidation of coal may be applied as a single-stage reaction. The mixed sulphuric and perchloric acids, of the same strength and proportions previously described, with added vanadium catalyst, serve to oxidize 2 g of Orient high V.C.M. coal using a 500-ml reaction flask.

The temperature after 2 minutes heating was 66°. White fumes filled the reaction flask. After three minutes the temperature was 110° and rapidly increasing. At 4 minutes the temperature was 225° and there was 50 mm of foam over the boiling reaction acids. At 5 minutes the foam had subsided and the reacting acids turned the colours black to red-brown; the temperature had fallen to 202°. At 8 minutes the temperature was 203° and the reaction mixture yellow in colour. With the reflux return cut off the temperature increased to 210° at the 14-minute interval and the oxidation was complete.

The fumes escaping from the water-condenser in this reaction were collected in a cold trap immersed in a dry ice-acetone bath. There were thus collected 2.35 g of condensate. There remained a yellow oil, weight 1.05 g, after warming to room temperature. This constituted the unoxidized volatile combustible matter from the coal oxidation. The reflux collected in the air-condenser had a volume of approximately 3.0 ml.

Essentially the same results were attained with 12.5 ml of sulphuric acid plus 15 ml of perchloric acid in the oxidation of 2 grams of the same coal. In this case the exothermic reaction carried the temperature to 202° in 7 minutes. At this point the reflux return was cut off and the reaction complete after 30 minutes with other results the same.

A 3-g sample of anthracite coal was similarly oxidized using 18 ml of sulphuric acid and 15 ml of perchloric acid again with 2-3 mg of vanadium as catalyst. In this case there was no appreciable foam formation. The exothermic reaction carried the temperature to 208° at the 8-minute interval. The return of reflux was cut off at 25 minutes and the reaction complete at 50 minutes. The cold trap condensate was 2.35 g reduced to approximately one gram at room temperature, with high volatile matter being lost.

Under the same conditions a 2 g sample of Pocahontas coal gave the same type results except that the starting acid mixture was 10 ml of sulphuric acid and 15 ml of perchloric acid. The reaction produced 15 mm of foam at the 5 minute interval at 224°, indicating again a markedly high exothermic reaction. At 13 minutes the reflux return was cut off and the reaction complete in 30 minutes. The reflux collected in the air condenser had a volume of 4.5 ml. The cold trap condensate again was approximately 1 ml at room temperature.

The determination of arsenic in coal following procedures as described presents the problem of the possible loss of arsenic by either volatilization or retention in the acid insoluble ash.

These same problems exist in a wet oxidation procedure which employs mixed nitric-sulphuric acid as reactants. By reasonable prediction, no arsenic will be lost by volatilization in wet ashing because of the high potential provided to maintain the arsenic in its higher valence state.

Loss by retention of arsenic by the ash residue must be proven following either wet or dry preliminary ashing procedures.

#### PRE-DIGESTION BY SULPHURIC ACID FOLLOWED BY FINAL OXIDATION WITH ADDED PERCHLORIC ACID

As previously shown, carbon as coconut charcoal or Darco decolorizing carbon, may be wet ashed employing boiling mixed sulphuric and perchloric acids with added vanadium catalyst. With the two concentrated acids, and equal volume mixtures, an effective perchloric acid of 100% strength is provided.



This suggests a preliminary digestion with concentrated sulphuric acid. The carbonization of the sample having been accomplished, the subsequent addition of perchloric acid rapidly completes the oxidation. Such a procedure is more time consuming but has the advantage that foam formation is avoided.

The wet oxidation of ion-exchange resin IR-120 was employed to demonstrate this type reaction.

The Bethge digestion apparatus with 500 ml reaction flask was charged by the addition of 2 grams of sample, 2 to 3 mg of vanadium and 15 ml of concentrated sulphuric acid. A 60-minute digestion period was employed for this reaction (at 15 minutes 180°, at 30 minutes 185° and at 60 minutes 220°). The inner side walls of the reaction flask at this point were well spattered with charred sample reactants and the solution well charred and jet black.

At this point there was added (by pouring through the water condenser) 5 ml of 70% perchloric acid.

In 2 to 3 minutes the temperature rose to 230° and receded to 210°. The side walls of the reaction flask were completely clear of black deposit. The reaction of oxidation was complete in 10 minutes of the second stage at a temperature of 203°. The cooled acid residue was turbid but dilution with an equal volume of water gave a clear solution.

This procedure was applied with equally good results to dried whole milk powder. It constitutes a general method of attack.

#### THE WET ASHING OF WOOL AT HIGH OXIDATION POTENTIAL

This reaction may be carried out by any one of three procedures.

1. By use of mixed nitric plus perchloric acid,<sup>2</sup> with and without vanadium as catalyst.
2. By reaction with 64.5% boiling perchloric acid,<sup>3</sup> with vanadium as catalyst.
3. By digestion with equal volumes of 96.3% sulphuric and 69.6% perchloric acid in the presence of vanadium for catalysis. Reaction 3 is the most rapid. It was demonstrated as follows:

The Bethge apparatus (250 ml flask) was charged with 1 g of wool yarn, 2 to 3 mg of vanadium and 15 ml of equal parts by volume of concentrated sulphuric acid and 69.6% perchloric acid.

The digestion was at low heat. At 2.5 minutes the sample was completely in solution (dark brown) and at 90°. At 3 minutes it was at 122° with brisk ebullition. At 3.5 minutes the temperature was 165° with foam formation of 10 mm. At 4 minutes the temperature was 200°C with 25 mm of foam formation and the colour changed from brown to green. At 4.5 minutes and 205° the foam subsided. At 5 minutes the temperature was the same and the reacting solution yellow. The reaction was complete in 6 minutes at 203° and orange in colour from pervanadic acid which indicates complete oxidation. The cool reaction mixture deposited crystals of ammonium perchlorate but gave a clear solution after dilution.

#### THE WET OXIDATION OF THE MOST OXIDATION-STABLE ORGANIC MATERIALS

The wet oxidation of quinoline serves as an example. A 2-ml sample (2.2 grams) was digested in the Bethge apparatus using a 250-ml flask. The oxidant was 15 ml of equal parts by volume of concentrated sulphuric acid and 96.6% perchloric acid with 2 mg of vanadium as catalyst (effective perchloric acid strength 100%).

With 4 minutes heating the temperature was 190° and vigorous reaction set in. The temperature after 5 minutes was 214° accompanied by the formation of 25 mm of foam. At 6 minutes the temperature was 225° and the solution changed from dark-brown to red-brown. At 8 minutes the temperature fell to 218° and the reactants were yellow in colour with no foaming. At 10 minutes the temperature was 225° and reaction complete as indicated by the pervanadic acid colour.

The wet ash residue was evaporated to remove excess acid. After removal of perchloric followed by sulphuric acid, there remained, upon cooling, a white crystalline residue soluble in water and strongly acidic in reaction. A sample of this residue was neutralized to pH 5.5 and copper sulphate added. A blue insoluble precipitate was obtained indicating the reaction product to be nicotinic acid.

Such oxidation has been employed for the patented procedure in the manufacture of nicotinic acid.

#### THE WET OXIDATION OF 8-HYDROXYQUINOLINE

The same reaction oxidant as employed for the oxidation of quinoline was employed. A 1-g sample of "oxine" was wet ashed with complete oxidation in less than 10 minutes digestion. The wet ash was

evaporated to remove the mixed acids and the catalyst and a small amount of ammonium sulphate only remained.

The oxidation of both ring structures of "oxine" was in this case complete as distinct from the partial oxidation of quinoline only to nicotinic acid.

A one-gram sample of Snyder's reagent (4:7-dihydroxy-1:10-phenanthroline) was oxidized under the same conditions. The reaction was complete in 10 minutes and the wet ash upon evaporation to remove the excess acids showed only the catalyst as a residue. This oxidation was accompanied by no carbonization by the hot acid medium.

#### WET OXIDATION OF SYNTHETIC FABRIC MATERIALS

This oxidation is difficult to carry out employing procedures other than high oxidation donors. The mixed acids used were equal parts of 96.3% sulphuric acid and 69.6% perchloric acid with 1 to 2 mg of vanadium as catalyst. The Bethge digestion apparatus with 250-ml reaction flask was employed at moderate heat. The results are given in Table I.

TABLE I. THE WET OXIDATION OF NYLON, DACRON AND ORLON

Time, <i>min</i>	1	1.5	2.0	2.5	3	3.5	4	5	6	7	8
Nylon	54°	—	66	90	123	194	213	213	210*	—	—
Dacron	47°	54	65	80	105	165	209	209	210	211	211*
Orlon	41°	150	192	218	218	215	214	214*	—	—	—

\* Oxidation complete.

All three materials were exothermic in reaction to a marked degree. No carbonization degradation products were formed. Foam formation was pronounced with Nylon and Orlon, but normal with Dacron. The residual acid solution of the ash was clear in each case when hot. When cool a precipitate of ammonium perchlorate formed in the case of Nylon and Orlon but not with Dacron. Upon dilution with water, all gave clear solutions except Orlon. With Orlon the oxidation was most rapid and the exothermic nature of the reaction the most pronounced.

#### THE WET ASHING OF RUBBER

The procedures previously employed were digestion with mixed nitric and perchloric acids. Their general adoption for routine analytical control has been retarded, due to fear of attending uncontrolled reaction rates.

For analyses, other than the determination of sulphur, predigesting with hot concentrated sulphuric acid is a recommended procedure.

A 1-gram sample of pure gum rubber, finely divided, was placed in a 250-ml Bethge apparatus flask. Concentrated sulphuric acid (7.5 ml) was added and 1 to 2 mg of vanadium. The pre-digestion period was 10 minutes at 200°. The inside walls of the flask were coated black from spray reaction products, the solution was carbonized and black, and sulphur dioxide escaped from the water-condenser.

The reaction mixture was cooled to 40° and 7.5 ml of 69.6% perchloric acid added by pouring through the water-condenser. Heating for 3 minutes imparted 100° to the reaction and oxidation was initiated with the formation of 50 mm of foam. At 5 minutes the reaction temperature was 200° and oxidation vigorous. At 8 minutes the solution was dark brown and at 215°. In the reaction period 8 to 20 minutes the temperature fell to 188°, the solution changed from brown, through red, then yellow, and finally to orange, to indicate completion of oxidation.

The wet ash was clear when hot, turbid when cold and clear again with dilution.

#### PROCEDURAL GENERALIZATIONS

By the application of one of the three general methods above cited in the oxidation of wool, practically any sample of organic composition may be successfully and rapidly wet ashed.

For recovery of sulphur in the wet ash residue, nitric acid must be one portion of the oxidizing acid mixture. Boiling 72.5% perchloric acid fails to retain sulphur quantitatively as sulphuric acid. Small portions, in the absence of nitric acid, are converted to sulphuryl chloride and evolved. Procedures (2) and (3) retain arsenic, phosphorus and metallic major and minor constituents quantitatively. Following reaction types (1) and (2) silica may be determined. This procedure requires evolution of nitric acid, if involved, dilution and filtration.

For the determination of arsenic, phosphorus and molybdenum there are available spectrophotometric procedures of high sensitivity. For the determination of Fe, Cu, and Co, the procedures may employ the chromophore group specifics, ( $=N-C-N=$ ) such as 1:10-phenanthroline or its many derivatives. These include "cuproïne," "neo-cuproïne," "bathophenanthroline," "bathocuproïne," "Snyder's reagent," "Terosite," terpyridine and bipyridine among other examples.

By all these processes the sensitivity is such that it is seldom necessary to wet ash samples larger than one gram.

The Bethge apparatus for digestion provides a ready means of removal of excess acid, with retention of the distillate. This provides for retention of any evolved elements for determination if loss by volatility is suspected.

There is available a wide range of oxidation potentials from moderate to the highest attainable. Static control of specific oxidation potentials is assured. The elimination of all hazard from uncontrolled reaction rates is assured. The study of reaction conditions resulting in the least requisite time may be made, employing a wide variety of acid mixtures, reagent concentrations and proportions including temperature control. All these variables create flexibility which cannot be duplicated, even remotely, by the use of oxidation media in the absence of perchloric acid.

*Boiling 72.5 per cent perchloric acid alone cannot be employed to oxidize cellulose, sugars, or alcohols or compositions rich in these ingredients. Violent reactions are certain to result.* By the simple expedient of oxidation with mixtures of nitric acid and perchloric acid combined, such oxidations are entirely practical and a very large number of routine control analyses without the least hazard are in constant routine application.

Boiling diluted perchloric acid (55% to 65%) concentration maintained by use of the Bethge apparatus through reflux return, is admirably adapted for the wet oxidation of products rich in cellulose, proteins and sugars.<sup>3</sup>

For organic compositions requiring the highest oxidation potential such as coal, ion-exchange resins, alkaloids, carbon and heterocyclic ring nitrogen structures such as caffeine, the use of mixed sulphuric and perchloric acids represents a very important series of reactions. The use of vanadium as catalyst serves to temper and shorten oxidation periods. The presence of sulphuric acid serves the same dual purpose.

In establishing correct procedures for any new type wet oxidation no hazard is involved. A 10-milligram sample may be first tested. If the particular reaction composition gives a controlled oxidation it may be increased to 100 mg, then to 500 mg and finally to 1 gram samples or larger. The use of an operator's protective scheme, such as a transparent reaction flask shield is not an admission of possible ensuing violent reaction, but is rather a sensible protection. This is a correct procedure with many reactions in which perchloric acid has no part.

Perchloric acid is, without fear of refutation, the most versatile analytical reagent

known. Study of its basic chemistry and familiarity with its multiplicity of applications receives far too little study. Its use contributes speed, accuracy, and convenience for hundreds of analytical operations. It is a fault to outlaw its use as a result of misinformation. One thus avoids the real labour of experimentation. Wet oxidations are indeed but a small part of the rich rewards of its multiplicity of reaction advantages.

#### FURTHER APPLICATIONS

Many specific applications in wet oxidation procedures besides those described have been omitted from this account although successfully applied. By the use of the apparatus described, and by following the considerably varied processes experimentally demonstrated herein, few if any situations defy successful methods of attack.

For a general review of the role of perchloric acid in procedures of wet oxidation consult H. Diehl and G. Frederick Smith.<sup>10</sup>

**Zusammenfassung**—Es wurde eine Untersuchung von oxydative Kraft (Potential) der Überchlorsäure und Schwefelsäure-Überchlorsäure Mischungen zwecks Zerstörung der organischen Substanzen nasser Veraschung vorgemommen. Das Oxydationspotential wurde an Fe-II bis Fe-III und Cr-III—CrO<sub>3</sub> angewandt geprüft. Die Gegenwart von Schwefelsäure vergrößert das Potential der Überchlorsäure, und stimuliert der Verlauf der Reaktion. Vanad in kleiner Menge (1–2 mg) dient dem gleichen Zwecke, und reguliert auch die Kinetik der Oxydation. Die bearbeitete Technik wurde auf Probe von Kohle, Ionaustaucherharze, Alkaloide und syntetische Stoffe angewandt, und befriedigend gefunden.

**Résumé**—Le potentiel d'oxydation de l'acide perchlorique à son point d'ébullition est une fonction de la température et de la concentration. A la température ordinaire, on ne peut déterminer aucun potentiel d'oxydation dans le domaine de concentration de 0 à 73,6%. A la température d'ébullition l'acide perchlorique à 50% ne réussit pas à oxyder Fe (II), si ce n'est très lentement. A une acidité de 72,5% (concentration azeotropique), l'acide bouillant (203°C) est un oxydant puissant. Par exemple Cr (III) est facilement oxydé en CrO<sub>3</sub>. Pour des concentrations comprises entre 50 et 72,5%, l'acide bouillant a des potentiels d'oxydation continuellement croissants. Par le contrôle de concentrations convenablement choisies au moyen de l'ébullition à reflux, on peut imaginer de nombreuses méthodes pratiques pour des oxydations contrôlées par voie humide de composés organiques.

Pour avoir des potentiels d'oxydation élevés, il faut de fortes concentrations d'acide perchlorique. Par addition d'acide sulfurique concentré en quantités variables en volume à de l'acide perchlorique à 70%, les concentrations effectives de ce dernier peuvent augmenter et atteindre 100%. De nouveau, par le contrôle de concentrations particulières des mélanges d'acides choisis au moyen de l'ébullition à reflux, on peut obtenir des potentiels d'oxydation extrêmement élevés, sous contrôle statique.

L'utilisation d'acide sulfurique dans de telles applications remplit la fonction supplémentaire importante de maîtriser la réaction et contrôler les vitesses de réaction. L'addition de 1 à 2 mg de vanadium comme catalyseur de la réaction a le même but. Le vanadium influence aussi favorablement la cinétique de la réaction tout en raccourcissant la période d'oxydation nécessaire.

Des méthodes utilisant cette réaction ont été démontrées ici expérimentalement. L'oxydation par voie humide d'échantillons tels que charbon, résines échangeuses d'ions, alcaloïdes, matériaux synthétiques servent d'exemples. Aucune réaction dangereuse n'a été rencontrée dans ce travail.

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## THE DETECTION OF CARBON IN SPOT TEST ANALYSIS\*

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**Summary**—If organic compounds are dry heated with mercuri-amido chloride or with a mixture of mercuric oxide and ammonium chloride, hydrogen cyanide results. The latter can be sensitively detected through the colour reaction (blue colour) when the gas phase is permitted to come into contact with filter paper moistened with a solution of copper acetate and benzidine acetate. This detection of carbon can be accomplished within the technique of spot test analysis; the limit of identification is 1  $\mu\text{g}$  carbon.

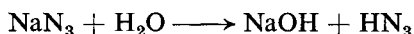
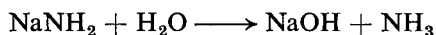
THE problem of detecting carbon or more correctly carbon-containing compounds arises when testing for the presence of metal-organic compounds, or in testing the purity of inorganic materials, and also when studying the evaporation residues of commercial waters. Emich<sup>1</sup> has described a microchemical method for detecting carbon based on the detection of carbon dioxide produced by burning the sample, but in addition to requiring delicate apparatus and exact handling, this method has the further disadvantage of not being applicable when carbonates are also present. Feigl and Goldstein<sup>2</sup> have described procedures for spot test purposes, which make use of sensitive redox reactions and which are not impaired by carbonates. However, oxidizing or reducing inorganic compounds do interfere and hence these must be completely removed before applying the test.

For these reasons, special interest resides in a procedure proposed by Mamose<sup>3</sup> and his associates, which though impaired by carbonates, which are readily removed, is not subject to interference by inorganic compounds that have oxidising or reducing properties. This test is based on the formation of sodium cyanide when organic compounds and inorganic compounds containing carbon are dry-heated with sodium amide (m.p. around 200°). Wöhler<sup>4</sup> found that sodium amide decomposes into its elements when heated and that sodium cyanide results on heating with carbon. Accordingly, the Mamose procedure probably involves the simultaneous production of free sodium, carbon and nitrogen, and also the marked combining power of the latter two elements. This view is supported by the finding of Mueller<sup>5</sup> that sodium cyanide results if organic compounds are heated with sodium azide, which itself decomposes when heated and gives sodium and nitrogen. Since very sensitive tests are available for cyanides, it could confidently be expected that sensitive tests for carbon might be developed on the basis of pyrolysis of the sample in the presence of sodium amide or sodium azide.

However, trials showed that, within the technique of spot test analysis, the formation of sodium cyanide by dry heating of organic compounds with sodium amide or azide occasionally fails completely or takes place to an unsatisfactory extent. Moreover, the explosive decomposition in the presence of sodium azide is a handicap. The reason for the failure was to be sought in an effect, which Feigl<sup>6</sup> has termed

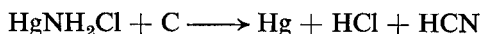
\* Translated by Ralph E. Oesper, University of Cincinnati, U.S.A.

pyrohydrolysis, and which he has employed in qualitative organic analysis. Pyrohydrolysis involves fundamentally the action of water that is released as quasi-superheated steam during the dry heating of metal salt hydrates or organic compounds; such steam is capable of bringing about reactions that by the wet method are not realizable at all, or not to more than a minor extent. Accordingly, when the organic compounds give off water when dry-heated in the vicinity of the melting- or decomposition-temperature of admixed sodium amide or sodium azide, the following hydrolysis occur:



Since these hydrolyses destroy the sodium amide or azide, the formation of cyanide during the pyrolysis steadily decreases and finally ceases. Hence the yield of cyanide will be insufficient in many cases to provide a satisfactory test.

It has now been found that a reliable production of cyanide can be achieved, without impairment by pyrohydrolysis, if the organic sample is dry-heated in the presence of mercuri-amido chloride, commonly known as infusible white precipitate. When the sample is heated in the presence of this compound hydrogen cyanide gas is formed, which can be readily detected in the gas phase by the well known and widely-used colour reaction of Sievert and Hermsdorf.<sup>7</sup> No experimentally substantiated statements can be made regarding the reaction path leading to hydrogen cyanide. However, the net reaction can be written:



The procedure given here has the following advantages. The method is applicable to all organic compounds; if certain precautions are taken, even volatile samples can be successfully tested. Organic compounds containing sulphur, which according to Mamose decrease the yield of sodium cyanide because of the formation of thiocyanate, do not interfere. Obviously the sulphur is fixed and immobilized as mercury sulphide. No pyrohydrolysis occurs. In contrast to sodium amide and sodium azide, the mercuri-amido chloride is neither hygroscopic nor does it explode on heating. A mixture of mercuric oxide and ammonium chloride may be substituted for the complex mercuric chloride.

*Procedure:* Conduct the test in a micro test tube fixed in an asbestos board support. Add a small amount of the solid or liquid material to be tested or a drop of its solution to a few cg of mercuri-amido chloride or a 1 : 5 mixture of mercuric oxide and ammonium chloride. Cover the mouth of the test tube with a disc of filter paper moistened with the reagent solution. Begin heating at the upper end of the test tube and proceed downward. A blue stain appears on the paper if the response is positive.

*Reagent solution:* Equal volumes of (a) and (b) are mixed before the use.

(a) 2.86 g of copper acetate in a litre of water.

(b) 675 ml of a solution of benzidine acetate, saturated at room temperature, and 525 ml water.

About fifty organic compounds of different types were examined and the limit of identification of 1  $\mu\text{g}$  carbon was obtained. Only urea fails to give a satisfactory sensitivity.

The test as described here has been proved effective for detecting organic materials in the evaporation residues of water samples. Tests directed towards the detection of organic dust particles are in progress.

*Acknowledgement*—The authors are indebted to Professor Fritz Feigl for valuable counsel in the course of these studies.

**Zusammenfassung**—Wenn organische Verbindungen im trocknen Zustande mit Merkuriamidochlorid oder mit einer Mischung von Merkurioxyd und Ammoniumchlorid erhitzt werden, entsteht Cyanwasserstoff. Dieser kann sehr empfindlich über die blaue Farbe, die aus der Reaktion zwischen mit Kupferacetat und Benzidinacetat angefeuchtetem Filtrierpapier und der Gasphase eintritt, bestimmt werden. Dieser Tüpfelnachweis auf Kohlenstoff weist eine Erfassungsgrenze von 1  $\mu\text{g}$  Kohlenstoff auf.

**Résumé**—Si on chauffe à sec des composés organiques avec du chloro-amidure de mercure ou avec un mélange d'oxyde mercurique et de chlorure d'ammonium, il se forme de l'acide cyanhydrique. On peut déceler ce dernier de manière sensible au moyen d'une réaction colorée (couleur bleue): on met en contact la phase gazeuse avec un papier filtre imprégné d'une solution d'acétate de cuivre et d'acétate de benzidine. On peut faire cette recherche du carbone par la méthode d'analyse à la touche. La limite d'identification est 1  $\mu\text{g}$  de carbone.

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## SPECTROPHOTOMETRIC DETERMINATION OF PALLADIUM WITH THIOMALIC ACID

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**Summary**—A procedure has been developed for the ultraviolet spectrophotometric determination of palladium<sup>II</sup> with thiomalic acid. Maximum absorbance of the yellow organo-palladium complex, PdR<sub>2</sub>, is at 350 mμ; the optimum pH range is 1.1 to 2.6.

The colour reaction is instantaneous and the complex is stable for several days. Temperature variation over the range 15° to 35° has no significant effect. The coloured complex obeys Beer's law and the practical sensitivity of the reaction is 0.05 ppm of palladium.

Tolerances to a number of ions have been established and palladium has been determined in a variety of synthetic samples with good precision and accuracy.

SEVERAL reagents have been reported for the spectrophotometric determination of palladium. The most sensitive of these are *p*-nitrosodiphenylamine, *p*-nitrosodimethylaniline and *p*-nitrosodiethylaniline proposed by Yoe and Overholser.<sup>6,10</sup> Later work by Cheng,<sup>1</sup> using 2-nitroso-1-naphthol, provided a relatively simple method which is free from most of the usual interference. His method is somewhat simpler and freer from interferences than the method of Yoe and Overholser; however, it requires the extraction of the palladium complex into toluene. A method which can be carried out in aqueous media and which is rapid, sensitive and relatively free from interferences is desirable. It is the purpose of this paper to present such a method.

### APPARATUS AND REAGENTS

#### *Instruments*

Absorbance measurements were made either with a Beckman ratio recording spectrophotometer, Model DK-2, using matched 1.00-cm quartz cells or with a Beckman spectrophotometer, Model DU, using matched 1.00-cm Corex cells.

All pH measurements were made with a Beckman glass electrode pH meter, Model G.

#### *Reagents*

**Thiomalic acid:** The thiomalic acid (mercaptosuccinic acid) was obtained from the National Aniline Division, Allied Chemical and Dye Corporation, Buffalo, N.Y. Results of analysis showed C = 31.95%, H = 4.15%; calculated, C = 32.0%, H = 4.03% based on the formula HOOCCH<sub>2</sub>CH(SH)COOH. The compound is colourless and highly soluble in water. Its melting range is 150° to 152° and its ionization constant is  $5.2 \times 10^{-4}$  at 20°. Aqueous solutions of thiomalic acid (henceforth abbreviated TMA) are slightly unstable. For this reason, fresh solutions in distilled water were prepared daily or when needed. This was entirely satisfactory because there is no effect on the colour reaction when the reagent solution is less than twenty-four hours old. Solutions used in this investigation were 0.01 molar.

**Standard palladium solution:** Eighty-five millilitres of concentrated hydrochloric acid was used to dissolve 1.74 grams of palladous chloride and distilled water was added to give a final volume of

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one litre. This gave a solution one molar in hydrochloric acid and containing approximately 1000 ppm of palladium. Standardization was carried out gravimetrically by the dimethylglyoxime method.<sup>3</sup> Triplicate analyses in good agreement gave an average value of 1054 ppm of palladium. A solution containing 100 ppm was prepared by taking an aliquot of the standard solution and diluting to the proper volume.

*Buffer:* A Clark and Lubs buffer of pH 2.0 was prepared by mixing 53 ml of 0.2*N* hydrochloric acid and 250 ml of 0.2*N* potassium chloride, and diluting to one litre.

*Solutions of diverse ions:* Reagent-grade salts were used to prepare solutions of the various ions; stock solutions generally contained 1 mg of the ion per millilitre of solution.

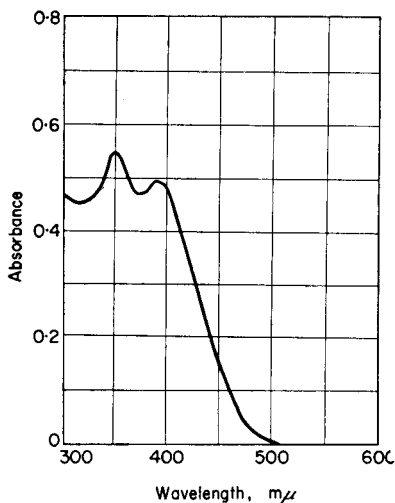


FIG. 1. Absorbance curve of the palladium complex with thiomalic acid.

#### EXPERIMENTAL AND DISCUSSION

When a drop of a 0.5% solution of TMA is added to a drop of palladium<sup>II</sup> solution (0.05 mg Pd) on a spot plate, a bright yellow colour is formed at once. This reaction was reported in 1948 by König and Crowell.<sup>5</sup>

The absorbance spectrum for the yellow organo-palladium complex is shown in Figure 1. The absorbance maximum is at 350  $m\mu$ ; the reagent does not absorb at wavelengths above 290  $m\mu$  and a water "blank" is satisfactory.

#### *Effect of pH*

The complex is formed at all pH's; however, maximum absorbance is obtained over the pH range 1.1 to 2.6. Ten millilitres of a Clark and Lubs buffer of pH 2.0 in a total volume of 25 ml is sufficient to maintain the pH well within the useful range.

#### *Concentration of reagent*

An excess of TMA is desirable since the absorbance of the complex is increased somewhat with increasing concentration of reagent. An excess of reagent also increases the tolerances to several diverse ions. Five millilitres of a 0.01*M* TMA solution was found satisfactory for a total volume of 25 ml.

### Order of addition of reagents

The order of addition of the acid solution containing palladium, the TMA, and the buffer is not critical. If the absorbance is to be measured immediately, however, the buffer must be added last. An hour is required for the colour reaction to reach maximum absorbance if the buffer is added first or second. The absorbance remains constant for at least three days.

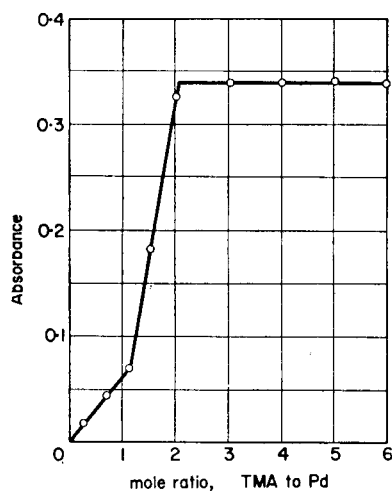


FIG. 2. Mole ratio of the palladium complex with thiomalic acid; palladium concentration constant, reagent concentration varied.

### Temperature

Temperatures over the range 15° to 35° have no significant effect on the palladium complex.

### Beer's law

Beer's law is obeyed over the concentration range 0.4 to 10 ppm of palladium, the most sensitive range being 2 to 7 ppm which give absorbances of 0.198 to 0.676.

### Structure of the palladium complex

Three methods were employed to establish the mole ratio of the complex in solution: (1) the mole ratio method of Yoe and Jones,<sup>9</sup> (2) the continuous variations method of Job<sup>4</sup> as modified by Vosburgh and Cooper,<sup>8</sup> and (3) the slope ratio method of Harvey and Manning.<sup>2</sup> Results of the three methods show a stable complex consisting of two molecules of TMA to one palladous ion. There is also a less stable one-to-one complex formed which does not absorb as strongly as does the two-to-one complex. (Figures 2, 3, 4.)

The following organic liquids were used in an attempt to extract the palladium complex from an aqueous solution (pH = 2.18): chloroform, ethyl acetate, diethyl ether, iso-amyl alcohol, cyclohexanol, *o*-dichlorobenzene. None of the liquids extracted the yellow complex to a visible extent, a strong indication that the complex is ionic in aqueous solution.

*Procedure*

The sample weight should be chosen so that a convenient volume will contain 50 to 175 ppm of palladium. Thus, a 1-ml aliquot of this solution, diluted to 25 ml, will contain 2 to 7 ppm of palladium.

Dissolve the sample by any appropriate method. Adjust the solution to the proper concentration and transfer a 1-ml aliquot by means of a pipette to a 25-ml volumetric flask. Add 5 ml of a freshly

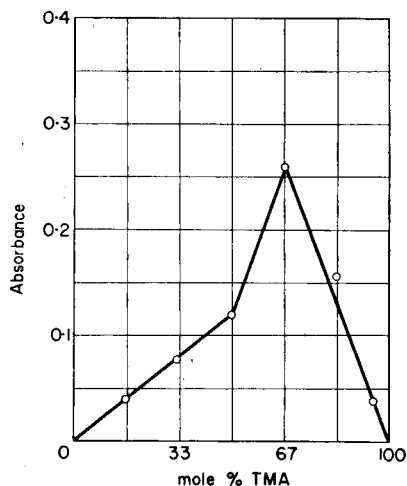


FIG. 3. Continuous variations of the palladium complex with thiomalic acid Curve (1), reagent in large excess; Curve (2), palladium in large excess.

*Note:* The first slope in Curve (2) is due to the formation of a 1 : 1 complex which absorbs less than the 2 : 1 complex. The second slope in Curve (2) was used to establish the 2 : 1 ratio.

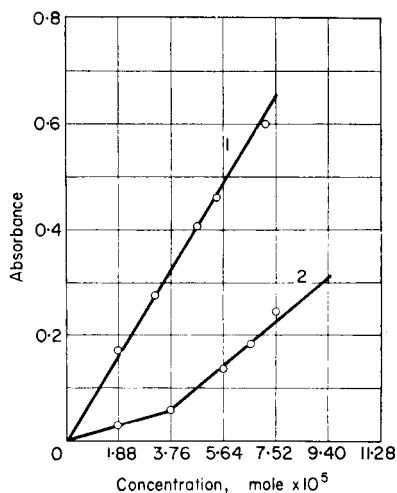


FIG. 4. Slope ratio of the palladium complex with thiomalic acid.

prepared 0.01M TMA solution and 10 ml of a hydrochloric acid-potassium chloride buffer of pH 2.0. Dilute the solution to the mark and thoroughly mix. Then measure the absorbance at 350 m $\mu$  and read the palladium concentration from a calibration curve prepared by the same procedure.

### Sensitivity

According to the Beer's law curve for the palladium complex, a concentration of 0.05 ppm of palladium should give an absorbance of 0.005 unit. Absorbance measurements of six solutions, each containing 0.05 ppm of palladium, gave values of 0.005, 0.006, 0.005, 0.005, 0.006, 0.005. Thus, 0.05 ppm of palladium may be taken as the practical sensitivity of the method. The sensitivity according to Sandell<sup>7</sup> is 0.010  $\mu\text{g Pd/cm}^2$ .

TABLE I. TOLERANCE TO DIVERSE IONS  
(4.00 ppm Pd)

Ion	Added as	Limiting concentrations <i>ppm</i>
Platinum <sup>IV</sup>	H <sub>2</sub> PtCl <sub>6</sub>	15
Rhodium <sup>III</sup>	RhCl <sub>3</sub>	4
Ruthenium <sup>III</sup>	RuCl <sub>3</sub>	3
Osmium <sup>VI</sup>	K <sub>2</sub> OsO <sub>4</sub>	3
Iridium <sup>IV</sup>	IrCl <sub>4</sub>	20
Gold <sup>III</sup>	AuCl <sub>3</sub>	1
Nickel <sup>II</sup>	Ni(NO <sub>3</sub> ) <sub>2</sub>	>100
Cobalt <sup>II</sup>	Co(NO <sub>3</sub> ) <sub>2</sub>	>100
Copper <sup>II</sup>	Cu(NO <sub>3</sub> ) <sub>2</sub>	0.6
Chromium <sup>III</sup>	Cr(NO <sub>3</sub> ) <sub>3</sub>	40
Iron <sup>III</sup>	Fe(NO <sub>3</sub> ) <sub>3</sub>	0.3
Vanadium <sup>IV</sup>	VOCl <sub>2</sub>	80
Sulphate	Na <sub>2</sub> SO <sub>4</sub>	>10,000
Nitrate	KNO <sub>3</sub>	>10,000

### Tolerance to diverse ions

A concentration of 4.00 ppm of palladium was used in this study. An ion was considered to interfere if the resulting solution differed by 0.005 absorbance unit from that containing palladium alone, *i.e.*,  $0.388 \pm 0.005$ .

Table I lists the tolerances to the metals commonly found with palladium.

### Analysis of synthetic solutions

The results of analyses of synthetic solutions are summarized in Table II. All samples were run in duplicate or triplicate. The values were in close agreement, the averages being recorded in the table.

### Precision

The precision was determined for a solution containing palladium alone (4.00 ppm Pd) and for synthetic solution No. 7 (Table II). In each case, eleven determinations were made. From these data the standard deviation,  $\sigma$ , was calculated from the formula  $\sigma = \sqrt{\frac{\sum d^2}{n-1}}$ , where  $d$  is the deviation from the mean and  $n$  is the number of determinations. The results are given below:

- (1) 4.00 ppm Pd only:  $\sigma = 0.019$  ppm, *i.e.*, 0.48%.
- (2) Synthetic soln. No. 7:  $\sigma = 0.022$  ppm, *i.e.*, 0.52%.

TABLE II. ANALYSIS OF SYNTHETIC SOLUTIONS  
Series A

No.	Pd Present ppm	Other Ions Present, ppm							Pd Found ppm
		Pt <sup>IV</sup>	Ni <sup>II</sup>	Co <sup>II</sup>	V <sup>IV</sup>	Cr <sup>III</sup>	Fe <sup>III</sup>	Cu <sup>II</sup>	
1	4.2	8	24	—	4	—	—	—	4.3
2	4.2	—	12	12	—	4	0.2	0.2	4.2
3	4.2	15	100	—	16	—	—	—	4.3
4	4.2	—	100	100	—	40	0.3	0.6	4.2

Series B

	Pd Present ppm	Other Ions Present, ppm						Pd Found ppm
		Pt <sup>IV</sup>	Rh <sup>III</sup>	Ru <sup>III</sup>	Os <sup>VI</sup>	Ir <sup>IV</sup>	Au <sup>III</sup>	
5	4.2	4	4	1.6	1.6	4	0.5	4.5
6	4.2	15	2	3	3	5	2	4.6
7	4.2	4	1	1	1	1	1	4.2
8	4.2	8	1.5	1.5	1.5	1.5	1	4.4

## CONCLUSIONS

Thiomalic acid has several advantages as a reagent for the spectrophotometric determination of palladium: It is colourless and water soluble; no extraction of the metal complex is required; the colour reaction is instantaneous and the complex is stable; the pH for maximum absorbance is easily controlled; it allows a high tolerance for many ions; laboratory fluctuations in temperature have no significant effect on the complex; the method is simple, rapid, and sensitive and its precision and accuracy are good.

**Zusammenfassung**—Zur spektrophotometrischen Bestimmung von zweiwertigem Palladium wurde der gelbe Komplex mit Thiomalinsäure, PdR<sub>2</sub>, der bei 350 m $\mu$  sein Absorptionsmaximum aufweist, herangezogen. Der geeignetste pH-Bereich liegt zwischen 1,1 und 2,6. Die Farbreaktion tritt rasch ein und der Komplex bleibt mehrere Tage stabil. Temperaturänderungen innerhalb 15 und 35° haben keinen merklichen Einfluss. Der gefärbte Komplex gehorcht dem Beerschen Gesetz, und die praktische Empfindlichkeit der Reaktion liegt bei 0,05 ppm Palladium.

**Résumé**—Les auteurs ont développé un procédé pour le dosage par spectrophotométrie dans l'Ultra-violet du palladium (II) par l'acide thiomalique. Le maximum d'absorption du complexe organo-palladeux jaune (PdR<sub>2</sub>) est à 350 m $\mu$ ; le domaine de pH le plus favorable est 1,1–2,6.

La réaction colorée est instantanée et le complexe est stable pendant plusieurs jours. Des variations de température dans le domaine 15–35° n'ont pas d'effet important. Le complexe coloré obéit à la loi de Beer et la sensibilité pratique de la réaction est 0,05 ppm de palladium.

On a établi des tolérances pour un certain nombre d'ions et on a dosé le palladium dans plusieurs échantillons synthétiques avec une bonne précision.

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## THE DETERMINATION OF CONDUCTIVITIES USING UNCONVENTIONAL ELECTRODE SYSTEMS\*

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**Summary**—An apparatus is described which permits the measurement of conductivities with non-contacting electrodes.

THE use of conventional dipping electrode systems in the determination of electrolytic conductivities is accompanied by a number of experimental difficulties many of which are directly associated with the electrodes themselves and which are often classified under the term "polarisation", whilst in concentrated solutions corrosion and fouling problems are all too common. Many attempts have been made to eliminate the use of immersed electrodes, mostly using high frequency alternating current.<sup>1</sup>

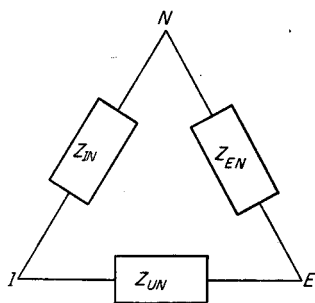


FIG. 1.

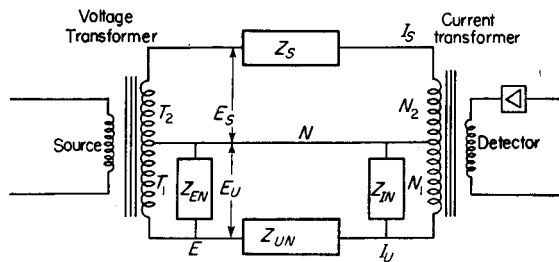


FIG. 2.

The electrode systems described here require the use of a three-terminal transformer ratio-arm bridge.<sup>2,4</sup> The basic circuit of a three-terminal network is shown in Fig. 1, where the impedance to be measured is  $Z_{UN}$  but the effects of stray impedances  $Z_{EN}$  and  $Z_{IN}$  must be removed. Fig. 2 shows the network applied to the bridge. Let E be the voltage terminal, I the current terminal and N the neutral. Assuming ideal transformers,  $Z_s$ , the standard impedance is adjusted to give zero voltage at the detector when there must then be zero core flux in the current transformer and

$$N_1 \cdot I_u = N_2 \cdot I_s \quad (1)$$

where  $N_1$  is the number of turns on the windings connected to the unknown,  $N_2$  the number of turns connected to the standard, whilst  $I_u$  and  $I_s$  are the currents in the unknown and standard.

Under the condition of zero core-flux there is zero voltage across the windings of

\* Presented at a meeting of the Polarographic Society, held at Nobel Division, Imperial Chemical Industries Ltd., Stevenston, Ayrshire, on 26 September 1958.



the current transformer. The connections to both  $Z_{UN}$  and  $Z_s$  on the current transformer side are thus at neutral potential and hence the voltage across  $Z_{UN}$  is  $E_u$  and across  $Z_s$  is  $E_s$  when

$$I_u = E_u/Z_{UN} \quad (2)$$

$$I_s = E_s/Z_s \quad (3)$$

and thus from equation (1)

$$N_1 E_u/Z_{UN} = N_2 E_s/Z_s \quad (4)$$

But the voltage ratio,  $E_u/E_s$  equals the turns ratio,  $T_1/T_2$ , so that at balance the equation becomes:

$$Z_{UN} = \frac{N_1}{N_2} \cdot T_1/T_2 \cdot Z_s \quad (5)$$

At balance  $Z_{IN}$  has no voltage across it and therefore draws no current. Its effect is to reduce the off-balance sensitivity by lowering the detector input impedance. This can be overcome by increasing the gain. The impedance  $Z_{EN}$  loads the source, and by

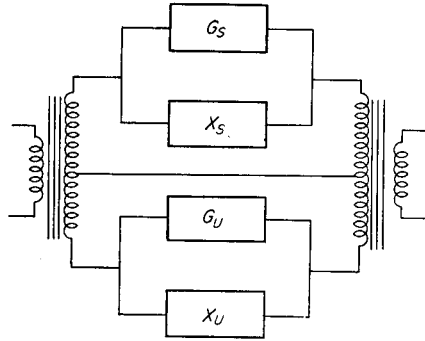


FIG. 3.

drawing current through the source impedance reduces the applied voltage  $E_u$ . The measurement, however, does not depend on absolute voltage but on the ratio  $E_u/E_s$ . In an ideal transformer this is a constant equal to the turns ratio, and a shunt on one winding reduces the voltages on all windings by the same proportions. Thus, if the transformers are ideal, neither  $Z_{EN}$  nor  $Z_{IN}$  cause any errors. In practice, whilst the transformers cannot be regarded as ideal and shunt impedances will produce small errors, careful construction can reduce the errors to negligible proportions, and in any case the effects of shunt loading can be compensated.

Equation (5) can be rewritten in terms of conductances

$$G_u = (G_s T_2) \cdot N_2/T_1 N_1 \quad (6)$$

Let  $(G_s T_2)$  represent the standard, then it will be seen that it is immaterial whether the number of turns be fixed and the conductance varied, or the conductance fixed and the number of turns varied. Using the latter method the number of standards can easily be reduced to one per decade. In practice the unknown is often a complex impedance, and Fig. 3 shows the bridge such that the standard and unknown impedance have been divided into resistive and reactive components and similar

arguments can be advanced for the determination of the reactive component. The measurements are dependent on the product of two turns-ratios and since each of these can easily be 1000 : 1, the overall ratio is a million to one. Further measurement of impedances remote from the bridge presents no great problem since the capacitance of long connecting leads and spurious impedances connected to the measuring terminals are counteracted by the use of the third terminal. The frequency is of little importance and measurements have been made at 100 c/s, 1592 c/s and 10 Kc/s.

Whilst the bridge can be used with conventional electrodes it also permits the determination of conductivity with non-contacting electrodes. Consider the case where  $T_1$  and  $N_1$  are made single turns, so that the balance equation becomes

$$G_u = N_2 \cdot T_2 \cdot G_s$$

The physical nature of the windings is unimportant and there is no reason why the cores of the voltage and current transformers, which in practice are wound on high permeability Mumetal toroidal cores, should not be linked by a closed annulus of

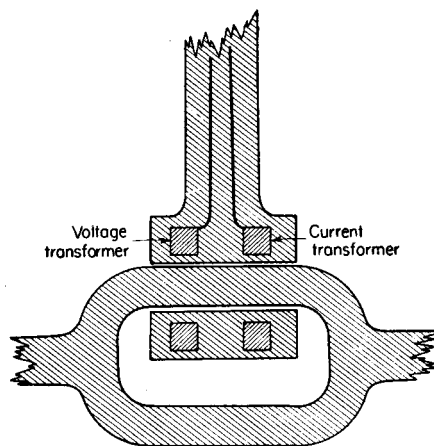


FIG. 4.

conducting liquid contained in an insulating, *e.g.* glass tube. A method of bringing this about is shown in Fig. 4, where an annular glass loop cell is used. The transformers are moulded into an insulating material, and where the electrolyte is inert with respect to the moulding, the probe may be immersed directly in the test-solution, provided the container is large in comparison with the probe. These types of units have been used to determine the conductivity of a variety of solutions, being especially suited to concentrated solutions. The electrolytes used have varied from potassium ferro- and ferricyanides through barium chloride to the conventional uni-univalent electrolytes *e.g.* hydrochloric acid, potassium bromide etc.

The ease with which the bridge determines the capacitance term enables it to be used as a "dielectric bridge." This has allowed the frequent use of the method to determine impurities, such as water, in organic liquids. For this purpose the "capacity cell" shown in Fig. 5 was used. It is necessary to use the "conversion formulae"

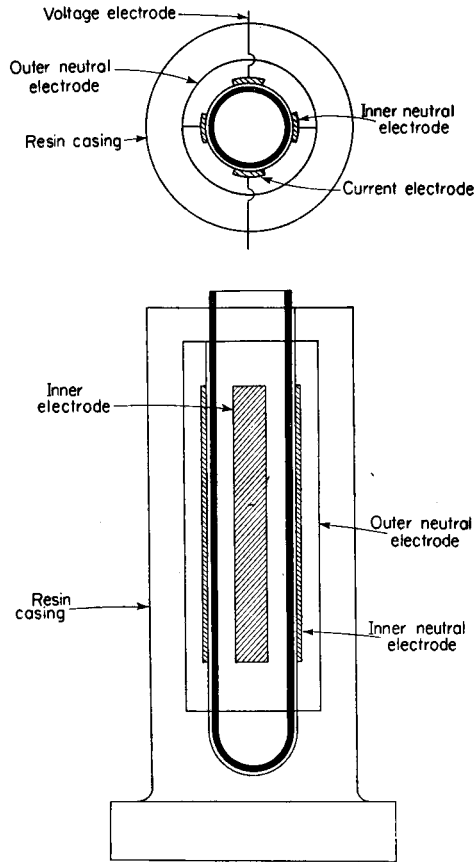


FIG. 5.

shown below where the parallel readings made with the bridge were converted to series readings, due allowance being made for the glass dielectric.

$$C_{ms} = C_{mp} + \frac{G_{mp}^2}{w^2 C_{mp}} \tag{8}$$

$$\frac{1}{C_{cs}} = \frac{1}{C_{ms}} - \frac{1}{C_g} \tag{9}$$

- where  $C_g$  = capacity of glass dielectric
- $C_{ms}$  = capacity of "measured series"
- $C_{mp}$  = capacity of "measured parallel"
- $C_{cs}$  = capacity of "corrected series"
- $G_{mp}$  = conductivity "measured parallel"
- $w$  = frequency in radians/sec.

Up to 5% water the results agree well with those of Akerlof and Short,<sup>3</sup> but above this concentration the dielectric constant value obtained is meaningless owing to the effect

of relatively small amounts of water (0.1%-3%) in organic liquids which have, when pure, low dielectric constants. Indeed, good results have been obtained for water-contaminated acetone (E 21) and also it has been possible to estimate acetone in synthetic cyclohexane-acetone mixtures, although with much less accuracy. For many purposes, where the conductivity term is negligible it has been possible to obtain results from a plot of the parallel against concentration of polar contaminant.

*Acknowledgement*—The author would like to express his grateful thanks to both Mr. R. Calvert and Mr. K. Fletcher of the Wayne-Kerr laboratories; and to Messrs. Wayne-Kerr laboratories for their generous support.

*Zusammenfassung*—Es wird ein Apparat beschrieben, welcher die Leitfähigkeitsmessung mit nicht berührenden Elektroden gestattet.

*Résumé*—L'auteur décrit un appareil qui permet la mesure des conductivités avec des électrodes sans contact.

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## THE DETERMINATION OF *vic*-DIOXIMES\*

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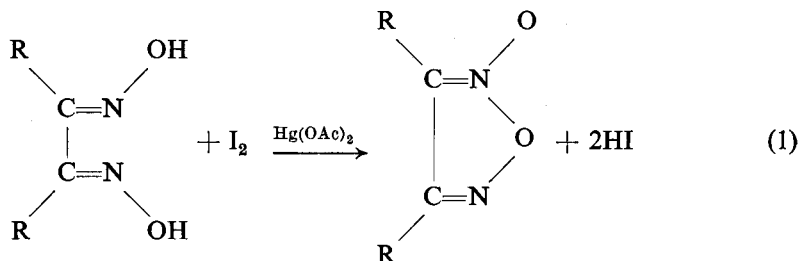
(Received 20 February 1959)

**Summary**—Iodine in the presence of mercury<sup>II</sup> acetate in non-aqueous media quantitatively dehydrogenates *vic*-dioximes to the corresponding furoxanes. This reaction was used to develop a titrimetric method for the quantitative determination of various aliphatic and alicyclic *vic*-dioximes. Fifteen different *vic*-dioximes were titrated successfully by this method. Several of the furoxanes of the *vic*-dioximes were isolated and their physical properties recorded.

### INTRODUCTION

THE purity of the *vic*-dioximes is frequently determined by elemental analysis and occasionally by gravimetric precipitation with an excess of nickel.<sup>1,2</sup> The titrimetric methods reported for the determination of nickel using dimethylglyoxime also can be used to assay various *vic*-dioximes. In the titrimetric methods the precipitate of bis(2:3-butanedionedioximato-N:N′)-nickel<sup>II</sup> is dissolved in acid and the resulting *vic*-dioxime is hydrolyzed to hydroxylamine which is then determined.<sup>3,4</sup> The precipitate also has been dissolved in glacial acetic acid and the resulting acetate groups titrated in a non-aqueous medium.<sup>5</sup> Elemental analysis and any method requiring the filtration of a nickel-*vic*-dioxime precipitate are always time consuming. For this reason a simple and fast oxidation method was devised.

Various chemical reagents have been used for the intramolecular dehydrogenation of *vic*-dioximes. Of the various reagents used—dinitrogen tetroxide,<sup>6,7</sup> sodium hypohalite,<sup>8</sup> alkaline ferricyanide,<sup>6,9</sup> nitrous acid,<sup>10</sup> and chlorine<sup>7</sup>—none possessed suitable characteristics for the development of an analytical method. It was found possible to quantitatively oxidize the *vic*-dioxime group to the furoxane structure using iodine in the presence of mercury<sup>II</sup> acetate.



The excess iodine is back-titrated to give the amount of *vic*-dioxime originally present.

Mercury<sup>II</sup> acetate increases the oxidation potential of iodine solutions because

\* No. XXIV in a series on *Chemistry of the vic-Dioximes*. Previous paper in this series is No. XXIII, *Analyt. Chim. Acta*, 1958, 19, 531.

† Contribution No. 723. Work was performed in the Ames Laboratory of U.S. Atomic Energy Commission.

iodide reacts with the mercury<sup>II</sup> acetate to give slightly dissociated mercury<sup>II</sup> iodide and mercury<sup>II</sup> iodide complexes. The oxidation potential increases to such an extent that an "auto-oxidation" of iodine to iodate takes place, removing free iodine from solution. In acid solution, the iodate reacts with iodide to re-form iodine.<sup>11,12</sup>

## EXPERIMENTAL

### Reagents

**Iodine solution:** Prepare an approximately 0.1*N* iodine solution by dissolving 12.5 g of resublimed iodine in one litre of dry carbon tetrachloride.

**Mercury<sup>II</sup> acetate solution:** Dissolve 30 g of C.P. mercury<sup>II</sup> acetate per litre of glacial acetic acid.

**Sodium thiosulphate solution:** Prepare approximately 0.1*N* sodium thiosulphate solution by dissolving 25.0 g of sodium thiosulphate 5-hydrate and 0.2 g sodium carbonate in one litre of water. Standardize the sodium thiosulphate solution against potassium iodate.

**Starch indicator solution:** Add 5 g of soluble starch which has been previously mixed with a little water to form a slurry to 500 ml of boiling water. Cool the solution and store under a thin layer of toluene.

**Potassium iodide solution:** Dissolve 75 g of potassium iodide in one litre of water.

### Procedure

Weigh the sample, containing  $(2 \text{ to } 7) \times 10^{-4}$  mole of *vic*-dioxime, into a 500-ml Erlenmeyer flask. Add 100 ml of carbon tetrachloride to the sample and also to an empty flask which serves as a blank. Then add exactly 25.00 ml of the iodine solution to both sample and blank, followed by approximately 25 ml of the mercury<sup>II</sup> acetate solution. If the sample does not readily dissolve, stir it in the stoppered Erlenmeyer flask until dissolution takes place. Allow approximately 30 min for the reaction to take place. Then add 75 ml of the potassium iodide solution to each flask and agitate the mixture vigorously. Titrate the excess iodine with the standard sodium thiosulphate solution, employing 2 ml of the starch solution as indicator. Observe the customary starch end-point in the aqueous layer. Calculate the results on the basis of equation (1). Table I lists the results obtained by the above procedure.

TABLE I. TITRATION OF *vic*-DIOXIMES WITH IODINE

<i>vic</i> -Dioxime	Sample size moles $\times 10^{+4}$	Average % found
Nioxime*	5.6-7.3	99.8 $\pm$ 0.03
4- <i>tert</i> -Amylnioxime	2.4-3.3	99.5 $\pm$ 0.25
4-Methylnioxime	5.1-6.4	99.7 $\pm$ 0.07
3-Methylnioxime	3.3-4.6	99.6 $\pm$ 0.18
4-Carboxylnioxime	4.3-5.4	99.3 $\pm$ 0.28
4-Ethoxycarbonylnioxime	2.6-2.8	100.3 $\pm$ 0.15
4- <i>iso</i> Propylnioxime	2.7-3.9	100.0 $\pm$ 0.15
3:3:6:6-Tetramethylnioxime	4.5-5.7	99.8 $\pm$ 0.05
4-Octylnioxime	3.2-4.4	99.6 $\pm$ 0.20
Heptoxime*	4.8-6.6	99.6 $\pm$ 0.23
Nioxime-urea complex	3.2-4.2	98.6 $\pm$ 0.83
Dimethylglyoxime	4.2-5.4	98.5 $\pm$ 0.03
Diethylglyoxime	3.7-4.8	99.2 $\pm$ 0.26
$\gamma$ -Benzildioxime	2.5-4.2	98.7 $\pm$ 0.03
$\beta$ -Benzildioxime	2.1-4.1	99.6 $\pm$ 0.10

\* Nioxime and heptoxime are the trivial names for 1:2-*cyclohexanedionedioxime* and 1:2-*cycloheptanedionedioxime*, respectively.

*Interferences*

The principal interferences in the titration were found to be easily oxidized materials, easily halogenated materials, primary amines, ketoximes, aldoximes, and monoximes of *vic*-diketones.

## DISCUSSION

All of the *vic*-dioximes were titrated readily with the exception of  $\alpha$ -benzildioxime, diaminoglyoxime, and  $\alpha$ -furildioxime. The first two were insoluble in the reaction mixture and with the latter high results were obtained because of oxidation of the furane rings.

Oximes and monoximes are oxidized first to the *gem*-iodonitroso compound as indicated by the immediate blue colour formation and then are further oxidized to some higher oxidation state upon addition of more oxidant. Hydroxamic acid iodides probably result from combinations of aldoximes and iodine. Reaction conditions could not be adjusted to obtain reproducible results for the titration of ketoximes, aldoximes, and monoximes.

## PREPARATION OF FUROXANES

Several of the *vic*-dioximes were dehydrogenated to their furoxane derivative in gram quantities. The melting points, boiling points, and percentage nitrogen are recorded in Table II.

TABLE II. PROPERTIES OF FUROXANES

Furoxane	B.P. at 6 mm., °C.	M.P., °C.	% Nitrogen	
			Calc.	Found*
<i>cyclo</i> Hexenfuroxane	121–122	43–44	19.99	19.56
3-Methyl <i>cyclo</i> hexenfuroxane	128–129	—	18.17	17.75
4-Methyl <i>cyclo</i> hexenfuroxane	136–136.5	—	18.17	17.98
4- <i>iso</i> Propyl <i>cyclo</i> hexenfuroxane	156–158	—	15.37	15.01
4- <i>tert</i> -Amyl <i>cyclo</i> hexenfuroxane	167–168	29–30	13.32	13.08
4-Octyl <i>cyclo</i> hexenfuroxane	—	53–54	11.10	11.28
4-Carboxyl <i>cyclo</i> hexenfuroxane	—	105–107	15.21	14.78
<i>cyclo</i> Heptenfuroxane	127–129	—	18.17	17.93
Diphenylfuroxane	—	114–115	13.08	12.87

\* Nitrogen determined by the micro-Dumas method.

*Procedure*

Dissolve iodine, 6.3 g (0.05 mole), in 400 ml of carbon tetrachloride in a 1000-ml Erlenmeyer flask. To this add 0.0025 mole of the *vic*-dioxime to be oxidized. Add a solution of 15.9 g (0.05 mole) of mercury<sup>II</sup> acetate dissolved in 250 ml of glacial acetic acid. Stir the mixture for 45 min and then transfer to an evaporation dish in a hood to permit evaporation of the carbon tetrachloride and acetic acid. When evaporation is complete extract the residue with two 150-ml portions of diethyl ether. Evaporate the ether and extract the residue again with two 100-ml portions of ether. After evaporation of the ether, repeat the process a third time. This removes most of the mercury iodide which is formed during the reaction. Dissolve the residue in a minimum of ether and vacuum distil in those cases where a liquid furoxane is obtained. If a solid is obtained recrystallize the residue from dilute aqueous ethanol and then from *cyclo*hexane.

The furoxanes listed in Table II were prepared also by oxidation of the *vic*-dioxime with sodium hypochlorite by the procedure of Boyer and Toggweiler.<sup>7</sup> In all cases the melting points and boiling points of the furoxanes obtained by the two different methods checked exactly. In general, the procedure given by Boyer and Toggweiler is to be preferred over the iodine reaction as a preparative method because of the difficulty involved in removing the last traces of mercury<sup>II</sup> iodide from the final product.

No attempt was made to determine whether the furoxanes formed by the oxidation of the substituted dioximes with either iodine or sodium hypochlorite were mixtures or one of a pair of isomeric furoxanes of unassigned structure, *e.g.*,



**Zusammenfassung**—Jod dehydriert in nicht wässrigen Medien und in Gegenwart von Quecksilber(II)acetat *vic*-Dioxim quantitativ zu den entsprechenden Furoxanen. Diese Reaktion wurde zur Entwicklung einer quantitativen massanalytischen Bestimmungsmethode für verschiedene aliphatische und alicyclische *vic*-Dioxime herangezogen. 15 verschiedene derartige Verbindungen wurden mit dieser Methode bestimmt und einige Furoxane isoliert sowie deren physikalische Eigenschaften beschrieben.

**Résumé**—L'iode en présence d'acétate mercurique en milieu non aqueux deshydrogène quantitativement les *vic*-dioximes pour donner les furoxanes correspondants. On a utilisé cette réaction pour développer une méthode titrimétrique pour le dosage quantitatif de différentes *vic*-dioximes aliphatiques et alicycliques. On a titré avec succès par cette méthode 15 *vic*-dioximes différentes. On a isolé plusieurs furoxanes correspondant a ces *vic*-dioximes et on a donné leurs propriétés physiques.

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# SPECTROPHOTOMETRIC DETERMINATION OF RHODIUM WITH THIOMALIC ACID AND THE SIMULTANEOUS DETERMINATION OF RHODIUM AND PALLADIUM

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**Summary**—A procedure has been developed for the ultraviolet spectrophotometric determination of rhodium with thiomalic acid. The maximum absorbance of the yellow rhodium complex is at 340  $m\mu$ ; the optimum pH range is 1 to 6.

The colour is formed at 100° and the complex is stable for several days. It obeys Beer's law and is sensitive to 0.055 ppm of rhodium.

Tolerances to several ions have been established and rhodium has been determined in synthetic samples with good precision and accuracy. Rhodium and palladium in several concentration ratios have been determined simultaneously.

THERE are few satisfactory methods for the spectrophotometric determination of rhodium.<sup>3</sup> In most of the existing methods interferences are serious and the procedures are tedious.

The authors have recently<sup>4</sup> presented a method for the spectrophotometric determination of palladium with thiomalic acid (abbreviated TMA). The same reagent can be applied to the spectrophotometric determination of rhodium. The method is fairly rapid, simple and relatively free from interferences. It is also possible to determine palladium and rhodium simultaneously.

## EXPERIMENTAL

### *Instruments*

Absorbance measurements were made either with a Beckman ratio recording spectrophotometer, Model DK-2, using matched 1.00-cm quartz cells or with a Beckman spectrophotometer, Model DU, using matched 1.00-cm Corex cells.

All pH measurements were made with a Beckman glass electrode pH meter, Model G.

### *Reagents*

*Thiomalic acid*<sup>4</sup>: A 0.05M solution of TMA in distilled water was prepared daily, or when needed.

*Standard rhodium solution*: A solution containing approximately 1000 ppm of rhodium was prepared by dissolving 0.68 g of  $RhCl_3 \cdot 4H_2O$  in 250 ml of 0.33N hydrochloric acid. It was standardized gravimetrically<sup>1</sup> by precipitating the rhodium as the hydrous oxide in the presence of sodium hydroxide and sodium bromate; filtering, washing, and igniting in air to  $Rh_2O_3$ . Duplicate analyses in close agreement gave an average value of 950 ppm of rhodium. A solution containing 100 ppm of rhodium was prepared by diluting an aliquot of the standard. A few drops of hydrochloric acid were added to the aliquot before dilution in order to prevent hydrolysis.

*Buffer solution*: A Clark and Lubs buffer of pH 2.0 was prepared by mixing 53 ml of 0.2N hydrochloric acid and 250 ml of 0.2N potassium chloride, and diluting to one litre.

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*Solutions of diverse ions:* Reagent-grade salts were used to prepare solutions of the various ions. Stock solutions contained 1 mg of the ion per ml of solution.

### DETERMINATION OF RHODIUM

When a dilute solution of rhodium chloride is heated at 100° with thiomalic acid, a bright yellow colour is formed.

The absorbance spectrum of the yellow TMA-rhodium complex is very similar to that of the TMA-palladium complex (Fig. 1). The rhodium complex has a maximum at 340 m $\mu$ ; the reagent does not absorb at wavelengths above 290 m $\mu$ . All measurements of the complex can be made against a water "blank."

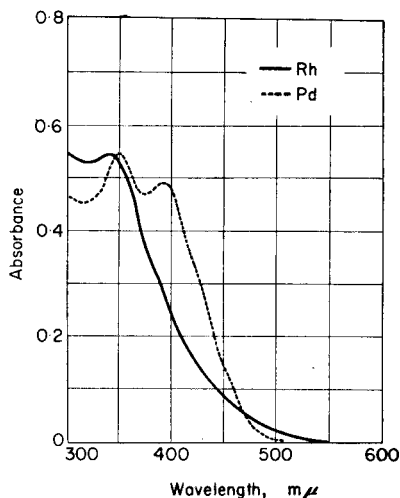


FIG. 1. Absorbance curves of the rhodium and palladium complexes with thiomalic acid.

#### *Effect of pH*

There is no noticeable effect of pH on the absorbance of the rhodium complex over the range 1 to 6. It is advisable, however, to maintain a low pH because rhodium salts hydrolyse easily.

In this study, 10 ml of a Clark and Lubs buffer of pH 2.0 were used in a total volume of 25 ml to maintain the pH close to 2.

#### *Concentration and heating time*

A boiling-water bath was employed as a source of heat for developing the rhodium complex. Addition of 1 ml of 0.05M TMA solution and a heating period of 40 minutes are the most favourable conditions for the formation of the rhodium complex. The complex is stable for at least a week.

#### *Temperature*

The effects of fluctuations of laboratory temperature on the measurement of the rhodium complex was studied. The temperature effect is negligible over the range of 15° to 35°.

#### *Structure*

No attempt was made to determine the structure of the Rh-TMA complex since TMA decomposes rapidly at the temperature of the complex formation (100°).

#### *Beer's Law*

The complex obeys Beer's law at 340 m $\mu$  and at 350 m $\mu$  over the concentration range 1.2 to 10 ppm, the most sensitive range being 2 to 7 ppm.

### Procedure

The sample weight should be chosen so that a convenient volume will contain 50 to 175 ppm of rhodium. Thus, a 1-ml aliquot of such a solution, diluted to 25 ml, will contain 2 to 7 ppm of rhodium.

Dissolve the sample by any appropriate method. Adjust the solution to the proper concentration range and transfer a 1-ml aliquot by means of a pipette to a 25-ml volumetric flask. Add 1 ml of a freshly prepared 0.05M solution of TMA. Heat the flask in a boiling-water bath for 40 minutes, then remove and cool the flask under the water tap. Add 10 ml of a hydrochloric acid-potassium chloride buffer of pH 2.0, dilute to the mark and thoroughly mix. Measure the absorbance at 340 m $\mu$  and read the rhodium concentration from a calibration curve prepared by the same procedure.

### Sensitivity

According to the Beer's law curve for the rhodium complex, a concentration of 0.055 ppm of rhodium should give an absorbance of 0.005 unit. Absorbance measurements of six solutions, each containing 0.055 ppm of rhodium, gave values of 0.005, 0.007, 0.006, 0.005, 0.005 and 0.007. Thus, 0.055 ppm of rhodium may be taken as the practical sensitivity of the method. The sensitivity according to Sandell<sup>2</sup> is 0.011  $\mu\text{g}/\text{cm}^2$ .

### Precision

The precision was determined for a solution containing 4.00 ppm of rhodium. Eleven determinations were made and the standard deviation,  $\sigma$ , was calculated from the formula

$$\sigma = \sqrt{\frac{\sum d^2}{n-1}},$$

where  $d$  is the deviation from the mean and  $n$  is the number of determinations.

$$\sigma = 0.023 \text{ ppm, i.e. } 0.57\%.$$

### Tolerance to diverse ions

A rhodium concentration of 4.00 ppm was used in this study. An ion was considered to interfere if it caused a difference of 0.005 absorbance unit from that containing rhodium alone.

Table I lists the tolerances to the metals commonly found with rhodium.

TABLE I.—TOLERANCE TO DIVERSE IONS (4.00 ppm Rh)

Ion	Added as	Limiting concentration, ppm
Platinum <sup>IV</sup>	K <sub>2</sub> PtCl <sub>6</sub>	0.5
Palladium <sup>II</sup>	PdCl <sub>2</sub>	0.05
Ruthenium <sup>III</sup>	RuCl <sub>3</sub>	0.2
Osmium <sup>VI</sup>	K <sub>2</sub> OsO <sub>4</sub>	1.0
Iridium <sup>IV</sup>	IrCl <sub>4</sub>	1.5
Gold <sup>III</sup>	AuCl <sub>3</sub>	0.2

### Analysis of synthetic solutions

The results of analyses of synthetic solutions are summarised in Table II. All samples were run in triplicate, the averages being recorded in the table.

TABLE II—ANALYSIS OF SYNTHETIC SOLUTIONS

No.	Rh present, <i>ppm</i>	Other ions present, <i>ppm</i>					Rh found, <i>ppm</i>
		Pt <sup>IV</sup>	Ru <sup>III</sup>	Os <sup>VI</sup>	Ir <sup>IV</sup>	Au <sup>III</sup>	
1	4.0	0.5	0.2	1.0	1.5	0.2	4.0
2	4.0	0.2	0.1	0.5	0.8	0.1	4.0

## SIMULTANEOUS DETERMINATION OF RHODIUM AND PALLADIUM

Fig. 1 shows that the absorbance spectra of the palladium and rhodium complexes are similar. Rhodium does not react with TMA at room temperature. On the other hand, the palladium complex forms instantaneously at room temperature but is stable at 100°. The absorbance of both complexes is measured at the same pH. Experiments showed that the absorbances of the palladium and rhodium complexes at 350 m $\mu$  are quantitatively additive.

A number of synthetic samples of known concentrations of palladium and rhodium were analysed in order to test the proposed method and to determine the maximum practical variation which could be allowed in the ratio of palladium to rhodium for their simultaneous determination. Ratios from 1 : 1 to 60 : 1 palladium to rhodium can be determined successfully (Table III).

TABLE III.—SIMULTANEOUS DETERMINATION OF PALLADIUM AND RHODIUM

No.	Pd added, <i>ppm</i>	Rh added, <i>ppm</i>	Pd Found, <i>ppm</i>	Rh Found, <i>ppm</i>
1	3.0	3.0	3.1	2.9
2	4.0	2.4	4.1	2.3
3	4.0	2.0	4.0	2.0
4	4.0	1.2	4.0	1.2
5	5.6	0.4	5.6	0.4
6	6.0	0.1	6.0	0.1

*Procedure*

The sample weight should be chosen so that a convenient volume will contain at least 50 ppm of palladium but not more than a total of 175 ppm of palladium and rhodium.

Dissolve the sample by any appropriate method and adjust the solution to the proper concentration range.

*Palladium:* Transfer a 1-ml aliquot by means of a pipette to a 25-ml volumetric flask. Add 1 ml of a 0.05M TMA solution and 10 ml of a hydrochloric acid-potassium chloride buffer of pH 2.0. Dilute the solution to the mark and mix thoroughly. Then measure the absorbance at 350 m $\mu$  and read the palladium concentration from a calibration curve prepared by the same procedure.

*Rhodium:* Transfer another 1-ml aliquot to a second 25-ml volumetric flask and treat as outlined above in the procedure for rhodium. Measure the total absorbance at 350 m $\mu$  and calculate the absorbance due to the rhodium complex.

$$A_s \text{ total} - A_s \text{ Pd} = A_s \text{ Rh}$$

Read the rhodium concentration from a Beer's law curve prepared for rhodium at 350 m $\mu$ .

## CONCLUSIONS

Thiomalic acid has several advantages as a reagent for the spectrophotometric determination of rhodium: It is colourless and water soluble; no extraction of the metal complex is required; the pH for maximum absorbance is easily controlled; iridium interference is not serious and palladium may be determined in the same sample; the method is simple and sensitive and its precision and accuracy are good.

**Zusammenfassung**—Es wurde eine UV-spektrophotometrische Methode zur Rhodiumbestimmung mit Thiomaleinsäure entwickelt. Das Absorptionsmaximum des gelben Rhodiumkomplexes liegt bei 340 m $\mu$ , und der günstigste pH-Bereich bei 1–6. Die Farbe wird bei 100°C gebildet und ist mehrere Tage beständig. Das Beer'sche Gesetz wird befolgt. Die Empfindlichkeit beträgt 0,055 ppm Rhodium.

Der Einfluss mehrerer Ionen wurde untersucht und Rhodium in synthetischen Proben mit guter Übereinstimmung und Genauigkeit bestimmt. Rhodium und Palladium konnten in verschiedenen Konzentrationsverhältnissen gleichzeitig bestimmt werden.

**Résumé**—On a développé une méthode de dosage spectrophotométrique dans l'Ultra-violet du rhodium par l'acide thiomalique. Le maximum d'absorption du complexe jaune du rhodium est à 340 m $\mu$ ; le domaine de pH le plus favorable est 1–6. La coloration est obtenue à 100° et le complexe est stable pendant plusieurs jours. La loi de Beer est suivie et la sensibilité est de 0,055 ppm de rhodium.

La présence de plusieurs ions peut être toléré et le Rhodium a été dosé dans des échantillons synthétiques avec une bonne précision. Le rhodium et le palladium, présents en proportions variables, ont été dosés simultanément.

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## A CRITICAL EVALUATION OF SPECTROGRAPHIC, FLUORESCENT X-RAY, AND POLAROGRAPHIC METHODS FOR THE DETERMINATION OF THE PLATINUM METALS

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**Summary**—This review covers pertinent publications up to June 1958. The methods are evaluated from the point of view of their analytical applications to assay beads and buttons, platinum metal precipitates, and alloys of platinum metals with and without base metal impurities.

No spectrographic method has been recorded for the direct determination of platinum metals in ores or concentrates. For the determination of palladium, platinum and rhodium in ores and concentrates the most accurate spectrographic methods involve a preliminary fire assay extraction to produce a lead button or a silver bead. For these, and for other alloys, precipitates, etc. the most accurate methods involve special efforts to produce uniformity of composition and to produce standards with identical metallurgical histories. No successful spectrographic method has been recorded for either the direct or indirect determination of iridium, ruthenium and osmium in ores, concentrates or complex alloys.

None of the frequent claims that spectrographic methods produce greater accuracy than wet methods has been substantiated and all are unacceptable. The few existing data indicate that with competent analysts and under optimum conditions the accuracies of the two methods are comparable.

For the qualitative examination of the purity of precipitates etc. containing a variety of metal traces the spectrographic method is incomparably superior to wet methods.

Polarographic methods for the platinum metals have been confined to systems with few constituents. No procedure has been recorded for the successful application to assay beads or buttons. Few detailed procedures have been recorded for the determination of any platinum metal and no method includes the usual processes of securing dissolution of multicomponent systems. Undoubtedly, polarographic methods could be useful competitors in areas below those in which classical methods apply. Furthermore, both spectrographic and polarographic methods provide the great advantage of speed when applied to large numbers of samples whose compositions are not widely different.

Too few X-ray spectrographic procedures have been recorded to estimate relatively their accuracy and precision.

PRACTICALLY the whole of the world's supply of the platinum metals is derived from ores whose precious metal content is close to or below the limit of detection of the most sensitive analytical methods. No direct method has been recorded for the quantitative or even the qualitative determination of any of the six platinum metals in ores. The lack of qualitative and field detection methods is, in the author's opinion, due to a lack of effort or interest on the part of the analytical researcher. The absence of direct quantitative procedures is, of course, due partly to the same situation, and partly to a strange tendency, on the part of the analytical researcher, to distinguish, and thus to avoid, these analytical problems by creating the artificial classification of fire assaying. For the relatively few engaged in this work, the high specificity of spectrographic methods has encouraged a persistent hope that this approach to platinum metal determinations may provide the much desired easy and positive application to ores. However, despite some rather extravagant claims, no

proved direct spectrographic application has been recorded; nor is one of general value likely to be evolved within the foreseeable future. The spectrographic methods available have been used largely for alloys of the platinum metals. Those of significant analytical value for the determination of platinum metals in ores have been applied, almost exclusively, subsequent to concentration by fire assay or other means. However, in the author's opinion, no analytical method provides the general efficiency attained by spectrographic procedures for the detection and determination of impurities in platinum metals alloys. In some cases colorimetric methods may provide comparable or even greater sensitivity and accuracy but only at the expense of more difficult techniques and the greater expenditure of time.

For those alloys, such as the silver bead or lead button, whose proportions of platinum metals are small, the relative accuracy and precision of spectrographic and spectrophotometric methods, a problem of some practical importance, has not been determined over sufficient ranges of concentration; the rather persistent claims for superiority of the former method must be dismissed for lack of evidence. Not a single publication has provided results to support these claims. However, one can predict with confidence that where both methods may be applied at all, competent operators will find comparable platinum metal values and the few results recorded<sup>1,2</sup> indicate this to be the case.

The general applications of the spectrograph for the determination of platinum metals as trace constituents are wide and invaluable. Gorbach and Windhaber<sup>3</sup> used the method to find traces of palladium, iridium, platinum, silver, etc., in Forest Honey. Fothergill, Withers and Clements<sup>4</sup> determined traces of platinum and palladium in the atmosphere of a platinum metals refinery. The author will make no attempt here to discuss the innumerable reports dealing with the spectrographic detection and determination of the platinum metals in all of their applications. This review will be concerned with the analytical treatment of assay beads and buttons obtained from platinum ores and concentrates; with alloys of which, at least, the principal constituent is one of the platinum metals; and with the determination of the purity of precipitates of the platinum metals.

## SPECTROGRAPHIC METHODS

### *Preparation of electrodes and samples*

As would be expected the choice of electrode material is sometimes determined by the physical character of the sample to be analysed and frequently by the necessity of avoiding a multiplicity of interfering lines. For aqueous and certain solid samples the most common choice has been the graphite electrode. The positive rod is drilled to receive the liquid which, by intermittent evaporations, may contain a large sample. The cavity may sometimes be coated with wax or other water-impervious materials to prevent diffusion beyond the area of effective electrical contact. The upper electrode is frequently sharpened to assist in the concentration of the electrical contact and to avoid wandering of the projected image beyond the slit area. For liquid samples various mechanical devices have been reported which permit each of a series of graphite rods to make regular and intermittent contact with the liquid sample; e.g. the rotating pin electrode technique which was recommended by Bardoćz and Varsányi.<sup>5</sup> With this method the ends of the carbon electrodes were

fastened like spokes on a slowly rotating horizontal shaft and were arranged to pass before a carbon counter-electrode. The solution to be analysed, into which the carbon rods dipped, was placed on a vertically adjustable shaft. The movement was timed by an adjunct device arranged to create the discharge only when one of the electrodes just passed the counter-electrode. The usual warming up phenomena associated with porous-cup techniques involving high energy excitation and with rotating disk techniques was reduced to an acceptable degree.

For solid samples various metallic electrodes have been used to which an alloy sample may be fastened mechanically or incorporated chemically; or the alloy sample may itself serve as the electrode.

Pasveer<sup>6</sup> converted the powdered standards to pellets, which were then annealed. The solid sample was rolled into sheet from which a disc was cut and fitted over a rod to duplicate the shape of the standard electrode. Pellet electrodes were also used by Hawley, Wark, Lewis and Ott<sup>7</sup> who mixed palladium or platinum black, prepared from solution by reduction with aluminium, with briquetting graphite. The mixture was compressed in a steel mould at 10,000 psi and the pellet was mounted in a brass adapter on the arc-spark stand. To produce a spark spectrum from a silver assay bead, Seath and Beamish<sup>8</sup> used a silver cup made from foil, inserted in one end of a glass tube and attached beneath, through a tube, to the lower terminal of the spark stand. The upper negative electrode was a gold wire. This equipment facilitated the removal of beads. The spectrographic method reported by Scobie,<sup>9</sup> one of the first generally useful procedures, involved the arcing of a silver assay bead containing platinum, palladium and rhodium. This author examined the applicability of various metal electrodes, rejecting cadmium, tin and zinc because of low melting points, copper because of mechanical failure, and steel and brass because of poor heat and electrical conductivity, and chose a silicon-copper rod. The upper electrode was graphite sharpened to give an end comparable in area to the 100-mg silver bead. The latter was cleaned, placed in a mould designed to allow deep punching of the silver bead at an included angle of 30°, and transferred to the copper electrode previously pointed at the same angle.

To achieve uniformity of composition in samples Lewis<sup>10</sup> fused silver- and gold-lead buttons under hydrogen. By this method platinum, palladium and rhodium were thus uniformly dissolved. Unfortunately the procedure has not yet been extended to include iridium and ruthenium. The lead alloy button thus prepared was mounted on a copper rod by pricking several small holes in the end of the rod with a sharp centre punch; the button, covered by a strip of heavy aluminium foil, was placed on the end of the rod and tapped lightly until flattened sufficiently to cover the end of the rod. The button was thus retained by filling the depressions in the copper rod. Lewis, Ott and Hawley<sup>11</sup> recorded interesting results concerning the relative efficiency of various standard methods of preparing samples together with electrode material. For the determination of impurities in rhodium they used rhodium solutions with both coated-electrode and porous-cup techniques. Solutions were evaporated in the flat end of electrodes of lead, zinc, aluminium, copper, mercury-coated copper, graphite, collodion-coated graphite, and Kerosene-impregnated graphite. The object was to find an electrode material on which the solutions would either plate or form a homogeneous salt layer. Most of the systems were rejected. Various metals reacted with rhodium solutions to form objectionable



salt mixtures. Coated or impregnated graphite electrodes resulted in thick and brittle salt layers. When the proportions of contaminants were high a salt crust formed on copper or mercury-copper electrodes, although in some cases plating did occur. Sensitivity was poor with copper electrodes. Under certain circumstances porous-cup graphite electrodes, wrapped in aluminium or lead foil, were sufficiently successful for chloride solutions of rhodium and for the contaminants iridium, palladium, iron, nickel, lead and silver. In the case of gold there was, as would be expected, some precipitation, which could be avoided to a degree by the addition of *aqua regia*, although the latter introduced corrosion of the clamps. The above difficulties, together with the necessity of long exposures to achieve adequate sensitivity were objectionable features of the carbon porous-cup techniques. The advantages were ease of obtaining uniformity of composition, good precision, and the facility with which standards could be prepared.

A fusion method which produced acceptable uniformity for the determination of palladium in a high-proportion silver alloy was described by Tomingas and Cooper.<sup>12</sup> The method involved prior fusion of silver-palladium alloys with the silver alloy to be analysed; or when copper was to be alloyed, addition of the latter in the form of wire to the base of the carbon crater, followed by the silver alloy; and subsequent pre-arcing for 30 seconds.

#### *Platinum metals in ores and concentrates*

*The assay bead:* While no spectrographic procedure for the direct determination of platinum metals in ores has been recorded within the past two decades, various spectrographic methods have been developed for these determinations subsequent to extraction from liquid solution by metals from whose line spectra there is relatively little interference. The extraction is usually arranged to provide the necessary degree of concentration of platinum metals and is generally accomplished by standard fire assay methods. The spectrographic techniques which have been used for these alloys are not unique; with the exception of a few novel methods of producing sample-electrode contact, the procedures are those previously accepted for general spectrographic applications. The improvement of methods for the platinum metals has followed chronologically the evolution of these spectrographic techniques in general. Laszlo<sup>13</sup> used the simple technique devised by Kiess and Stimson<sup>14</sup> of relating the concentration of platinum in silver assay beads to the disappearance of certain platinum lines in a condensed spark spectrum; the last ones to disappear were designated as *raies ultimes*. The method involved the preparation of standard silver-platinum electrodes containing 5% to 0.01% platinum, creating a condensed spark under identical conditions for a measured time and ascertaining the number of the platinum lines from each alloy. The silver beads were prepared by cupellation and by a fusion process. Care was taken to ensure alloys of uniform composition. The beads were cut in half and the flat side of each hemispherical section was soldered to a short piece of brass wire thus forming the electrode. An accuracy of about 20% was obtained, but the method was unsatisfactory for concentrations of less than 0.04%. Neither this spectrographic technique nor the method of bead preparation are recommended. The former is unnecessarily tedious and the latter could not be used successfully with the normal assay bead where uniformity of composition is seldom, if ever, attained, particularly when the more insoluble platinum metals are

present. A similar objection can be made to the method of Peters<sup>15</sup> who gave directions for the collection by fusion with lead acetate and subsequent cupellation. The claim that the volatilisation of osmium was prevented by partial cupellation can be accepted only with reservations.<sup>16</sup> Determinations were made for silver, gold and the six platinum metals. Seath and Beamish<sup>8</sup> had little success with the above spark method applied to assay beads containing platinum and palladium. They found the arc spectrum less sensitive to variations in electrical conditions, and since small beads were consumed the problem of non-uniformity of alloy composition was of much less significance. These authors preferred graphite electrodes and silver beads of about 10 mg. Threshold lines for arc and spark spectra of silver and gold beads and their corresponding limits of concentration of platinum and palladium were recorded. The work was essentially qualitative and a claim was made for a sensitivity on 10-mg silver beads of 0.04  $\mu\text{g}$  of platinum or palladium, which is beyond that usually accepted. The relative sensitivity of arc excitation and chemical methods for ores was discussed by Azcona and Pardo.<sup>17</sup> The former was considered superior when applied to concentrates obtained by cupellation or electrolytic methods. The authors used a molybdenum line as an internal standard and recorded a sensitivity of about 0.5  $\mu\text{g}$  for platinum, palladium, ruthenium and gold; and about 200  $\mu\text{g}$  for iridium.

The adverse influence of copper on the spectrographic determination of palladium in Doré Metal and silver assay beads was described by Tomingas and Cooper.<sup>12</sup> The Doré Metal contained 90–95% silver, 5–10% gold, 0.3–0.8% platinum and 45–80 ppm of palladium. An AC arc was used with carbon electrodes, the upper cone-shaped and the lower with a crater, and solid samples. It was found that copper in excess of 0.4% influenced the intensity of both the silver line 3469, used as the internal standard, and the palladium lines; furthermore the fluctuations in copper content eliminated compensation by the silver and also compensation by the background method. A relatively high lead concentration was also objectionable since it resulted in sputtering during the arcing and low palladium results. Generally the lead proportion could be reduced by a pre-exposure or by subsequent addition of silver to the silver bead, kept small initially for this purpose. The deleterious effect of copper was met by establishing separate working curves constructed from the palladium:silver intensity ratio with sets of alloys containing appropriate amounts of copper. The applicable curve was determined by the copper:silver line ratio. The standards were prepared by melting and shotting Doré drillings containing 0.4% to 0.5% copper. Palladium, as required, was incorporated by addition of a palladium-silver alloy and subsequent melting. Copper was alloyed by placing the required weight in wire form on the bottom of the carbon electrode crater, adding the Doré metal, and subjecting the mixture to a 30-sec pre-exposure. Samples to be analysed and requiring salting with copper, etc., were similarly treated to ensure uniformity of composition and metallurgical history. In practice the sample was excited and viewed visually for evidence of a green colour before analysis, to determine if the copper content was below 0.4%, in which case the palladium lines were too weak for measurement. Gold, in concentrations greater than 9%, interfered with the palladium determination. The accuracy of the method, as compared to polarographic methods (unfortunately these were not described), indicated very acceptable uniformity of the alloys prepared by the prescribed fusion methods. The method

was recommended for the determination of palladium as low as 0.05 ppm in ores, concentrates, blister copper and other metallurgical products. Various Russian analysts<sup>18-20</sup> have used copper sulphide as a collecting medium for platinum, palladium, gold, etc., to produce finally a copper pearl which was then analysed spectrographically. Van'kin and associates<sup>18</sup> precipitated by sodium thiosulphate. Bufatin and associates<sup>19</sup> separated platinum and palladium from uranium by hydrogen sulphide in sulphuric acid solutions, with copper sulphide as the collector. For the spectrographic analysis gold was used as the internal standard; line 2675.95 for gold against 2659.45 for platinum; and line 3122.78 for gold against 3421.24 for palladium. Livshitz and Kashlinskaya<sup>20</sup> used thiosulphate to precipitate the sulphides of platinum, palladium, rhodium and gold, together with copper added in amounts to produce a final bead of 100 to 200 mg. Prior to extraction by a variety of mineral acids the sample was treated to concentrate the platinum metals. Unfortunately the authors provide no data concerning the efficiency or the character of the concentrating process. Furthermore the statement that the maximum loss of platinum metals due to deficiencies in the wet extraction was less than 5% can apply only to the samples examined; such dissolution procedures can result in serious losses. The copper bead containing as little as 5  $\mu\text{g}$  of platinum metal was placed in a depression on the lower carbon electrode and subjected to an alternating arc of 220 volts and 4.0 amps. The copper line, 2445.0 was used for comparison with 2675.95 for gold, 2659.45 for platinum and 2447.91 for palladium. For rhodium 3434.89, the copper comparison line was 3375.67. The few results reported indicated a good recovery for samples containing very small amounts of the platinum metals. Excluding the possibility of misinterpretation through translation, it would seem that the proposed spectrographic method involved amounts of the platinum metals considerably below the sensitivity generally accepted. The authors make the usual claim for superiority of accuracy over wet methods, with the usual omission of any description of the character of the methods or any acceptable data. It is a fact that the amounts of platinum metals involved in the analysis falls well within the range of the most acceptable spectrophotometric methods. Presumably the tendency toward these unsubstantiated claims is not confined to regional literature and in this instance, as in all others recorded in this review, there is the suggestion that the wet methods were uncritically chosen, incorrectly applied, or applied by operators lacking in efficiency. It may be well to suggest here that these authors' approach toward spectrographic analysis for the platinum metals through the preparation of a copper bead offers good promise if it can be incorporated within the new scheme involving a collection from ores by iron-copper-nickel buttons.<sup>1,2</sup>

Scobie<sup>9</sup> used a low voltage AC arc method for the spectrographic determination of platinum, palladium, rhodium and gold in ores subsequent to collection of silver beads. Standard beads were prepared from standard platinum metals and silver solutions evaporated in lead boats, and the residue was subsequently cupelled. The upper graphite electrode was pre-burned for a period of  $2\frac{1}{2}$  minutes. A pre-arc period of 30 sec was considered desirable followed by a 2-min exposure period. Intensity measurements of the appropriate platinum metals lines were made relative to the background of silver line 3233.25. Continued routine practice indicated this procedure to be superior to that of line compensation. The range of concentration, 0.001% to 0.1% of platinum and palladium, was covered by one line and for rhodium

by two lines. The author claimed a sensitivity of 1  $\mu\text{g}$  of platinum metals per assay ton of ore, with the probability of increasing this to 0.1  $\mu\text{g}$ . All of the precious metals could be determined by one spectrographic arcing with an accuracy of about 5% average deviation from absolute values. The author's claim that the procedure offered the advantage of speed over existing wet methods of platinum metals analysis is beyond dispute but the claim for greater accuracy was not substantiated and is unacceptable. A conclusion such as this, too frequently made in spectrographic literature of the platinum metals, loses any significance when comparisons are made with wet methods, the character of which is not described, and the source of the data being unstated. In the present instance the author offered no data for platinum metals values obtained by wet methods. The author's calculations of accuracy and precision, were, in some cases, incorrect and the claim of a 6% accuracy is well on the optimistic side.

Presumably Scobie found no difficulty attaining uniformity of composition with the silver beads. In the case of platinum, palladium, and to a lesser degree, with rhodium, careful fusions with lead and silver may result in a uniform distribution of these three platinum metals. However, later investigators have encountered evidence of some segregation, with the result that one cannot now accept without reservations the direct application of spectrographic spark methods to assay beads. Low voltage arc methods in which beads are entirely consumed may avoid the difficulty but suitable quantitative procedures have not been recorded. Hawley, Lewis and Wark<sup>21</sup> applied a low voltage spark method to determine the platinum and palladium content of minerals and ores. The difficulties of assuring uniformity in the normal assay bead and in standards was avoided, in the latter case, by the preparation of a gold-mercury-platinum or palladium amalgam subsequently dissolved and reduced by zinc, in the former case by the normal assay fusion and cupellation to produce a gold-platinum-palladium bead, followed by weighing and, as in the case of standards, by dissolution in acids and reduction by zinc to produce platinum and gold precipitate. Subsequent to the purification of the black precipitate the latter was treated to form a mercury amalgam in the same manner as the standards. For spectrographic determination gold lines were used as the internal standard. This paper will be of considerable interest to those concerned with the mineral origins of platinum and palladium. Rhodium, iridium, ruthenium and osmium were not detected in the minerals examined. Presumably the authors did not consider that their wet treatment of the gold bead could eliminate these four elements from subsequent detection by spectrographic analysis.

A method for the spectrographic determination of platinum, palladium and rhodium in ores, slimes and tailings was recorded by Nedler.<sup>22</sup> The procedure involved a fire assay to produce a silver bead, division of the bead and shaping each section to form a cylinder tipped to a dull wedge, excitation between these two sections by a high voltage spark, measurement of line length relative to silver lines by a logarithmic sector, and the application of a correction curve derived from a silver fixation line pair correlated with concentration errors and made necessary by wide variations in excitation conditions. For platinum determinations five line pairs were required for the range 0.02%–1%, for palladium three line pairs over the range 0.2%–1%, and for 0.2%–1% of rhodium, two pairs. The method introduces no new principle and in the opinion of the present author is cumbersome, relatively inaccurate

and inapplicable to those materials which contain iridium, ruthenium and even large proportions of rhodium. While the author commendably recognises the difficulties arising out of irregular distribution of platinum metals in ores, the deleterious effects of variations in the metallurgical history, size, shape, etc. of the silver alloy electrode, he suggests very little to overcome most of these problems. The use of a fixation line pair to arrive at a correction factor to reduce errors of the order of 50% to 10% or 15% is scarcely an encouraging feature. The failure to recognise that a silver assay bead is seldom free of interfering impurities may be excused by the acceptance of a 10%–20% inaccuracy but it is not a recommendation for the technique used in view of the fact that modifications may be used to produce a greater accuracy. The physical method used to shape the silver alloy electrode is objectionable and can be accepted with reservations only when one is assured of homogeneity, a factor which received inadequate attention. The inclusion for comparison of the results of wet methods of analysis is an excellent feature and an improvement over many of the more acceptable spectrographic publications, but it is regrettable that the wet methods were not identified. The author's justification for the acceptance of a 10%–15% precision, on the grounds of as much as an 80% heterogeneity of platinum metals in ores, is acceptable only with considerable reservations.

*Lead button.* In a later paper Hawley and co-workers<sup>23</sup> stated that the above mercury amalgam method<sup>21</sup> sometimes failed to provide uniformity. The proposed new method involved the formation of a platinum metal alloy with enough lead to reach a concentration of platinum metals falling within the sensitivity range of the spectrographic method. Obviously this might be most readily accomplished by a carefully controlled cupellation. However, the normally associated base metal content of a partially cupelled lead button introduced objectionable interferences. The author's fire assayed the ore samples in the normal manner, adding gold or silver as a collector in amounts which provided "weighable gold or silver beads". The latter, together with sufficient lead to constitute 90% to 95% of the resulting alloy, were fused on a charcoal block, weighed to determine the lead content and fused with solder to a copper electrode. There was no appreciable interference from the solder. Master standard beads, containing the required ranges of concentration of gold or silver and platinum metals were prepared by a similar fusion on a charcoal block. Subsidiary standards and beads simulating the composition of silver assay beads were prepared by suitable dilutions and fusions with lead. Variations in lead content and high silver content did not affect the spectrographic determinations. High gold content affected adversely the results from the lead button. The spectrographic analysis was made with a 15,000-volt condensed spark and calculations of concentration were based on the mutual or variable internal standard method. This procedure involved the determination from the alloy standards of working curves recording intensity ratios to either of two lead lines of each of appropriate lead, gold, silver, palladium, platinum, rhodium and bismuth sensitive lines. For assay beads, converted to lead alloys, the working curves permit a determination of the relative per cent of each constituent of the lead alloy, which in turn allows a calculation of the total lead content. This must agree within experimental error with the amount of lead as determined by direct weighing of the lead added to the assay beads. With this condition satisfied the per cent of each platinum metal is readily calculated in suitable terms. The sensitive lines used for the determination of the ratio of element

to lead were arc lines with a few exceptions although a condensed spark was applied to the electrodes. The precision of the method was about 6%. The size of button or electrode was without any appreciable effect on the accuracy of the method. The accuracy attainable, determined from salted samples, indicated a recovery for palladium, platinum and rhodium within about 5%. The accuracy of recovery as determined on assay beads prepared from ores was not determined. In its present form the method will not prove applicable to such assay beads containing iridium, ruthenium or osmium. Iridium is collected mechanically by lead and hence uniformity of composition will not normally be achieved. Ruthenium, sometimes incorrectly described as volatile in a lead button, may offer both mechanical and spectrographic difficulties. Osmium is largely lost during cupellation to form a silver or gold bead. Indeed, with large proportions of osmium in a silver assay bead, the latter will explode violently. Hawley and Rimsaire<sup>24</sup> applied the above techniques to the determination of Canadian uranium and sulphide ores. Tentative results are included for ruthenium, iridium and osmium. The authors acknowledge the deficiency of their method for these three metals. The sensitivity of the authors' method based on the lead collection from one assay ton of ore with the production of a ten-mg lead bead was reported to be 0.003 ppm for platinum and 0.0008 ppm for palladium and rhodium. These values are not supported by results and cannot be accepted without verification. Here it is well to realise that the accuracy of methods such as the above and the related methods described below, applied to assay beads from ores or concentrates, may be subject to errors not discussed by the various authors. Where ores contain an unusually high amount of platinum metal "insolubles", the latter may well include alloys, resulting from the heat treatment or occurring in ores as minerals, which contain proportions of platinum, palladium and particularly rhodium. To the degree that these "insolubles" are present, there may be some lack of uniformity in the distribution of the above three metals. In practice the proportion of "insolubles" is usually very small in which case the error would be insignificant.

There is a further condition which can lead to errors in these methods which depend upon uniformity of bead or button composition. The collection of platinum metals by silver or gold is accomplished at elevated temperatures, during which period metals such as rhodium or its alloys will, in some cases, become resistant to corrosive reagents which normally encourage dissolution processes. One cannot assume that rhodium in this condition will become uniformly distributed, particularly when the proportions in the bead are large.

Lewis<sup>10</sup> examined critically the spectrographic determination of platinum metals in lead buttons obtained by a variety of fire assay methods applied in a number of different laboratories. This excellent reconnaissance survey not only provided assurance of the practical efficiencies of fire assay techniques but included a description of the most acceptable procedure for the preparation of platinum, palladium, rhodium-lead alloys so far recorded.

Master standards were prepared by fusing macro amounts of the platinum metals under hydrogen to produce alloys containing either 5% gold or 10% silver together with platinum, palladium and rhodium from 0.001% to 1.0%. Working sets of either gold or silver standards were made by diluting the master standards. For analysis, the gold or silver fire assay beads were fused under hydrogen with sufficient lead to produce the 5% gold or the 10% silver-lead alloy.

The samples were mounted on copper rods as described above under electrode preparation and sparked with a high-voltage spark from a High Precision Source unit. Intensity ratios of platinum metals, gold and silver were calculated with lead as an internal standard. The dissimilarity of physical properties of lead and precious metals produced no appreciable error in measurements of relative intensity.

#### *The analysis of precipitates and commercial alloys*

Spectrographic methods are, in general, incomparably superior to all chemical procedures for the detection and, to a lesser degree, for the determination of metal impurities in precipitates. In those cases where the impurity is one of the more insoluble platinum metals the great advantages of the spectrographic analysis is obvious, as it is also when precipitates may contain traces of a number of metals. Usually this analysis is essentially qualitative and one spectrogram will suffice for the whole gamut of metal impurities. The problem of attaining uniformity can often be avoided by acceptable precipitating procedures. However, where accurate measurements of impurities are required and where a high voltage-low amperage spark excitation is used, the analyst will do well to recall that the processes of contamination of precipitates are not always conducive to uniform distribution. This possibility has, to the author's knowledge, received no recognition in the various publications dealing with these determinations. Perhaps it is not too irrelevant to refer here to the growing practice of evaluating the efficiency of a standard gravimetric procedure by a spectrographic examination of the precipitate and the corresponding filtrate for the distribution of constituents. Particularly in those instances where the completeness of recovery is sensitively related to conditions of precipitation, such investigations may result in an evaluation of the operator as much as, or more than, in an evaluation of the procedure. In any case the practical efficiency of an analytical method is usually much more effectively determined by a reconnaissance survey than by the results obtained by an isolated investigation. However, one cannot over-emphasise the usefulness of spectrographic methods in determining the purity of precipitates nor the need for this information when new methods are proposed.

For the detection of impurities in solids the arc method of excitation is generally the most sensitive. Typical of the procedures for a general examination of impurities in solids is that described by Raper and Withers<sup>25</sup> who used the arc with graphite electrodes, the lower of which contained a cavity to hold the platinum sample. Spectra were photographed, first of the pure platinum, then of the sample, and finally of *R.U.* powder, on a plate on which the wave length scale was printed. The authors recorded the lower limits of detection in percentage by weight of silver, lead, nickel, palladium, iron, ruthenium, arsenic, antimony, rhodium and iridium.

In a series of papers Ayres and co-workers<sup>26-29</sup> provided spectrographic procedures for the determination of palladium, platinum, rhodium and iridium in samples containing as low as 5 ppm of a single platinum metal. The problem of uniformity was avoided by using aqueous-acid solution. A high voltage spark source, altered by an increase in the inductance of the spark circuit to give more arc-like excitation, was used and the porous-cup graphite electrode was recommended. Cobalt was added as the internal standard and line pairs of the platinum metals used with the cobalt line 3354.2 were included. The authors varied the relative concentrations of the platinum metals over wide limits and reported an accuracy of 2.8% and 2.4%

average deviation of the intensity ratios. A 180-sec exposure was required for an acceptable sensitivity. Because of variable porosity, pre-sparking of the electrodes was necessary. Within the concentrations recommended, the line intensity ratio of one platinum metal was unaffected by variations in concentrations of the remaining two metals. Ayres used these or related procedures for the evaluation of the efficiencies of standard separations of palladium from platinum, iridium and rhodium,<sup>26</sup> of rhodium from iridium<sup>27</sup> and of platinum from palladium, rhodium and iridium.<sup>28</sup> The lower limits of detection were 5 ppm for palladium, 20 ppm for platinum, 10 ppm for rhodium and 25 ppm for iridium.<sup>29</sup> For the investigation of the rhodium-iridium separation by titanium<sup>III</sup> chloride the lower limits of detection were 0.5 ppm for rhodium and 50 ppm for iridium. Smaller amounts of iridium were determined spectrophotometrically. For the evaluation of the platinum isolation by hydrolytic separation<sup>28</sup> the authors used a direct current arc excitation with carbon rods, the lower of which was shaped to form a cup and the upper sharpened to a point. The dry sample together with the cobalt salt was mixed with carbon, and the mixture in the graphite cup was covered with lithium carbonate to prevent mechanical loss and to reduce the cyanogen band background. The spectrochemical method showed a precision of 4.7% and an accuracy of 5.3%. The authors stated that there was a slight compensation of errors, which were insignificant except where the amounts of the metals were 20 mg or less. Van Der Voort<sup>30</sup> prepared platinum and palladium by standard procedures and discussed the relative advantages of various methods of excitation for determining the palladium content of platinum. With arc analysis the palladium spectrum decreased in intensity with time. The interrupted arc was useful if the platinum retained its form but the accuracy was not great. The spark excitation was suitable for larger amounts of metal containing 0.1% of palladium or more. Under certain conditions a glow discharge at atmospheric pressure with a current of 0.25 amp at 370 volts was promising.

In order to attain uniformity of composition and grain size, Hawley and co-workers<sup>7</sup> utilised precipitation methods for the determination of impurities in platinum and palladium sponges and refinery samples. The samples were dissolved by standard procedures and treated with aluminium to produce the finely divided "black." Standards of suitable purity were similarly dissolved, salted with the appropriate impurities and similarly precipitated. The black precipitates were mixed with carbon, compressed to form pellets and, with the major constituent serving as an internal standard, analysed spectrographically with excitation by a Multisource spark discharge. The range of concentrations of impurities were those common to refinery samples. The accuracy of the methods was of the order of 3%. The authors were of the opinion that spectrographic analyses yielded "a much higher degree of accuracy than the chemical analyses".

Inexplicably, this claim of superior accuracy is repeated in various publications. Statements to the effect that spectrographic methods for the determination of minor contaminants are "far superior to wet chemical methods and should be used, if not exclusively, as a check in the chemical determinations" really mean that a purely empirical analytical procedure should be accepted as the primary standard.

Lewis and Ott<sup>31</sup> found good agreement between their "black" technique and a method involving the preparation of palladium sponge. The direct analysis of platinum metals sponges was rejected because of the probable lack of homogeneity,



the difficulty experienced in properly salting spectrographic standards and in duplicating metallurgical history. These difficulties were overcome by dissolution of both samples and standards, salting the latter with appropriate metals, evaporation to salts, mixing in a mortar, reduction to sponge by hydrogen, mixing again in a mortar and reducing again with hydrogen. The sponge was then mixed with graphite, and pellets were prepared by a modification of the method discussed above.<sup>7</sup>

Excitation of the pellet was accomplished by a high-voltage spark, and various filters were used to reduce the intensities of lines of such impurities as gold, silver and copper. The addition method of analysis<sup>32</sup> was used except where the proportion of the contaminant was 0.005% or below, in which case spectrographically standardized palladium sponge was used. The authors preferred the more practical "analytical samples" as standards and by prior examination chose the sponge containing the lowest degree of contamination. After the determination of the proportion of the residual contaminant, true concentrations were plotted on logarithmic paper against intensity ratios of the chosen line for the contaminant and a palladium line as the internal standard. The authors' results, which indicate excellent precision and accuracy, reveal also the peculiar tendency to values higher than those indicated by "check" samples. There were no indications of elements which could depress the intensity of spectral lines. It was concluded that while, in general, comparable results were obtained by the "black" and "sponge" techniques, the former was superior for the determination of silicon, lead, bismuth and iridium. Of particular significance is the conclusion that the sensitivity of methods decreases in the order, "black," "sponge," "solution" and finally, "salt" methods. The "sponge" and "black" procedures were also examined, with the former prepared as described for palladium and the latter prepared by reduction in alkaline medium, by hydrazine dihydrochloride. The resulting pellets, prepared as described above<sup>7</sup>, were excited by a high-voltage spark discharge in the case of the "sponge" and by the direct current arc in the case of the "black". To determine silica a modified "sponge" procedure is described in which the addition method of analysis is used. The precision obtained for the impurities varied between 2% and 7%. With direct-current arc discharges the precision was of the order of 15%. The authors concluded that the "sponge" technique was most suitable for the determination of iridium, palladium, iron and copper. The preparation of the black was preferred for other impurities. Further application of the "sponge" and "black" techniques was recorded by the authors who examined rhodium spectrographically for iridium, palladium, platinum, ruthenium, copper, nickel, cobalt, silver, gold and silica.<sup>11</sup> The samples and standards were prepared as described above.<sup>11</sup>

A procedure for the determination of rhodium in platinum alloys was discussed in an interesting and useful paper by Barđoćz and Varsányi.<sup>5</sup> The range of concentrations investigated was about 0.5 to 12% of rhodium in platinum. Because of the difficulty in duplicating size, shape and metallurgical history in the standards and samples, the authors preferred to work with aqueous solutions and in order to avoid the deleterious effects of warming up of the solutions on the electrodes and also to permit a continuous feeding process, the rotating pin technique, described above, was applied. Both arc and spark excitation methods could be used. The porous-cup electrode was unsatisfactory due to lack of precision caused by varying porosity; pre-exposure of the electrode only partially corrected the difficulty.

Furthermore the porous-cup technique limited the choice of excitation methods, eliminating the higher sensitivity energy spark discharge because of the tendency toward excessive heating. For the same reason the rotating-disc technique was rejected, although here the problem of porosity is avoided. The relative warming effects of the rotating-pin and rotating-disc methods were well illustrated. For the determinations the author used a low voltage condensed spark source directed electronically at 1000 volts with an effective pre-sparking time of 7.5 sec and effective exposure time of 15 sec. The line pairs were 3434.89 or 3396.85 for rhodium and 3408.13 for platinum. The pair (3396.85–3408.13) applies for the lower rhodium values. Although the lines lay in the rising area of the gamma curve they were sufficiently close together to permit a single density curve. With the technique employed the background in the neighbourhood of the lines was weak.

Koehler<sup>33</sup> used the spark and the interrupted arc for foil samples of platinum-rhodium alloys to be used as catalysers and for thermoelements. A technique was recorded for the estimation of some fourteen trace impurities, and included also is a list of the most sensitive undisturbed lines of silver, arsenic, gold, phosphorus, lead, antimony, silicon, tin and zinc.

For the determination of the platinum content of precious metal alloys, jewellers' scrap, etc., Manning and Coull<sup>34</sup> applied the Constant-Pair Method in which the added internal standard, molybdenum, at concentrations equal to platinum, provided lines of equal intensity for both metals. While no calibration curve was required, in the present author's opinion the laborious process of selecting the appropriate volumes of the standard molybdenum solution far outweighs the work involved in producing a working curve. As would be expected the accuracy of the method was not good; applied to a series of dental alloys the errors were about 15%.

Oberlander<sup>35</sup> recorded a list of suitable line pairs to be used for the determination of gold, palladium, rhodium, copper, iron, silver in platinum. For the determination of 0.00014–0.058% of gold and 0.0001–0.05% palladium in platinum wires, Ishitsuka<sup>36</sup> used the arc between carbon electrodes in one of which the wire was inlaid. Platinum was used as the internal standard. Gerlach and associates<sup>37,38</sup> discussed the precautions to be observed in the determination of impurities in platinum, iridium and rhodium. The most sensitive lines for the determination of the impurities were recorded. Homologous pairs of lines and their applications for the determination of iridium and rhodium in platinum are also included.

Stauss<sup>39</sup> discussed the use of the spectrograph in the platinum industry from the viewpoint of identification of alloys, special analyses for minor impurities and control of the purity of platinum and its alloys. In most instances the methods were essentially qualitative. The spectrographic control analysis for the platinum metals was also advocated by Pastore and Occhialini,<sup>40,41</sup> who wound wire samples around a copper rod and inserted the spirals between two carbon electrodes. Lines for the determination of platinum, gold and silver were recorded.

Babaeva and co-workers<sup>42–45</sup> have published a number of articles dealing with conventional spectroscopic determinations of small amounts of one or more platinum metals in precious metal alloys and salts. To determine small quantities of iridium and rhodium in complex platinum salts,<sup>42</sup> the authors used the direct current arc and carbon electrodes, the anode of which contained 2.5 mg to 3 mg of dried salt. Standards were prepared by evaporating solutions of suitable salts, and grinding the

residue. Platinum lines were used as the internal standard. Because of the necessity of burning large samples and the fact that the accuracy attainable was only about 10–20%, the authors preferred activation by the spark method. The 3-mg sample was fastened to the carbon electrode by a drop of collodion and pressed in by grinding the carbon on a glass plate. The upper electrode was pointed. For concentrations of 0.5% to 0.05% iridium in platinum the lines 3220.79 for iridium and 3230.29 for platinum were used. Below 0.05% the platinum line was 3212.9. For rhodium the lines were 3396.8, or below 0.005%, 3434.9 with the platinum line 3427.92. The line pairs used were identical for either the bivalent or quadrivalent platinum and the working curves were consistent when one used the same compositions for the standard and unknown. The errors did not exceed 4.5% and the sensitivity was about 0.001%.

In a second paper<sup>43</sup> the authors recorded control methods for the determination of palladium in platinum, platinum in palladium and rhodium in iridium. The procedures contributed very little of value to spectrographic methods. A condensed spark and medium quartz spectrograph were used. The palladium in platinum varied from 10% to 0.001%; the platinum in palladium, from 5% to 0.001%; the rhodium in iridium, from 1% to 0.001%. The authors used the principal constituent for comparison and they recorded the most suitable lines for each of the three metals. They were unable to determine small proportions of iridium in rhodium. Standard solutions of pure platinum salts were evaporated, and the powder was added to graphite electrodes in two or more charges. For platinum and palladium determinations the mean error did not exceed 6.5%. For rhodium in iridium the mean error was 11%.

The authors also dealt with the determination of iridium, platinum, palladium in refined rhodium<sup>44</sup> and platinum and palladium in refined silver.<sup>45</sup>

For the determination of small quantities of iridium, platinum and rhodium in high purity palladium, Kheyfits<sup>46</sup> used both arc and spark with carbon electrodes, the upper and lower of which, subsequent to warming, were impregnated by adding aliquots of 0.01 ml of aqueous solutions.

The sensitivity of the spark method for platinum and iridium was 0.001% as compared to a range of 0.0005–0.02% for the AC arc. The accuracy ranged from  $\pm 3\%$  to  $\pm 5\%$ . In the case of the rhodium standards, which, of necessity, were prepared as sodium hexachlororhodate, the inaccuracy was increased due to the instability of the arc. However, in the presence of sodium salts the intensity of the palladium reference lines was increased. The authors used one of six palladium reference lines, lines 2929.79 or 2997.97 for platinum; 2924.79 or 3220.78 for iridium; and 3396.85 for rhodium.

#### X-RAY SPECTROSCOPIC METHODS

The applications of X-ray analytical methods to the platinum metals has been the subject of only a few papers. In one of the earliest publications Schreiber<sup>47</sup> discussed techniques which would avoid the serious errors resulting from excessive heating of the anticathode. This is not a significant problem in modern X-ray methods which employ secondary or fluorescent emission. MacNevin and Hakkila<sup>48,49</sup> used the latter method for the determination of palladium, platinum, rhodium and iridium. These metals were applied as liquid solutions to heavy chromatographic

paper and subsequently dried. This method avoided the variations in fluorescent energy caused by changes in tube-to-target distances. Calibration curves were constructed from known amounts of the metals plotted against the time required for 19,200 counts. In the case of mixtures there was some interference;  $K_{\alpha}$  lines for palladium and rhodium were coincident, as were also the  $L_{\alpha_2}$  for platinum and the  $L_{\alpha_1}$  lines for iridium. To estimate the interference a correction curve, which indicated the counts per second attributed to the interfering element, was required. This method of ascertaining a correction factor becomes less valid as the proportion of the interfering metal is increased. To correct for instrument fluctuations, corrected counts per second were compared with the counts from a standard determined simultaneously rather than with a permanent calibration curve. This difficulty is analogous to that associated with intensity measurements of single lines in emission spectroscopy and constitutes one of the objectionable features of the fluorescent X-ray method. The error in positioning the sample, sample preparation, and counting for one standard deviation was found to be 1.86%.

Background corrections were required for each iridium determination and also for each palladium determination when the sample size exceeded 2 mg. The platinum background, assumed to be constant, was obtained by extrapolating the concentration-intensity curve to zero concentration.

The sensitivities, expressed as the mg per ml giving a count of 10% above background, was 0.10 for platinum,  $L_{\beta_1}$ ; 0.20 for palladium,  $K_{\alpha}$ ; 0.14 for rhodium,  $K_{\alpha}$ ; and 0.02 for iridium,  $L_{\alpha_1}$ .

The effect of foreign metals was discussed briefly. The enhancement and absorption of lines by associated base metal was assumed to be small because of the low concentrations of metals in the sample. The authors provided no experimental data dealing with interferences from line proximity of foreign elements.

#### POLAROGRAPHIC ANALYSIS OF PLATINUM METALS

Analytical literature contains no polarographic procedure for either the direct or indirect determination of platinum metals in ores, concentrates or complex alloys. Of the six platinum metals, potentially useful methods have been recorded for palladium, rhodium and osmium. None of the publications includes analytical data to indicate specific areas of application. The problems of interference from associated base metals are rarely discussed and, in general, little useful information is provided to indicate the effect of other platinum metals. Indeed the present author has found no polarographic report which deals with the questions of dissolution and subsequent preparation of the solutions to be analysed. Little of any immediate analytical value has been published for iridium. Most of the polarographic results are concerned with rhodium and with palladium. One cannot avoid the conclusion that there is here a fertile field of research. Polarographic methods will meet an analytical need in millimolar concentration ranges, and more important still, will provide some clarification concerning the character of dissolved species, of mixtures of valence states and, in general, useful descriptive data. Specifically, there could be value in polarographic methods applied to the various alloys obtained from fire assay processes. The advantages over classical methods of speed and simplicity could outweigh the greater accuracy of the former. Compared to spectrographic methods, applied to alloys when the maximum accuracy is required, the speed of polarographic

methods may in some instances at least outweigh the labour involved in securing uniformity in solid electrodes.

### *Palladium*

Willis<sup>50</sup> published a variety of potentially applicable polarographic methods for palladium. The work was almost entirely descriptive, with no attempt to provide procedural techniques nor analytical data. The most important problem of interferences from associated metals was not discussed. Obviously any forthcoming useful applications must await further researches. This author found a wave at  $-1.757$  volts (SCE) for palladium<sup>II</sup> dissolved in  $0.1M$  potassium cyanide- $M$  potassium chloride. The dissolved constituent  $K_2[Pd(CN)_4]$  was reduced to palladium. In  $M$  ammonia- $M$  ammonium chloride solutions of palladium<sup>II</sup> tetra-ammino chloride, a well defined analytical step was obtained whose half-wave potential varied considerably with the palladium concentration. With  $M$  pyridine- $M$  potassium chloride a step was produced which varied with the palladium concentration. The half-wave potential at  $5 \times 10^{-3}M$  was  $-0.361$  V, and at  $2 \times 10^{-4}M$ , it was  $-0.313$  V. Under certain conditions ethylenediamine-potassium chloride solutions could also be used to produce an analytical step. With all of the above methods reduction involved a 2-electron change. The author concluded that the stability of the palladium amine complex increased with the basic strength of the co-ordinating amine; and with increased stability the reduction of the complex became less reversible. He correlated some interesting observations on the increase in negativity of the half-wave potential toward the base of each of the three groups of metals in column VIII of Mendeleeff's Table.

Wilson and Daniels<sup>51</sup> recorded a polarographic method for the determination of palladium following isolation by dimethylglyoxime. The authors compared their method favourably with the gravimetric methods which they incorrectly evaluate as "the most generally accepted methods now in use". The proposed procedure was applied to concentration ranges of  $0.18$  to  $2.72$  m-moles of palladium contained in ammonia-ammonium chloride buffer. A gelatin solution was used as a maximum suppressor. The diffusion currents corrected for residual current were measured at  $-1.10$  volts (SCE). The precision ranged from  $1\%$  to  $0.3\%$  over a tenfold change in concentration; with concentrations of less than  $0.35m-M$  there were greater deviations. Iridium, rhodium and platinum interfered. No results were included for osmium or ruthenium. Of the platinum metals examined only platinum<sup>IV</sup> gave fairly reproducible waves. The presence of equimolar concentrations of silver, chromium, copper and nickel was permissible. With nickel as a contaminant the voltage was adjusted to  $-1.0$  rather than  $-1.1$ . Gold, iron<sup>III</sup> and titanium interfered seriously. This method will find very limited applications. The necessity for isolation by precipitation will encourage rejection in favour of various spectrophotometric methods.

Various authors have recorded procedures for the polarographic determination of palladium in the presence of gold and platinum. Linhart<sup>52</sup> recommended a solution of  $0.1N$  lithium hydroxide in which the half-wave potential was  $-1.25$  V. He proposed to use the method for the analysis of white gold, noting that cadmium interfered and must be removed, and for the determination of palladium and gold in platinum. No procedure was included and no analytical data were provided. Tomiček and

co-workers<sup>53</sup> discussed the polarographic behaviour of palladium, gold and silver in various electrolytes. The three metals could be determined in the presence of each other. Bardin and Lyalikov<sup>54</sup> successfully used solid platinum electrodes in a supporting electrolyte of 0.1*N* sodium nitrate to produce a clear-cut irreversible wave at 0.6–0.7 V. Since the polarographic process involved the deposition of palladium black on the platinum cathode an applied voltage which produced hydrogen was avoided. Dissolution of the latter resulted in a distorted polarogram which, at saturation, resulted in a current-voltage curve rising almost at zero. Regeneration of the cathode can be accomplished readily by treatment with hot nitric acid. In the absence of hydrogen, successive polarograms showed good agreement. To avoid the objectionable maximum the palladium solutions were treated with a small amount of hydrochloric acid. Within the concentration range studied there was a good analytical relationship between palladium content and wave length. The maximum error was 6% and the average error was 3%. The authors erroneously compare the results favourably with those to be obtained from gravimetric procedures. By applying a rotating electrode modification, results were obtained three to four times faster than with the stationary electrode and a greater sensitivity was attained, *e.g.*, 0.05 mg of palladium in 10 ml of solution (5  $\mu\text{g}$  per ml). Polarographic and polarometric studies of noble metals were made by Beran and associates.<sup>55</sup> These authors examined the polarographic reactions of palladium, gold and some sixteen other elements in various mixtures of ethylenediamine tartrate and Complexones I, II and IV. The proposed procedure was recommended for dental alloys containing palladium and gold.

### Platinum

Very few procedures have been proposed for the polarographic determination of platinum. English<sup>56</sup> devised a procedure for the determination of platinum in catalysts in which the metal is adsorbed on carbon. The procedure required a preliminary selective dissolution of base metals by hydrochloric acid containing titanium<sup>III</sup> chloride. The organic residue containing carbon was oxidized and dissolved in *aqua regia*, and the solution was neutralized by sodium hydroxide with methyl red indicator and buffered with a mixture of citric acid and disodium phosphate. Gelatin was added and electrolysis was started at zero applied potential (SCE). The platinum<sup>IV</sup> wave rose quickly to a well defined analytical level at about  $-0.6$  V then dropped sharply to a second and lower plateau at  $-1.2$  V. Since no starting horizontal was formed, the step height was taken as the vertical distance from the starting line to the intersection of the median line starting at the  $-0.3$  V ordinate. The method involved standardisation difficulties arising from the instability of platinum<sup>IV</sup> and resulting in errors as great as 6%. Reproducibility depended upon adherence to a prescribed procedure and could be maintained for a period of several hours. A further difficulty which could become serious in applications to complex platinum mixtures arises from the necessity of maintaining a prescribed volume of acid following dissolution processes. Larger volumes of acids increased the concentration of the supporting electrolyte which affected the step height. Further work will be necessary to extend the limited usefulness of this method, which has some potential value. Bardin and Lyalikov<sup>57</sup> determined platinum<sup>II</sup> polarographically in a solution of 0.1*N* sodium nitrate as the supporting electrolyte and with solid platinum

electrodes. A platinum needle served as the cathode and a platinum plate as the anode. Oxygen interfered so much that the nitrogen, passed through for 45 minutes, was treated by copper to remove traces of oxygen. Two well-defined waves were produced at potentials of 0.7 V and 1.6 V. While within certain limits the effect of polarization was insignificant, the waves produced by a previously prepared platinum electrode coated with platinum black were appreciably distorted and less clearly defined. The results presented by the authors indicate a good analytical application for both waves. A modification of the equipment permitted polarographic determinations for platinum in concentrations of the order of  $10^{-3}$  mg per ml.

In a second paper<sup>58</sup> the authors showed that the height of the second wave increased with increase in acidity and decreased with the addition of sodium hydroxide, from which it was concluded that the second wave was a hydrogen reduction wave. Because of this characteristic the second wave was not recommended for analytical application. On the other hand the height of the first wave, produced through the reduction of quadrivalent platinum to bivalent platinum was proportional to the platinum concentration and could be used analytically.

For proportions of platinum of less than  $10^{-6}M$ , Slendyk<sup>59</sup> used a catalytic hydrogen step at  $-1.0$  V vs SCE from  $2M$  hydrochloric acid solutions. While the analytical step was roughly proportional to the platinum concentration, neutral salts decreased the height of the plateau and this was accentuated with an increasing cation charge.

### Rhodium

Willis<sup>60</sup> recorded a number of potentially useful polarographic methods for rhodium. Rhodium trichloride with excess of complexing reagent was used, the latter serving also as a supporting electrolyte. No analytical data were included. With  $M$  ammonium chloride a reversible two-electron analytical step was found at  $-0.928$  V (SCE). The half-wave potential in  $0.02M$  ammonium chloride decreased to  $-0.799$  V. In  $M$  ammonium chloride- $M$  ammonium hydroxide a step occurred at  $-0.928$  V, the height of which was proportional to a concentration range of  $0.5 \times 10^{-4}$  to  $2.5 \times 10^{-4}$  molar. With the chloropentamine rhodium complex in  $M$  potassium nitrate or potassium sulphate and gelatin,  $E_{\frac{1}{2}}$  was  $-0.962$  V and again a two-electron exchange was involved. With  $3.8 \times 10^{-4}M$  rhodium trichloride in thiocyanate solutions a step was obtained at  $-0.394$  V. Zuman<sup>61</sup> used  $0.9M$  potassium thiocyanate solution and found a step with a half-wave potential of  $-0.43$  volts vs SCE. In  $0.5M$  sodium fluoride there were two steps with half-wave potentials of  $-0.1$  and  $-1.0$  volts. For analytical work Willis<sup>60</sup> preferred a  $M$  pyridine- $M$  potassium chloride medium. With concentrations of  $3.8 \times 10^{-4}M$  rhodium chloride solutions a step occurred at  $-0.414$  V: the complex postulated was  $K_3[RhPy_6]$  reduced to  $K_2[RhPy_6]$ . Repin<sup>62,63</sup> investigated the possible applications of a variety of complexing reagents for the polarographic determinations of rhodium and concluded that the only complexes of analytical use were formed with pyridine-hydrochloric acid added to produce a pH of 7. With ammonium hexachlororhodate a wave of reduction to divalent rhodium is formed. The wave becomes a peak and loses its analytical value in the presence of higher concentrations of pyridine or with rhodium concentrations greater than 40 mg per litre. At 1 mg of rhodium per litre the error may be as little as 2-4%. In the presence of platinum and iridium, rhodium can be determined by

adding to the pyridine-hydrochloric solution of the ammonium salts of tervalent rhodium and quadrivalent iridium a few drops of sodium sulphite to produce bivalent platinum, whose proportions must not exceed 94% of the rhodium and platinum total. The rhodium wave was separated by 0.3 V from the catalytically depolarized hydrogen.

### *Osmium*

While no complete polarographic method for the determination of osmium has been recorded some data of procedural value have been published. Crowell and co-workers<sup>64</sup> studied the character of the polarographic reduction of solutions of octovalent osmium oxide and of potassium osmate. Of various basic solutions, that in saturated lime water provided the most satisfactory polarographic waves. A dropping mercury cathode was used, with an anode of mercury covered with a thin layer of mercuric oxide in contact with lime water saturated with both calcium hydroxide and mercuric oxide. To avoid reduction of the osmium compound by mercury the two compartments were separated by a short arm with a stopcock. The potential of the half-cell at 25° was -0.091 volts vs NCE. With octovalent osmium oxide three steps appeared; the first representing a reduction to hexavalent osmium, the second to quadrivalent and the third to tervalent. The concentrations used varied between  $1.9 \times 10^{-4}M$  to  $7.1 \times 10^{-4}M$   $OsO_4$ . With potassium osmate in lime water only two waves were evident, corresponding to the reduction of hexavalent and quadrivalent states. The half-wave potentials for these two reductions are respectively -0.44 volt and -1.20 volts vs NCE. No analytical results were provided, but the authors stated that by a direct comparison method with standard osmium solutions an accuracy of better than 5% could be attained. It is to be hoped that the method will be examined with a view to ascertaining its analytical value.

A polarographic method applicable to small amounts of osmium after isolation of the volatile oxide was proposed by Kolthoff and Parry.<sup>65</sup> The oxide in the presence of hydrogen peroxide, in an acetate buffered solution at pH 5, yields a kinetic or catalytic current whose maximum is measured at +0.23 volt vs SCE. Under the same conditions the rate of reduction of the octovalent oxide by the mercury pool anode was 2% a minute. The kinetic current was approximately linear in 8mM hydrogen peroxide over an osmium concentration range between 2M and  $10 \times 10^{-7}M$ . A calibration curve was recommended for analytical applications. The explanation for the catalytic current involved the reduction of the octovalent oxide to the hexivalent state and a rapid oxidation in the presence of hydrogen ions and hydrogen peroxide.

### *Ruthenium*

The polarography of ruthenium in chloride-free perchloric acid was examined by Niedrach and Tevebaugh.<sup>66</sup> The authors postulated the existence in equilibrium of two distinct hydrolysed dissolved constituents of quadrivalent ruthenium. Due to the slow rate of change, two polarographic waves were found for the 1-electron reduction of these two species. In *M* perchloric acid the half wave potential of the first wave was +0.65 NHE; and for the second wave, +0.45 NHE. The reduction was irreversible. A third wave at -0.09 volts involved a reduction to bivalent ruthenium which could be re-oxidized slowly by perchloric acid to the quadrivalent



form. The polarographic behaviour of ruthenium and of other platinum metals in acid solutions with a dropping mercury electrode was discussed by Slendyk and Herasymenko.<sup>67</sup> With ruthenium, catalytic hydrogen deposition occurred in three stages. In hydrochloric acid the deposition of hydrogen for various platinum metals, including ruthenium, compared with that for mercury at  $-1.17$  volts SCE, occurred over the following ranges:  $0.5-0.6$ ;  $0.7-0.8$ ;  $0.9$  volts, the exact values depending upon the pH and the concentrations of the platinum metals. This catalytic activity decreased from ruthenium to palladium, and from iridium to platinum. The authors' explanation involved, in all cases, a reduction to metal and a type of alloy formation with mercury. The theory seems untenable in view of its dependence upon the existence of distinct stages in the character of alloy development. Aside from confirmation of the existence of multiple catalytic hydrogen stages this report has little or no analytical significance. Šušič<sup>68</sup> discussed the polarographic determination with the dropping mercury electrode of amounts of ruthenium of the order of  $1 \times 10^{-8}$  g to about  $30 \times 10^{-8}$  g in solutions of  $0.9M$  perchloric acid, or EDTA, or EDTA together with ammonium acetate. With perchloric acid the single wave was a catalytic hydrogen wave and the ratios of concentration to the diffusion current showed a surprising precision. The EDTA with the same solutions of  $Ru^{III}$  and  $Ru^{IV}$  yielded three catalytic hydrogen waves, the highest of which was identical with the wave in the perchloric medium. The first wave had a half-wave potential of  $-0.88$  to  $-0.96$  V (SCE) between pH  $1.06-2.3$ ; the half-wave potential of the second wave under the same conditions varied from  $-1.16$  to  $-1.24$  V. With increasing pH the second wave was eliminated. The latter was recommended for determinations of quantities of ruthenium greater than  $1 \times 10^{-7}$  g per ml, with  $0.001\%$  gelatin and a pH  $> 5.4$  in either the EDTA or in EDTA with ammonium acetate as supporting electrolyte. Undoubtedly this polarographic method can be applied analytically, but further work and some modification will be required. The author provides no analytical procedure and, as in most polarographic papers, the methods of dissolution and of avoiding interference are not discussed.

**Zusammenfassung**—Ein kritischer Überblick der Methoden zur spektrographischen und polarographischen Bestimmung der Platin-Metalle zum Juni 1958 wird angegeben.

**Résumé**—Cette mise au point concerne les publications appropriées examinées jusqu'en juin 1958. Les méthodes ont été jugées du point de vue de leurs applications analytiques aux essais de perle, aux précipités de platine métallique et aux alliages des métaux de la mine du platine avec ou sans impuretés des métaux principaux.

Aucune méthode spectrographique n'a été signalée pour le dosage direct des métaux de la mine du platine dans les minerais et les concentrés. Pour le dosage du palladium, du platine et du rhodium dans le minerais et les concentrés, les méthodes spectrographiques les plus exactes nécessitent une extraction préliminaire par voie sèche pour obtenir un culot de plomb ou une perle d'argent. Pour ces derniers, pour d'autres alliages, pour des précipités, etc. . . , les méthodes les plus exactes impliquent des traitements spéciaux pour obtenir une composition uniforme et réaliser des étalons ayant des passés métallurgiques identiques. Aucune méthode spectrographique satisfaisante n'a été signalée pour le dosage direct ou indirect de l'iridium du ruthenium et de l'osmium dans les minerais, les concentrés ou les alliages complexes.

Aucune des fréquentes affirmations selon lesquelles les méthodes spectrographiques fourniraient une plus grande exactitude que les méthodes par voie humide, n'a été confirmées et elles sont toutes inacceptables. Les quelques données existantes montrent qu'avec un analyste compétent et dans les meilleures conditions l'exactitude des deux méthodes est du même ordre.

Pour l'examen qualitatif des impuretés d'un précipité etc. contenant des traces de nombreux métaux, la méthode spectrographique est nettement supérieure aux méthodes par voie humide.

Pour les métaux de la mine du platine les méthodes polarographiques ne concernent que des mélanges à peu de constituants. Aucun procédé n'a été signalé permettant leur application satisfaisante aux essais de perles ou de culots. Peu de procédés détaillés ont été signalés pour le dosage de chaque métal de la mine du platine et aucune méthode ne comporte les procédés usuels permettant la dissolution d'un système à constituants multiples. Les méthodes polarographiques peuvent être, sans aucun doute, d'utiles rivales dans les domaines de concentrations en dessous desquelles les méthodes classiques ne sont plus applicables. De plus les deux méthodes spectrographiques et polarographiques possèdent le grand avantage de la rapidité lorsqu'il s'agit d'un grand nombre d'échantillons de compositions voisines.

Trop peu de méthodes par spectrographie aux rayons X ont été signalées pour juger leur précision.

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# ANALYTICAL APPLICATIONS OF XYLENOL ORANGE—II

## SPECTROPHOTOMETRIC STUDY ON THE ZIRCONIUM-XYLENOL ORANGE COMPLEX

K. L. CHENG

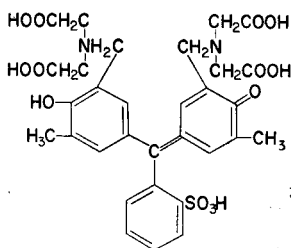
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**Summary**—The purplish-red complex formed from zirconium and Xylenol Orange has been studied by spectrophotometric methods and shown to contain zirconium and reagent in the ratio 1 : 1. The formation constant of this complex has been measured as  $4.0 \times 10^7$ .

In Part I of this series,<sup>1</sup> Xylenol Orange has been proven to be a sensitive and highly selective reagent for zirconium (and hafnium), and its use in the determination of small amounts of zirconium in high temperature alloys has been described elsewhere<sup>2</sup>. This paper presents the results of a spectrophotometric study on the zirconium-Xylenol Orange complex.

Xylenol Orange, which has the following structure, is an analogue of EDTA and therefore would be expected to form a 1 : 1 complex.



Xylenol Orange

### EXPERIMENTAL

#### Reagents

*Xylenol Orange solution:* 0.065 g of the sodium salt (as supplied by CHEMAPOL) was dissolved in water and diluted to 1 litre. This gave a  $1 \times 10^{-7}M$  solution.

*Zirconium solution:* A  $2 \times 10^{-7}M$  solution was prepared from zirconium tetrachloride in 0.8*N* perchloric acid and standardized by EDTA.<sup>3</sup>

Absorption measurements were made with a Beckman Spectrophotometer, Model DU using 1-cm silica cells.

### THE ZIRCONIUM-XYLENOL ORANGE COMPLEX

The spectra of Xylenol Orange and its zirconium complex in 0.8*N* perchloric acid medium have been determined.<sup>1</sup> The complex has a maximum absorption at 535  $m\mu$ .

The mole ratio of the zirconium-Xylenol Orange complex was investigated by the mole ratio method and Job's method.<sup>4</sup> In the mole ratio method,  $9.5 \times 10^{-7}$  mole of zirconium were mixed with various amounts of Xylenol Orange ( $1 \times 10^{-7}M$

solution) in approximately 0.8*N* perchloric acid. The total volume was 50 ml. The solution was set aside for more than 30 minutes before making the absorbance measurement using water as blank (see Fig. 1). In Job's method, mixtures of varying proportions of equimolecular solutions of zirconium and Xylenol Orange were prepared, keeping the total volume at 50 ml, and their absorbances were measured at 535 m $\mu$ . The data are plotted against the composition of the mixtures (Fig. 2). Since Xylenol Orange solution absorbs slightly at 535 m $\mu$ , a correction was made. Both methods indicate that a 1 : 1 complex was formed under the conditions investigated.

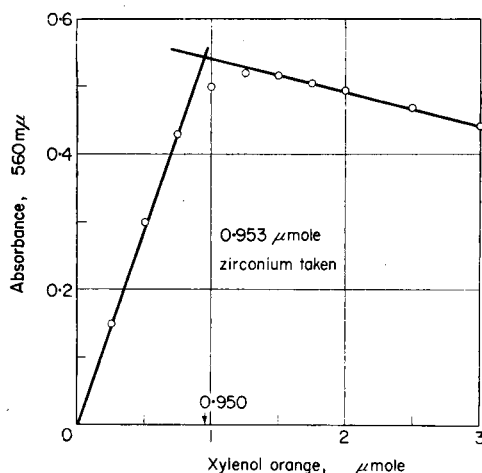
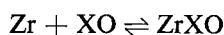


FIG. 1.

#### FORMATION CONSTANT OF THE ZIRCONIUM-XYLENOL ORANGE COMPLEX

The formation constant of the complex has been calculated from Fig. 2 by the method similarly used for a similar purpose by Majumdar and Chakrabartty.<sup>5</sup> The formation is in accordance with the following equation



where XO represents the molecule of Xylenol Orange.

Hence

$$K = \frac{[\text{ZrXO}]}{[\text{Zr}] \cdot [\text{XO}]} \quad \text{or} \quad \frac{[x]}{[a-x][b-x]} \quad (1)$$

The concentrations of free zirconium and Xylenol Orange in the solution can be found if the concentration of the zirconium Xylenol Orange formed  $[x]$ , the total concentration of zirconium  $[a]$  and the total concentration of Xylenol Orange  $[b]$  are known. By drawing a line to intersect curves I<sub>c</sub> and II<sub>c</sub> at A and B, where solutions A and B have the same concentration of Zirconium-Xylenol Orange complex,  $[x]$  can be calculated from the following relation:

$$K \text{ (formation constant)} = \frac{[x_1]}{[a_1 - x_1][b_1 - x_1]} = \frac{[x_2]}{[a_2 - x_2][b_2 - x_2]}$$

Since  $[x_1] = [x_2]$  we obtain,

$$[x] = \frac{[a_1 b_1 - a_2 b_2]}{[a_1 + b_1] - [a_2 + b_2]} \quad (2)$$

The concentrations of zirconium  $[a_1]$  and Xylenol Orange  $[b_1]$  used in solution A and those of zirconium  $[a_2]$  and Xylenol Orange  $[b_2]$  used in solution B can be easily found at points  $A_1$  and  $B_1$  from Fig. 2. The formation constant  $K$  is then calculated from equation (1). This is a very convenient way of measuring the formation constant of a coloured complex with the mole ratio 1 : 1.

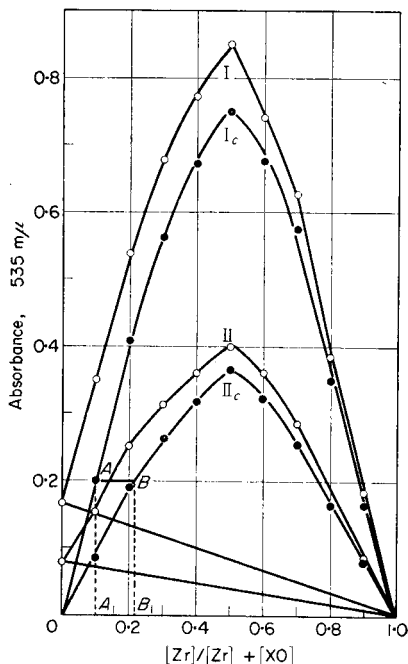


Fig. 2.

Application of this method gave a value of  $K = 4.0 \times 10^7$ . This value is not high as compared with that of the stability constant for the zirconium-EDTA complex ( $10^{19.9}$ ). Therefore Xylenol Orange can serve as a metal indicator in the EDTA titration of zirconium, and its zirconium complex is easily masked by other strong complexing agents such as EDTA, fluoride, phosphate, oxalate, and large amounts of sulphate.

**Zusammenfassung**—Es wurde der purpurrote Zirkon Xylenol Orange Komplex auf spectrophotometrischem Wege untersucht. Das Verhältnis von Zirkon und Reagens betrug 1 : 1. Die Bildungskonstante dieses Komplexes wurde als  $4.0 \times 10^7$  bestimmt.

**Résumé**—Le complexe rouge-pourpre du Zirconium avec le Xylenol Orange a été étudié par Spectrophotométrie. On a montré qu'il contient le Zirconium et le réactif dans le rapport 1 : 1. La constante de formation de ce complexe a été mesurée, et est égale à  $4,0 \times 10^7$ .

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## SPECTROPHOTOMETRIC DETERMINATION OF RUTHENIUM WITH N:N'-BIS-(3-DIMETHYL-AMINOPROPYL)DITHIO-OXAMIDE\*

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**Summary**—N:N'-Bis-(3-dimethylaminopropyl)dithio-oxamide, a derivative of rubeanic acid, reacts with ruthenium in a strong hydrochloric acid solution to give a soluble blue complex which has been made the basis for the determination of trace quantities of the element. Optimum conditions for the use of the reagent have been studied. Well-known distillation techniques have been successfully applied to quantities of ruthenium ranging from 14.8  $\mu\text{g}$  to 177.9  $\mu\text{g}$ . The sensitivity is 0.020  $\mu\text{g}/\text{cm}^2$ .

### INTRODUCTION

SEVERAL investigations have been carried out in recent years on the spectrophotometric determination of ruthenium. Ayres and Young<sup>1,2</sup> have studied thiourea and dithio-oxamide (rubeanic acid), and DeFord<sup>3</sup> thiourea, as colorimetric reagents for this metal. Currah, Fischel, McBryde and Beamish<sup>4</sup> investigated the reaction between ruthenium and *p*-nitrosodimethylaniline. Breckenridge and Singer<sup>5</sup> studied the ruthenium-5-hydroxyquinoline-8-carboxylic acid system. Recently Steele and Yoe<sup>6</sup> have proposed 1-naphthylamine-3:5:7-trisulphonic acid for the determination of ruthenium.

In this paper N:N'-bis-(3-dimethylaminopropyl)dithio-oxamide is recommended as a reagent for the spectrophotometric determination of ruthenium. This compound has recently been applied by Jacobs and Yoe<sup>7</sup> to the simultaneous spectrophotometric determination of cobalt, nickel and copper. The latter reactions are carried out at pH 9 with immediate development of colour at room temperature. The reaction with ruthenium requires heat in the presence of high concentrations of hydrochloric acid.

### EXPERIMENTAL

#### *Apparatus*

*Spectrophotometers:* Beckman spectrophotometers, Model DK-2 and Model DU, with 1-cm matched Corex cells were used for all absorbance measurements.

*Distillation apparatus:* The still used for the distillation of ruthenium was the same as the one proposed by Steele and Yoe.<sup>8</sup>

#### *Reagents*

*Standard ruthenium solution:* Approximately 0.4 g of ruthenium chloride was dissolved in distilled water. Concentrated hydrochloric acid was added to give a final concentration of one molar in 500 ml. The solution was standardized gravimetrically by precipitating the ruthenium as the hydrated oxide, igniting in air and then in hydrogen to the metal. The solution contained 0.593 mg of ruthenium per ml. More dilute solutions were prepared as needed.

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*Reagent solution.* A  $3 \times 10^{-3}M$  solution of *N,N'*-bis-(3-dimethylaminopropyl)dithio-oxamide was prepared by dissolving 87 mg of the compound in 100 ml of 95% ethanol.

*Other reagents:* All other reagents were analytical grade and were used without further purification.

#### Absorbance curves

Fig. 1 shows absorbance curves of the reagent ( $1.8 \times 10^{-4}M$ ) and the ruthenium complex (3.56 ppm). The hydrochloric acid concentration in both solutions was approximately 7.5*M*. The solutions were heated in a boiling-water bath for 15 minutes. The ruthenium complex has a maximum absorbance at 630  $m\mu$ . The reagent does not absorb above 400  $m\mu$ , so distilled water was used as a reference.

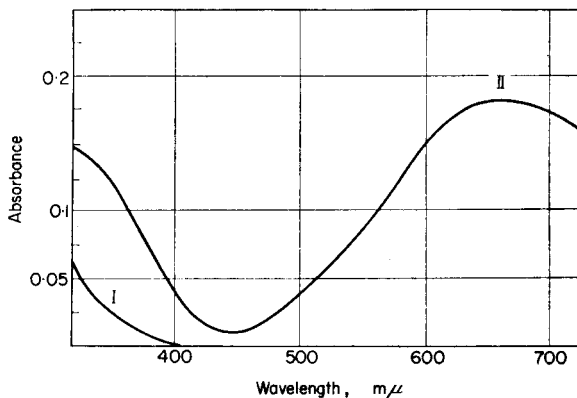


FIG. 1. Absorbance curves for reagent (I) and its ruthenium complex (II).

#### Effect of molarity of hydrochloric acid

Table I illustrates the effect of the concentration of hydrochloric acid on the intensity of the colour reaction. The absorbance of the complex was found to increase up to a concentration of hydrochloric acid corresponding to approximately 7.5*M*.

TABLE I. EFFECT OF CONCENTRATION OF HYDROCHLORIC ACID ON ABSORBANCE OF RUTHENIUM COMPLEX (3.56 ppm of Ru)

Molarity of HCl	$A_s$ at 630 $m\mu$
0.80	0.115
1.6	0.141
2.4	0.150
3.2	0.157
4.0	0.165
6.4	0.170
7.5	0.179
8.6	0.180

#### Effect of time of heating

Maximum colour development was reached after heating 15 ml of the sample in a boiling water bath for 15 minutes. The 15 ml of solution contained 3 ml of the reagent solution ( $3 \times 10^{-3}M$ ) and

10 ml of concentrated hydrochloric acid along with the desired quantity of  $\text{Ru}^{\text{III}}$ . After this heating period the solution was cooled and diluted to 25 ml with distilled water. It is necessary to use about a 10-fold excess of reagent in order to assure complete colour development.

#### *Conformity to Beer's law*

Beer's law was found to be obeyed by the complex over the range investigated, 0.27 ppm to 9.52 ppm ruthenium.

#### *Effect of diverse ions*

It was found that concentrations of  $\text{Rh}^{\text{III}}$  and  $\text{Ir}^{\text{IV}}$  comparable to the amount of  $\text{Ru}^{\text{III}}$  present hindered the development of the ruthenium complex. It appears that these ions form colourless complexes with the reagent. No colour could be developed with the ruthenium in the presence of these two ions even when three times the normal amount of reagent solution was used.  $\text{Pt}^{\text{IV}}$  forms a rose colour with the reagent *when heated*, but not in the cold. This is probably due to a  $\text{Pt}^{\text{II}}$  complex resulting from the reduction of  $\text{Pt}^{\text{IV}}$  to  $\text{Pt}^{\text{II}}$  upon heating with excess reagent. Platinum interferes with the development of the ruthenium complex when present in amounts equivalent to the amount of ruthenium present. A bright yellow complex is formed when  $\text{Pd}^{\text{II}}$  reacts with the reagent in strong hydrochloric acid. This reaction takes place at room temperature. It offers promise of being a good reaction for palladium and is currently being investigated. Palladium can be tolerated as long as its concentration is no more than twice that of the ruthenium present. Osmium, as the osmate ion, forms a complex with the reagent whose colour changes from a green to red and finally to brown. The nature of the final product is such that it is difficult to characterize spectrally.

These studies indicate the advisability of a prior separation of the ruthenium. This is accomplished by distillation of the ruthenium as ruthenium tetroxide.

#### *Distillation of ruthenium*

The apparatus employed for the distillation of ruthenium is the same as the one reported by Steele and Yoe.<sup>8</sup> In our work only the first receiver is used, since osmium is removed in a prior treatment. If osmium is present, the sample is heated with 6*M* nitric acid *in a hood* for 15 minutes, thereby converting the osmium to the volatile osmium tetroxide.

*Recommended distillation procedure:* If the sample contains chlorides, it must be heated with sulphuric acid to fumes of sulphur trioxide to remove chlorides, since their presence hinders the volatilization of ruthenium tetroxide. Place the sample in a 200-ml flask and dilute to about 25 ml with distilled water. Add concentrated sulphuric acid to give a final concentration of about 10% by weight. Add twenty-five ml of a 10% (by weight) solution of sodium bromate and distil the sample for 15 minutes. Collect the ruthenium tetroxide in 10 ml of 6*M* hydrochloric acid and carry through the procedure for analysis.

#### *Procedure for analysis*

Evaporate the distillate containing the ruthenium tetroxide to about 1 ml and then wash into a 25-ml volumetric flask with 1 or 2 ml of distilled water. Then add 10 ml of concentrated hydrochloric acid and 3 ml of the reagent solution. Heat the sample in a boiling water bath for 15 minutes, cool, and dilute to the mark with distilled water. Measure the absorbance of the solution at 630  $\text{m}\mu$  against a distilled water blank. Then determine the concentration of ruthenium from a calibration curve.

#### *Analysis of synthetic samples*

Synthetic samples containing ruthenium alone and in the presence of other platinum metals were carried through the distillation procedure and then analysed by the recommended procedure. The results are given in Table II.

TABLE II. ANALYSIS OF SYNTHETIC SAMPLES

Sample	$\mu\text{g Ru added}$	$\mu\text{g Ru found}$	% Recovery
1	59.4	62.5	105
2	29.7	31.3	105
3	14.8	13.3	90
4	89.1	85.5	96
5	59.4	60.5	102
6	118.6	117.5	99
7	29.7	28.8	97
8	117.9	177.5	100
9*	29.7	27.3	93
10*	59.4	60.5	102
11*	89.1	87.5	98

\* Os, 250; Pd, 1000; Pt, 1000; Ir, 1000; Rh, 1000.

#### Sensitivity

The sensitivity of the colour reaction as defined by Sandell<sup>9</sup> is  $0.020 \mu\text{g}/\text{cm}^2$ .

#### Standard deviation

The standard deviation was based upon ten samples which contained 89.1 micrograms of ruthenium. Each sample was carried through the distillation procedure and analysed according to the recommended procedure. The standard deviation was 0.003 absorbance unit or 0.06 ppm ruthenium.

### CONCLUSIONS

The proposed reagent has the advantage over rubeanic acid and thiourea in that the ruthenium complex is much more soluble than the complexes of these two compounds. The time of heating is about one-half that of the rubeanic acid and thiourea systems. The sensitivity of the new colour reaction is less than that claimed by Ayres and Young for rubeanic acid. In our hands, however, the sensitivity claimed for rubeanic acid was not obtained, perhaps through inexperience with the method. The sensitivity of the new reagent is slightly greater than the ruthenium-thiourea reaction.

*p*-Nitrosodimethylaniline is more sensitive than the new reagent but here again the new complex is more soluble and maximum intensity is reached in 15 minutes, whereas the ruthenium complex with *p*-nitrosodimethylaniline requires 50 minutes for maximum colour development.

*N,N'*-bis-(3-dimethylaminopropyl)dithio-oxamide should be a valuable reagent for the determination of trace quantities of ruthenium. The procedure is more rapid and the accuracy compares favorably with existing methods.

*Acknowledgement*—The authors wish to express their thanks to the Mallinckrodt Chemical Works for their gift of the *N,N'*-bis-(3-dimethylaminopropyl)dithio-oxamide used in this work.

*Zusammenfassung*—Zur Bestimmung von Rutheniumspuren wird der lösliche blaue Komplex, der mit *N,N'*-bis(3-dimethylaminopropyl)dithio-Oxamid (ein Derivat der Rubeanwasserstoffsäure) in stark salzsaure Lösung entsteht, herangezogen. Die besten Arbeitsbedingungen wurden studiert und bekannte Destillationsverfahren bei Rutheniummengen von 14,8–177,9  $\mu\text{g}$  angewendet. Die Empfindlichkeit beträgt  $0,020 \mu\text{g}/\text{cm}^2$ .

**Résumé**—La N-N'-bis-(3-diméthylamino propyl)dithio-oxamide, dérivé de l'acide rubéanique, réagit avec le ruthénium en solution acide chlorhydrique fort pour donner un complexe bleu soluble qui est à la base du dosage de traces de cet élément. Les auteurs ont étudié les meilleures conditions d'utilisation de ce réactif. Ils ont appliqué avec succès des techniques de distillation bien connues à des quantités de ruthenium allant de 14,8  $\mu\text{g}$  à 177,9  $\mu\text{g}$ . La sensibilité est 0,020  $\mu\text{g}/\text{cm}^2$ .

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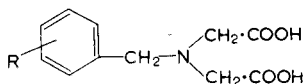
## PRELIMINARY COMMUNICATIONS

### New chelons based on pyridine

(Received 20 October 1958)

SELECTIVITY in chelometric titration has been achieved principally through applying selective metallochromic indicators, masking or demasking agents, and selective titrants. Within the last few years numerous metallochromic indicators have been synthesized and studied for their applicability in chelometric titrations and these have been recently reviewed by Barnard, Broad, Flaschka.<sup>1</sup> The unique properties of certain of these indicators have widened the scope of metal ion analysis with EDTA tremendously and undoubtedly more studies of this nature will be forthcoming. Recently the proposal of new chelons suitable for selective titration has brought increased attention. Aside from the classical EDTA the chelons triethylenetetramine (trien), tetraethylenepentamine (tetren), and ethylene glycol-*bis*( $\beta$ -aminoethyl ether)-*N*:*N'*-tetra-acetic acid (EGTA)<sup>5-7</sup> have been proposed as titrants because of some unique behaviour which allows them to be employed as selective titrants. For example EGTA complexes calcium ( $\log K = 11$ ) much more tightly than magnesium ( $\log K = 5.2$ ) and thereby permits selective titrations of the former.<sup>6,7</sup> Polyamines, such as trien and tetren, form stable complexes with a fairly restricted group of metal ions (namely the later transition metals) and may be utilized for the titration of these particular metals in the presence of alkaline earths, the rare earths and heavy metals.

In this laboratory a number of new chelons based upon pyridine have recently been synthesized and are under current investigations. These may be designated as derivatives of 2-aminomethyl pyridine-*N*:*N*-diacetic acid (abbreviated PADA).



Where R corresponds to  $-\text{H}$ ,  $-\text{SO}_3^-$ ,  $-\text{COO}^-$ ,  $-\text{CH}_3$ , or  $-\text{CH}_2-\text{N}(\text{CH}_2\text{COOH})_2$ . This paper represents the preliminary report of some of the unusual properties of the 6-methyl derivative.

Unlike EDTA, the 6-methyl PADA does not form stable complexes with the alkaline earths and rare earths, but is otherwise similar. Unlike the polyamines, 6-methyl PADA reacts with lead and bismuth in acid solution. Thus by judicious choice of chelons and the proper use of the pH effect, selective titrations can be achieved with rather complicated mixtures of metal ions.

Potentiometric detection of end-points was chosen for this study because of the rather specific activity of this type of end-point detection; in other words, non-titrated metals which may block the action of metallochromic indicators do not block the detection of end-points with the mercury electrode. Also the mercury electrode is applicable over almost the entire pH range and thus selectivity by the pH effect is readily obtained. Some of the results are illustrated in Fig. 1 for titrations with 6-methyl PADA. Studies are now under way to determine the stability constants for these chelons with a representative group of metal ions and this work will be reported in detail later.

### EXPERIMENTAL

#### Potentiometric end-point

The electrode system consisted of a mercury indicator electrode and a calomel reference electrode;<sup>2</sup> the potential being followed by means of Leeds and Northrop pH meter (Cat. No. 7664). In the titration of every ion except mercury,<sup>11</sup> a drop of  $10^{-3}$  M mercury<sup>II</sup>-chelona<sup>II</sup> is added to establish a reasonably meaningful potential.<sup>3</sup>

*Reagent and solutions*

*6-methyl PADA standard solutions.* 3.144 grams of the solid dipotassium dry salt was dissolved in demineralized water and diluted to 100 ml to prepare 0.1M solution.

*Metal salt solutions:* These were prepared by weighing the approximate amounts of salts (using high purity chemicals) to prepare 0.01M solutions and standardized against EDTA solution.

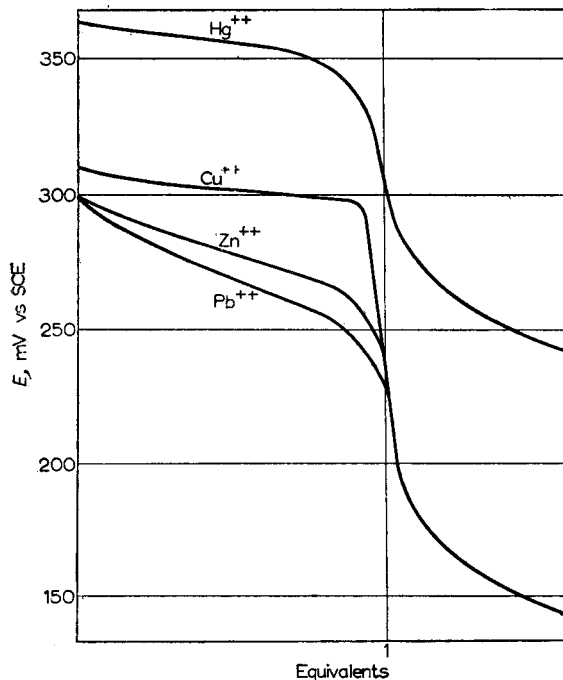


FIG. 1. Titration curves with 6-methyl PADA using mercury electrode. Acetate buffer (pH 5.5). Alkaline earths, rare earths, scandium, yttrium, aluminium do not interfere.

*Buffers:* Ammonia, triethanolamine and acetate buffers were prepared by mixing one mole of base and of nitric acid and diluting to 1 litre. These were stored in polyethylene bottles.

*Mercury<sup>II</sup>-chelionate:* 0.001M prepared by mixing 10 ml of 0.002M mercuric nitrate with an equivalent amount of 6-methyl PADA and neutralizing with sodium hydroxide to pH 7.0.

### PROCEDURE

The titrations of different metal ions were carried out in 50 ml titration cell equipped with a magnetic stirrer and a glass electrode to check the pH during the titration. Samples containing  $10^{-3}M$  metal ion and at most  $10^{-2}M$  buffer and 1 drop  $10^{-3}M$  mercury<sup>II</sup>-chelionate were titrated with 0.1M solution of the chelon from a Gilmont microburette (total displacement 1 ml, subdivided into 0.0002 ml).

### RESULTS

Fig. 1 shows the potentiometric curve of different metal ions titrated with 6-methyl PADA in acetate buffer at pH 5.5. Rare earths and alkaline earths are not titrated and do not interfere at this pH. The direct titrations of copper, cobalt, nickel, zinc and lead in ammonia buffer (pH 9.5) were feasible with fairly sharp breaks. Calcium, strontium, and barium do not titrate at this or higher pH. Bismuth at pH 1.5 as well as mercury<sup>II</sup> nitrates could be titrated in nitric acid.

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### Metalfluorechromic indicators

(Received 23 January 1959)

As a result of the examination of sixteen metalfluorechromic indicators, it has become apparent that metal ions are capable of forming two kinds of complexes with these indicators.

The "normal complex" is demonstrated by the quenching of the fluorescence of calcein W by copper ions.<sup>1</sup> In this instance the free indicator exists in a form  $H_n I^{n-6}$  which fluoresces. The formation of the copper complex results in the quenching of the fluorescence and must be interpreted as bringing about the electronic configuration found in the indicator anion  $I^{-6}$ . This type of reaction would be expected with metalfluorechromic indicators since an analogous phenomenon takes place with metallochromic indicators. That is the formation of a metal complex with a metallochromic indicator results in the appearance of the "alkaline colour" of the free indicator at a pH at which an "acid colour" would normally exist. With the metalfluorechromic indicators studied to date, copper, manganese, nickel, cobalt and palladium are capable of forming the 'normal complex' at appropriate pH values.

A second type of reaction which I prefer to call an "indicator reversal complex" is also demonstrated by calcein W. This is used in the titration of calcium with EDTA.<sup>2</sup> In this case the free indicator at a high pH exists in the form  $I^{-6}$ , which does not fluoresce. The addition of calcium causes the fluorescence to appear even though the pH of the solution is so high that the free indicator does not fluoresce. This phenomenon must be interpreted as an indication that calcium brings about the electronic configuration of a fluorescing anion  $H_n I^{n-6}$  presumably in the form  $CaH_n I^{n-4}$ . In addition to calcium, barium, strontium, mercury, zinc, lead and others react in this manner.

In no case has an element been found which will take part in both types of complex formation.

A mechanism for this phenomenon may be suggested in the possibility of the formation of two geometrically different chelates at the fluorechromic site. These two configurations are illustrated in Fig. 1.

Fig. 1a illustrates the normal complex which results in the quenching of the fluorescence of the free indicator. The copper ion is attached to the phenolic oxygen and thus alters the part which this portion of the molecule can contribute to fluorescence.

Fig. 1b illustrates a second configuration which can exist with this functional group. In this instance the metal ions (Ca, Sr, Ba, Hg, etc.) do not chelate in a manner which binds the phenolic oxygen. This explains why these elements do not quench the fluorescence of the free indicator.

The enhancement of the fluorescence by the metal ions which form "an indicator reversal complex" also may be explained by this mechanism. Function groups of this type form complexes of the type MHL. In addition it is not unusual for  $\log K_{MHL}^M$  and  $\log K_{ML}^M$  to differ by only a single order of

magnitude.<sup>3,4</sup> Under these conditions it is reasonable to expect that the addition of a metal ion to a solution of the indicator in the "alkaline form" will result in some formation of the complex MHL and thus return the fluorechromic portion of the indicator to the "acid colour." This reaction can be expected only with elements which form the geometric configuration illustrated in Fig. 1b.

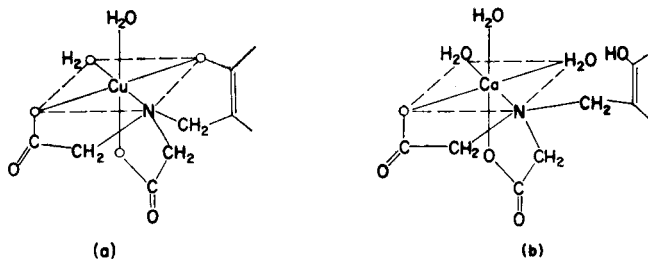


FIG. 1.

The phenomenon which has been referred to as a "blocking reaction" with metallochromic indicators<sup>5</sup> can be explained by the same mechanism.

This phenomenon is being examined in considerable detail and will be reported on at a later date.

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### Rapid method for coulometric analysis using an I-Q recorder

(Received 19 March 1959)

A RAPID method which employs an I-Q recorder has been developed for controlled potential coulometric analysis. This I-Q recorder uses the bevel gear differential as main mechanism. The recorder shows the electrolysis current,  $i$ , along the Y-axis and the quantity of electricity,  $Q$ , (the integrated value of the electrolysis current,  $i$ ) along the X-axis. This is unlike most recorders which show time  $t$  along the X-axis. The current integration is performed by the differential gear, a tachogenerator to stabilize, and various motors.<sup>1</sup> This integrating mechanism derives a chart instead of the counter used in the direct-reading current integrator. Integration of current from the neighborhood of zero percent of rated current is possible; also background current is mechanically cancelled from the total electrolysis current which passes from the cell. The value of  $Q$  on the chart is the net electrolysis current. The background current is assumed to be always constant.<sup>2</sup>

In coulometric analysis with controlled potential,

$$i_t = i_0 10^{-Kt} \quad (1)$$

and

$$Q = \int_0^t i_t dt \quad (2)$$

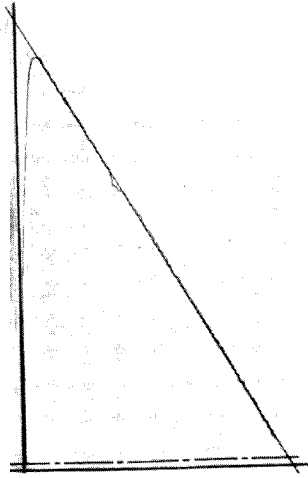
where  $i_0$  = initial current at zero time.

$i_t$  = current at time  $t$ .

$K$  = constant.

$Q$  = quantity of electricity.





From equations (1) and (2) it is found<sup>3</sup> that

$$Q = \frac{i_0 - i_t}{2.303 K} \quad (3)$$

The current plotted against the quantity of electricity shows that the relation is effectively a straight line. Therefore measurement of the electrolysis current for only the initial few minutes is sufficient, since the current is large and the recording distance of  $Q$  is greatest at this time. The inclination of the entire curve is determined by extending a line from this recorded section. By extrapolation, the estimated resultant quantity of electricity is found at the intersection with the X-axis.

The experimental determination of semimicro amounts of copper has confirmed the relation shown in equation (3). Fig. 1 shows the chart obtained in the determination of 0.5 mg of copper.

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## SHORT COMMUNICATION

### The heterolytic and homolytic dissociation of bromine chloride and determination of the bromine formed during homolytic dissociation

(Received 9 February 1959)

WHILE developing the iodometric method for the determination of bromide ions already reported<sup>1</sup> and in further experiments, the chemical behaviour of bromine chloride was subjected to a thorough investigation. We observed<sup>2</sup> that, in the molecule of bromine chloride, bromine possesses a  $+\delta$  charge whilst chlorine has a  $-\delta$  charge. Accordingly, bromine chloride dissociates in aqueous solution to bromine ions of positive  $\delta$  charge and to chloride ions of negative  $\delta$  charge. Applying this assumption, all the reactions of bromine chloride studied by us could be interpreted, in general, with success. However, we were unable to explain the phenomenon then mentioned<sup>3</sup> that when stoichiometric bromine chloride, *i.e.* containing equivalent amounts of bromine and chlorine, reacted in aqueous solution with excess cyanide, and the bromine cyanide formed was measured by iodometry, it was found that only 97–98 % of bromine chloride was converted into bromine cyanide. A similar observation was reported by L. Molnár.<sup>4</sup> In the presence of excess chlorine, bromine chloride quantitatively yielded bromine cyanide.

In the course of the investigation of the standard bromine chloride solution, a method was also evolved for the determination of the content of elementary bromine in the aqueous solution of bromine chloride. This method, which is given in detail below, essentially consists in treating the solution with excess hydrogen cyanide, when bromine chloride is converted into bromine cyanide and chloride ions whilst elementary bromine yields bromine cyanide and bromide ions. Bromine cyanide and excess hydrogen cyanide are then removed from the solution by an inert gas ( $\text{CO}_2$ ) or by cautiously boiling the boric acid solution. The residual bromide ions, the amount of which is equivalent to the original content of elementary bromine, are determined by the bromine cyanide method<sup>1</sup> already mentioned.

By this method, we investigated solutions of bromine chloride prepared from equivalent amounts of bromine and chlorine and other solutions of bromine chloride containing different quantities of elementary chlorine and elementary bromine. No elementary bromine was found in solutions of bromine chloride prepared with excess chlorine. However, in solutions prepared from equivalent amounts of chlorine and bromine we found, on removal of excess hydrogen cyanide and bromine cyanide formed during the cyanide reaction, a quantity of bromide just equal to the deficiency in the reaction between bromine chloride and cyanide already mentioned. In solutions of bromine chloride prepared by excess bromine we obtained, within the limits of experimental errors, the quantity of bromine which was in excess. The deficiency of bromine found in investigating stoichiometric bromine chloride apparently did not now occur.

From this phenomenon we concluded that, in addition to the heterolytic dissociation (to  $\text{Br}^+$  and  $\text{Cl}^-$ ) characteristic of bromine chloride in aqueous solution, there must also be a homolytic dissociation (to  $\text{Br}_2$  and  $\text{Cl}_2$ ) to a small extent.\* This is ascribed to the relatively small difference in the electron affinities of bromine and chlorine. This dissociation is suppressed by the presence of elementary chlorine or bromine. Recently, we described<sup>6</sup> a similar phenomenon in connection with iodine bromide. The reaction of stoichiometric bromine chloride and cyanide is due to the homolytic dissociation which takes place to a small extent. The bromine liberated during homolytic dissociation reacts with cyanide ions, and affords bromine cyanide and bromide ions.

As already mentioned elsewhere, these parallel dissociations make the analytical application of iodine bromide difficult. The elementary bromine liberated during the homolytic dissociation of iodine bromide reacts with aromatic compounds at a rate higher than that of iodine of bond (oxidation) number +1 which forms during heterolytic dissociation.<sup>7</sup> Accordingly, iodine bromide has partly an

\* It is known<sup>5</sup> that in solvents of low dielectric constant the homolytic dissociation of interhaloid compounds predominates whilst solvents of high dielectric constant, such as water, encourage heterolytic dissociation.

TABLE 1.—DETERMINATION OF THE CONTENT OF ELEMENTARY BROMINE IN SOLUTIONS OF BROMINE CHLORIDE

Number	Composition of the solution, ml			Br <sub>2</sub> found, ml of 0.01N Br <sub>2</sub> solution	Deviation		Bromine formed during homolytic dissociation %
	0.1N aqueous solution of bromine chloride	0.1N Br <sub>2</sub> -water	0.1N Cl <sub>2</sub> -water		ml of 0.01N Br <sub>2</sub> solution	%	
1	10.00	—	—	1.80	—	—	1.80
2	10.00	—	—	2.20	—	—	2.2
3	10.00	—	5.00	0.00	—	—	—
4	10.00	—	1.00	0.05	—	—	—
5	10.00	1.00	—	10.08	+0.08	+0.8	—
6	10.00	5.00	—	4.95	(0.1N Br <sub>2</sub> -solution) -0.05	-1.0	—
7	10.00	10.00	—	10.12	+0.12	+0.2	—

iodinating and partly a brominating effect. (In an aqueous solution, under certain conditions, the iodinating effect can be raised to 90–94% or even to 100%).

However, the two different types of dissociation of bromine chloride do not interfere with the analytical application of this reagent. Bromine of bond (oxidation) number +1 which forms during the predominant heterolytic dissociation reacts with aromatic compounds at a rate appreciably higher than that of elementary bromine liberated during homolytic dissociation and particularly than that of chlorine. Thus, bromine chloride in aqueous solution behaves in its aromatic substitution reactions as a brominating agent. Therefore, it is possible to use a standard solution of bromine chloride analytically with success.<sup>3</sup>

### DETERMINATION OF FREE BROMINE IN SOLUTIONS OF BROMINE CHLORIDE

#### Reagents

These were all of analytical grade.

*Potassium cyanide*: 5% solution, neutralised with sulphuric acid in the presence of methyl red as indicator.

*Carbon dioxide*: from steel flask.

*Chlorine water*: freshly prepared, free from bromine.

*Potassium iodide*: solid.

*Hydrochloric acid*: 20% distilled (bromide-free), prepared according to Pharm. Hung. V, Vol. I, p. 295.

*Sodium Thiosulphate*: 0.01*N*.

*Sodium hydroxide*: 2*N*,

*Sulphuric acid*: 2*N*.

#### Method

A 10.00 ml portion of the approximately 0.1*N* stoichiometric solution of bromine chloride to be tested is transferred to a 100-ml Erlenmeyer flask with a ground glass stopper, and is mixed, in a well-ventilated hood, with 2 ml of 5% potassium cyanide solution previously neutralized in the presence of methyl red indicator. Carbon dioxide is bubbled through the solution at a vigorous rate for half an hour, in order to remove excess bromine cyanide and hydrogen cyanide. The solution is neutralised in the presence of methyl red indicator and chlorine water is added dropwise until the liquid turns light straw-yellow. Half as much 5% potassium cyanide solution is added as the volume of added chlorine water. The liquid is shaken and allowed to stand for 2–3 minutes and 0.2 g of potassium iodide is added to the reaction mixture which is acidified with 5 ml of 20% hydrochloric acid. After allowing the liquid to stand for 20 minutes, the amount of liberated iodine is measured by titration with 0.01*N* sodium thiosulphate solution.

1 ml of 0.01*N* sodium thiosulphate solution is equal to 0.1998 mg (log 0.30060) of bromine. Half of the total quantity of elementary bromine ( $\text{Br}_2$ ) was removed as bromine cyanide and the titration indicates only the residual amount of bromide ion. Thus, the equivalent weight is one-quarter of the atomic weight.

On investigating in this way a solution of bromine chloride of stoichiometric composition, it was found that 1–3% of bromine forms during homolytic dissociation (Table 1).

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## LETTER TO THE EDITOR

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### A comment on the purity of water prepared by ion-exchange methods

SIR:

Schenkel and Kitchener (*Nature*, 1958, **182**, 131) have recently reported that conductivity water prepared by ion-exchange methods produces anomalous surface effects which they attribute to traces of a weakly basic substance, probably polymer fragments dissolved from the resin. We also have observed evidence of such contamination and agree with these authors that the "conductivity value is a dangerous index" of the purity of water treated with an ion-exchange resin. It is our experience that the contaminant appears to be removed by passage through Millipore filters (Millipore Filter Corp., Watertown, Mass.). This work is described fully in an article entitled "The Nucleation and Precipitation of Silver Chloride from Homogeneous Solution", to appear in this journal.

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LOUIS GORDON

27 March 1959

## OBITUARY

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### THOMAS BROOKS SMITH

The death of Dr. T. B. Smith at his home in Sheffield on Friday, 21st November, 1958, although coming after several years of comparatively poor health, was nevertheless very unexpected. He had retired prematurely in December 1956 from his appointment as Senior Lecturer in Analytical Chemistry in the University of Sheffield and had hoped to make use of his retirement to fulfil many of the tasks that a busy life had inevitably left undone. He had become a member of the Advisory Board of this journal when it was founded.

Thomas Brooks Smith was born in Newcastle-upon-Tyne in the year 1893, was educated at Hull and then studied chemistry at Imperial College, London (then the Royal College of Science), where he came under the influence of J. C. Philip and T. E. Thorpe. In 1914 he took a junior post in the chemistry department of the University of Sheffield which at that time was one of the youngest of the provincial universities. Conditions were difficult and the department was highly under-staffed by modern standards, but the requirements of war service soon took "T.B." (he was always known as "T.B.") off with the allied army as Divisional Gas Officer to Salonica, where his outstanding personal qualities of resourcefulness and ingenuity saw him safely through those grim years.

After the war, in 1919, "T.B." returned to Sheffield as lecture-demonstrator, but soon became involved in the tremendous task of organising and equipping the chemistry department to meet the new demands of the post-war situation. Professor W. P. Wynne soon gave him complete charge of all teaching of inorganic chemistry above the intermediate level, and this position "T.B." retained until his retirement in 1956. The only facilities afforded during the whole period—nearly forty years—comprised a temporary laboratory in a wooden hut; this hut was only removed when the new chemistry buildings came into use in 1955.

It will for ever remain a mystery how "T.B." managed to find either space or time to carry out his research projects; his experiments were always done in some odd corner of this teaching laboratory and suffered constant interruption by reason of the never-ending demands of enthusiastic students. Despite these difficulties many analytical problems were investigated and solutions found, though of these only a small proportion ever reached the stage of publication in research journals.

Experimental work was always done in short bursts of rather feverish activity, alternating with longer periods of quiet rumination during which his active mind would be at work on some new idea which would eventually form the nucleus of another investigation. Even during the active periods, however, a serious enquirer seeking advice was never refused a hearing. Indeed, the enquirer could always expect a lengthy and objective discussion of the problem from every possible point of view,

with perhaps a trip to the library to ensure that no stone be left unturned in obtaining every grain of information; but after all this he would be left to think the problem out anew and to draw his own conclusions.

As a teacher "T.B." never gave a simple and straightforward presentation of subject matter with all the difficulties judiciously ironed out—the method so much beloved by bad students. His process instead was to awaken the student to the realisation that things are not always as simple as they seem, that many of the views commonly accepted even by the writers of textbooks will not bear more than superficial exploration without revealing alarming weaknesses, and that ability to think in quantitative terms is of the essence of progress in a subject where tradition sometimes tends to over-ride critical judgment. It is no cause for surprise that his examination questions were always highly unconventional and that his lecture times tended to disregard the clock. His lecture demonstrations did not usually involve elaborate apparatus but were always very much to the point and were expertly carried out.

The final outcome of his many researches into, and thoughts about, analytical methods was the publication of the book *Analytical Processes* for which his name is so well-known. In it the reader may discover for himself the profundity and keenness of its author's mind and the originality with which the problems are treated. Many generations of students have perused its pages and have there discovered the results of concentrated study and active thought about all those processes which are most important to the analyst; from it they will have learned how to tackle new problems, how to discover where the main dangers lie, and how best to seek for a solution. The book is without doubt a landmark in the development of analytical theory, and the change that has taken place in analytical thinking since its first publication in 1929 reveals how much ahead of his day the author was.

But T. B. Smith was much more than a good scientist. He put his unusual degree of manual dexterity to good use in watch-making, in piano-playing, and in repairing anything of a mechanical nature that came his way. No household gadget was allowed to escape his dissecting enthusiasm, and the domestic inconvenience caused by this quality was at times considerable. He was also a conjuror of quality, giving displays that were always elaborately planned to suit the occasion.

Finally, "T.B." would be the first to want to acknowledge the tremendous debt that he owed to his wife Ursula, whom he married in 1927 and who survives him. She it was who accomplished the difficult task of getting the ideas contained in *Analytical Processes* into print, who put his work before all other interests, who nursed him through his many illnesses and who gave to him the ideal counterpart to his own rather wayward temperament. Among the many interests that they shared, the study of ethical and philosophical problems loomed large, and all who knew "T.B." were aware that he was a man not merely of wide knowledge and true understanding but that he possessed the much rarer gift of wisdom. His insight even in problems far removed from his special field was remarkable, and he certainly believed that there are more things in heaven and earth than are dreamed of in the average scientist's philosophy. His death is indeed a great loss both to his friends and to the world of analytical chemistry.

P. WOODWARD



## BOOK REVIEWS

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**Elementary Practical Organic Chemistry, Part III. Quantitative Organic Analysis.** ARTHUR I. VOGEL. Longmans, Green and Co., London, 1958. Pp. xii + 645-840 + xxxii. 21s.

A GOOD maxim for every chemist to remember is that everything depends ultimately on quantitative analysis. Thirty years ago the research, and often the honours student, had to perform a number of quantitative experiments such as carbon and hydrogen, nitrogen, alkoxy, halogen and acetyl determinations; the accuracy required for success added greatly to the skill of the operator. In these days of micro and semimicro specialists the quantitative aspects of organic analysis tend to be neglected; this volume will give a new stimulus to students and teachers alike. The author is well-known for his previous books on analysis; the present small volume is the last of his recent trilogy, the preceding ones having dealt with small scale preparations and qualitative organic analysis respectively; he has now covered the whole field of organic laboratory work. The chapter, page and section numbers run continuously throughout the trilogy which has also appeared as an omnibus volume.

Semi-micro methods for determining nitrogen, halogens and sulphur, with descriptions of apparatus are given; it seems a pity that the now equally important phosphorus and fluorine determinations are not included. The general account of titration in non-aqueous solvents covers modern ideas on acids and bases and discusses their titrations with indicators. A special feature is made of this type of titration and many examples occur in the text under, for example, amines, phenols, acids, enols. Potentiometric titration is also exemplified with diagrams of suitable apparatus.

Succeeding chapters deal with the estimation of the following:—hydroxyl (alcohols,  $\alpha$ -glycols, phenols); amino; amine, including quaternary ammonium, salts; amino-acids; carboxyl and salts; anhydride; ester; carbonyl; sugars; nitro, nitroso, azo; unsaturation; alkoxy; *c*-methyl; *n*-acetyl; active hydrogen; enol; imide; sulphonamide; thiol; sulphide; disulphide;  $\alpha$ -epoxy. The use of ion-exchange resins, the Karl Fischer reagent and special determinations complete the list.

Each section begins with a brief outline of the reaction, with equations; often two, or more, types of determination are described under the headings "Reagents" and "Procedure", *e.g.* for glycols both the iodometric and acidimetric methods are given, with five and two examples respectively. The "Calculation" of results is finally detailed. Some methods are not up-to-date, for instance the acetylation of phenols and especially of alcohols.

Many standard methods for determining unsaturation are given. Catalytic hydrogenation is described for platinum oxide and Raney nickel (stabilized) catalysts, but no mention is made of palladium catalysts which are often so useful and selective with double bonds. Both the Wijs and the Hanus methods for determining iodine numbers, and the bromate-bromide and the pyridine sulphate dibromide methods for unsaturation are included.

Active hydrogen is estimated by the older Zerewitinoff reaction (methyl magnesium iodide in anisole, ether, etc.), and by the more recent lithium aluminium hydride method. The section on anion- and cation-exchange resins gives a general outline of the principles involved; a few suitable resins are mentioned and there is a list of salts of organic acids and of a few organic bases which give good results in ion-exchange chromatography. Procedures include salts of organic acids, salts of organic bases, alkaloidal salts, and saponification equivalents of esters.

The Karl Fischer reagent is described in some detail. It is useful in determining the water content of (listed) hygroscopic and water-miscible liquids and of water of crystallization (some examples). It has also been employed in a number of reactions with other substances of which the following are mentioned:—organic acids, anhydrides, carbonyl compounds, primary and secondary amines, cyanides. The preparation of the reagent and apparatus for its use are detailed. Hydroxyl in all classes of monohydric alcohols may also be determined by this method.

Special methods include:—formaldehyde (two reactions); acetone; aryl hydrazines; urea (two

methods); organic peroxides and hydroperoxides; *isothiocyanates* and *isocyanides*; carboxyl by the *isothiuronium* salt method and subsequent titration with acetous perchloric acid; alcohols.

The following items form an appendix:—atomic weights; bibliography of 15 works on quantitative organic analysis; vapour pressures of water; four- and five-figure logarithms.

Any student who masters all the techniques described here will emerge with confidence to perform any practical problems which the future may hold for him.

A. MCGOOKIN

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**The Chemical Behavior of Zirconium.** WARREN B. BLUMENTHAL. D. Van Nostrand Company Inc., Princeton, N.J., New York, Toronto, London, 1958. Pp. 398 + vi. \$11.00.

In the preface the author tells us that only one book has previously appeared on the chemistry of zirconium, in 1922. His task has included therefore not only a coverage of both the earlier and more recent literature on zirconium but also a recasting of the earlier literature into contemporary language and theoretical understanding.

The nine chapters are headed:—The Element, Zirconium; Interstitial Solutions and Intermetallic Compounds; Zirconium Halogenides; Zirconium Oxides and the Zirconates; Zircon and the Complex Silicates; The Sulfatozirconic Acids, Sulfates, and Sulfonates; Compounds of Other Inorganic Acids; Carboxylates of Zirconium; Organic Compounds Other than the Carboxylates. The inorganic analyst who has to deal with this not so rare metal can read them all with profit: chapter 4 on the oxides and the zirconates and chapters 7, 8 and 9 on the compounds of inorganic acids, the carboxylates, and organic compounds other than the carboxylates, are especially important.

The reverence in which the reviewer has always held Berzelius is deepened by the number of references to his early work with this element. His metal prepared in 1824 was 93.7% Zr but eighty years later it was found that his reaction product could be 98% pure if it was first treated with absolute alcohol instead of water and then washed with dilute acid. He made the carbide as early as 1817 and his figure of 89.46 for the atomic weight compares favourably with the present value of 91.22 when allowance is made for the oxygen content.

In the chapters on the carboxylates and on other organic compounds there is much of interest to the analyst. The almost unique reaction with mandelic acid is discussed (p. 335) and on page 340 we learn that "The zirconium atom is practically never available for reactions which occur by the pairing of oppositely charged ions or by the pairing of odd electrons," and again, "after its reactions, zirconium must always contain at least 8 electrons in its valence orbitals (4d and 5sp) and all reactions of zirconium may be regarded as initiated by the donation of lone pairs of electrons from other atoms to the zirconium atoms."

The price of this book seems high by British standards but it is a most authoritative work and lives up to the claim on the cover that it "brings unity and clarity to a mass of miscellaneous data." It can be recommended without reserve.

R. C. CHIRNSIDE

## NOTICES

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### The following meetings have been arranged:

*Monday-Friday 22 June-3 July 1959: Residential Course on Radiation Health Hazards:* Wolverhampton and Staffordshire College of Technology, Wulfruna Street, Wolverhampton: Organisers: F. SCOTT, B.Sc., F.R.I.C. and E. WILLIAMS, B.Sc., A.Inst.P.

Although primarily intended for safety officers in Technical Colleges, applications are also invited from others interested in this aspect of the usage of ionising radiations.

*Friday 26 June 1959: Polarographic Society: Society for Analytical Chemistry, Scottish Section: Symposium on Polarography.* This joint meeting will be held in the Department of Chemistry, David Keir Building, The Queen's University of Belfast. Papers will be presented between 10.0 a.m. and 12.30 p.m., and between 5.0 p.m. and 7.0 p.m. in the Lecture Theatre of the Department of Chemistry. In the afternoon there will be a tour of the Laboratories of the new Building.

The programme of papers is as follows:—

*The Polarographic Investigation of Some Copper Complexes in Non-aqueous Solution:* Dr. Z. ZAGORSKI, Chemistry Dept., Q.U.B. and University of Poznan, Poland.

*Aspects of the Polarographic Behaviour of Rhenium and Technetium:* Dr. R. J. MAGEE, Chemistry Dept., Q.U.B.

*The Application of Polarography to Tissue Respiration:* Dr. I. S. LONGMUIR, Institute of Diseases of the Chest, London.

*A Potentiometric Method for Acid-base Titrations in Certain Acetone-water solutions:* Mr. G. F. REYNOLDS, Chemical Inspectorate, Woolwich Arsenal.

*The Polarographic Determination of Nitroglycerine:* Mr. A. F. WILLIAMS, I.C.I. Ltd., Nobel Division.

*Polarography in Fused Salts:* Mr. R. L. FAIRCLOTH, U.K.A.E.A., Harwell.

A limited amount of accommodation will be available as required in University Hostels; if hotel residence is preferred, intending delegates are requested to make their own arrangements.

Anyone intending to be present at this meeting should notify Mr. J. Brooks (Hon. Secretary, S.A.C., Scottish Section), Analytical Research Section, Research Department, I.C.I. Ltd., Nobel Division, Stevenston, Ayrshire, as soon as possible stating whether University Hostel accommodation is required.

*Monday-Friday 6-17 July: Residential Course on Spectrochemical Techniques:* Wolverhampton and Staffordshire College of Technology, Wulfruna Street, Wolverhampton, Staffs. Course Tutor: W. B. FOSTER, B.Sc., A.R.I.C.

This course is intended to cover the fundamental theoretical and practical aspects of emission spectrography, ultra-violet and infra-red spectrophotometry, and flame photometry. Emphasis will be placed on practical work in all branches, and there will be opportunity for course members to select techniques for more detailed study. Additional evening lectures will be given by visiting specialists.

*Wednesday-Saturday 9-12 September 1959: Polish Chemical Society: Sixth Jubilee Congress.* The Polish Chemical Society is organising the Jubilee Congress in honour of the 40th Anniversary of the Society. The Congress will be held in Warsaw. General meetings and section meetings will be devoted to plenary lectures and short communications. The following sections are planned: inorganic chemistry, organic chemistry, physical chemistry, analytical chemistry, radiochemistry and chemical technology and engineering. A three-day excursion programme to Cracow, Oswiecim and Wieliczka is planned in connection with the Congress. The address of the Organising Committee is Warszawa, Pałac Kultury i Nauki, pokój 2011, Poland.

*Thursday-Saturday 1-3 October 1959: Verein Österreichischer Chemiker:* In conjunction with I.U.P.A.C. in the II Chemischen Universitäts-Institut, Vienna, IX, Währingerstrasse 38. The meeting will be concerned chiefly with electrochemistry, and especially with electrocrystallisation. Those wishing to contribute should notify the Sekretariat des Verein Österreichischer Chemiker, Wien, I, Eschenbachgasse 9, Austria, before 30 June. It is hoped to be able to distribute the programme of the meeting in July 1959.

*Monday-Wednesday 26-28 October 1959: Oak Ridge National Laboratory: Third Conference on Analytical Chemistry in Nuclear Reactor Technology: The Analysis of Reactor Materials Following the Operation of Nuclear Reactors.*

The Oak Ridge National Laboratory has announced that the Third Conference on Analytical Chemistry in Nuclear Reactor Technology will be held at Gatlinburg, Tennessee, on October 26, 27 and 28, 1959.

The general theme of this conference, analysis of reactor materials following the operation of nuclear reactors, complements sequentially those of previous meetings which dealt with, (1) advances in the chemical analysis of important reactor materials, and (2) the role of analytical chemistry in the startup and operation of nuclear reactors.

The subjects which will be emphasized at this conference are: chemical analysis as related to the estimation of corrosion and erosion rates, re-processing of fuels and blanket materials, and the analytical chemistry of fission product mixtures, of plutonium, and of the transplutonic elements.

The contribution of papers pertaining to these or closely related subjects is solicited. Presentations on new developments or improvements in methods of chemical analysis, including advances in instrumentation, are especially invited although review papers and those involving pertinent theoretical discussions may well prove to be of equal interest and should be submitted for consideration.

To facilitate the completion and distribution of the programme well in advance of the conference, speakers are requested to submit abstracts of about 500 words not later than August 1, 1959, and to indicate the time required for their presentation, not to exceed 30 minutes.

The Proceedings of the conference will be published. In order to be included in the Proceedings, manuscripts must be submitted before the opening of the conference. Publication in the Proceedings is not mandatory, but desirable. If a paper is not to be published in the Proceedings, the abstract and a reference to another source of publication, if any, will be made.

All communications relative to the conference, including the submission of manuscripts and abstracts, should be directed to: C. D. SUSANO, Oak Ridge National Laboratory, P.O. Box Y, Oak Ridge, Tennessee, U.S.A.

Inquiries with respect to accommodations or requests for reservations should be addressed to: Mr. TOM WOODS, Manager, Mountain View Hotel, Gatlinburg, Tennessee, U.S.A.

Probably a morning and afternoon session will be held on each of the three days of the conference. If greater interest is evidenced in certain aspects of this subject matter, arrangements will be made to increase the number of sessions but within the scheduled period of three days. Every effort will be made to avoid conflicts of interest in scheduling concurrent sessions.

Since it is intended that the scope of the programme will necessarily encompass only a limited portion of the field of analytical chemistry as it pertains to the analysis of materials after they have been involved in an operating reactor, the general topics for each of the six sessions will be essentially as follows:

*Monday 26 October*

Morning—*The Analysis of Spent Reactor Fuels*

Afternoon—*Analytical Chemistry of Exposed Blanket Materials*

*Tuesday 27 October*

Morning—*Analytical Chemistry in the Reprocessing of Fuels and Blanket Materials*

Afternoon—*The Analysis of Corrosion and Erosion Products*

*Wednesday 28 October*

Morning—*The Analysis of Fission Product Mixtures*

Afternoon—*Analytical Chemistry of Plutonium and Transplutonic Elements*

In addition to the formal technical programme, an informal dinner and dance will be held on Tuesday evening. Arrangements are now being made to secure a prominent speaker in the field of analytical chemistry or some closely related field to address the group after the dinner.

The conference is being conducted on an unclassified basis and all interested persons, regardless of affiliation, are invited to attend or participate in all or any portion of the meeting.

There will be no registration fee, but for those who partake of the dinner a nominal charge will be made.

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The *B.S.I. News* announces, among others, the following new standards:

BS 2511 (PD 3201): *Determination of water by the Karl Fischer method*: Addendum 1, 1959: *Determination of water in ketones*. This indicates the modifications required to the methods given in Parts 1 and 2 of the standard to enable water to be determined in ketones by the Karl Fischer method using an electrometric end-point. (Price 2s.)

BS 1121: *Methods for the analysis of iron and steel*: Part 39, 1959: *Nitrogen in steel*. This specifies a method applicable to all types of steel containing up to 0.25 per cent of nitrogen. Using this method, complete nitrogen recovery cannot be obtained from steels containing silicon nitride. (Price 4s.)

BS 1902 (PD 3325): *Methods of testing refractory materials*: Addendum 2, 1959: *Additional methods*. This specifies an alternative method for the determination of silica and methods for the determination of size, bulk density and warpage. Full details of the individual methods are given. (Price 3s.)

Revised British Standards have been issued as follows:

BS 350, 1959: *Conversion factors and tables, Part 1, Basis of tables, Conversion factors*. The scope of Part 1 of B.S.350 has been considerably augmented by its revision, and now covers a wide range of subjects of measurement falling under the general headings Metrology, Mechanics and Heat. Part 1 gives extended basic information on units, together with the standard abbreviation for each unit or combination of units considered. The standard does not deal with purely electrical units. A feature of the standard is the inclusion of comprehensive tables of conversion factors, showing the relationship between any pair of units used in the measurement of a given physical quantity. Summary tables of units and conversion factors are included, together with an appendix on thicknesses of sheets and diameters of wires. A list of the detailed conversion factors which will be included in Part 2 is also given. (Price 15s.)

B.S. 753, 1959: *Density-composition tables for aqueous solutions of sulphuric acid*. The tables, based on the International Critical Tables, give density in grams per millilitre of the aqueous solution, mass in grams of  $H_2SO_4$  in 100 grams of aqueous solution and mass in grams of  $H_2SO_4$  in 1 litre of aqueous solution. Notes on the use of B.S. density or specific gravity hydrometers are added, including the corrections to be applied in various circumstances, with worked examples. (Price 15s.)

B.S. 903: *Methods of testing vulcanised rubber*: Part B 17, 1959, *Determination of total copper*. This gives details of reagents and procedure. (Price 3s.)

B.S.I. Publications may be obtained from the B.S.I. Sales Branch, 2, Park Street, London, W.1.

## BOOKS RECEIVED

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- Laboratory Distillation Practice.** E. A. COULSON and E. F. G. HERINGTON. George Newnes Limited, London, 1958. Pp. x + 166. 25s.
- Laboratory Glassblowing.** L. M. PARR and G. A. HENDLEY. George Newnes Limited, London. 1956. Pp. iv + 160. 21s.
- Annotated Bibliography of Alpha-Benzildioxime.** CHARLES V. BANKS, MICHAEL J. MAXIMOVICH, NELSON J. FOWLKES and PETER A. BEAK. United States Atomic Energy Commission, Research and Development Report ISC 1038. 1958. \$1.75.
- Tables of Constants and Numerical Data.** Pergamon Press, Ltd., London and New York. Vol. 9, **Pouvoir Rotatoire Naturel, II. Triterpènes.** J.-P. MATHIEU and G. OURISSON. Pp. 302. 1958. £7. Vol. 10, **Pouvoir Rotatoire Naturel, III, Amino-Acides.** J.-P. MATHIEU, P. DESNUELLE and J. ROCHE. Pp. 61, 1959. 40s.

## PAPERS RECEIVED

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- New Contributions to the Halogenating Effect of Iodine Bromide. E. SCHULEK and K. BURGER. (20 March 1959).
- Contributions to the Chemistry of Selenium and Selenium Compounds-II. New Contributions to the Iodometric Measurement of Selenocyanide. E. SCHULEK and L. BARCZA. (20 March 1959).
- Contributions to the Chemistry of Selenium and Selenium Compounds-III. Microdetermination of Selenite through Bromocyanogen. E. SCHULEK and L. BARCZA. (20 March 1959).
- Contributions to the Chemistry of Selenium and Selenium Compounds-IV. Detection and Determination of Minute Amounts of Selenite in the Presence of Selenate. E. SCHULEK and L. BARCZA. (20 March 1959).
- Solvents for Ultraviolet Spectrophotometry. D. D. TUNNICLIFF. (2 April 1959).
- An EDTA-Polarographic Method for the Determination of Tellurium in the Presence of Lead. ZBIGNIEW ZAGORSKI and MARIA CYRANKOWSKA. (6 April 1959).
- The Determination of Ultramicro Quantities of Silver in Platinum Sponge by Neutron Activation Analysis. D. F. C. MORRIS and R. A. KILLICK. (9 April 1959).
- Vereinfachte Schnellmethode zur Sulfatbestimmung durch Ionenaustausch. J. A. MIKES and J. SZÁNTÁ. (20 April 1959).
- Bestimmung der Abriebfestigkeit von Ionenaustauschern. J. A. MIKES and L. KOVÁCS. (20 April 1959).
- Organic Analysis-XV. Some Observations on the Infrared Spectra of the Tetralin Series. TSUTOMU MOMOSE, YO UEDA and HIROSHIGE YANO. (22 April 1959).
- The Redox Properties of Some Alkoxy-Substituted Benzidines. D. I. REES and W. I. STEPHEN. (5 May 1959).
- The Wet Oxidation of Bone: Digestion with 100 per cent Sulphuric Acid Followed by the Addition of Dioxonium Perchlorate. G. FREDERICK SMITH and HARVEY DIEHL. (12 May 1959).
- Komplexometrische Bestimmung von Bor neben Barium. OTTO BORCHERT. (14 May 1959).
- Utilisation of Ternary Complexes in Chemical Analysis, I. Selective Extraction and Colorimetric Determination of Traces of Iron as "Ferroul Iodide." FRANTISEK VYDRA and RUDOLF PRIBIL. (14 May 1959).
- Spectrophotometric Determination of Thorium with Neo-thorone. TAKEO TAKAHASHI and SHINGO MIYAKE. (16 May 1959).
- Studies on Uronic Acid Materials, II. The Variation in Composition of Gum Nodules from *Combretum Leonense*. D. M. W. ANDERSON, E. L. HIRST and N. J. KING. (16 May 1959).
- Analytical Applications of Xylenol Orange, III. Spectrophotometric Study of the Hafnium-Xylenol Orange Complex. K. L. CHENG. (18 May 1959).
- Titration of Oxalic Acid with Cerium<sup>IV</sup> at Room Temperature Using Ferroul as Internal Indicator. V. PANDURANGA RAO and G. GORALA RAO. (20 May 1959).
- 2-Mercaptoacetic (Thioglycollid) Acid as a Reagent for Zirconium. SUSEELA B. SANT and BHARAT R. SANT. (20 May 1959).
- A Study of the Conditions for the Determination of Boron with Dianthrimide. LARS DANIELSSON. (23 May 1959).
- The Determination of Boron in Iron and Low-Alloy Steels with Dianthrimide: A Colorimetric Method that does not require Preliminary Separations. LARS DANIELSSON. (23 May 1959).
- The Application of Zone Electrophoresis and Polarography in the Analysis of Complex Mixtures. W. HOYLE and T. S. WEST. (25 May 1959).
- The Polarographic Determination of Nitroglycerine. A. F. WILLIAMS and D. KENYON. (26 May 1959).
- The Semi-micro Determination of Silicon and Phosphorus in Organic Compounds. T. R. F. W. FENNELL and J. R. WEBB. (30 May 1959).

## NOTES FOR CONTRIBUTORS

## 1. General

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

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

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

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

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

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

## 2. Script Requirements

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

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

3. Summaries will not be required for short or preliminary communications. For other contributions the essential contents of each paper should be briefly recapitulated in a summary at the beginning of the

paper. This should be in the language of the paper, but for German or French papers an English version should also be provided wherever possible. Summaries of papers will be printed in all three languages, and authors who are able to provide translations of their summaries are asked to do so.

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



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

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

<sup>1</sup> J. B. Austin and R. H. H. Pierce, *J. Amer. Chem. Soc.*, 1955, **57**, 661.

<sup>2</sup> S. T. Yoffe and A. N. Nesmeyanov, *Handbook of Magnesium-Organic Compounds*. Pergamon Press, London, 2nd Ed., 1956. Vol. 3, p. 214.

<sup>3</sup> A. B. Smith, *The Effect of Radiation on Strengths of Metals*. A.E.R.E., M/R 6329, 1962.

<sup>4</sup> W. Jones, *Brit. Pat.* 654321, 1959.

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

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

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



## CONTENTS

DONALD H. WILKINS and LOUIS E. HIBBS: The determination of copper with triethylenetetramine using a metalfluorechromic indicator	201
HARVEY DIEHL and G. FREDERICK SMITH: Wet oxidation of organic matter employing mixed perchloric and sulphuric acids at controlled temperatures and graded high potentials	209
ALCIDES CALDAS and VICENTE GENTIL: The detection of carbon in spot test analysis	220
VERNON L. WAGNER, Jr. and JOHN H. YOE: Spectrophotometric determination of palladium with thiomalic acid	223
V. S. GRIFFITHS: The determination of conductivities using unconventional electrode systems	230
CHARLES V. BANKS and JOHN J. RICHARD: The determination of <i>vic</i> -dioximes	235
VERNON L. WAGNER, Jr. and JOHN H. YOE: Spectrophotometric determination of rhodium with thiomalic acid and the simultaneous determination of rhodium and palladium	239
F. E. BEAMISH: Spectrographic, fluorescent X-ray, and polarographic methods for the determination of the platinum metals	244
K. L. CHENG: Analytical applications of Xylenol Orange - II. Spectrophotometric studies on the zirconium-Xylenol Orange complex	266
WILLIAM D. JACOBS and JOHN H. YOE: Spectrophotometric determination of ruthenium with N:N'-bis-(3-dimethylaminopropyl)thio-oxamide	270
Preliminary Communications:	
DAVE C. PRIEST, FAWZY S. SADEK, J. F. BUNNETT and CHARLES N. REILLEY: New chelons based on pyridine	275
DONALD H. WILKINS: Metalfluorechromic indicators	277
SHIGEKI HANAMURA: Rapid method for coulometric analysis using an I-Q recorder	278
Short Communication:	
E. SCHULEK and K. BURGER: The heterolytic and homolytic dissociation of bromine chloride and determination of the bromine formed	280
Letter to the Editor:	
D. H. KLEIN and LOUIS GORDON: A comment on the purity of water prepared by ion-exchange methods	283
Obituary:	
THOMAS BROOKS SMITH	284
Book Reviews	286
Notices	288
Books Received	291
Papers Received	292