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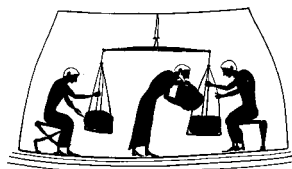
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## THE SEPARATION OF CARRIER-FREE $^{234}\text{Th}$ ( $\text{UX}_1$ ) FROM URANIUM BY ANION-EXCHANGE

S. S. BERMAN, LORNA E. MCKINNEY\* and M. E. BEDNAS  
 Division of Applied Chemistry, National Research Council,  
 Ottawa, Canada

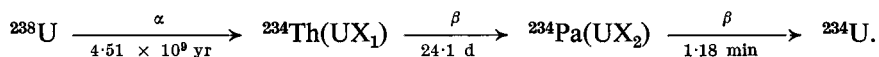
(Received 30 November 1959)

**Summary**—A relatively simple procedure for the preparation of large quantities of carrier-free  $^{234}\text{Th}$  for use as a tracer has been devised. A 9.6M hydrochloric acid solution of uranium is fed into an anion-exchange column. The uranium complex is adsorbed and the daughter thorium is washed through the resin bed, resulting in a substantially quantitative separation of  $\text{UX}_1$  from as much as 50 g of uranium. The uranium may be readily recovered by elution with 0.1M hydrochloric acid solution, or may be left on the column to be periodically washed with 9.6M hydrochloric acid solution to produce fresh batches of  $\text{UX}_1$ .

### INTRODUCTION

IN the course of investigations in this laboratory it was found desirable to employ a radioactive tracer to follow the behaviour of thorium in various analytical procedures.  $^{234}\text{Th}$  ( $\text{UX}_1$ ) has proved to be an excellent isotope for this purpose for three reasons: (i) it can be prepared in the laboratory from readily available materials, (ii) its half-life of 24.1 days allows for convenient handling, and (iii) its short-lived (1.18 min) daughter,  $^{234}\text{Pa}$  ( $\text{UX}_2$ ), is a very energetic  $\beta$  emitter so that the detection of  $\text{UX}_1$  is greatly facilitated.

$^{238}\text{U}$  disintegrates according to the familiar uranium series with the following first three steps:



The third product,  $^{234}\text{U}$ , has a half-life of  $2.48 \times 10^5$  years. Thus any uranium compound obtained from a chemical supplier will, in effect, contain only  $^{238}\text{U}$ , equilibrium quantities of  $\text{UX}_1$  and  $\text{UX}_2$ , and  $^{234}\text{U}$ , since the original decay products of the uranium series will have been removed in the purification process, and the build up of new products arrested at  $^{234}\text{U}$  due to its long half-life. Since 1 gram atomic weight of uranium produces an equilibrium amount of  $3.5 \times 10^{-3}$  micrograms of  $\text{UX}_1$ , the preparation of  $\text{UX}_1$  becomes a problem of separating a submicro quantity of thorium from a macro amount of uranium.

About 10 minutes after a separation has been effected an equilibrium amount of  $\text{UX}_2$  will again be present. This is a fortunate occurrence in our case since this constant companion of  $\text{UX}_1$  produces a very hard  $\beta$  emission (2.3 Mev) which can be counted, instead of the soft  $\beta$  radiation (0.19, 0.10 Mev) of  $\text{UX}_1$ . Thus all weak emitters which may be present can be screened out and the detection of  $\text{UX}_1$  greatly enhanced.

The separation of  $\text{UX}_1$  from uranium has been the centre of much interest since its discovery by Crookes<sup>1</sup> in 1900 and an excellent review of the work in this field up to

\* Present address: Department of Oncology, University of Wisconsin, Madison, Wisconsin.

1950 is given by Dyrssen<sup>2</sup>. The methods are generally based on the solvent extraction of uranium into ether, precipitation of  $UX_1$  with a carrier, or adsorption of  $UX_1$  on charcoal or some other adsorbent. None of these procedures is quantitative and only the involved and lengthy method of Erbacher, Herr and Wiedemann<sup>3</sup>, which employs both ether extraction and carrier precipitation, produces a substantially carrier-free isotope.

Recently, several ion-exchange procedures have been proposed for this separation. Bane<sup>4</sup> adsorbed the  $UX_1$  from a uranyl nitrate solution on a cation-exchanger, allowing the uranium to pass through the bed. The  $UX_1$  was eluted with a sodium bisulphate solution. A similar procedure has been developed by Dyrssen<sup>2</sup> who removed the thorium isotope with an oxalic acid solution. Chen<sup>5</sup> adsorbed the  $UX_1$  on an anion-exchanger from a 7.5M nitric acid solution, and later washed it off with water. Forty grams of uranyl nitrate (19 g uranium) could be handled in this manner in comparison with the 1-gram uranyl nitrate samples processed by Dyrssen. Recoveries of greater than 85% of the original  $UX_1$  are reported.

The authors, after a brief examination of some of the above procedures, decided that ion-exchange would probably yield the most efficient and simple method for producing relatively large quantities of the carrier-free thorium isotope. Attempts to utilise the methods of Dyrssen and Chen were unsuccessful. In order to produce large yields of  $UX_1$  fairly concentrated solutions (1.3M) of uranium were used. Considerable leakage of  $UX_1$  in the feed effluent occurred and great difficulty was encountered in removing much of the isotope from the resin in both cases.

In view of the recent success of several workers<sup>6-8</sup> in separating thorium from uranium by anion-exchange in hydrochloric acid solution it was decided to investigate this approach. It was felt that the apparent disadvantage of having to adsorb the major component on a very large bed would be balanced by the fact that there would be no problem of removal of the  $UX_1$  from the resin.

#### APPARATUS AND METHODS OF ANALYSIS

The ion-exchange column used was of conventional design, 3.1 cm in internal diameter and 1 metre high. The bed consisted of 500 ml (approx. 1 lb) of 20-50 mesh Amberlite IRA-400 anion-exchange resin of analytical grade supported on a wad of glass wool. The resin was stirred for 1 hour with 2M hydrochloric acid solution before transferring it to the column, to ensure complete conversion to the chloride form.

The column volume above the resin bed (250 ml) served as a reservoir and was closed off by a rubber stopper through which a glass tube was inserted which extended almost to the resin bed. Flow rates of solutions were controlled by regulating the influx of air into the reservoir through this tube. The outlet tube of the column was fitted with a stop-cock so that the flow could be arrested at any time.

Activity measurements were made on suitable aliquots which were evaporated to dryness on aluminium dishes 1 inch in diameter. Hydrochloric acid solutions were evaporated to dryness in glassware and taken up in nitric acid before this step. Measurements were made with an appropriately shielded Nuclear-Chicago D34 end-on GM tube with a 1.4 mg/cm<sup>2</sup> mica window. The output of this tube was fed into an Atomic Instrument Company Model 1070B multiscaler unit. In each case the sample was covered with an aluminium absorber of 32 mg/cm<sup>2</sup> thickness which served to screen out all soft radiations, including that of the  $UX_1$  itself, so that only the strong  $\beta$  emission of the  $UX_2$  was registered.

Analysis of uranium effluents was done gravimetrically. Suitable aliquots were treated with carbonate-free ammonia solution to precipitate ammonium diuranate which was then filtered, washed, ignited at 800°, and weighed as  $U_3O_8$ .

The uranium used was the yellow trioxide, which, on analysis, was found to be quite free of other metals but hydrated as  $UO_3 \cdot 0.5 H_2O$ .

## EXPERIMENTAL

Initial experiments with a small ion-exchange column ( $1.0 \times 20$  cm) verified that uranium can be adsorbed on an anion-exchanger from concentrated hydrochloric acid solutions while  $\text{UX}_1$  passes through into the effluent. Since maximum adsorption of uranium was desired, 4:1 (9.6M) hydrochloric acid solution was used throughout this work because, at this concentration, the distribution coefficient between the uranium-chloro complex and the exchanger is at its maximum<sup>9</sup>. These experiments also indicated the ease of removal of uranium from the resin with 0.1M hydrochloric acid solution and showed that 500 ml of resin should be able to adsorb at least 65 g of uranium before leakage occurred. This is approximately 120 times the amount indicated by Tomic *et al.*<sup>7</sup> who adsorbed uranium from a 6.5M hydrochloric acid solution.

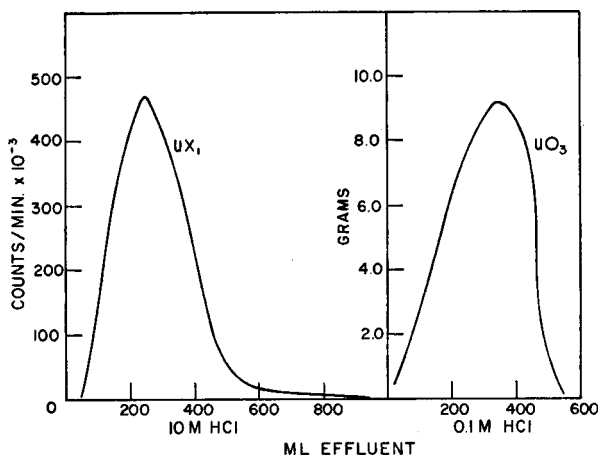


FIG. 1.—Typical elution curves for  $\text{UX}_1$  and uranium.

Before feeding the uranium solution on to the large column, the resin bed was washed with 9.6M hydrochloric acid solution until the effluent was of this concentration. Sixty g of the uranium trioxide (48.4 g uranium) were dissolved in 150 ml of the hydrochloric acid solution, and the solution was poured into the column with the effluent stopcock closed. As the dense uranium solution came into contact with the resin, particles rose through the solution until about two-thirds of the bed had been displaced. At this point sufficient uranium had been adsorbed on the resin to (i) lower the density of the solution and (ii) increase the density of the particles so that the bed quickly resettled. This displacement provided excellent contact between the two phases, ensuring optimum adsorption of the uranium complex. Once the bed had resettled the effluent stopcock was opened, and the bleeder tube was adjusted so that the uranium solution, now much depleted in concentration, passed through the bed at the rate of about 4 ml per minute. Very little further movement of the uranium band was observed.

Elution of the  $\text{UX}_1$  was continued with three 250-ml portions of the acid solution. The effluent was usually collected in 50-ml fractions which were analysed radiometrically for  $\text{UX}_1$ . A typical elution curve is shown in Fig. 1. Much tailing is noted in this elution, with the activity never dropping to zero. This may be explained by the fact that the uranium in the column is continually producing  $\text{UX}_1$  at a rate which makes it impossible to wash the resin free of thorium activity. For example, during the hour it takes to pass 250 ml of eluent through the bed new  $\text{UX}_1$  has been produced in sufficient amount to cause an increased activity of  $4.3 \times 10^4$  disintegrations per minute.

A sample of  $\text{UX}_1$  in hydrochloric acid solution was passed through the column following the procedure described above, except that the total effluent was collected, evaporated and analysed radiometrically. This experiment indicated recovery of at least 99% of the  $\text{UX}_1$ .

Fractions of  $\text{UX}_1$  effluents from a sample which had been separated from uranium by the above method were evaporated to dryness and the residues (mainly small quantities of organic matter from the resin) were examined spectrographically and were all found to be free of uranium, indicating complete separation of the thorium isotope.

The uranium could be eluted quite simply from the resin with 0.1M hydrochloric acid solution. The column was first washed with 250 ml of the acid solution at the rate of 5 ml per minute, and the effluent was discarded, as it contained no uranium. Elution with another 600 ml of this eluent produced a complete recovery of the uranium (Fig. 1). This elution curve was prepared from gravimetric analyses of 50-ml fractions of the effluent. The beginning and end of the uranium elution can be easily noted by eye because of the sharpness of the leading and trailing edges of the band and the intense yellow colour imparted to the solution by the metal.

The uranium, however, need not be removed from the column if a continuous supply of  $UX_1$  is desired. Depending on the needs of the laboratory the column may be "milked" periodically to produce  $UX_1$ . For example, 14 days after the removal of  $UX_1$  from the uranium another quantity of the isotope, which will have one-third the activity of the original batch, may be recovered by elution with the 9.6M hydrochloric acid solution. With each elution of the bed the uranium band moves less than 1 inch down the column, and since the band has a very sharp leading edge several "milkings" are possible before any uranium appears in the effluent. We were able to recover 5 batches of  $UX_1$  from a column which was "milked" at two-week intervals, before any uranium was found in the effluent. In this way one column supplied our needs for 2 months before it was necessary to remove the uranium and recharge the resin bed with a fresh uranium solution. Eluted uranium solutions are evaporated to dryness and stored for re-use since in 4 months 97% of the equilibrium quantity of  $UX_1$  is regenerated and 99% in 5½ months.

Impurities in the uranium should not present too much of a problem if a fairly pure reagent is used. Rare earths, alkali metals, alkaline earths and other elements such as Al, Ni and Cr, which are not adsorbed from concentrated hydrochloric acid solutions, will appear in the effluent with the  $UX_1$ . However, they will be removed with the first batch of the thorium isotope and future batches should not contain them. Other elements which are adsorbed or partially adsorbed (e.g.  $Fe^{III}$ , Cu,  $Mo^{VI}$ , Zn, Cd, etc.) may appear in various batches but their concentration will be very low, and since only a very small percentage of a batch of  $UX_1$  is usually used in any one tracer experiment, the interference of any of these metals in any particular experiment would probably be negligible.

#### RECOMMENDED PROCEDURE

Dissolve approximately 50 g (0.2 mole) of uranium, as the oxide or chloride (but not the nitrate), in 150 ml of 9.6M hydrochloric acid solution. Transfer the solution to the ion-exchange column which has previously been washed with the acid solution. When the resin has resettled allow the solution to pass through the bed at the rate of 4 ml per minute. When the level of the liquid has just reached the top of the resin bed add another 250 ml of the acid. Repeat with another 250 ml of this solution and collect the total 650 ml of effluent, which will contain about 97% of the  $UX_1$  present in the original uranium solution. More activity may be eluted with another batch of acid but the increased yield is generally not worthwhile.

The column may then be periodically eluted with 750 ml of the acid solution until it is noticed that the uranium band has almost reached the bottom of the resin bed. The interval between elutions is determined by the needs of the laboratory and the 24.1 day half-life of  $UX_1$ .

To remove the uranium the column is washed with 250 ml of 0.1M hydrochloric acid solution at the rate of 5 ml per minute. This effluent is discarded. Elution is continued with 600 ml of this solution, resulting in the quantitative recovery of the metal.

**Zusammenfassung**—Eine relativ einfache Methode zur Herstellung grösserer Mengen von trägerfreiem  $^{234}Th$  wird beschrieben. Eine 9.6-m salzsaure Lösung von Uran wird durch eine Anionenaustauschersäule geschickt. Der Urankomplex wird absorbiert und das Tochter-Thorium wird durchgelassen. Hierbei wird eine praktisch quantitative Trennung des  $UX_1$  von bis zu 50 g Uran erzielt. Das Uran kann leicht wiedergewonnen werden, indem man mit 0.1-m Salzsäure eluiert. Man kann es aber auch auf der Säule belassen und in periodischen Eluierungen mit 9.6-m Salzsäure weitere Mengen von frisch gebildetem  $UX_1$  gewinnen.

**Résumé**—On a imaginé un procédé relativement simple pour la préparation de grandes quantités de  $^{234}Th$  libre d'entraîneur utilisable comme traceur. On introduit une solution d'uranium dans de l'acide chlorhydrique 9,6 M dans une colonne échangeur d'anions. L'uranium complexé est fixé et le Thorium issu par descendance, est éliminé par lavage de la résine, fournissant une séparation pratiquement quantitative de  $UX_1$  de quantités aussi importantes que 50 g d'uranium. L'uranium



peut être récupéré facilement par élution avec une solution d'acide chlorhydrique 0,1 M, ou peut être laissé sur la colonne pour être lavé périodiquement à l'acide chlorhydrique 9,6 M produisant de nouveaux échantillons de UX<sub>1</sub>

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## UTILISATION OF TERNARY AND ION-ASSOCIATION COMPLEXES IN CHEMICAL ANALYSIS—II

### POLAROGRAPHIC DETERMINATION OF INDIUM

MILOSLAV KOPANICA and RUDOLF PŘIBIL

Laboratory of Analytical Chemistry, Chemical Institute, Czechoslovak Academy  
of Sciences, Prague, Czechoslovakia

(Received 8 December 1959)

**Summary**—Conditions have been found for the formation of phenanthroline-thiocyanate complexes of indium, cadmium and other metals and their compositions have been determined. The influence of EDTA on the formation of these complexes has been observed. At pH 3 indium remains bound in the soluble EDTA complex, while cadmium, zinc, copper and other ions form water-soluble phenanthroline-thiocyanate complexes which can be separated from the aqueous phase into butanol. It is then possible, after acidification with hydrochloric acid, to determine indium polarographically in the aqueous phase. Using this method it is possible to determine from 0.05% of indium in metallic cadmium.

WITHIN the framework of the systematic study of analytically utilisable ternary complexes, further attention has been paid to certain complexes of the type metal-phenanthroline-thiocyanate. As is known, phenanthroline with bivalent and trivalent cations forms complex ions of the type  $\text{Me}^{\text{II}}(\text{Phen})_2^{2+}$  and  $\text{Me}^{\text{III}}(\text{Phen})_2^{3+}$ , which, in contrast to similar pyridine complexes, behave as chelates. They are characterised by increased stability and, in the presence of halides or thiocyanate, they form insoluble compounds for which the composition  $\text{Me}(\text{Phen})_m\text{X}_n$  can be assumed. Their most significant property is their slight solubility in water and their solubility in organic solvents. Therefore they are suitable—as has been shown with the complex phenanthroline-iron-iodide<sup>1</sup>—for the extraction of certain metals and their separation.

It has been proved that a number of cations, in the presence of thiocyanate, also form insoluble precipitates over a wide pH range with phenanthroline. Some of these are readily extractable by an organic solvent; others can be thoroughly dispersed (e.g. in butanol) without making impossible a subsequent separation of the aqueous and organic phase. The presence of other complex-forming substances, principally EDTA, through the formation of other complexes, decreases the number of reacting cations so that it is possible to obtain a selective separation. So, for example, at pH 3 indium is firmly bound by EDTA against phenanthroline and thiocyanate whereas other elements occurring with it may continue to exist in the form of phenanthroline-thiocyanate complexes. This fact makes possible the separation of indium from cadmium and zinc and its determination in the aqueous phase, either polarographically or complexometrically. In this work the conditions have been elaborated for this separation of indium when it is subsequently determined polarographically.

### EXPERIMENTAL

#### *Reagents and solutions*

Standard indium solution was prepared from reagent grade indium metal. Its titre was determined complexometrically.

A solution of 1:10-phenanthroline (0.05M) was prepared by dissolution of a precisely calculated and weighed quantity of 1:10-phenanthroline, Guaranteed Reagent (Lachema, Brno) in warm redistilled water acidified by a minimum quantity of nitric acid. The pH of the solution resulting was 3 to 4.

The disodium salt of ethylenediaminetetra-acetic acid (EDTA) was prepared in 0.05M concentration. The product "Chelaton 3" (Lachema, Brno) was employed.

Solutions of various metal salts were prepared from reagent grade chemicals. The concentrations of these solutions were controlled complexometrically.

A 30% solution of ammonium thiocyanate was prepared from the reagent grade chemical.

The indicator used was a 0.1% Xylenol Orange solution (Chemapol, Praha).

The buffer solution was prepared from formic acid and ammonium formate.

#### *Apparatus*

Adjustment of the pH of the solution was controlled potentiometrically with a glass electrode. The measurement was carried out with an electronic pH meter (Kovodružstvo, Praha).

Polarographic measurements were carried out by a photoregistering polarograph of the type LP-55 (Laboratorní přístroje, Praha) and in a polarographic cell with a separate calomel electrode.

### RESULTS AND DISCUSSION

#### *Phenanthroline-thiocyanate complexes of cadmium, indium and zinc*

In solutions containing phenanthroline complexes of cadmium, indium and zinc, in the range of pH 1 to 5, on addition of thiocyanate in excess, a white voluminous precipitate is produced. The formation of this precipitate is not greatly influenced by the pH of the solution; for example, in the case of cadmium the precipitate is formed in strongly acidic solutions (1N HCl), in neutral, or in weakly alkaline solutions. It may be assumed that a change in acidity of the solution may influence the structure of the resulting complex. In the present work the structures of the complexes were studied in the range of pH 3 to 3.5 since this pH value, as will later be shown, is the most suitable for the separation of indium from the interfering elements.

The phenanthroline-thiocyanate complexes of cadmium, indium and zinc were prepared by the addition of solid ammonium thiocyanate (50 times the amount of the metal nitrates) to solutions of nitrates of these metals after adjusting the pH of the solutions with formate buffer to 3. This solution was then treated with saturated phenanthroline solution until precipitate no longer formed. The solution was then allowed to stand for 2 to 3 hours, and was then decanted and filtered. The precipitate on the filter was washed with water until the washings gave no reaction with silver ions. The material thus obtained was dried *in vacuo*. In the case of indium, the phenanthroline-thiocyanate complex of which is partly soluble in water, the precipitated complex was washed with ether and then also dried *in vacuo*.

Analysis was carried out by oxidative melting of the prepared complex with sodium peroxide in a sintered corundum crucible; after extraction of the melt with water, the content of sulphur was determined gravimetrically by precipitation with barium chloride in the presence of EDTA;<sup>2</sup> the metal constituent was then determined chelatometrically and polarographically.

Determination of the ratio of metal to phenanthroline in the complexes studied was carried out by amperometric titration. Since these materials are water-insoluble, the dependence of the concentration of the thiocyanate complex of cadmium (or indium or zinc) on the quantity of added phenanthroline has been studied. Since the metals in thiocyanate medium yield polarographic waves,<sup>3</sup> it is possible to follow the

development of the complex amperometrically. The amperometric titration can easily be carried out using a rotating platinum electrode—the titration curve has, in this case, a normal course, and the current drops during the titration; at the point of equivalence it reaches a constant value. The employment of a mercury dropping electrode is less suitable—the reading of the equivalence point of the titration is inaccurate because of the influence of deformations which occur in the diffusion currents of cadmium, indium or zinc in the presence of phenanthroline.

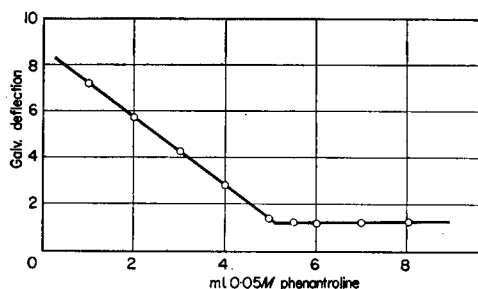


FIG. 1.—Amperometric titration of cadmium thiocyanate complex with phenanthroline. Titrated solution: 5 ml of 0.05M  $\text{Cd}(\text{NO}_3)_2$ , 5 ml of 30%  $\text{NH}_4\text{CNS}$  solution in a 50-ml volume, pH 3.1; recorded at  $-0.80$  V vs. S.C.E., rotating platinum electrode.

The titrations were carried out as follows: the metal nitrate solution in 1M ammonium thiocyanate solution was adjusted with formate buffer to a pH value of 2.5–3 and, after the removal of oxygen by nitrogen, the titration was carried out with 0.05M phenanthroline solution at an applied voltage for zinc of  $-1.10$  mV, for cadmium of  $-0.75$  mV and for indium of  $-0.80$  mV vs. S.C.E. Fig. 1 shows the course of this type of titration.

On the basis of these titrations it was ascertained that in the case of phenanthroline-thiocyanate complexes of cadmium, indium and zinc the ratio of the metal to phenanthroline under the conditions described is always 1:1. From the content of sulphur and metal and using the determined ratio of phenanthroline to metal, it is possible to determine the formula of the compounds studied:

Zn complex

	<i>found</i>	<i>calculated</i>
S	15.45%	16.10%
Zn	16.73%	16.46%
Phen : Zn = 1:1		
<i>Formula:</i> $\text{Zn}(\text{Phen})(\text{CNS})_2 \cdot 2\text{H}_2\text{O}$		

Cd complex

	<i>found</i>	<i>calculated</i>
S	14.76%	14.45%
Cd	25.95%	25.53%
Phen : Cd = 1:1		
<i>Formula:</i> $\text{Cd}(\text{Phen})(\text{CNS})_2 \cdot 2\text{H}_2\text{O}$		

In complex

	<i>found</i>	<i>calculated</i>
S	18.85%	18.20%
In	22.42%	24.50%
Phen : In = 1:1		
<i>Formula:</i> $\text{In}(\text{Phen})(\text{CNS})_3$		

Similar complexes are formed under similar conditions with a number of other metals. Their compositions have not been studied in detail since it does not belong to the framework of this paper. In the majority of cases the complexes concerned are substances slightly soluble in water but soluble in certain organic solvents. As the aim of this work was to find the conditions for the separation of indium from the accompanying elements, the extraction of indium in the form of the phenanthroline-thiocyanate

TABLE I.—DEVELOPMENT AND SOLUBILITY OF PHENANTHROLINE-THIOCYANATE COMPLEXES AT pH 3

Metal	Solubility in water	Formation of complexes in the presence of EDTA
Cd <sup>II</sup>	insoluble	insoluble
Zn <sup>II</sup>	insoluble	insoluble
Pb <sup>II</sup>	insoluble	no complex develops
Mn <sup>II</sup>	insoluble	insoluble
Cu <sup>II</sup>	insoluble	insoluble
Ni <sup>II</sup>	insoluble	insoluble
Fe <sup>III</sup>	insoluble	no complex develops
Fe <sup>II</sup>	insoluble	insoluble
Al <sup>III</sup>	insoluble	no complex develops
Th <sup>IV</sup>	no complex develops	no complex develops
Tl <sup>I</sup>	no complex develops	no complex develops
Bi <sup>III</sup>	insoluble	no complex develops
V <sup>V</sup>	insoluble	no complex develops
Ti <sup>IV</sup>	insoluble	no complex develops
UO <sub>2</sub>	insoluble	no complex develops
Mo <sup>VI</sup>	insoluble	insoluble
W <sup>VI</sup>	no complex develops	no complex develops
Cr <sup>VI</sup>	no complex develops	no complex develops

complex has been studied first. This complex can readily be extracted by butanol, methyl propyl ketone or other ketones but this method of extraction is not very selective and it is less suitable than, for example, extractions of the thiocyanate<sup>4</sup> or iodide<sup>5</sup> complexes of indium.

#### *Separation of indium from cadmium and other metals*

The influence of the presence of EDTA on the development of phenanthroline-thiocyanate complexes was further studied. It was ascertained that in the range of pH 2–3, the compound In(Phen)(CNS)<sub>3</sub> does not develop and indium remains bound in the form of the soluble EDTA complex. Under the same conditions, on the other hand, the insoluble complexes of cadmium, zinc, copper and other metals are formed. Table I contains a survey which summarises the formation of phenanthroline-thiocyanate complexes at pH 3 in the presence and absence of EDTA. From this survey it is evident that indium can be separated from a number of elements by the utilisation of the formation of phenanthroline-thiocyanate complexes. A suitable organic solvent for the complete extraction of phenanthroline-thiocyanate complexes has not been found. But in butanol, which does not dissolve the phenanthroline-thiocyanate complexes, they readily disperse without hindering the separation of the aqueous and organic phase.

The experiments were carried out as follows: 50 ml of aqueous solution containing 2 ml of the standard indium solution, 4 ml of 30% ammonium thiocyanate solution and 2 ml of 0.05M phenanthroline solution, were stirred rapidly by a magnetic stirrer with 50 ml of butanol, and then the two phases were separated in a separatory funnel. In preliminary experiments the content of indium in the aqueous phase was determined by complexometric back-titration with a standard thorium nitrate solution, using Xylenol Orange as indicator.

In this manner it was ascertained that indium remains quantitatively in the aqueous phase as an EDTA complex and in this way it can be separated from cadmium, zinc and other metals. Further, it was observed that phenanthroline alone forms with thiocyanate an insoluble ion-association complex which also disperses in butanol. Therefore, it is possible to remove phenanthroline quantitatively from the aqueous phase by addition of thiocyanate and by separation of the complex which is formed in butanol. From the structure of the cadmium complex of phenanthroline thiocyanate it is evident that the same molar quantity of phenanthroline is necessary for its precipitation. But since the thiocyanate complex of cadmium is extracted into butanol, it is evident from a number of experiments that, for the separation of cadmium into butanol in the presence of excessive thiocyanate, two-thirds of the stoichiometric quantity of phenanthroline is sufficient.

*Polarographic determination of indium after separation of interfering elements in the form of phenanthroline-thiocyanate complexes*

Since indium is a good depolariser and the determination of low concentration of this element is frequently required, special attention has been paid to its polarographic determination. A number of methods have been elaborated in which, almost always, the interfering influence of cadmium is considered. Some authors solve this problem by precipitation,<sup>7,8</sup> others by extraction,<sup>9</sup> or by chromatographic separation;<sup>14</sup> others use complex-forming electrolytes.<sup>11-15</sup>

If indium is separated from cadmium and other elements, as described above by means of the formation of phenanthroline-thiocyanate complexes in the presence of EDTA, the indium remains in the aqueous phase as a stable soluble EDTA complex which does not manifest itself polarographically. But on acidification of the solution it decomposes, and indium can then be determined polarographically. For this reason hydrochloric acid solutions of different molarity were tested as base electrolyte. The development of the polarographic wave of indium in hydrochloric acid medium depends on the existence of chloro-indic complexes as has been proved by Kolthoff<sup>16</sup> and Schufle<sup>17</sup> who studied the polarographic behaviour of indium in 1M to 8M HCl.

The influence of *o*-phenanthroline on the wave of indium in 1M HCl was studied further. It was ascertained that in this base electrolyte *o*-phenanthroline yields a double wave. The first (more positive) wave is badly developed and its height is about one-sixth of the total height of the wave. The half-wave potential of the more negative wave is  $-0.71$  V vs. S.C.E. This wave is shown in Fig. 2, curve 1.

*o*-Phenanthroline influences very unfavourably the otherwise well-developed wave of indium in 1M HCl. If the ratio of indium to phenanthroline is 1:3 or greater, the current drops steeply after the limiting current for indium is reached; for ratios of 1:2 and 1:1 this decline is not so obvious and a residue of the wave of phenanthroline is still maintained. A similar drop of the current in the polarographic curves of indium has been explained by Bulovová<sup>14</sup> as an effect of slightly deformable anions.

This explanation could be applied equally well to the reduction of the phenanthroline complex of indium but, since in the presence of phenanthroline the development of the minimum on the polarographic curve occurs also in the waves of other cations (copper, cobalt), the half-wave potential of which is substantially different from the potential at which the dropping mercury electrode has no charge, the explanation of this feature will require further study. The presence of *o*-phenanthroline in the solution to be analysed therefore makes a polarographic determination of indium impossible. It is

TABLE II.—DEPENDENCE ON TIME OF HEIGHT OF THE POLAROGRAPHIC WAVE OF INDIUM IN 3*M* HCl AND 0.1*M* NH<sub>4</sub>CNS (SOLUTION SATURATED WITH BUTANOL).

time, <i>min</i>	height, <i>mm</i>	$E_{\frac{1}{2}}$
10	40	-0.644
60	39.5	-0.644
120	40	-0.644
180	42	-0.644
240	44	-0.662
300	46	-0.662
900	53	-0.696

$E_{\frac{1}{2}}$  = half-wave potential in V vs. S.C.E.  $t = 0$  is the mixing time of the solution after separation with hydrochloric acid.

necessary, in consequence, in removing the phenanthroline-thiocyanate complexes of cadmium and other metals into butanol, to use thiocyanate in excess so as to transfer the total phenanthroline to the organic phase as described earlier. The aqueous solution with the separated indium then still contains excess of EDTA, thiocyanate and a residue of butanol dissolved in water (the solubility of butanol in water<sup>18</sup> is 79 g/litre at 20°). This solution is acidified with hydrochloric acid so as to make the resulting concentration of HCl 3*M* and, after removing oxygen by nitrogen, the polarogram of the solution is recorded, beginning at -0.30 V vs. S.C.E. In this medium indium produces a well-developed step with a half-wave potential of -0.64 V vs. S.C.E. This must result from the reduction of chloro-indic complexes, since in such a strongly acidic solution the existence of thiocyanate complexes cannot be assumed. Proof of this is also provided by the value of the half-wave potential, which in reduction of the indium thiocyanate complex is -0.717 V vs. S.C.E.<sup>3</sup>

On acidification of the aqueous phase after the separation of cadmium and other elements an interesting feature may be observed. The solution becomes faintly pink in colour and this colour disappears after about 3 hours. During this time the solution has a slight odour of hydrogen sulphide, and the presence of this gas can be confirmed by a paper impregnated with lead acetate solution. This reaction can be accelerated by increasing the temperature. At room temperature its course is slow and it can be explained by assuming reduction of thiocyanate. This reaction influences both the height and the half-wave potential of the indium wave. For 2 hours after acidification, the height of the wave remains constant; the half-wave potential then shifts to more negative values and the height of the wave increases slightly. The results indicating this phenomenon are presented in Table II.

Because of the high solubility of butanol in water, the diffusion coefficient of the analysed solution differs from that of an aqueous solution of hydrochloric acid and the wave of indium in 3M HCl solution, saturated with butanol, is somewhat lower. For the evaluation of polarograms it is therefore necessary either to prepare solutions for the construction of a calibration curve for indium by the procedure used for the sample, or to use the standard addition method.

*Procedure for the determination of indium after separation of cadmium*

In a solution containing the mixture of the two ions adjust the pH to a value of 3 by addition of buffer (formic acid and ammonium formate, pH 3), then add 0.02M EDTA solution at a concentration

TABLE III.—POLAROGRAPHIC DETERMINATION OF INDIUM AFTER SEPARATION OF CADMIUM

Present		In found, mg	Error, %
Cd, mg	In, mg		
39.2	0.55	0.57	+5
39.2	1.90	1.96	+3
39.2	2.70	2.67	-1
39.2	3.50	3.48	-0.6
196	1.90	1.95	+3
196	0.80	0.83	+4
294	0.80	0.78	-3
588	0.80	0.82	+3

which will produce EDTA in excess, in comparison with the concentration of indium. To the solution adjusted in this manner add 30% ammonium thiocyanate solution to make its total concentration amount to 2-3% and then add 0.05M *o*-phenanthroline solution for as long as a precipitate of CdPhen(CNS)<sub>2</sub> is produced. Now add the same volume of butanol and stir the mixture thoroughly for 3 min by a magnetic stirrer. Separate the two phases in a separatory funnel and repeat the stirring with half the volume of butanol for 2 min. Normally the organic phase will then be clear. Again separate the two phases in the separatory funnel, pour the bottom (aqueous) layer into a 50-ml volumetric flask, wash the butanol twice with 5 ml of water, and add this water to the volumetric flask. Acidify the solution in the volumetric flask with 12 ml of concentrated HCl, add 1 ml of 1% glucose solution and make up with water to the mark. It is necessary to carry out the polarographic recording of indium within 2 h after mixing. The wave height for indium is compared, for the evaluation of the analysis, with the wave height for a standard indium solution prepared by the same procedure, or the determination is carried out by the standard addition method. Several curves obtained after separation of a larger amount of cadmium are shown in Fig. 3, and Table III presents the results of several analyses of indium after its separation.

*Procedures for the determination of indium after separation of other metals*

It is also possible to separate zinc, copper, manganese, cobalt, nickel, iron<sup>II</sup> and molybdenum<sup>VI</sup> from indium in the same way. For the polarographic determination of indium, the most important of these elements is copper which, it is true, does not interfere polarographically; but at high concentration (in comparison with indium) it interferes in the determination because of its more positive half-wave potential. Iron<sup>II</sup> can be separated from indium in the form of the phenanthroline-thiocyanate complex; since, however, iron<sup>II</sup> does not interfere in the polarographic determination, it is simpler not to carry out a separation, but merely, before the polarographic determination proper, to reduce iron<sup>III</sup> with hydroxylamine (or iron powder, reduced by



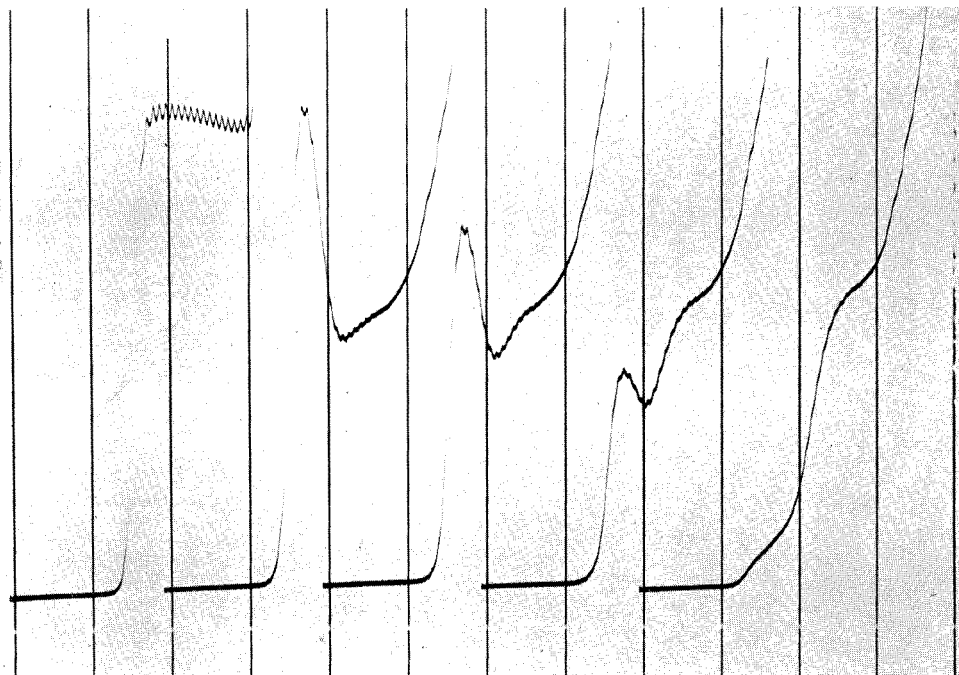


FIG. 2.—Influence of phenanthroline on the wave of indium in 1M HCl

(1) 10 ml of 1M HCl, 1 ml of 1% glucose, 1 ml of 0.05M phenanthroline.

(2) the same solution as (1) with 0.5 ml of 0.01M  $\text{In}(\text{NO}_3)_3$

(3) the same solution as (1) with 0.5 ml of 0.01M  $\text{In}(\text{NO}_3)_3$

(4) the same solution as (1) with 0.5 ml of 0.01M  $\text{In}(\text{NO}_3)_3$

(5) 11 ml of 1M HCl, 1 ml of 1% glucose, 1 ml of 0.01M  $\text{In}(\text{NO}_3)_3$

[All the curves begin at  $-0.30$  V, 200 mV/abscisse, sensitivity 1/70, S.C.E., the curves (1)–(5) from right to left.]

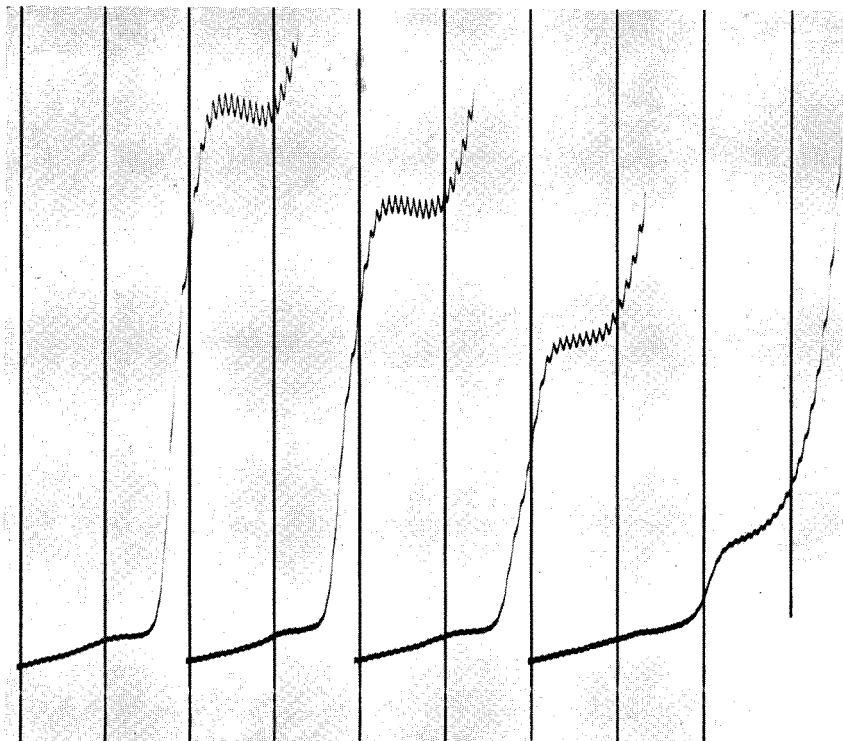


FIG. 3.—Polarographic curves of indium after separation of cadmium

Before separation 50 ml of solution contained

(1) 0.55 mg of In, 39.2 mg of Cd

(2) 1.90 mg of In, 39.2 mg of Cd

(3) 2.70 mg of In, 39.2 mg of Cd

(4) 3.50 mg of In, 39.2 mg of Cd

[All the curves start at  $-0.30$  V,  $200$  mV/abscisse, sensitivity  $1/70$ , S.C.E., the curves (1)–(4) from right to left.]

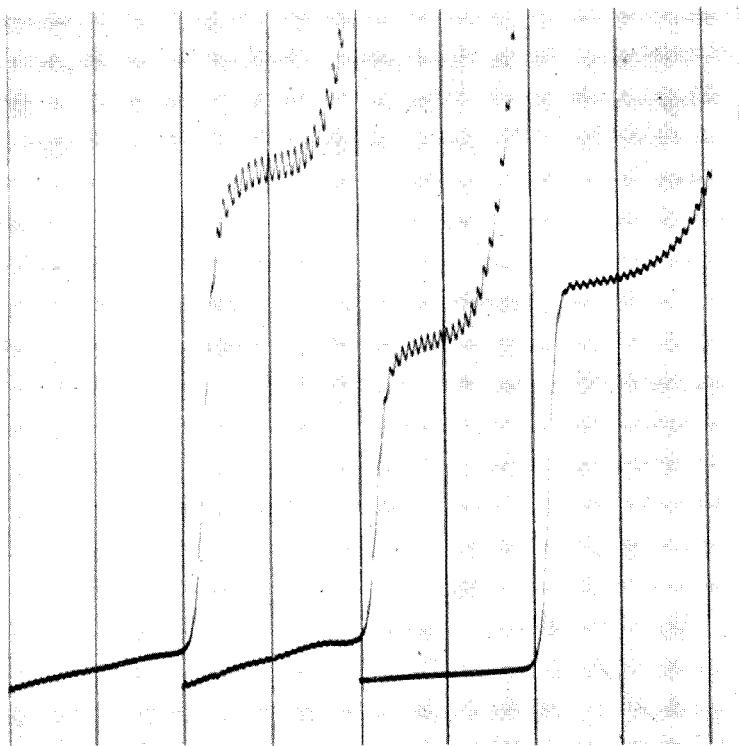


FIG. 4.—Polarographic curves of indium after separation of cadmium, copper and zinc  
 (1) Before separation, 50 ml of solution contained 2.70 mg of In, 294 mg of Cd, 32 mg of Zn  
 (2) Before separation, 50 ml of solution contained 1.68 mg of In, 196 mg of Cd, 63 mg of Cu, 65 mg of Zn  
 (3) Curve of indium in 3M HCl without separation  
 [All the curves start at 0.30 V, 200 mV/abscisse, sensitivity 1/30, S.C.E., the curves (1)–(3) from right to left.]

hydrogen). Fig. 4 shows polarographic curves obtained after the separation of copper, zinc, cobalt, nickel and cadmium.

In the analyses of synthetic samples containing cadmium as the principal component, with an indium content of 0.05–0.5%, the error of determination varies from  $\pm 3$  to  $\pm 5\%$ ; when the indium content ranged from 0.5 to 5% results were obtained with the normal accuracy of polarographic analysis, *i.e.*  $\pm 2\%$ . The sample weights were chosen in such a manner that the quantities of indium involved in the separation were at least 0.8 mg (at 0.1% content of indium in metallic cadmium). Only higher concentrations of lead and bismuth in the analysed sample interfere in the determination of indium carried out in this manner, because the half-wave potentials of these metals are more positive than the half-wave potential of indium.

**Zusammenfassung**—Die Bedingungen für die Bildung der Phenanthroline-Thiocyanat-Komplexe von Indium, Cadmium und anderen Elementen wurden studiert und die Zusammensetzung der Komplexe wurde bestimmt. Der Einfluss von EDTA auf die Bildung der Komplexe wurde untersucht. Bei pH 3 bleibt Indium als EDTA-Komplex gebunden, während Cadmium, Zink, Kupfer und andere Ionen wasserlösliche Phenanthroline-Thiocyanat-Komplexe bilden, die mit Butanol ausgeschüttelt werden können. Nach Ansäuern der verbleibenden wässrigen Phase kann Indium polarographisch bestimmen werden. Mit dieser Methode ist es möglich, noch 0.05% Indium in Cadmiummetall zu bestimmen.

**Résumé**—Les auteurs ont établi les conditions dans lesquelles on peut former les complexes phénanthroline-thiocyanate de l'indium, du cadmium et d'autres métaux; la composition de ces complexes a été déterminée et l'influence de l'EDTA sur la formation de ceux-ci a été observée. A pH 3 l'indium reste engagé dans un complexe soluble de l'EDTA, tandis que le cadmium, le zinc, le cuivre et d'autres ions forment des complexes phénanthroline thiocyanate solubles dans l'eau, qui peuvent être séparés de la phase aqueuse par extraction dans le butanol. Il est alors possible, après acidification par l'acide chlorhydrique, de doser l'indium polarographiquement dans la phase aqueuse. En utilisant cette méthode il est possible de doser jusqu'à 0,05% d'indium dans le cadmium métallique.

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## ACID CHLORIDES OF SUBSTITUTED SUCCINIC AND GLUTARIC ACIDS AS HYDROLYTIC REAGENTS FOR THE DETERMINATION OF WATER

R. BELCHER, L. OTTENDORFER\* and T. S. WEST

Chemistry Department, The University, Edgbaston, Birmingham 15, England

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**Summary**—Some alkyl substituted succinyl and glutaryl chlorides have been examined as hydrolytic reagents for the determination of water. The best reagents are methylethylglutaryl and dimethylglutaryl chlorides; the former compound is recommended because it is less volatile.

Water of crystallisation in several hydrates has been determined satisfactorily using this reagent.

Naphthalyl chloride and cyclohexyl diacetyl chloride were also examined, but were unsuitable.

THE method of determining water in a gas stream by passing it through an acid chloride and titrating the hydrochloric acid formed was first used by Lindner<sup>1</sup> in his titrimetric procedure for the determination of carbon and hydrogen in organic compounds. Lindner's original reagent was  $\alpha$ -chloronaphthylidichlorophosphine oxide, but later he used naphthylidichlorophosphine oxide.<sup>2</sup> Hydrogen chloride produced from the hydrolysis is absorbed in water contained in a bubbler and is determined alkalimetrically. A few other reagents have been suggested by later investigators.<sup>3</sup>

In the course of an examination of titrimetric procedures for the determination of carbon and hydrogen, it was found that succinyl chloride had advantages over earlier reagents in speed of reaction.<sup>4,5</sup> Although succinyl chloride reacts rapidly with water and yields hydrogen chloride almost immediately, it would be desirable to have available a reagent which yields lower blank values. A number of alkyl substituted succinyl chlorides have now been examined because it was expected that they would be less volatile and that the nature of the alkyl groups would lead to acid chlorides of greater reactivity. Glutaryl chloride and alkyl substituted glutaryl chlorides were also examined because it was envisaged that the six membered ring of the acid anhydride formed in the reaction would possess a stability similar to that of the five membered anhydride ring of the succinic acid series. The stable nature of these anhydrides probably has some influence on the efficiency of the reaction.

The following compounds were therefore prepared and examined:—

Succinyl chloride  
 $\alpha$ : $\alpha$ -Dimethylsuccinyl chloride  
 $\alpha$ : $\alpha$ -Diethylsuccinyl chloride  
Glutaryl chloride  
 $\beta$ : $\beta$ -Dimethylglutaryl chloride  
 $\beta$ -Methyl- $\beta$ -ethylglutaryl chloride  
 $\beta$ : $\beta$ -Diethylglutaryl chloride  
Cyclohexyl-1':1'-diacetyl chloride  
Naphthalyl chloride

\* Present address: Institut für anorganische und allgemeine Chemie, Technische Hochschule, Wien VI, Getreidemarkt 9, Austria.

Attempts to make tetramethylsuccinyl chloride and dicyclohexyl-1:1-diacetyl chloride were unsuccessful.

Barium chloride dihydrate was used for most of the tests. Samples obtained from different sources were checked gravimetrically; in all cases their water content varied only slightly ( $\pm 0.07\%$ ) from the theoretical value of 14.75%. Sodium acetate trihydrate, copper sulphate pentahydrate and cadmium chloride ( $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ ) were also used in some experiments and were satisfactory. These hydrates were heated in a stream of dry nitrogen which was passed through a reaction vessel containing the reagent. The hydrogen chloride liberated from the reagent passed over and was collected in an absorber containing distilled water.

To obtain the best results from a given reagent it is necessary to keep the gas bubbles in the reaction vessel as small as possible. This is best achieved by passing the gas directly upwards into the liquid through a sintered-glass disc, but limitations are imposed by the back pressure of the gas. When a No. 3 glass sinter-disc (20 mm diameter) was used a pressure of about 80–120 mm Hg was required to maintain a flow rate of 50 ml/min. The pressure was considerably lower and the bubble size was still reasonably small with a No. 2 sinter-disc. However, the surface area exposed to the reagent increases with the square of the radius of the bubble and the volume with the cube of diameter, whereas the efficiency of the reaction depends on the size of *active* interface per unit volume.

For each reagent the time of contact depends mainly on the viscosity and therefore on the temperature. Surface-tension and the formation of foam also have to be considered.

It was found that a spiral path inside the reaction vessel did not markedly improve the results, and a possible explanation seems to be that the small bubbles emerging from the sinter-disc usually combine when they ascended the spiral. The increased contact time thus obtained appears to offset the decrease in surface area caused by the merging of the small bubbles.

Two other factors which require consideration are the amount of hydrogen chloride retained by the reagent and the time taken for it to pass over from the reaction vessel to the absorber. The most favourable conditions were established experimentally.

The column of reagent used in the reaction vessel must be long enough to allow sufficient contact time. This factor depends on the shape of the reaction vessel and the dead space enclosed between reagent and absorbent. It is desirable to keep the quantity of reagent small, to minimise retention of hydrogen chloride.

A volume of about 5 ml of the reagent is suitable in most cases. This amount of reagent is usually sufficient for at least 700–800 mg of water. Special care was taken to design the reaction vessel in such a way that the maximum amount of the reagent was in permanent contact with the gas-stream. The gas-bubbles themselves gave the necessary stirring effect.

The reproducibility of results and, of course, of blanks, depends essentially on the volume of gas which is passed, and varies only slightly with the flow rate. This means that for a given volume of gas, the flow rate may be altered over rather a wide range without undue effect on the constancy of blanks, provided that the cooling-system used to counteract the volatility of the reagents is efficient. It is also necessary to ensure that aerosol formation does not lead to the passage of reagent into the absorbing vessel. Glass-wool or silica-wool filters inserted in the cooling trap are not very

TABLE I.—COMPARISON OF ACID CHLORIDES AS REAGENTS FOR WATER

Reagent and b.p.	Reagent temp, °C	Blank analyses, ml of 0.05N NaOH		Amt. of H <sub>2</sub> O, mg	Time required, min	Accuracy (Deviation from 100% recovery)	Comments
		No trap	Cooling trap				
Succinyl chloride 75°/12 mm	70	1.0-4.0	0.3-0.5	3-10	30	-2.7%	High blanks Slow removal of HCl
α:α-Dimethylsuccinyl chloride 88-92/12 mm	20-50	2.0-3.0	1.6-1.9				High blanks Difficult conditions
α:α-Diethylsuccinyl chloride 117°/12 mm	20-50 90	0.8-1.2 1.5-1.7	0.7-1.0				Sluggish at low temp. High blanks at elevated temp.
Glutaryl chloride 101-104/14 mm	20 70-90	1.5-1.7 1.4-1.7	0.1-0.45	3-10	60	0-11%	High blanks Low blanks with cooling trap but slow removal of HCl.
β:β-Dimethylglutaryl chloride 122-125°/15 mm	70-100	0.4-0.8	0.1-0.2	10 10-20	30 60	±1%	Low and stable blanks Recommended. Flow rate up to 30 ml/min
β-Methyl-β-ethylglutaryl chloride 115°/12 mm	40-70	0.2-0.3	Not necessary	25	30	±2%	Highly recommended Flow rate 30-50 ml/min
β:β-Diethylglutaryl chloride 127°/11 mm		0.6-0.7	0.4-0.5				High blanks
Cyclohexane-1:1-diacetyl chloride 141°/12 mm		0.1	Not necessary	5	30	-10%	Low capacity. Slow release of HCl.

useful, as their surface is rather big and it may be that hydrogen chloride as well as the reagent is retained.

### Examination of reagents

The behaviour of the various reagents examined during this investigation is summarised in Table I. As already mentioned, the use of succinyl chloride has been described elsewhere<sup>4</sup> but it is included in the table for the sake of comparison. The chief comment to be made on this reagent is that the blank values, though reproducible,

TABLE II.—DETERMINATION OF H<sub>2</sub>O IN BaCl<sub>2</sub>·2H<sub>2</sub>O USING DMGC

Analysis No.	H <sub>2</sub> O, mg		Recovery, %
	Taken	Found	
1	5.032	5.056	100.5
2	6.328	6.315	99.8
3	8.557	8.503	99.4
4	9.894	9.917	100.2
5	12.03	11.98	99.6
6	14.61	14.57	99.7
7	16.96	16.98	100.1
8	19.98	20.00	100.1

Analyses 1-4 Flow rate 15-20 ml/min. Volume of gas passed 500 ml. Blank deducted 0.07 mg H<sub>2</sub>O  
Analyses 5-8 Flow rate 20-30 ml/min. Volume of gas passed 1000 ml. Blank deducted 0.14 mg H<sub>2</sub>O

are large in comparison to those of other reagents described below. They were reduced by means of a cooling trap and a more efficient design has since improved them further. Results obtained invariably tend to be low.  $\alpha$ : $\alpha$ -Dimethylsuccinyl chloride gives higher blanks, even with a cooling trap, and possesses no advantage over succinyl chloride. The corresponding diethyl-substituted succinyl chloride reacts very sluggishly with water so that only 40-60% recovery was obtained. In the glutaryl chloride series the parent substance yielded promising results when maintained at 70-90° and used in conjunction with an ice-salt cooling trap to counteract the volatility of the reagent. However, the release of hydrochloric acid gas is rather slow.  $\beta$ : $\beta$ -Dimethylglutaryl chloride proved to be an extremely satisfactory reagent, superior to any yet examined. When maintained at 70-100° and used in conjunction with an ice-salt trap, low and reproducible blanks were obtained under a variety of conditions of flow rate up to 30 ml/min. In almost all cases the recovery of water was quantitative (*cf.* Table II.)  $\beta$ -Methyl- $\beta$ -ethylglutaryl chloride gave more variable results, but it has the advantage of being much less volatile and not requiring a cooling trap. Flow rates of up to 50 ml/min can be used and the evolution of hydrogen chloride is rapid and quantitative (*cf.* Table III.) The corresponding diethyl-substituted glutaryl chloride was, rather surprisingly, found to be inferior. It gave low recoveries, and high blanks, and was sluggish in its reaction. The substitution of the carbon atom of a cyclohexane ring in place of the  $\beta$ -methylene group of glutaryl chloride yielded the cyclohexyl-1:1-diacetyl chloride. It was thought that the higher molecular weight would decrease the volatility of the reagent and that the tendency for hydrogen chloride to be retained would be minimised, but the removal of hydrogen chloride was



slow; although the blanks were low under normal conditions they increased considerably with rise of temperature. The reagent has a low capacity ( $<1$  mg/H<sub>2</sub>O per ml). Naphthalyl chloride (not shown in Table I) was used in the molten form at 80°, but it is unstable and gives recoveries of water varying from 40–70%. The deposited anhydride is difficult to remove.

TABLE III.—ANALYSIS OF HYDRATES BY MEANS OF MEGC; FLOW RATE 5–30 ML/MIN

Hydrate	Gas volume	H <sub>2</sub> O, mg		Recovery, %
		Taken	Found	
BaCl <sub>2</sub> ·2H <sub>2</sub> O	500 ml	3·647	3·687	101·2
		5·580	5·626	100·8
		7·846	7·830	99·8
		10·02	10·07	100·5
BaCl <sub>2</sub> ·2H <sub>2</sub> O	1000 ml	12·23	12·16	99·4
		15·60	15·57	99·8
		17·88	18·04	100·9
		20·12	20·20	100·4
NaC <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ·3H <sub>2</sub> O	500 ml	2·334	2·320	99·2
	1000 ml	9·665	9·656	99·9
CuSO <sub>4</sub> ·5H <sub>2</sub> O	500 ml	3·099	3·117	100·6
	1000 ml	15·85	16·01	101·0

Blank on 500 ml gas volume  $\equiv$  0·09 mg H<sub>2</sub>O

Blank on 1000 ml gas volume  $\equiv$  0·14 mg H<sub>2</sub>O

### Discussion of results

Table I shows that there is no apparent pattern in the behaviour of the various reagents. It was expected that under comparable conditions, the blank analyses would at least bear a direct relationship to the vapour pressure or boiling point of the reagents. It is surprising to note, therefore, that  $\alpha$ : $\alpha$ -dimethylsuccinyl chloride gave blank analyses of 1·6–1·9 ml of 0·05*N* sodium hydroxide as compared to 0·3–0·5 ml for succinyl chloride although the respective boiling points are 88–92°/12 mm and 75°/12 mm. Even  $\alpha$ : $\alpha$ -diethylsuccinyl chloride (117°/12 mm) gives twice the blanks of succinyl chloride.

As a result of this examination it appeared that the choice of reagent lay between  $\beta$ : $\beta$ -dimethylglutaryl chloride (DMGC) and  $\beta$ -methyl- $\beta$ -ethylglutaryl chloride (MEGC). The latter was selected because it was less volatile and eliminated the need for a cooling trap. Results obtained for the analysis of several hydrates using both reagents are shown in Tables II and III.

These results reveal that both MEGC and DMGC are suitable as reagents for the determination of water.

### EXPERIMENTAL

#### Synthesis of reagents

The acid chlorides were prepared by treatment of the corresponding acids with a 20% excess of phosphorus pentachloride. After refluxing for several hours, the excess of PCl<sub>5</sub> was distilled off, first at atmospheric and then at slightly reduced pressure. The main fraction was eventually redistilled

and the product stored in sealed tubes. The chlorine content of the reagents was determined by hydrolysing samples with 40% sodium hydroxide solution and applying the Volhard procedure.

The  $\alpha$ : $\alpha$ -dialkyl substituted succinic acids and  $\beta$ : $\beta$ -disubstituted glutaric acids were prepared by conventional procedures.<sup>6,7</sup> In the case of the  $\beta$ : $\beta$ -diethylglutaric acid, however, a modified method was used owing to the failure of the ammonium salt of 4:4-diethyl-3:5-dicyanoglutarimide to separate. This was as follows.

200 ml of anhydrous ethanol saturated with  $\text{NH}_3$  at  $-5^\circ$  were treated with 1 mole of ethyl cyanoacetate (113 g) and 0.5 mole of diethyl ketone in a wide necked 750-ml stoppered bottle and stored in an ice box for 24 h. Subsequently the mixture was transferred to a distillation flask and the ammonia was removed by aspirating dry air through the mixture for 5 h. 250 ml of water were then added and 250 ml of the mixture were distilled. The residue was acidified with hydrochloric acid after being cooled and the free "Guareschi" imine which separated was purified and hydrolysed as described elsewhere.<sup>7</sup>

The cyclohexyl-1:1-diacetic acid was prepared by the method described by Thole and Thorpe.<sup>8</sup>

### Apparatus

The apparatus used is shown in Fig. 1. Nitrogen from a cylinder is fed through a side-arm into the combustion tube after passage through a scavenging train packed with Anhydrone and soda asbestos to remove moisture and acid gases. The working end of the delivery tube is provided with a B.14 cone and cap; this latter arrangement permits safe loading of the combustion boat into the tube without risk of contamination from grease. The combustion tube is supported horizontally, with an aluminium heating block mounted two thirds of the way along the tube. The delivery arm between the combustion tube and the reaction vessel is kept warm by means of an electrically heated tape, and the part of the reaction vessel below the condenser is similarly maintained at an appropriate temperature. Evaporation of the reagent is minimised by the water cooled condenser round the upper part of the vessel and by a cold-finger condenser as shown in Fig. 1. The gas stream is finally passed (where necessary) through a U-tube cooled in ice/salt and then through an absorber where the hydrochloric acid is removed by distilled water. The gas emerging from the absorbing vessel is then passed into a bottle so that it displaces an equal volume of water into a graduated 1-litre measuring cylinder.

When the apparatus is assembled the reaction vessel is charged with 5 ml of the appropriate acid chloride, the temperature of the heating tape is adjusted as necessary, and the absorber vessel is charged with a few ml of distilled water. The temperature of the heating block is raised to  $150^\circ$  and gas is passed at a rate of *ca.* 20 ml/min for 3–4 h. A blank analysis is then conducted to establish whether the reagent has been run-in sufficiently (*cf.* Table I.)

### Method of analysis using $\beta$ -Methyl- $\beta$ -ethylglutarylchloride

The absorber is charged with *ca.* 6 ml of distilled water, and the sample of hydrate contained in a platinum micro-combustion boat is placed into the tube and pushed along into the heating zone whilst the nitrogen flushes out of the tube. The cap is then placed in position and the gas is allowed to flow through the train at a rate of *ca.* 18–22 ml per min. Dehydration of  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  is said<sup>9</sup> to begin at  $42^\circ$  and to be complete at  $110$ – $120^\circ$ . Thus the temperature of the heating block is raised quickly to  $60^\circ$  and then to  $120^\circ$  over the next 10 min and finally up to  $150^\circ$  during the last 10 min. At the end of the experiment (*ca.* 500 ml gas passed over 25–30 min) the absorber is detached and its contents are washed out into a conical flask. The hydrochloric acid content is determined by titration with 0.05N sodium hydroxide, with neutral red as indicator. The blank analysis is determined by carrying out an identical operation except that an empty platinum boat is used. It is not necessary to carry out a blank determination with each analysis, for the true blank value can be found in each case by correcting the standard blank for the volume of gas passed during a determination. This value is deducted from the appropriate titre.



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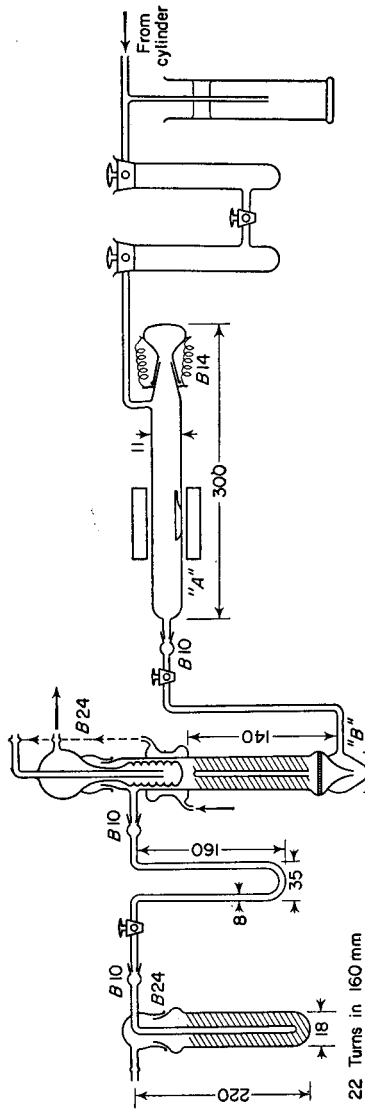


FIG. 1.—Apparatus used for determination of water. A heating tape is wound round the glassware from "A" to "B". All dimensions in mm.

**Zusammenfassung**—Einige alkylsubstituierte Succinyl- und Glutarylchloride wurden in Hinblick auf ihre Brauchbarkeit zur Bestimmung von wasser untersucht. Besonders studiert wurden Methyl-Äthyl-Glutarylchlorid und Dimethylglutarylchlorid. Die erstere ist mehr zu empfehlen wegen seiner geringeren Flüchtigkeit. Kristallwassergerhalte in verschiedenen Hydraten wurde zufriedenstellend bestimmt. Naphthylchlorid und Cyclohexyldiacetyl chlorid wurden ebenfalls untersucht, sind jedoch ungeeignet.

**Résumé**—Quelques dérivés alkyl substitués de chlorures de succinyl et de glutaryl ont été étudiés comme agents hydrolytiques pour le dosage de l'eau. Les réactifs test sont les chlorures de méthyl éthyl glutaryl et de diméthyl glutaryl; le premier composé est recommandé comme étant moins volatil.

L'eau de cristallisation de certains hydrates a été déterminée d'une façon satisfaisante avec ce réactif.

Les chlorures de naphталyl et de cyclohexyl-diacétyl ont aussi été étudiés mais ne convenaient pas.

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## ESTIMATION OF SMALL AMOUNTS OF AMINES BY MEANS OF CATIONITE PAPER

A. LEWANDOWSKI and A. JARCZEWSKI

Department of General Chemistry, Poznań University, Poznań, Poland

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**Summary**—The use of paper with an incorporated cation-exchanger for estimation of microgram amounts of amines is described. Several chain amines and carbocyclic amines have been estimated with an error of 1–3%.

### INTRODUCTION

SINCE 1954, when the first report of the making and analytical use of filter paper with incorporated ion-exchangers was submitted,<sup>1</sup> this new chromatographic technique has been utilised for different analytical purposes.<sup>3–16</sup> The first reports<sup>1</sup> had shown the usefulness of such paper, not only for separating, but also for quantitative estimation of inorganic ions. Subsequently, organic ions *e.g.* alkaloids,<sup>12–13</sup> amines, heterocyclic bases, amino acids, amides of carbonic and sulphonic acids, urea and its derivatives were also successfully estimated. In the present paper the use of paper charged with cation-exchanger for estimation of chain amines and carbocyclic amines is considered.

As such paper will have wide applications it would be useful to shorten the term “paper with incorporated ion-exchanger” or “paper charged with ion exchanger”. In the present communication the term “ionite paper” is used. To avoid any misunderstanding it is stressed that ionite paper must be distinguished from ion-exchanger paper with chemically changed cellulose fibres (*e.g.* sulphonated, phosphorylated or aminated cellulose fibres).

Ionite paper offers unlimited possibilities for estimation of small amounts of any kind of ionic substance. Ions differing sufficiently in affinity for the ion-exchanger have already been separated and estimated simultaneously on the same strip of ionite paper.<sup>1</sup> Adjacent zones may be determined when the colours of zones belonging to the separated ions are different. In the case of aniline and dimethyl- or diethylaniline, the yellow zone of the *p*-nitrosocompound belonging to the substituted aniline differs distinctly from the violet zone of the diazo compound of aniline with naphthylamine. Components of mixtures of these amines may be easily determined. Promising results were obtained when mixtures of compounds were first separated by partition chromatography on common chromatographic paper (*e.g.* Whatman No. 1) and then the single compounds were transferred to the ionite paper. The 5–10% error arising in direct determinations from partition chromatograms diminished to about 2% when, in addition, ionite paper was used.

### EXPERIMENTAL

#### *Ionite paper*

The ionite paper<sup>3</sup> and the required phenolsulphonic ion-exchanger were prepared in our Institute. Ionite paper containing about 10% ion-exchanger in hydrogen form was generally used. In some cases less ion-exchanger (2%) was taken. A high percentage shows more brilliant colours but leaves

smaller zone areas. Lower contents of ion-exchanger assures a sufficiently great zone area when very small amounts of substances are estimated.

The paper was cut into strips 80 mm long and 10 mm wide.

### Reagents

Chemically pure amino compounds were used. The chain amines were estimated from aqueous solutions whilst benzidine was dissolved in 10% ethyl alcohol. The aminobenzoic acids were dissolved in 3 ml of ethyl alcohol and diluted with water to 100 ml. The remaining compounds enumerated in Table I were dissolved in water acidified with an equivalent amount of hydrochloric acid. The actual concentrations during the experiments correspond to the one-, two-, three- and fourfold weight units of amines in 1.0 ml of solution. The weight units are indicated in Table I. Lower amounts, down to 1  $\mu\text{g}$ , were also estimated.

$\alpha$ -Naphthylamine (1% solution in butanol) was used for spraying.

TABLE I. AREA OF ZONE AS A FUNCTION OF AMOUNT OF AMINE

Amine	Value of one weight unit, $\mu\text{g}$	Zone-area, $\text{mm}^2$			
		1 $\times$	2 $\times$	3 $\times$	4 $\times$
Methylamine	38	28	64	108	150
Dimethylamine	45	61	131	202	270
Triethylamine	91	37	80	124	168
Ethanolamine	127	86	178	265	350
Triethanolamine	185	59	134	211	284
Aniline	34	70	126	187	247
Toluidine	50	57	90	123	152
Phenyldimethylamine	32	67	95	123	152
Phenyldiethylamine	31	75	109	138	170
$\alpha$ -Naphthylamine	78	76	132	184	238
<i>o</i> -Phenylenediamine	50	59	106	160	215
<i>m</i> -Phenylenediamine	50	101	188	278	362
Benzidine	100	61	106	145	192
<i>o</i> -Aminobenzoic Acid	100	149	247	352	442
<i>p</i> -Aminobenzoic Acid	100	106	184	262	340
Phenylhydrazine	93	107	189	270	362
Phenylhydroxylamine	100	94	171	237	307

Note: Different amines have been estimated on papers with different ion-exchange content.

### General procedure

For analysis the samples of amine were placed on a spot test plate. On the same plate five standards of various concentrations were also placed. It is essential to use equal volumes (*e.g.* 1.0 ml) of all solutions. The ionite paper strips, joined with narrow (2–3 mm) feeding strips of Whatman No. 1 paper, were hung over the plate in such a way that the ends of the feeding strips dipped into the solutions. The feeding strips were used to diminish the speed of flow and to prevent static equilibrium on the lower end of the ionite paper (when dipped immediately into the solution). A piece of lignin lying on the upper ends of the strips soaked up all surplus liquid which travelled upwards. In a suitable arrangement the solutions may also travel to horizontally mounted ionite paper.<sup>14</sup> In both cases the whole system was enclosed in a glass chamber.

When the solutions had passed the strips, two drops of water or diluted acid of the same pH as the solution were added to wash away the excess of amines resting on the feeding strip and the lower parts of the zones. In order to visualise the zones occupied by amines, convenient reagents were spread on the strips. In all experiments coloured zones with sharp boundaries (Fig. 1) appeared.

After spraying, the strips were dried and the areas of the zones were measured by means of transparent mm-grid paper. As the strips were accurately 10 mm wide it was easy to define the areas with an accuracy of 1 mm<sup>2</sup>. The areas of the standards were plotted against micrograms of compounds and the "unknown" was found graphically from the resulting graph. For different series of estimations papers with different contents of ion-exchanger were used. The areas were therefore comparable only within the same series *i.e.* in Table I in respect to one amine.

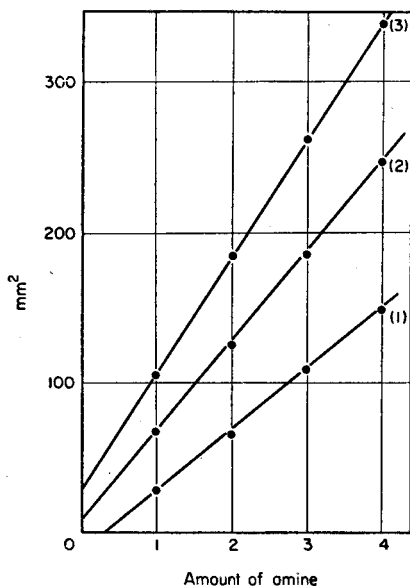


FIG. 2.—Graphs showing the linear dependence between area of zone and amount of amine. 1—Methylamine, 2—Aniline, 3—*p*-Aminobenzoic acid.

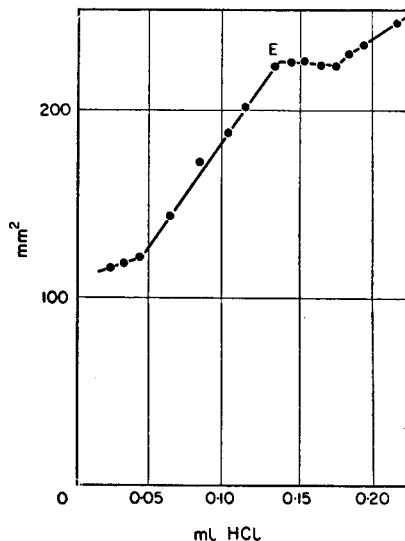


FIG. 3.—Areas of zones of toluidine as a function of added 0.05M hydrochloric acid. E—Equivalent point.

## RESULTS AND DISCUSSION

Numerous estimations that were performed show, as expected, linear dependence between areas and  $\mu\text{g}$  of amines. Fig. 2 presents graphs illustrating this dependence. An error of 1–3% was found.

Ionite paper with less ion-exchanger (about 2%) enables one to estimate about 1  $\mu\text{g}$  of amine with the same error.

In Table 1 one series of several estimations of each amino compound is cited. Chain amines enumerated in this table were estimated in the way just mentioned. The zones were made visible by means of Congo Red. The quantitative evaluation of the zones offers no difficulties.

Most of the aromatic amino compounds were estimated from acidified solutions. Benzidine and *o*- and *p*-aminobenzoic acids were absorbed from acid-free slightly alcoholic solutions. Phenyltrimethylaniline and phenyldiethylaniline were rendered visible by means of gaseous nitric oxide which produced coloured *p*-nitroso compounds (brown fading to yellow). *o*-Phenylenediamine and benzidine were located by dipping in a 2% potassium dichromate solution acidified with sulphuric acid. The remaining aromatic compounds were diazotised on the moist strips by gaseous nitric oxide and covered with  $\alpha$ -naphthylamine solution. Violet zones appeared.

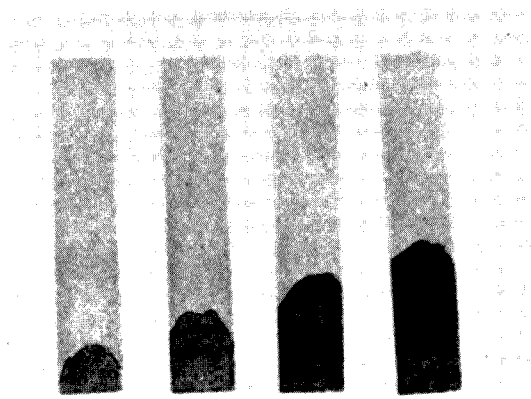


FIG. 1.—Zones of aniline on strips of cationite paper.



The areas of zones are influenced by the relative amounts of aromatic amine and hydrochloric acid. For equivalent amounts, less acid causes the appearance of smaller zones whilst a greater excess of acid causes the formation of larger zones. On graphs where areas are plotted against added acid (Fig. 3), there is a sharp change at the equilibrium point (E). In the presence of a small excess of acid the areas remain constant but grow when much acid is added. It may be mentioned that this behaviour has been utilised in our Institute in so called chromatographic titrations<sup>17</sup> of weak amines. The areas of the zones served as indicator. Details about this will be published elsewhere. Here, this fact must be taken into consideration when unknown concentrations of amines are to be estimated and the usual accuracy is desired.

In the case of estimation of unknown concentrations of weak (*e.g.* aromatic) amines a few equal samples of the unknown were placed in the cavities of a spot test plate and increasing volumes of hydrochloric acid were added. The final volume of the samples was adjusted to 10 ml by means of water. The resulting solutions were taken up by the ionite paper as mentioned above. For quantitative evaluation the zone appropriate to the equivalence point, *i.e.*, which demonstrated the greatest area resulting from increasing amounts of acid, was compared with the standards. Standards were obviously prepared with equivalent amounts of acid. As just quoted, a slight excess of acid causes no significant error.

**Zusammenfassung**—Die Verwendung von Papier mit einverleibten Ionenaustauschern zur quantitativen Bestimmung von verschiedenen organischen Aminen wird beschrieben. Mikrogrammengen wurden mit 1–3% Fehler bestimmt.

**Résumé**—Les auteurs décrivent l'utilisation d'un papier avec échangeur d'ion incorporé pour le dosage des amines organiques. Microgrammes des amines sont dosées avec une erreur de 1–3%.

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## 2:5-DIHYDROXY-*p*-BENZOQUINONE AS AN ANALYTICAL REAGENT FOR THE GRAVIMETRIC DETERMINATION OF THORIUM AND ZIRCONIUM

B. D. JAIN and S. P. SINGHAL

Department of Chemistry, Delhi University, Delhi, 8, India

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**Summary**—2:5-Dihydroxy-*p*-benzoquinone precipitates thorium alone and completely from 1*N* hydrochloric acid solution even in presence of large quantities of cerium<sup>3+</sup> and cerium<sup>4+</sup>, lanthanum and uranium. It also precipitates zirconium alone and completely from 1*N* hydrochloric acid solution in presence of titanium<sup>4+</sup>. The precipitate in each case can be ignited to oxide and weighed.

### INTRODUCTION

2:5-DIHYDROXY-*p*-BENZOQUINONE is a yellowish-brown crystalline solid, soluble in alcohol and acetic acid. It is slightly soluble in cold water but appreciably so in hot water, giving a red solution and the colour of the solution changes to yellow at pH lower than 2.5. It is a dibasic acid,  $pK_1 = 5.18$ ,  $pK_2 = 2.73$ .<sup>1</sup>

2:5-Dihydroxy-*p*-benzoquinone has been stated to give complexes with a large number of cations.<sup>2</sup> The thorium chelate has been shown to contain two dihydroxy-*p*-benzoquinone groups to one thorium.<sup>3</sup> We have now found that Th<sup>4+</sup> is completely precipitated by this reagent from 1*N* hydrochloric acid solution, whereas Ce<sup>4+</sup>, Ce<sup>3+</sup> and La<sup>3+</sup> are only precipitated at pH 2-3, and UO<sub>2</sub><sup>2+</sup> at pH 7. Th<sup>4+</sup> can thus be readily separated from Ce<sup>4+</sup>, Ce<sup>3+</sup>, La<sup>3+</sup> and UO<sub>2</sub><sup>2+</sup>. Zr<sup>4+</sup> is precipitated alone and completely by this reagent from 1*N* hydrochloric acid solution even in presence of Ti<sup>4+</sup>. The Th<sup>4+</sup> and Zr<sup>4+</sup> chelates on ignition give the corresponding oxides. Sulphate ions do not interfere in the above determinations.

For the determination of thorium and its separation from rare-earths (except Ce<sup>4+</sup>) and from uranium, *m*-nitrobenzoic acid,<sup>4</sup> ferron,<sup>5</sup> tetrachlorophthalic acid,<sup>6</sup> and benzoic acid<sup>7</sup> have been used. 1-Hydroxy-3-methoxyxanthone separates thorium from a ten-fold excess of cerite earths and a five-fold excess of cerium<sup>4+</sup> and uranium.<sup>8</sup> We have found that 2:5-dihydroxy-*p*-benzoquinone completely precipitates thorium even in the presence of fifteen times its weight of cerium<sup>3+</sup>, lanthanum and uranium.

Propylarsonic acid<sup>9</sup> and mandelic acid<sup>10</sup> have been used for the determination of zirconium and for its separation from titanium. We have now found that 2:5-dihydroxy-*p*-benzoquinone completely precipitates zirconium even in the presence of ten times its weight of titanium.

### EXPERIMENTAL

All reagents used were of A.R. quality.

2:5-Dihydroxy-*p*-benzoquinone was prepared by the oxidation of hydroquinone with hydrogen peroxide in the presence of sodium hydroxide.<sup>11</sup> The sodium salt of 2:5-dihydroxy-*p*-benzoquinone so formed was converted into the reagent by treatment with concentrated hydrochloric acid at 10°.

#### *Procedure for the determination of thorium*

One hundred and fifty ml of a solution containing 50 mg of thorium is treated with about 0.4 g of the solid reagent or its aqueous solution. The resultant solution is boiled for 1-2 min, cooled to

room temperature and filtered through Whatman No. 40 filter paper. The precipitate is washed with 0.2% aqueous solution of the reagent, dried and ignited at 900° to the oxide. The results obtained from a standard solution of thorium nitrate by this method are shown in Table I.

TABLE I

ThO <sub>2</sub> taken, mg (Oxine method)	53.6	53.6	48.6	48.6	9.8	9.8
ThO <sub>2</sub> found, mg	53.6	53.6	48.6	48.6	9.8	9.8

*Properties of the thorium chelate*

The chelate is violet in colour; it is slightly soluble in water, dilute alcohol and dilute acetic acid. It is slimy at pH higher than 0.5 and crystalline at lower pH.

*Effect of pH on the precipitation of thorium*

The pH of the thorium solution was adjusted by adding various amounts of dilute hydrochloric acid. Thorium was then precipitated from the solution as described above. The results are recorded in Table II.

TABLE II

ThO <sub>2</sub> taken, mg (Oxine method)	53.6					
ThO <sub>2</sub> found, mg	53.6	53.6	53.6	53.6	53.6	53.6
pH	3	2	1	0.5	1N HCl	2N HCl

*Precipitation of cerium<sup>4+</sup> and the effect of pH on its precipitation*

The procedure employed is the same as described for thorium. Cerium<sup>4+</sup> is completely precipitated by this reagent at pH 3; at lower pH the precipitation is incomplete (Table III).

TABLE III

CeO <sub>2</sub> taken, mg (Oxine method)	17.6		
CeO <sub>2</sub> found, mg	17.6	15.1	1.6
pH	3	2	1

*Properties of the cerium<sup>4+</sup> chelate*

The properties of the cerium<sup>4+</sup> chelate are similar to those described for the thorium chelate.

*Separation of thorium from cerium<sup>4+</sup>, cerium<sup>3+</sup>, lanthanum<sup>3+</sup> and uranyl*

After the addition of different amounts of cerium<sup>4+</sup>, cerium<sup>3+</sup>, lanthanum and uranyl salts to a thorium salt solution, its acidity was adjusted to 1N with hydrochloric acid and thorium precipitated as described above. The precipitate was then washed with about 200 ml of 0.2% solution of the reagent which had been made 1N with HCl. The results obtained are given in Table IV.

TABLE IV.

ThO <sub>2</sub> taken, mg (Oxine method)			48.6				
CeO <sub>2</sub> added (as Ce <sup>4+</sup> ), mg	ThO <sub>2</sub> found, mg	CeO <sub>2</sub> added (as Ce <sup>3+</sup> ), mg	ThO <sub>2</sub> found, mg	La <sub>2</sub> O <sub>3</sub> added, mg	ThO <sub>2</sub> found, mg	U <sub>3</sub> O <sub>8</sub> added, mg	ThO <sub>2</sub> found, mg
50	48.6	50	48.6	50	48.6	50	48.6
100	48.6	100	48.6	100	48.6	100	48.6
250	48.4	250	48.6	250	48.6	250	48.6
500	48.8	500	48.6	500	48.6	500	48.6
750	48.6	740	48.8	750	48.4	750	48.4

TABLE V.

ZrO <sub>2</sub> taken, mg (Oxine method)	38.4	38.4	35.0	35.0	9.6	9.6
ZrO <sub>2</sub> found, mg	38.4	38.4	35.0	35.0	9.6	9.6

TABLE VI.

ZrO <sub>2</sub> taken, mg (Oxine method)	35.0					
ZrO <sub>2</sub> found, mg	35.0	35.0	35.0	35.0	35.0	35.0
pH	3	2	1	0.5	1N HCl	2N HCl

TABLE VII.

ZrO <sub>2</sub> taken, mg (Oxine method)	35.0
TiO <sub>2</sub> added, mg	ZrO <sub>2</sub> obtained, mg
21.6	35.0
43.2	35.0
108.0	35.0
216.0	34.8
324.0	34.8

*Precipitation of zirconium and the effect of pH on the precipitation*

The procedure employed is the same as described for thorium. The results are presented in Tables V and VI.

*Properties of the zirconium chelate*

The properties of the zirconium chelate are similar to those described for the thorium chelate.

*Separation of zirconium from titanium*

After the addition of different amounts of titanium<sup>4+</sup> solution to the zirconium solution, the acidity of the solution is adjusted to 1*N* hydrochloric acid and zirconium precipitated as described above. The precipitate is washed with about 200 ml of 0.2% solution of the reagent which has been made 1*N* with hydrochloric acid. The results are shown in Table VII.

Iron<sup>3+</sup> interferes in the determination of zirconium by this method and must be absent.

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**Zusammenfassung**—2:5 dioxy-*p*-benzochinon fällt Thorium allein und vollständig aus 1*N* HCl selbst in Gegenwart grosser Mengen von Cer(III) und Cer(IV), La(III) und UO<sub>2</sub>(II). Das Reagens fällt auch Zirkonium allein und vollständig aus 1*N* HCl Lösung neben Titan(IV). Die Niederschläge können in beiden Fällen versucht und die Oxyde gewogen werden.

**Résumé**—La 2,5 dihydroxy-*p*-benzoquinone précipite le thorium seul et complètement en solution HCl *N*, même en présence de grandes quantités de cérium III et cérium IV, La(III) et UO<sub>2</sub>(II). Elle précipite aussi le zirconium seul et complètement en solution HCl *N* en présence de titane IV. Dans chaque cas, le précipité peut être calciné jusqu'à obtention de l'oxyde et pesé.

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## CALCEIN BLUE—A NEW METALFLUORECHROMIC INDICATOR FOR CHELATOMETRIC TITRATIONS

DONALD H. WILKINS

General Electric Research Laboratory, Schenectady, New York, U.S.A.

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**Summary**—A new metal fluorechromic indicator is described for the chelatometric titration of metal ions. Calcein Blue (a condensation product of 4-methylumbelliferone, formaldehyde, and imino-diacetic acid) may be used for the chelatometric determination of metal ions which form highly coloured complexes with chelatometric reagents. A procedure based on reaction rates is given for the determination of nickel and chromium in mixtures without prior separations. Calcein Blue serves as an indicator for the direct titration of the alkaline earth elements as the result of the formation of an indicator-reversal complex.

THE colour of the complexes of EDTA with elements such as copper, cobalt, chromium, etc., has caused considerable difficulty in chelatometric titrations. The use of conventional and visual indicators is limited to solutions containing only a few milligrams of elements which form highly coloured complexes. The introduction of Calcein and Calcein W as metalfluorechromic indicators has eliminated much of the difficulty previously encountered with these elements.<sup>2-4</sup> An extensive study of metalfluorechromic indicators has led to the preparation of many new indicators similar to Calcein W. This paper deals with some applications of a new indicator, Calcein Blue,\* which is a condensation product of 4-methylumbelliferone, formaldehyde and imino-diacetic acid. Although the metalfluorechromic properties of Calcein Blue and Calcein W are very similar, the former is a superior indicator for chelatometric titrations. Calcein Blue exhibits its maximum fluorescence when activated by a wavelength of 370  $m\mu$  (in alkaline solution) and 330  $m\mu$  (in acid solution), whereas Calcein W exhibits its maximum fluorescence when activated with light of much longer wavelengths. Since most sources of ultraviolet light exhibit a maximum output of radiation at 366  $m\mu$  or 250  $m\mu$  it can readily be seen that Calcein Blue, in alkaline solutions, approaches the ultimate in matching the maximum output of the ultraviolet source with the wavelength of maximum activation of fluorescence. This fortuitous circumstance leads to a much more sensitive indicator for titrations under ultraviolet radiation. The parent compound (4-methylumbelliferone) is an acid-base indicator of the coumarin series. The addition of a chelating functional group that is *ortho* to the phenolic oxygen imparts metafluorechromic properties to the resulting indicators. Calcein Blue exhibits a brilliant blue fluorescence (445  $m\mu$ ) up to a pH of 11. The addition of copper ions to a solution of the free indicator at a pH from 4 to 10 results in the quenching of the blue fluorescence. Palladium also quenches the fluorescence over the pH range of 4 to 10, but the reaction is too slow to be of use in chelatometric titrations. Manganese, nickel and cobalt also quench the fluorescence of Calcein Blue, but this reaction is confined to the alkaline region in which the free indicator fluoresces.

If the pH of a solution containing Calcein Blue is raised above 12, the free indicator

\* G. Frederick Smith Chemical Co., Columbus, Ohio.

no longer fluoresces. The addition of calcium, barium or strontium ions to this solution results in the formation of a complex with the indicator which does fluoresce. It should be noted that this indicator complex exhibits the "acid colour" of the free indicator.<sup>5</sup> This phenomenon has been referred to as the formation of an indicator-reversal complex. The titration of metal ions which form highly coloured complexes with chelating agents is most conveniently carried out by adding a standard excess of the chelating agent and performing a back-titration with a standard copper solution. In this manner, macro amounts of nickel, cobalt, copper, iron and titanium (in the presence of peroxide), as well as elements which do not form highly coloured complexes such as aluminium, manganese, zinc and mercury, can be carried out with a single standard solution. The selection of an appropriate pH for the back-titration can be derived from pY-pH curves for the chelating agent in question.<sup>1</sup> Back-titrations with a standard copper solution are carried out by adding an excess of an appropriate chelating agent, for example, trien, EDTA or tetraethylenepentamine to a solution of the metal ion to be determined. The pH is then adjusted, a few drops of a 0.1% solution of Calcein Blue added, and the solution back titrated with a standard solution of copper to the quenching of the blue fluorescence of the free indicator.

## METHODS

### *The determination of nickel and chromium mixtures*

To an acid solution of nickel and chromium add a measured excess of EDTA over that which would be necessary to complex the nickel present in the solution. Dilute to 100–150 ml with water, add 10 ml of a sodium acetate-acetic acid buffer (pH approximately 4.8) and 2–3 drops of the indicator solution. Back-titrate the excess of EDTA with a standard copper solution to the quenching of the blue fluorescence of the free indicator. To the solution in which the nickel was just titrated add a measured excess of EDTA over that which would be necessary to complex the chromium present in the solution. Place the beaker on a hot plate and boil for 10–15 minutes in order to form the chromium-EDTA complex. Back-titrate the excess EDTA with a standard copper solution to the quenching of the blue fluorescence of the free indicator. Both titrations should be done with ultra-violet light as the sole source of illumination. From the two back titrations calculate the mg of nickel and chromium present.

### *The determination of calcium, strontium and barium*

In the determination of these elements use is made of the formation of an indicator-reversal complex. To a solution containing calcium, barium or strontium, add a few drops of a 0.1% solution of Calcein Blue, adjust the pH to a value of 13–14 (in the case of strontium add a two-fold excess of potassium tartrate) and titrate the solution with standard EDTA. The end-point is characterised by the quenching of the fluorescence due to the alkaline earth-indicator complex.

## DISCUSSION

The determination of nickel and chromium in mixtures without prior separation is based on the slow reaction rate for the formation of a chromium-EDTA complex. The solution containing the nickel and chromium should be maintained near room temperature until after the nickel determination is completed. The titration should be completed shortly after the addition of EDTA for the nickel determinations, since a long period of standing, even at room temperature, could lead to the formation of the chromium-EDTA complex or to the precipitation of chromium.

Other binary mixtures in which one of the ions to be determined is chromium<sup>III</sup> may be analysed by the procedure given here for nickel-chromium mixtures. The criteria for the determination are that the second element must react with EDTA at

room temperature, and must form a complex which can be back-titrated with a standard copper solution at a pH of 4.8.

In the determination of calcium, strontium and barium, the pH may be adjusted by the addition of a 1M solution of potassium hydroxide or by the addition of pellets of potassium hydroxide. In either case, one should use a low-carbonate potassium hydroxide, such as reagent grade potassium hydroxide, which contains approximately 2% potassium carbonate. The presence of an excessive amount of carbonate leads to a residual fluorescence after the end-point in the titration. The continued use over a period of several months of a large stock bottle of 1M potassium hydroxide or of potassium hydroxide pellets can lead to a selection of an excessive amount of carbonate, causing a gradual deterioration of the end-point. This can easily be avoided by maintaining a small stock bottle of alkali for daily use. In this manner the supply of alkali is consumed before an excessive amount of carbonate is accumulated. Potassium hydroxide is superior to sodium hydroxide for the adjustment of the pH in the determination of the alkaline earths. The use of sodium hydroxide leads to a high residual fluorescence after the end-point—an indication that sodium also forms a weak indicator-reversal complex.

Zinc, as well as some other elements which form indicator-reversal complexes, may also be determined by the procedure given for the alkaline earths. These elements, however, are conveniently determined by back-titration with a standard copper solution.

**Zusammenfassung**—Ein neuer metallfluorochromer Indicator zur chelometrischen Bestimmung von Metallionen wird beschrieben. "Calceinblau" (ein Kondensationsprodukt von 4-Methylumbelliferon, Formaldehyd und Iminodiessigsäure) kann für die chelometrische Bestimmung auch solcher Metallionen verwendet werden die mit dem chelometrischen Reagens stark gefärbte Komplexe bilden. Eine Vorschrift zur Bestimmung von Nickel und Chrom in einer Lösung ohne vorhergehende Trennung wird beschrieben. Das Verfahren beruht auf der Verschiedenheit der Reaktionsgeschwindigkeit beider Metalle bei der Komplexbildung. Calceinblau dient auch als indicator bei der direkten Titration von alkalischen Erden.

**Résumé**—L'auteur décrit un nouvel indicateur métallique fluorochromique pour le dosage des ions métalliques par complexométrie. Le bleu de calcéine (un produit de condensation de 4 méthyl ombelliférone, de formaldéhyde et d'acide iminodiacétique) peut être utilisé pour le dosage complexométrique d'ions métalliques qui forment des complexes fortement colorés avec les réactifs complexants.

Une méthode basée sur les vitesses de réaction est donnée pour le dosage de mélanges de nickel et de chrome sans séparations préalables. Le bleu de calcéine sert d'indicateur pour le dosage direct des alcalino-terreux, étant donnée la formation d'un complexe réversible de l'indicateur.

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# A NEW GENERAL PROCEDURE IN THE LOW-TEMPERATURE WET OXIDATION OF ORGANIC COMPOSITIONS

## PERCHLORIC AND PERIODIC ACIDS AS OXIDANTS "THE PERIODIC ACID LIQUID FIRE REACTION"

G. FREDERICK SMITH

The Noyes Laboratory, University of Illinois, Urbana, Illinois, U.S.A.

and

HARVEY DIEHL

Department of Chemistry, Iowa State University, Ames, Iowa, U.S.A.

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**Summary**—The substitution of periodic acid for nitric acid in the much employed "liquid fire reaction" for destructive oxidation of organic compositions is described. The advantages attained are extended general applicability, low temperature requirements, and the noteworthy reactivity of periodic acid in downgrading heavy, complex organic molecules to fragments more readily soluble in perchloric acid used as companion reagent. These fragments are more easily oxidised by 66 to 69 or 70% strengths of this acid. The reactions described cover organic compositions which are essentially cellulose, sugars and proteins. Coal, leather, polymerised products and other commercially important products may be readily oxidised. The reactions involved are hazard free.

### INTRODUCTION

PERCHLORIC acid is the most adaptable oxidant in general use for the wet oxidation of organic compositions. With added nitric acid, these combined oxidants serve to constitute the "liquid fire reaction."<sup>1</sup> These mixed reactants are of extensive general applicability. Mixtures of sulphuric and perchloric acids have also been employed.<sup>2,3</sup> The highest oxidation potentials available are thus provided. A wide variety of wet oxidations result from the individual use of perchloric acid.<sup>4</sup> For such reactions the perchloric acid is employed at controlled concentrations and temperatures.

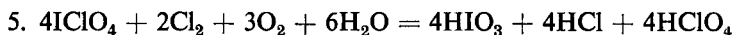
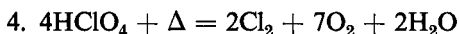
In all these wet oxidation procedures, conditions are defined, and suitable apparatus has been designed, to ensure hazard-free reaction kinetics.

Employing periodic acid in preferential applications, as a substitute for nitric acid, has marked advantages. This modification effects improvements in extensive general applicability. Lower reaction temperatures may be employed. Periodic acid serves not only as oxidant, but contributes to the ready fragmentation of large molecular species, by degradation, to smaller organic entities. The effective oxidation potentials cover the range 1.6 to 2.0 V. The present contribution describes the new procedure, designated "the periodic acid liquid fire reaction."

### REACTIONS INVOLVED

The following reactions are fairly well established and appear to apply concurrently in the reaction mixture:





The effective degradation of the large complex molecules of organic compositions by periodic acid, to form fragmentation products of lesser molecular weight, is of major importance to the reaction mechanism. Such reactions are extensively applied in a wide variety of reactions of practical analytical determinations and studies of related structural significance. The extent to which these reaction types contribute to the wet oxidation reactions being described, is not well established. The reactions in strong perchloric acid, at moderately elevated temperatures (150–200°), are undoubtedly much more extensive and complicated than those which apply in neutral or moderately acid solutions. Evidence will be submitted which demonstrates the reality and extent of the periodic acid fragmentation reactions which contribute effectiveness to the periodic acid liquid fire reactions.

In the reactions stated above the oxidants simultaneously operative are periodic, iodic and perchloric acids, iodine and iodine perchlorate, oxygen and chlorine.

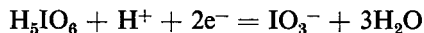
Reaction (1), the thermal dissociation of periodic acid in hot concentrated perchloric acid, is relatively slow. Tests in boiling 70% perchloric acid indicate that 3 to 5 min are required. In lesser strength acid, a longer interval is required. In the wet oxidation mixture, therefore, the periodic acid is available for a sufficient period to provide both for fragmentation and oxidation.

Reactions (2) and (3) occur simultaneously at low temperature (40–70°), in the presence of organic matter dispersed in concentrated (60–70%) perchloric acid. These reactions are markedly exothermic. Perchloric acid concentrations should be selected which minimise reaction (2) to such rates that reaction (3) keeps pace with reaction (2). Both iodine and iodine perchlorate may be evolved. They may be retained by the use of a reaction apparatus of the vapour refluxing principle.

Reaction (4) increases in rate as the perchloric acid concentration is augmented from 60 to 72.5% and at its boiling point.

Reaction (5) is slow, but intensifies with increases under the same conditions as reaction (4). Iodine is oxidised to iodic acid, following the intermediate formation of iodine perchlorate, under the same conditions. Total destruction of organic matter often occurs before reactions (4) and (5) have become jointly complete.

The standard reduction potential of the periodic-iodic acid couple<sup>5</sup>



has been estimated to be 1.6 V. The oxidising power of perchloric acid depends upon its concentration and temperature. Exact measurements of its reduction potential have not, and perhaps cannot, be made. Even the exact nature of the reduction products is not known with certainty. On the basis of its effects at different concentrations approximate values can be assigned. Thus, since in 58 to 60% perchloric acid<sup>3</sup> at 150° to 160° ferrous iron is oxidised to ferric, the potential is estimated to be 0.8 V. For progressively increasing concentrations, from 60 to 72.5%, the boiling temperature increases in almost direct proportion (to 203° at 760 mm for the 72.5% water-perchloric acid azeotrope), and the oxidising power rises markedly and approximately in direct proportion, reaching an estimated value of 2.0 V.

In the periodic acid-perchloric acid mixture, the former brings about the initial reaction in oxidation of organic compositions at moderate temperature and with controlled intensity. Fragmentation of organic compositions by periodic acid is well known. It reacts rapidly upon organic material bearing hydroxyl or amino groups on adjacent carbon atoms, aldehydes and ketones being assumed to be hydrated. Degradation products, formic acid and probably oxalic acid among other simple formulations, are then readily oxidised to carbon dioxide through the medium of hot concentrated perchloric acid.

Fragmentation is more extensive in the reactions at hand owing to the presence of concentrated perchloric acid. As the temperature increases following initiation of oxidation by periodic acid, which is exothermic, the perchloric acid provides more extensive fragmentation before final conversion of carbon to carbon dioxide. The perchloric acid has an additional function. It effects dissolution of organic matter of a wide range of structures, both in hot or cold concentrated acid, without being accompanied by char formation. The periodic acid liquid fire reactions are thus seen to have many unusually effective reaction advantages.

## EXPERIMENTAL

### *Reagents*

*Periodic acid:* Colourless, crystalline, non-hygroscopic, reagent grade para-periodic acid,  $H_5IO_6$ . Free adsorbed water, at 85°, not more than 0.3%. Non-volatile after ignition, not more than 0.01%. Assay 99-98%. Sulphate and heavy metal free. Commercially available.

*Perchloric acid:* Reagent grade vacuum distilled. Assay 66.0, 68.0, 70, and 72%. Non-volatile matter, as sulphate, not in excess of 0.003%. Sulphate, chloride phosphate and iron free. Intermediate concentrations are obtained by blending. Commercially available.

*Vanadium:* Used in mg amounts as catalyst.  $NH_4VO_3$  or  $V_2O_5$ , reagent grade.

### *Apparatus*

The most suitable apparatus has been previously described and its design designated by line drawings.<sup>1,2,3,4</sup> The Bethge apparatus serves best for general use. The apparatus employed in the liquid fire reactions may serve for many applications of the new periodic acid liquid fire reaction, for example in the determination of heavy metal trace elements in the wet ash residue. Vycor reaction flasks are preferable but Pyrex glass may be substituted. The Bethge apparatus provides for reflux retention of volatile products. This maintains a fixed concentration of the original perchloric acid employed. The complete retention of volatilised spray formation is assured. By use of the three-way stopcock of the Bethge apparatus, an increase in the concentration of perchloric acid wet ash residue is made operative.

### *Oxidation of cellulose*

To 1.0 g of cellulose, in the 250-ml conical flask of the Bethge apparatus, was added 15.0 ml of 68% perchloric acid and 1.5 g of para-periodic acid. The mixture (both reactants cellulose and periodic acid, being soluble in the perchloric acid) was heated gently to initiate the reaction, which began at 40 to 50°. The reaction was markedly exothermic and, in 15 to 20 sec after initiation, the temperature rose to 100 to 110° without further heating. Heat was again applied and the oxidation of the cellulose was complete in 2 to 5 min. Continued heating to the boiling point completed the conversion of the iodine perchlorate formed to iodic acid. The latter operation is favoured by cutting off the return of condensate. The course of the temperature during the operation is shown graphically in Fig. 1.

### *Oxidation of wool*

Wool yarn was subjected to the periodic-perchloric acid treatment under the same conditions given above for cellulose. Wool is not measurably attacked by concentrated perchloric acid when

cold, but it is dissolved when the acid is heated. The initial reaction is exothermic, but to a lesser degree than with cellulose. Little or no iodine was evolved. Oxidation was complete in 5 min, the final temperature being 170°. The course of the reaction temperature effects is shown in Fig. 2.

#### *Oxidation of sucrose*

Cane sugar is soluble, without charring, in concentrated perchloric acid. Its oxidation under conditions identical with those given above for cellulose followed. The reaction began at about 40° and was markedly exothermic. Iodine was liberated, then oxidised to iodine perchlorate. Oxidation was complete in 5 to 6 min, the final temperature being 190°, with most of the time taken to effect oxidation of the iodine perchlorate to iodic acid. The results are shown graphically in Fig. 3.

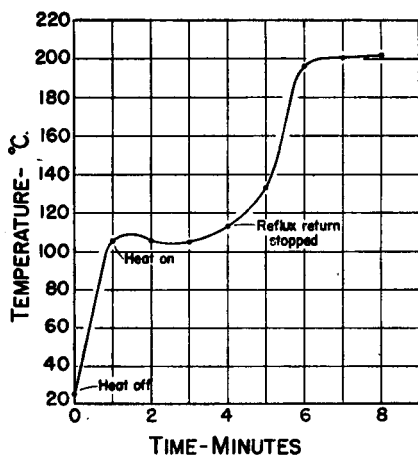


FIG. 1.—Cellulose oxidation.

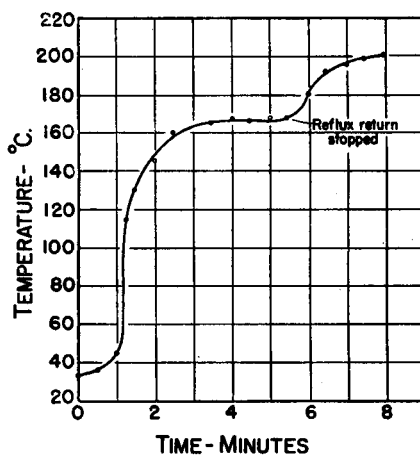


FIG. 2.—Wool oxidation.

#### *Oxidation of vegetable and chrome tanned leather*

Vegetable tanned leather was treated in duplication of conditions given for the oxidation of cellulose. The initial reaction occurred at approximately 40° and the reaction was complete in 14 to 15 min, the final temperature being 175°. In the initial reaction considerable iodine was formed, soon to be converted to iodine perchlorate. The results are shown in Fig. 4. Chrome tanned leather is often fortified by incorporation of such additives as paraffin and barium sulphate. The presence of 3 to 6% of chromium in the tanning process also increases the difficulty in its wet oxidation. The same method of attack was applied to a sample of such type chrome tanned leather as that applied to vegetable tanned leather, except that 2 mg of vanadium was added as catalyst. At the initial reaction temperature, 50°, the temperature rose rapidly to 150° in 4 min. At 5 min the solution of wet ash acids has a green colour, with considerable turbidity, and oxidation was essentially complete with the flask walls coated with paraffin still unoxidised. After 9 min the reflux was cut off and at 13 min and at 198° the reaction mixture was orange coloured from dissolved chromic acid, indicating complete removal of organic matter. The boiling wet ash solution was clear but, upon cooling, a precipitate of barium sulphate was present.

#### *Wet oxidation of various types of coal*

The wet oxidation of soft coal<sup>2</sup> (high and low V.C.M.) has recently been described. The major objective of the present study was to provide conditions of wet oxidation suited to the subsequent determination of arsenic. It was postulated that the periodic acid liquid fire reaction would provide more suitable reaction conditions than in the previously cited method. This was found to be the case. In the previous study, the wet oxidation procedure developed the condition that the volatile combustible matter of coal was evolved as in the case of the regularly applied V.C.M. determination in the standard (proximate analysis) analytical routine. By the use of the present procedure the volatile combustible matter in coal is oxidised rather than volatilised. In addition, the presence of periodic

and iodic acids, as well as iodine perchlorate, ensures more favourable conditions for retention of arsenic in the wet ash residue.

Coal samples of all types may be boiled in contact with 70% perchloric acid for periods of 1 to 3 h before complete oxidation results. The presence of a few mg of chromium shortens the required boiling period to 30 min. The addition of 1 or 2 mg of vanadium in place of chromium catalytically shortens the required boiling period to 15 min. The reaction mechanism accounting for this valuable catalyst influence has been previously described.<sup>1</sup>

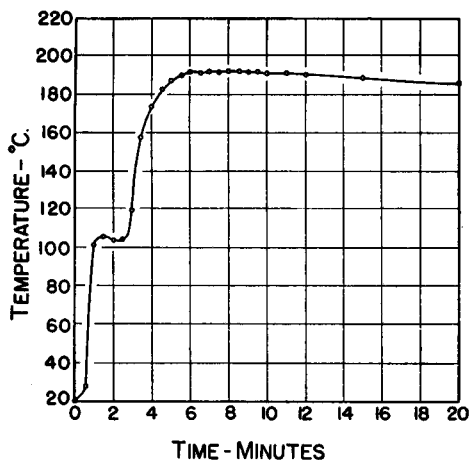


FIG. 3.—Sucrose oxidation.

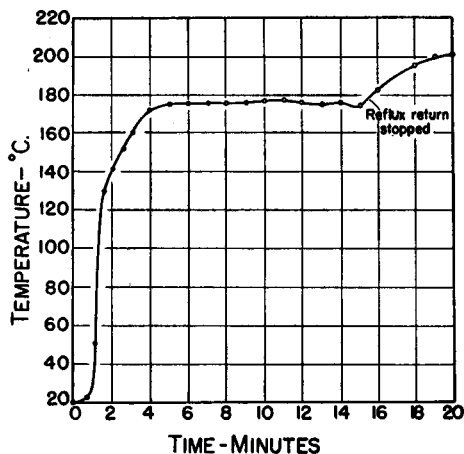


FIG. 4.—Vegetable-tanned leather oxidation.

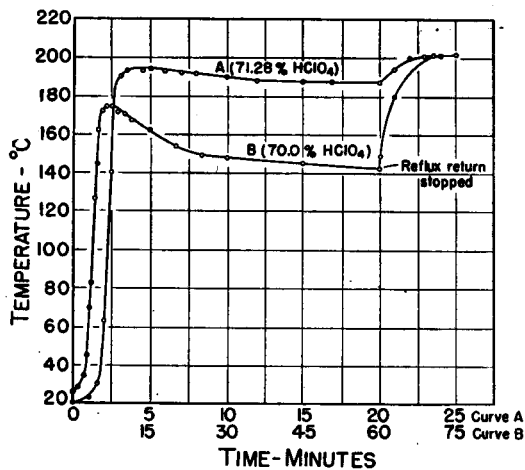


FIG. 5.—Anthracite coal oxidation.

The time required for the oxidation of coal by the new procedure varies to a large extent with the initial concentration of perchloric acid. Thus, for anthracite (see Fig. 5), a 1 h digestion was required using 70.0% perchloric acid concentration, but only 20 min using 71.28% concentration. With either concentration of perchloric acid, the initial reaction set in at 30 to 40° and was exothermic. For the lower acid concentration the formation of iodine perchlorate was very pronounced; at the higher concentration little was formed and its conversion to iodic acid was rapid. The results for the oxidation of anthracite coal are shown graphically in Fig. 5.

Soft coals containing a moderate amount of volatile combustible matter, such as Pocahontas coal, require less concentrated perchloric acid for their rapid oxidation. Considerable foam, a layer 25 to 40 mm thick, was formed but did not interfere. Relatively little iodine was formed. Starting with

69.5% perchloric acid, the reaction was practically complete in 5 min and assuredly complete in 10 min at 200°; with 69%, the time was about doubled. The results are shown in Fig. 6.

Bituminous coal containing high volatile combustible matter, such as the Orient coal of Southern Illinois, was oxidised expeditiously with high initial concentrations of perchloric acid, 70.0 and 71.28%. Considerable foam, a layer of approximately 50 mm thick, was present during the early stages of the reaction. Some iodine was formed in the 70% perchloric acid digestion but little or none

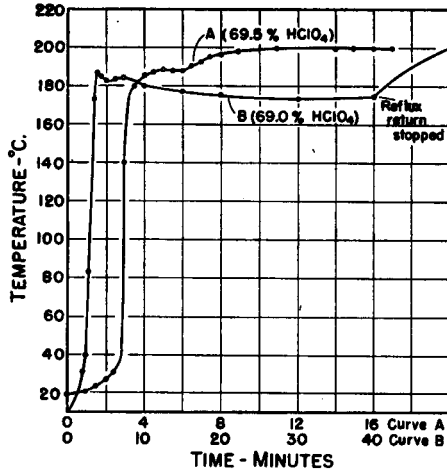


FIG. 6.—Pocahontas coal oxidation.

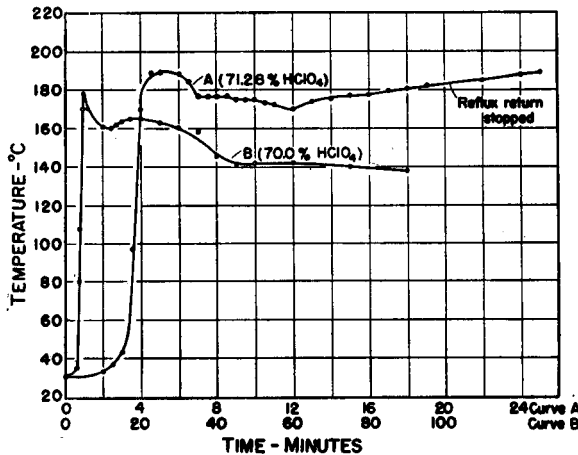


FIG. 7.—Orient coal oxidation.

in the 71.28% mixture. The effect of the initial acid concentration on the time required is shown in Fig. 7.

As was expected, the ash remaining following the periodic-perchloric acid digestion of coal was less than that obtained by dry ashing: Pocahontas 6.83 and 9.72%, respectively; Orient coal 4.60 and 7.50%, respectively.

#### *Oxidation of adipic acid*

Because of the use of adipic acid in Nylon synthesis its wet oxidation was studied. The Bethge apparatus reactants were: 1.0 g of adipic acid, 15.0 ml of 65.5% perchloric acid, 1.5 g of para-periodic acid, both with and without vanadium. The results were as follows:

1. Without vanadium, the reaction was smooth and complete in 10 min. The maximum temperature was 162°. The evolution of iodine was excessive for best conditions.

2. With 1.0 mg of vanadium added, the reaction was smooth, more rapid and the evolution of iodine retarded in favour of iodine perchlorate. The oxidation was complete in 8 min at a maximum temperature of 159°.

3. With 2.0 mg of vanadium added, the best conditions were attained. The reaction was complete in 6 min and the maximum temperature was 157°.

The last of these conditions was applied to the oxidation of Nylon with the exception that the perchloric acid concentration was augmented.

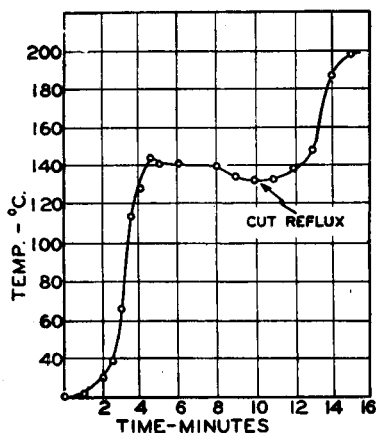


FIG. 8.—Nylon oxidation.

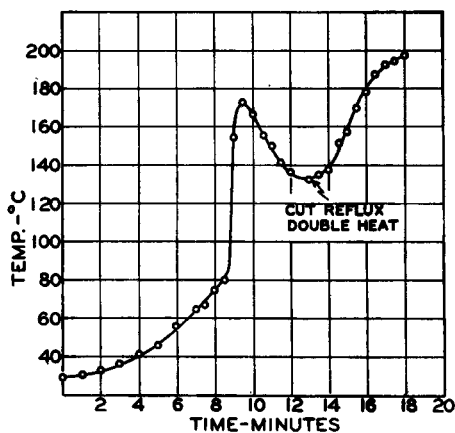


FIG. 9.—Methyl methacrylate oxidation.

#### Oxidation of nylon

For Nylon oxidation (polymerised adipic acid and hexamethylenediamine), the use of 69.5% perchloric acid was found to favour iodine perchlorate formation with little iodine. The data for this oxidation is given in Fig. 8. Nylon is seen to be completely oxidised at a maximum temperature of 145°. The ashed acid residue, upon cooling, deposited ammonium perchlorate. The wet ash was soluble in water, except for its titanium dioxide additive.

#### Oxidation of uric acid

Uric acid was investigated as an organic type involving heterocyclic ring nitrogen structure. Also, because it is a component of urine and of many types of faecal matter. One gram of uric acid with 1.5 g of periodic acid, 15.0 ml of 65.5% perchloric acid and 2 mg of vanadium, was digested in the Bethge apparatus. The initial exothermic reaction was at 45–50°, evolving a modest amount of iodine, followed by iodine perchlorate. Reaction was complete after 5 to 6 min at a maximum temperature of 150°. The cold wet ash residue deposited ammonium perchlorate and was completely soluble upon dilution with water.

#### Oxidation of methyl methacrylate or methyl methacrylate polymer P-1 and lucite

Methyl methacrylate is miscible with 68.5% perchloric acid. It is smoothly oxidised by the use of the periodic acid liquid fire reaction. Low temperature treatment retards foam formation. Vanadium, as catalyst, is effective. One gram samples were oxidised in 15 ml of perchloric acid in 17 min without vanadium. Ten minutes were required with 2 mg of catalyst. 1.5 g of para-periodic acid constitutes a generous excess. The polymer of methyl methacrylate, du Pont P-1, in the presence of vanadium, was similarly oxidised in 16 to 17 min. Lucite was similarly oxidised in the same time interval. The production of iodine perchlorate as the reduction product of periodic acid predominated. At a lesser perchloric acid concentration iodine was formed initially. The oxidation of polymerised methyl methacrylate is shown in Fig. 9.

As shown in Fig. 9 reaction is initiated exothermally at 80°. It would appear that, in all these reactions, the oxidation follows the same course as for methyl methacrylate. The initial exothermic reaction is followed by a second stage of oxidation contributed by perchloric acid. This latter oxidation accounts for the catalysis by vanadium.

*Iodine perchlorate as the reduction product of periodic acid*

A 60-g sample of the volatile orange coloured reduction product from the periodic acid oxidation of organic matter was collected for examination of its composition. Upon distillation the sample dissociated materially to liberate iodine. The most stable fraction had a constant boiling point of 112.5°. This fraction was subjected to analysis for iodine by titration of its solution in excess potassium iodide using sodium thiosulphate. A sample weight of 0.5261 g required 26.60 ml of 0.0930N thiosulphate, corresponding to 0.5770 g of  $I(ClO_4)_3$ . The problem was not studied further. The conclusion was postulated that the reduction products of periodic acid in the oxidation of organic matter consists of iodine monoperchlorate which dissociates to liberate iodine, thus accounting for random ratios of iodine to the perchloric acid anions. In the reactions as described, iodine and iodine perchlorate are oxidised to iodic acid by boiling with concentrated perchloric acid.

*Polyethylene oxidation*

Polyethylene is well known to be non-reactive in contact with hot concentrated perchloric and periodic acids. The periodic acid liquid fire reaction could thus be predicted to be ineffective. This was experimentally substantiated. Evidence was produced that oxidation was progressing due to the formation of iodine perchlorate and by the exothermic reaction properties, but the time that would be required for complete oxidation would be excessive.

The rapid oxidation of polyethylene is provided by boiling 70–72% perchloric acid with added ceric ion. This reaction, at 200°, is rapid (10 to 15 min), and the wet ash residue is completely soluble when hot and, after dilution, when cold. The low oxidation equivalent weight of cerium requires the use of considerable amounts. These tests indicate that polyethylene requires the application of 1.9 to 2.0 V for rapid destructive oxidation.

*Procedural treatment of residual wet ash solution*

If the removal of iodic acid from the wet ash solution is desirable, this is accomplished by its dilution by addition of an equal portion of water followed by a stream of sulphur dioxide from a small lecture demonstration pressure bottle. Boiling will remove the iodine, leaving a perchloric acid solution. If perchloric acid is objectionable, the addition of sulphuric acid and boiling to expel it may be easily provided. In many procedures for determination of wet ash concentrates neither iodic nor perchloric acids are interferences. An excess of sulphur dioxide causes the formation of hydriodic acid. It is, therefore, an advantage to add the sulphur dioxide to the boiling diluted wet ash residue. Small amounts of sulphuric acid only are formed by the sulphur dioxide reduction of iodic acid.

#### ADVANTAGES IN THE APPLICATION OF THE PERIODIC ACID LIQUID FIRE REACTION

The new procedure, herein described, is the most widely applicable of any process which may be applied in wet ashing techniques. It is seen to apply to the rapid wet oxidation of cellulose, sugars and other polyhydric organic compositions, proteins and protein rich materials.

The special feature of these reactions is the much lower temperatures required.

The most important reaction property is that of heavy molecular weight degradation reactions to produce smaller fragments which are readily destroyed through simultaneous contact with concentrated perchloric acid. The effective catalysis of the oxidation by very small amounts of vanadium is thus made operative to a greater extent.

The oxidation of coal at the lowest temperature which is effective in complete removal of organic matter is an attractive procedure in preparation for the determination of arsenic.

The special property of periodic acid in fragmentation of polymeric compositions has made the wet oxidation of such products as nylon, methyl methacrylate polymers and other comparable products easily operative.



Owing to the use of low strength perchloric acid it is postulated that all amino nitrogen of organic compositions is retained in the wet ash digestion residue. This assumption is now being investigated.

The wet oxidation of cellulose type products such as dried feeds, which is a much employed procedure in the determination of calcium, magnesium, sulphur, phosphorus and the alkali metals as applied by the routine animal nutritionists using the nitric acid liquid fire reaction almost entirely, may now be preferentially replaced with gains in many considerations.

The periodic acid wet oxidation procedure has been applied to cellophane, Dacron and Orlon fabrics, dried clover, corn leaves and ground corn stocks, honey, dried beef, Lucite, Du Pont Mylar, and starch, with equal success. Many other applications are deemed attractive.

Because of the use of much less highly concentrated perchloric acid in the reactions described, and the need for only lower temperatures of reaction, there is no tendency to encounter uncontrolled reaction rates.

**Zusammenfassung**—Der Ersatz von Salpetersäure durch Periodsäure zur nassen Veraschung organischer Substanzen wird vorgeschlagen. Die erzielten Vorteile sind: allgemeinere Anwendungsmöglichkeit, niedrigere Temperatur und eine bemerkenswerte Aktivität der Periodsäure bei der Zerstörung starke komplexer organischer Molekeln unter Bildung von Fragmente, die in der als weiteres Reagens anwesenden Perchlorsäure wesentlich leichter löslich sind. Diese Verbindungen werden dann in 66–70% iger Perchlorsäure leichter oxydiert. Die beschriebenen Reaktionen beziehen sich Vorwiegend auf organische Verbindungen des Types Cellulose, Zucker und Eiweiss. Auch Kohle, Leder, polymere Produkte und ander handelsübliche wichtige Materialien werden ebenfalls leicht oxydiert. Die Reaktion ist ungefährlich.

**Résumé**—Les auteurs décrivent la substitution de l'acide périodique à l'acide nitrique dans la réaction très employée "liquid fire" pour l'oxydation destructrice des composés organiques. Les avantages obtenus sont les suivants: possibilité d'application générale étendue, nécessités de basse température, réactivité intéressante de l'acide périodique dans la dégradation de molécules complexes organiques lourdes en fragments plus facilement solubles dans l'acide perchlorique utilisé comme réactif d'accompagnement. Ceux-ci sont plus facilement oxydés par cet acide pour des concentrations de 66 à 69 ou 70%. Les réactions décrites s'appliquent à des composés organiques, en particulier à la cellulose, aux sucres et aux protéines. Le charbon, le cuir, les produits polymérisés et d'autres matériaux importants au point de vue commercial peuvent être facilement oxydés.

Les réactions mises en jeu ne dépendent pas du hasard.

#### REFERENCES

- <sup>1</sup> G. Frederick Smith, *Analyt. Chim. Acta*, 1953, **8**, 397.
- <sup>2</sup> G. Frederick Smith and Harvey Diehl, *Talanta*, 1959, **3**, 41.
- <sup>3</sup> Harvey Diehl and G. Frederick Smith, *ibid.*, 1959, **2**, 209.
- <sup>4</sup> G. Frederick Smith, *Analyt. Chim. Acta*, 1957, **175**, 1957.
- <sup>5</sup> W. H. Latimer, *Oxidation Potentials*, Prentice Hall, Inc. 2nd Ed., 1952, p. 66.



Using the flux of  $10^{12}$  neutrons  $\text{cm}^{-2} \text{sec}^{-1}$  available in the Harwell Pile BEPO and measurement of the  $\beta^-$ -activity of  $^{182}\text{Ta}$ , it has been estimated that as little as  $1 \times 10^{-10}$  g of tantalum may be determined under ideal conditions.<sup>12</sup> The decay scheme for  $^{182}\text{Ta}$  is shown in Fig. 1.

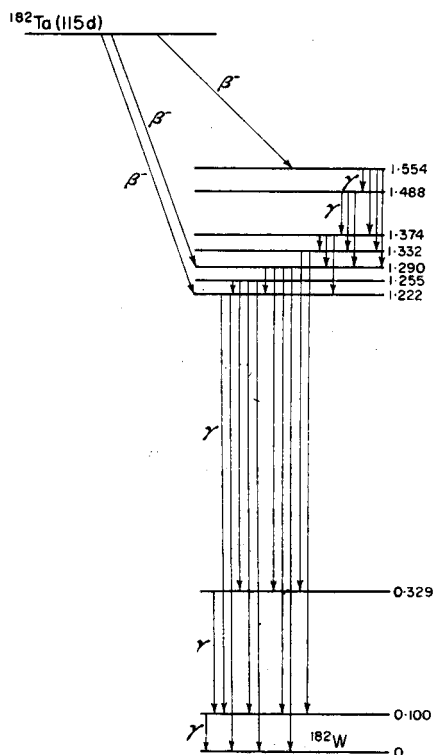


FIG. 1.—Decay scheme for  $^{182}\text{Ta}$ , energies in MeV.

## EXPERIMENTAL

### Irradiation

Samples of the powdered rocks of about 0.5 g were accurately weighed out and sealed in 6-mm internal-diameter silica irradiation tubes. Standards were prepared by weighing out 0.1-ml aliquots of a dilute standard solution of tantalum<sup>v</sup> (50 mg Ta/litre, in oxalic acid solution) into 4-mm internal-diameter silica irradiation tubes, which were then sealed. Samples and standards were packed together in a standard 3-in.  $\times$  1-in. screw-top aluminium can and sent for irradiation in the Harwell Pile BEPO. Irradiation was usually for a period of 1 week with pile factor 10.

### Radiochemical separation

Following delivery from Harwell after irradiation, the samples and standards were left to "cool" for a few days, and then were assayed radiochemically for  $^{182}\text{Ta}$ . A procedure involving carrier chemistry, precipitation, and solvent extraction, was employed for the separation of tantalum from the irradiated rock samples. Steps involving solvent extraction with tri-*n*-butyl phosphate were based on distribution data of Morris *et al.*<sup>14,15</sup>

### Reagents

Ta carrier, 10 mg Ta/ml (see preparation of carrier)  
 $\text{KNO}_3$ , solid  
 $\text{K}_2\text{CO}_3$ , solid

HNO<sub>3</sub>, conc  
 H<sub>2</sub>SO<sub>4</sub>—HF solution, 12*N* in H<sub>2</sub>SO<sub>4</sub> and 10*M* in HF  
 HF, conc  
 HF, 0.5*M*  
 NH<sub>4</sub>OH, conc  
 NH<sub>4</sub>NO<sub>3</sub>, solid  
 NH<sub>4</sub>NO<sub>3</sub>, 2% solution in H<sub>2</sub>O  
 Tri-*n*-butyl phosphate (TBP), purified by the method of Alcock *et al.*<sup>18</sup>  
 Petroleum ether  
 Ethyl alcohol, absolute

#### *Preparation of tantalum carrier*

Dissolve a weighed quantity of "Specpure" Ta<sub>2</sub>O<sub>5</sub> in a mixture of conc HNO<sub>3</sub> and conc HF. Make up to a volume with 5*M* HF to give 10 mg of Ta per ml of solution. Store in a stoppered polythene bottle.

#### *Radiochemical separation procedure for tantalum in rocks*

*Step 1.* Remove the irradiation tubes from the can, open them at the constriction, and transfer the powdered rock samples quantitatively to platinum crucibles. To each add 4 g of powdered K<sub>2</sub>CO<sub>3</sub> and 0.1 g of KNO<sub>3</sub>; mix thoroughly. Fuse in an electric muffle furnace, heating carefully at a low temperature first, and then at 850–900°. When decomposition is complete, remove the crucible from the furnace, allow it to cool somewhat, then grasp it with the tongs and carefully distribute the melt in a thin shell over the interior walls by imparting a slow rotary motion to the crucible as it cools. Transfer the cooled melt to a 250-ml polythene beaker, add 20 ml of H<sub>2</sub>O and break up the melt with a glass rod flattened at one end. Acidify carefully with HF, add 2 ml of Ta carrier, and stir for 5 min with a polythene rod. Filter the supernate into a 50-ml polythene centrifuge tube and discard any residue.

*Step 2.* Add 1 g of solid NH<sub>4</sub>NO<sub>3</sub>, and make the solution just ammoniacal with conc NH<sub>4</sub>OH. Centrifuge and discard the supernate. Wash the precipitate of hydrous tantalum<sup>v</sup> oxide with two 10-ml portions of conc HNO<sub>3</sub>. Centrifuge and discard the supernate.

*Step 3.* Dissolve the precipitate in 10 ml of a solution 12*N* in H<sub>2</sub>SO<sub>4</sub> and 10*M* in HF. Add 10 ml of TBP and mechanically stir the phases for 2 min using a polythene stirring rod. Centrifuge, transfer the organic (upper) layer with a polythene transfer pipette to a clean 50-ml polythene centrifuge tube, and discard the aqueous layer. Wash the TBP phase with two 5-ml portions of 0.5*M* HF. Discard the aqueous washings.

*Step 4.* Add 10 ml of petroleum ether to the TBP phase and stir it with 10 ml of 6*M* NH<sub>4</sub>OH. Centrifuge at high speed and separate and discard the organic and aqueous layers. Wash the precipitate twice with 10-ml portions of hot 2% NH<sub>4</sub>NO<sub>3</sub> and transfer to a 50-ml glass centrifuge tube.

*Step 5.* Centrifuge and discard the supernate. Wash the precipitate twice with 10-ml portions of boiling conc HNO<sub>3</sub>. Centrifuge and discard the supernate.

*Step 6.* Transfer the precipitate to a porcelain crucible with 2 ml of distilled water; heat to dryness. Ignite at 900° for 15–20 min, and allow to cool in a desiccator.

*Step 7.* Add 1 ml of ethyl alcohol to the Ta<sub>2</sub>O<sub>5</sub> in the crucible and grind with the polished end of a stirring rod. Slurry the Ta<sub>2</sub>O<sub>5</sub> with the ethyl alcohol on to a weighed aluminium counting tray (A.E.R.E. cat. no. 4-3/1068). Dry thoroughly under a radiant heater lamp taking care to ensure that the resulting deposit on the tray is uniform. Cool and weigh to determine the chemical yield. (The precipitate is very loose and powdery and great care is necessary). Fix the precipitate to the tray by the addition and evaporation of a few drops of collodion solution (2 mg/ml).

#### *Treatment of the irradiated tantalum standards*

At a suitable time open the irradiation tubes containing the tantalum standards. Using a polythene transfer pipette drawn out almost to a point, transfer the tantalum solution quantitatively to a 50-ml polythene centrifuge tube and rinse thoroughly with 5*M* HF. Add 2 ml of Ta carrier, mix thoroughly, then make just ammoniacal with conc NH<sub>4</sub>OH. Proceed as from Step 5 of the radiochemical procedure for rock samples.

*Counting of the Ta<sub>2</sub>O<sub>5</sub> precipitates*

In the present study final precipitates of Ta<sub>2</sub>O<sub>5</sub> were counted through a standard Al-Pb sandwich absorber with a  $\gamma$ -scintillation counter type 1186A.

In order to check for the radiochemical purity of the radiotantalum, decay measurements on the final precipitates were performed. Decay curves obtained from a sample and a standard are shown in Fig. 2, and are straight lines corresponding well with published values<sup>12</sup> for the half-life of <sup>182</sup>Ta. A further check for radiochemical purity was made by measuring the  $\gamma$ -spectra of final precipitates with a single NaI(Tl) crystal  $\gamma$ -scintillation spectrometer. Typical results are shown in Fig. 3.

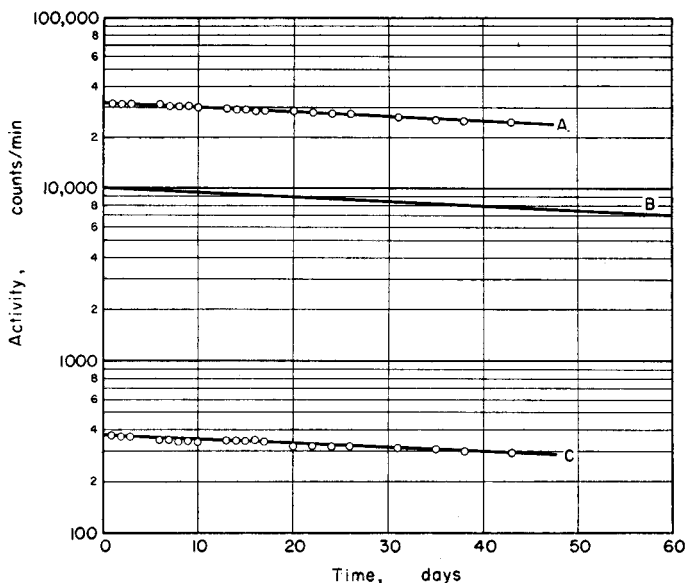


FIG. 2.—Decay curves: A, tantalum activity of a standard. B, line of slope corresponding to a nuclide of half-life 115 days. C, tantalum activity from a rock sample.

## RESULTS

If  $A_1$  is the activity (corrected for background and chemical yield) from a rock sample and  $A_2$  is the corresponding activity from a tantalum standard, at a given time

$$\frac{A_1}{A_2} = \frac{w_1}{w_2}$$

where  $w_2$  is the weight of tantalum in the standard and  $w_1$  is the weight of tantalum in the rock sample.

Typical analysis results obtained by the radio-activation method are shown in Table 1. These refer to the standard granite G1 from Westerley, Rhode Island, and the standard diabase W1 from Centreville, Virginia, which have been distributed as standards for both major and minor constituents of igneous rocks.<sup>17</sup>

## DISCUSSION

In the determination of tantalum by neutron-activation, consideration must be given to the possibility of formation of <sup>182</sup>Ta through nuclear reactions involving

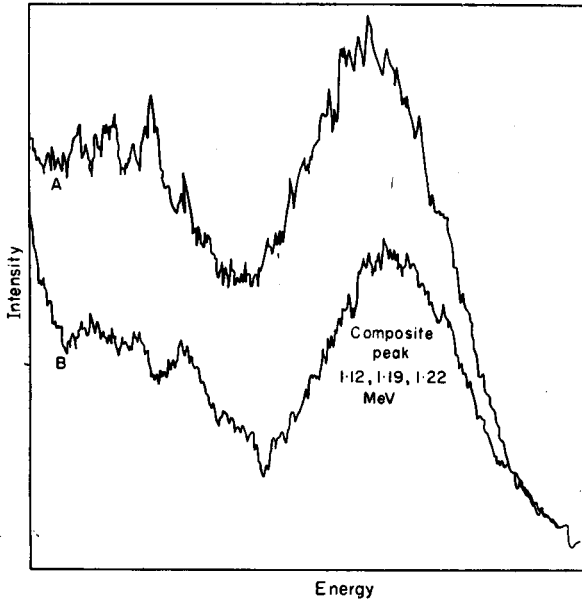
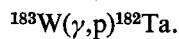
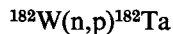
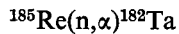


FIG. 3.—Gamma ray spectra: A, activity of a standard. B, activity from a rock sample

TABLE I.—TANTALUM CONTENTS OF THE STANDARD GRANITE G1 AND THE STANDARD DIABASE W1 DETERMINED BY NEUTRON-ACTIVATION ANALYSIS

G1	W1
3.1 ppm	0.95 ppm
2.8	0.88
2.9	0.89
3.1	1.06
3.1	0.99
3.1	0.84
2.7	Average 0.93
2.9	
Average 3.0	

elements other than tantalum. For example,  $^{182}\text{Ta}$  could be produced by the following reactions:



The first two of the above nuclear reactions may be brought about by the fast neutron flux in the pile, which flux Mellish *et al.*<sup>18</sup> calculated to be 0.17 of the slow flux in the centre of BEPO. The cross-sections for these reactions are likely to be very much lower than for the reaction  $^{181}\text{Ta}(n,\gamma)^{182}\text{Ta}$ , and since the abundance of rhenium in

igneous rocks is extremely low, 0.001 ppm,<sup>1</sup> the first reaction is clearly not troublesome in the present work.

To check on any possible interference arising from the production of <sup>182</sup>Ta from nuclear reactions of tungsten, samples of pure WO<sub>3</sub>, together with pure Ta standards, were irradiated in the Pile for 1 week. The tantalum activity was separated and counted as before. The experimental results indicated that if a rock contained 70 ppm W (the crustal abundance of tungsten has been quoted<sup>1</sup> as 1.5–69 ppm), this could give rise to a maximum spurious tantalum content of only 10<sup>-5</sup> ppm.

Any interference of importance due to the formation of radio-isotopes of tantalum other than <sup>182</sup>Ta would have been apparent from the decay and energy measurements on the final precipitates from analysis samples.

*Note added in proof.*

Since the acceptance of this paper, Atkins and Smales<sup>19</sup> have published details of the determination of tantalum by neutron-activation analysis. Our results for the tantalum content of G1 and W1 do not correspond with the values obtained by these investigators. Atkins and Smales point out and discuss the possibility of contamination of the rock samples during pulverisation, and this may account for the discrepancy. Our samples were provided in a powdered condition by the U.S. Geological Survey.

*Acknowledgment*—The authors wish to record their thanks to Mr. G. W. J. Kingsbury of the National Chemical Laboratory, Teddington, for the loan of "Specpure" tantalum pentoxide.

**Zusammenfassung**—Neutronenaktivierungsanalyse wurde zur Bestimmung von Tantal in Gestein angewandt. Radiochemische Abtrennung unter Verwendung von Trägern beruhte hauptsächlich auf der Fällung von Tantalhydroxyd und Solventextraktion mit Tri-n-butylphosphat. Radiochemisch reines Tantal wurde schliesslich als Pentoxid gefällt und der chemische Gehalt gravimetrisch ermittelt. Zur Verhinderung von Fehlern durch Selbstabschirmung wurden verdünnte Lösungen von Tantal als Standards verwendet und zugleich mit den Proben bestrahlt. Die Ergebnisse der Analysen von Standardgestein G1 und W1 werden mitgeteilt.

**Résumé**—L'analyse par activation des neutrons a été appliquée au dosage de traces de tantale dans les roches. Les séparations radiochimiques après addition d'entraîneur ont été basées principalement sur la précipitation du tantale à l'état d'oxyde tantaleux, et sur l'extraction par solvant avec le phosphate de tri-n-butyl. On précipite finalement le tantale radiochimiquement pur à l'état de pentoxyde et le rendement chimique a été déterminé par gravimétrie.

Pour éviter les erreurs dues au phénomène d'auto-absorption on utilise comme étalons des solutions diluées de tantale irradiées simultanément avec l'échantillon à doser.

Les résultats relatifs à la teneur en tantale d'échantillons de roches étalons G<sub>1</sub> et W<sub>1</sub> sont indiqués.

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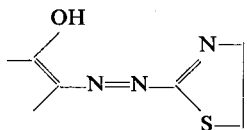
## PRELIMINARY COMMUNICATION

### Thiazolyl analogues of 1-(2-pyridylazo)-2-naphthol

(Received 9 March 1960)

AMONG the metallochromic indicators of the azo-dye series, 1-(2-pyridylazo)-2-naphthol (PAN)<sup>1</sup> has an outstanding position. In contrast to the analogous *o*:*o'*-di-substituted azo dyes of the Eriochrome Black T type—where the transforming functional groups<sup>2</sup> are represented by phenolic hydroxyls—the chelating grouping of the indicator PAN contains a heterocyclic nitrogen atom with a lone electron pair as one of the ligands. Due to this fact, pyridylazonaphthol possesses an increased ability to form coloured complexes with bivalent metal ions (*e.g.* with Cu<sup>II</sup>, Cd<sup>II</sup>, Ni<sup>II</sup>, Co<sup>II</sup>, Hg<sup>II</sup>, Pb<sup>II</sup> etc.) which display an especially strong affinity towards the nitrogen as a donor atom. The advantageous metallochromic properties of this substance have, in recent years, inspired several attempts to find other analogous indicators. In all these attempts the approach has been limited to modification of the phenolic part of the PAN molecule, resulting in the preparation of 4-(2-pyridylazo)-resorcinol (PAR),<sup>3</sup> and derivatives of H-acid and chromotropic acid.<sup>4</sup> From the analytical viewpoint, however, among all these substances only the indicator PAR may be considered successful.<sup>3,5</sup>

A novel and especially valuable group of analogues of the PAN and PAR indicators has now been found in thiazolyl azo dyes of the type I. With a view to studying the metallochromic properties of these substances the condensation products of diazotised 2-aminothiazole with a number of phenols, naphthols and naphthol-sulphonic acids have been prepared.



I

Their preparation is very simple, since 2-aminothiazole (as opposed to 2-aminopyridine) requires no special conditions for diazotisation or condensation; and the products are obtained in relatively good yields and—in most cases—in a fairly pure form. Among all the substances synthesised, the best properties were displayed by derivatives of 2-naphthol, of Schäffer's acid, of R-acid, of chromotropic acid and especially of resorcinol. Some of these dyes were synthesised earlier by Traumann,<sup>6</sup> however, their metallochromic properties and the possibility of their analytical application have not so far been studied.\* With the exception of the dye derived from 2-naphthol, all these substances (and especially their alkali salts) are readily soluble in water; 1-(2-thiazolylazo)-2-naphthol resembles its pyridine analogue in its solubility in water and other solvents.

In aqueous solution the substances studied behave as acid-base indicators with the point of colour change varying for individual compounds over the pH range 6-10. In the case of derivatives containing the naphthalene ring, the acid-base colour change is one from yellow (or wine-red in the case of the chromotropic acid derivative) to purple or even violet; 4-(2-thiazolylazo)resorcinol changes from yellow to bright red. In the acid region the thiazolyl azo dyes form complexes with a number of metal ions, *e.g.* Cu<sup>II</sup>, Cd<sup>II</sup>, Ni<sup>II</sup>, Co<sup>II</sup>, Zn<sup>II</sup>, Pb<sup>II</sup>, Hg<sup>II</sup>, Fe<sup>III</sup>, Ti<sup>III</sup>, Sc<sup>III</sup>, In<sup>III</sup>, La<sup>III</sup> etc., which are coloured purple to violet (naphthalene derivatives) or bright red to purple (derivative of

\* After the completion of the present work two abstracts appeared in *Z. analyt. Chem.*, 1960, 171, 435, 444 of papers by T. Yanagimara, N. Matano and A. Kawase, *Bunseki Kagaku*, 1959, 8, 10, 14, describing the application of 2-(2-hydroxy-5-methoxyphenylazo)-4-methylthiazole to the determination of Zn, Ni and Co.

resorcinol). The condensation product of diazotised aminothiazole with chromotropic acid reacts with metal ions within a narrow range of pH only (5–7), and gives a distinct and practically applicable reaction only with copper (a pure blue coloration). With alkaline earth metals these substances show no colour reactions.

Most coloured metal complexes of 1-(2-thiazolylazo)-2-naphthol can be extracted with organic solvents such as amyl alcohol, chloroform, carbon tetrachloride etc. Metal complexes of the resorcinol derivative are extractable with more polar solvents only (amyl alcohol). Among the sulphonated dyes only the mercury complex of 1-(2-thiazolylazo)-2-naphthol-6-sulphonic acid is soluble in amyl alcohol and even this is insoluble in chloroform or carbon tetrachloride.

As far as their analytical application is concerned, the thiazolyl azo dyes referred to can be used almost in all instances where the use of the PAN or PAR indicators has been recommended. Moreover, the water-soluble sulphonated derivatives, which have not yet been prepared in the pyridine series (*cf.*<sup>5</sup>), may be used with advantage. Selected substances from this new group have fully met expectations as metallochromic indicators in chelatometric titrations of a number of metal ions. In this respect those dyes which are derived from Schäffer's acid, chromotropic acid and especially from resorcinol appear to be the most promising. The end-point colour change of the latter (from bright red or purple to lemon yellow), on titrating *e.g.* Cu<sup>II</sup>, Cd<sup>II</sup>, Zn<sup>II</sup>, Pb<sup>II</sup>, Ti<sup>III</sup>, Sc<sup>III</sup>, La<sup>III</sup> and In<sup>III</sup> with ethylenediaminetetra-acetic acid, equals in its distinctness and sharpness those of the best metallochromic indicators used hitherto. Although the applicability of these thiazolyl dyes as chromogenic reagents for spectrophotometry has not so far been studied in detail, successful applications may also be expected here owing to the high sensitivity of the reactions and the excellent colour properties.

*Note added in proof*—The author's attention has been drawn to an abstract dealing with some of these compounds (*Chem. Abs.*, 1960, 54, 4541g) which appeared while the present paper was in the press.

V. SVOBODA

*Spolana, N. E.,*  
*Research Centre of the Lachema Plant,*  
*Brno, Czechoslovakia*

**Summary**—A new group of metallochromic indicators, the thiazolyl analogues of 1-(2-pyridylazo)-2-naphthol, is described. These can be used in almost all instances where PAN or PAR indicators have been recommended, and their water-soluble sulphonated derivatives are also of value. Other properties are being studied.

**Zusammenfassung**—Eine neue Gruppe metallochromer Indicatoren, die Thiazolyl-derivate des 1-(2-pyridylazo)-2-naphthols, wird beschrieben. Die Indicatoren können in nahezu allen Fällen verwendet werden, in denen PAN oder PAR empfohlen werden. Die wasserlöslichen, sulfonierten Derivate sind ebenfalls wertvoll. Andere Eigenschaften werden studiert.

**Résumé**—L'auteur décrit un nouveau groupe d'indicateurs métalochromiques, les dérivés thiazolyl du 1-(2 pyridylazo)-2 naphthol. Ces indicateurs peuvent être utilisés dans presque tous les exemples où les indicateurs PAN ou PAR ont été recommandés, et leurs dérivés sulfonés solubles dans l'eau sont aussi intéressants. D'autres propriétés sont étudiées actuellement.

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## SHORT COMMUNICATIONS

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### A self-sampling indicator tube for oxygen

(Received 4 February 1960)

ALTHOUGH oxygen is not usually numbered amongst the toxic or dangerous gases, a local deficiency or excess of oxygen in the atmosphere can constitute a serious hazard. Irrespective of any simultaneous production of other gases, such as carbon dioxide, a reduction to 10-15% in the oxygen content of the air can cause a degree of distress varying with the individual. On the other hand, an increase in the oxygen content of the air to above 30% can greatly augment the fire hazard due to increase in the ease of ignition and rate of burning of combustible materials.

Instruments available for the determination of oxygen are usually too expensive, bulky or fragile for convenience, whilst chemical methods depending on the extraction of oxygen from air by absorbents and the measurement of the residue tend to be lengthy and to be awkward in manipulation. The need for a simple field test has now been met by the use of an evacuated glass tube containing an intimate mixture of silica gel and manganous oxide. Air is admitted to the tube by breaking the end and very rapidly changes the colour of the absorbent from green to brown. The oxygen content of the atmosphere is determined by measurement of the lengths of green and brown material. The evacuated silica gel tube acts as its own pump and no other sampling apparatus is required.

The nature and ubiquity of oxygen impose special problems in the design of a field test which do not normally arise in the determination of toxic gases, usually present in small proportions in the atmosphere. Since the oxygen content may be large, the sample must be small enough to be commensurate with the absorptive power of the reagent, and the absorbent must be very reactive and capable of dealing with a wide range of oxygen content in the sample. Air must be excluded from the absorbent before sampling and from the unused portion of it after sampling.

A suitable absorbent was found in manganous oxide, which can be prepared in a suitable form by heating manganous carbonate, by the method of Schulek and Pungor,<sup>1</sup> who have used this oxide in gas analysis because of its high sensitivity to oxygen. The problems of protecting the manganous oxide from oxidation before sampling, and of providing the means of taking a small sample of air, were solved simultaneously by preparing the reagent *in situ* by heating manganous carbonate with a silica gel base in the tube, under reduced pressure, then vacuum sealing.

Manganous carbonate is prepared by pouring a solution of manganous chloride into a solution of sodium bicarbonate, filtering, washing successively with water, 96% alcohol, and pentane, and drying.<sup>1</sup> The manganous carbonate is then thoroughly mixed in an atmosphere of carbon dioxide in a rotating drum with eight times its own weight of silica gel (chromatographic grade, 50-100 mesh) previously dried at 430°. The gel granules are now completely covered with an adherent layer of carbonate. The granules, still maintained in an atmosphere of carbon dioxide, are transferred to glass tubes of 5-mm bore, sealed at one end, to a height of about 20 cm, and plugged with a disc of asbestos paper and steel gauze. The tubes are evacuated, heated *in vacuo* at 430° for 45 min and sealed.

The actual determination of oxygen in the atmosphere can be carried out in less than 1 min. The end of the sample tube is broken and, after 20 sec, the length of the brown layer,  $y$ , and the total length of the brown and green layers,  $L$ , are measured. The percentage of oxygen,  $P$ , is

$$P = \frac{100cy}{s(L - y) + cy} \quad (1)$$

where  $c$  = volume of oxygen in ml absorbed per cm length in the brown layer,  
and  $s$  = volume of nitrogen in ml per cm length in the green layer.

Equation (1) can be more conveniently expressed as

$$P = \frac{100aF}{1 - F + aF}$$

where  $a$ , the batch constant,  $= \frac{c}{s}$ ,

and  $F = \frac{y}{L}$ .

Actual measurement of the layer lengths in each determination can be avoided by placing the tube on a specially constructed chart and reading off the ratio  $F$  directly. From the value for  $F$ , the percentage of oxygen,  $P$ , can be read off on a batch calibration curve based on equation (2). A knowledge of the actual volume of sample taken is not necessary.

As the sample of air enters the evacuated tube, the oxygen component is rapidly absorbed by the manganous oxide, which it turns brown, and the nitrogen passes to the end of the tube containing unchanged green reagent. The boundary between brown and green layers is always sharp and well-defined. This process, which is extremely rapid at first, slows down slightly towards the end, but is complete, for practical purposes, within 20 sec. If the tube is now allowed to stand, air slowly percolates through the packing and the whole tube becomes brown at the end of 10 to 30 min. The difference between the rates of the initial rush and of the diffusion process is normally so great, however, that the error due to diffusion is negligible when the oxygen content does not exceed 40%.

Evacuated silica gel was found capable of adsorbing about 0.8 ml per g of gel of either air, oxygen or nitrogen. In the operation of the field test, it is probable that nitrogen is adsorbed throughout the length of the tube. The validity of equation (1) did not appear to be affected by this complication. Presumably  $s$  measures the nitrogen content of the air sample denuded of oxygen, irrespective of what proportion of this nitrogen content occupies the free space above the unused portion of reagent mixture, or is adsorbed by it.

Carbon dioxide is adsorbed by the silica gel far more avidly than nitrogen and, if a few per cent of carbon dioxide is present in the atmosphere, it will be adsorbed in the first few cm of granules. In these circumstances,  $P$  in equation (1) will express the oxygen content not of the atmosphere, but of the atmosphere denuded of carbon dioxide. If an appreciable amount of carbon dioxide is present in the sample, this gas should be separately determined.

At ordinary indoor temperatures and at pressures varying little from 760 mm, the field test gives results reproducible within 1 part in 20 of the oxygen content of the air. An increase in the ambient temperature results in an apparently lower oxygen concentration, whereas an increase in pressure gives an apparently higher oxygen concentration. If more exceptional temperatures and pressures are encountered, the following empirical formula can be used

$$P = P_1 \left( \frac{100}{120 - t} \right) \left( \frac{980}{p + 220} \right)$$

where  $P$  = percentage of oxygen (corrected),

$P_1$  = apparent percentage of oxygen,

$t$  = temperature ( $^{\circ}\text{C}$ ),

and  $p$  = barometric pressure (mm).

The method shares the drawback of batch calibration with most tests using tubes containing reagent based on silica gel. The necessity of excluding air during the preparation of the tubes is somewhat onerous. In operation, however, the field test could not be simpler, the sole apparatus required being the tube itself and a blue pencil to mark the colour boundary. The tubes appear to suffer no deterioration on keeping for at least two years.

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*Laboratory of the Government Chemist  
Clement's Inn Passage, Strand  
London, W.C.2*

B. E. DIXON  
P. R. KIFF

**Summary**—Oxygen is absorbed by manganous oxide which has been prepared *in situ* on a silica gel base. The percentage oxygen is found in less than one minute.

**Zusammenfassung**—Sauerstoff wird an Manganooxyd absorbiert, welches *in situ* auf einer Silicagel-grundlage erzeugt wurde. Der Prozentgehalt an Sauerstoff wird in weniger als einer Minute ermittelt.

**Résumé**—L'oxygène est absorbé par de l'oxyde manganoux qui a été préparé *in situ* sur un support de silica gel. Le pourcentage d'oxygène est trouvé en moins d'une minute.

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### Lithium chloride in non-aqueous potentiometric titrations

(Received 26 March 1960)

INSTRUMENT instability is often a problem in the use of non-aqueous solvents in potentiometric measurements or titrations. Various means have been used, such as special electrode holders and special cells with the tips of the electrodes placed very close together, to help stabilise the instrument. Lithium chloride was used by Fritz and Lisciki<sup>2</sup> as a means of reducing the resistance between the electrodes and thus increasing the stability of the instrument. This fact appears to be little known, and its limits of use are apparently much less known.

#### Equipment

The Beckman Model H-2 pH meter and the Leeds and Northrup pH Indicator were used for these observations. The glass-calomel electrode combination was used in all of the titrations. In addition the glass-silver:silver chloride electrode combination was also used when chlorobenzene, dioxane, and benzene were used as individual solvents.

#### Discussion

Glacial acetic acid was used as the solvent for the titration of aluminium oxinate,<sup>3</sup> salts,<sup>4</sup> and pyridine<sup>1</sup> with 0.1*N* perchloric acid. The instruments were reasonably stable and the use of lithium chloride did not appreciably improve their stability. Actually its use in these cases was undesirable, since the change in potential per increment of titrant near the inflection point of the potentiometric curves was much less when lithium chloride was used. The same results were observed for the use of lithium chloride when chlorobenzene<sup>1</sup> was used as the solvent for the titration of pyridine with perchloric acid. When the G-H mixture<sup>5</sup> was used as the solvent, lithium chloride had no effect on the stability of the instrument or the shape of the titration curves. The attempted titration of pyridine in inert solvents such as dioxane and benzene, with or without lithium chloride, failed.

The real usefulness of lithium chloride was found in the titration of weak acids with sodium methoxide in neutral or weakly basic solvents. In benzene-methanol solutions at a ratio of 3 : 1 or lower, the pH meters were stable due to the influence of the methanol. For the titration of acids such as benzoic or stearic in benzene-methanol solutions in a ratio of 4 : 1 or greater, the lithium chloride definitely increased the stability of the instruments. With the 8 : 1 benzene-methanol solution the instrument was extremely unstable, but stabilised when lithium chloride was added. Actually the instrument was stable enough to start a titration and obtain a reasonably good potentiometric curve with benzoic acid in 50 : 1 benzene-methanol solution titrated with sodium methoxide. However, titrations of these weak acids in pure benzene were not possible.

In these titrations, the change in potential per increment of titrant near the inflection point was also increased by approximately a factor of two. This may have been because the lithium chloride prevented the ionisation of the salt formed during the titration, thus reducing the common-ion effect

on the weak acid. In the titration of stearic acid a precipitate began to form shortly after the start of the titration (no precipitate formed in the absence of lithium chloride) which removed the common-ion effect on the weak acid.

The presence of lithium chloride also improved the stability of the instrument and increased the rate of change in potential per increment of titrant near the end-point when benzoic acid was dissolved in dimethylformamide and titrated with sodium methoxide.

The lithium chloride improved the stability of the pH meters using the glass-calomel electrode combination and caused an increase in  $\Delta E/\Delta V$  near the end-point when using solvent mixtures with high ratios of benzene to methanol, and dimethylformamide. It was of no value or was detrimental in acidic solvents such as glacial acetic acid.

E. L. GROVE

*School of Chemistry  
University of Alabama  
University, Alabama, U.S.A.*

**Summary**—The use of lithium chloride for improving instrument stability in non-aqueous potentiometric titrations is discussed, and its limitations are indicated.

**Zusammenfassung**—Der Gebrauch von Lithiumchlorid zur Erhöhung der Stabilität des Instrumentes bei potentiometrischen Titrationen in nichtwässrigem Medium wird diskutiert. Grenzen der Einsatzmöglichkeiten werden aufgezeigt.

**Résumé**—L'auteur discute l'utilisation du chlorure de lithium pour l'amélioration de la stabilité des instruments dans les titrages potentiométriques en milieu non aqueux, et indique ses limitations.

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### Determination of carbon disulphide by chloramine-T

(Received 12 April 1960)

It has been shown that chloramine-T brings about a rupture between S—S and N—S linkages and oxidises all the sulphur quantitatively to sulphuric acid.<sup>1</sup> It was of interest to find out whether the oxidant can break a C—S linkage and bring about a similar oxidation. Experiments carried out by the present authors indicated that carbon disulphide, after treatment with alcoholic potash, could easily be oxidised by chloramine-T quantitatively converting all the sulphur to sulphuric acid. This oxidation is described as an analytical procedure in this paper.

#### EXPERIMENTAL

**Chloramine-T:** About 15 g of a recrystallised sample of pure chloramine-T were dissolved in 1 litre of water and stocked in an amber coloured bottle. The solution was standardised iodimetrically in an acid medium as described earlier.<sup>2,3</sup>

**Carbon disulphide:** A weighed amount (about 0.200 g) of pure redistilled carbon disulphide, free from elemental sulphur, taken in a sealed thin-walled glass bulb, was broken under 5–6 ml of freshly prepared alcoholic potash (10%) in a stoppered conical flask. The carbon disulphide, on reacting with alcoholic potash, gave the corresponding amount of potassium ethyl xanthate. The yellowish white product was dissolved in water and filtered to remove the glass pieces, and the solution was made up in a standard volumetric flask (250 ml.). Aliquots of this solution were used for oxidation reactions.

### Procedure

An aliquot portion of the xanthate (carbon disulphide) solution (about 5 ml) was added to a known excess of acidified chloramine-T solution (20 ml of 0.1*N* chloramine-T with 10 ml of 2*N* HCl) in a stoppered conical flask. To the mixture was added 10 to 25 ml of ethyl alcohol. The reactants in the flask were set aside for at least half-an-hour. At the end of this period, 10 ml of 10% potassium iodide solution were added and the liberated iodine was titrated against thiosulphate solution. The amount of chloramine-T consumed by the xanthate was thus obtained from the titre value and the number of equivalents of the oxidant required per mole of carbon disulphide was calculated. With freshly prepared alcoholic potash no blank correction was necessary.

The analytical values were found to be reproducible and the results of a few representative experiments are given in Table I.

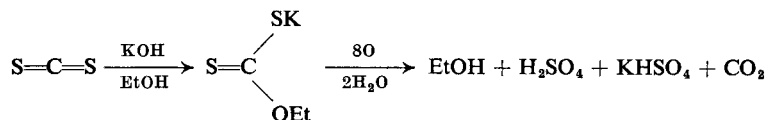
TABLE I. OXIDATION OF CARBON DISULPHIDE BY CHLORAMINE-T

Expt. No.	Amount of carbon disulphide taken $\times 10^6$ , moles	No. of equivalents of oxidant consumed $\times 10^6$	No. of equivalents of oxidant per mole of carbon disulphide	Oxidant
1	5.367	74.86	13.94	Chloramine-T
2	5.590	78.20	13.99	Chloramine-T
3	10.61	149.60	14.10	Chloramine-T
4	11.26	11.20	0.995	Iodine
5	11.26	11.20	0.995	Iodine

Similar experimental results were obtained when the reaction was carried out at 50° for 1 hour by immersing the flask containing the reactants in a hot water bath, except for a small correction in the blank experiment (about 0.5 ml).

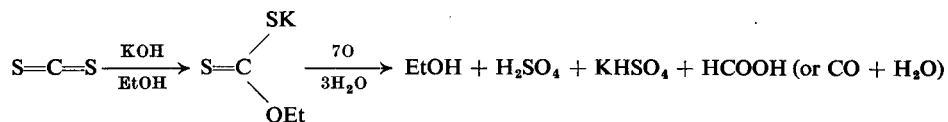
### RESULTS AND DISCUSSION

It can be seen from the results quoted in Table I that 14 equivalents of chloramine-T are consumed by 1 mole of carbon disulphide. If the carbon disulphide were to be oxidised completely, resulting in the conversion of carbon to carbon dioxide and sulphur to sulphuric acid, it would take 16 equivalents of oxidant, according to the equation:



Ethyl alcohol is regenerated and is not oxidised by chloramine-T under the experimental conditions as described in the present investigation.<sup>1</sup>

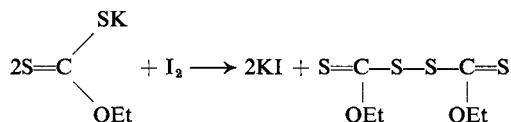
As observed in the actual experiments carried out, only 14 equivalents of the oxidant are consumed by carbon disulphide converted to the form of xanthate. The probable products of oxidation may, perhaps, be sulphuric acid and formic acid or carbon monoxide. Formic acid or its salt are not oxidised further by chloramine-T. Such an oxidation can be represented by the equation



The fact that formic acid was not oxidised further to carbon dioxide and water by chloramine-T was established by separate experiments. Aliquots of chloramine-T, with and without formic acid (2 ml), when standardised against thiosulphate, gave the same titre.

It is well known that xanthic acid is liberated on acidifying a xanthate, and the free acid easily decomposes into ethyl alcohol and carbon disulphide. Carbon disulphide is found to be oxidised by hypochlorous acid, alkali hypochlorite or alkali hypobromite. The resulting solution was observed to contain sulphide, sulphate, formate and carbonate<sup>4,5</sup> but no quantitative data are available as the reaction appears to be too complicated. Chloramine-T resembles hypochlorite in many oxidation reactions. The procedure resulting from the present investigations offers a better and a more accurate method of determination of carbon disulphide, since 14 equivalents of the oxidant are consumed for every mole of carbon disulphide.

Iodimetric oxidation of xanthate in neutral solution to dixanthogen is a quantitative reaction which at present is used quite generally for the determination of xanthate or carbon disulphide.<sup>6,7</sup> The oxidant consumed in such a reaction is only 1 equivalent for 1 mole of xanthate or carbon disulphide, since the oxidation proceeds to the stage of formation of dixanthogen according to the equation:



Experimental results obtained for the determination of xanthate by this method are also given in Table I.

The dixanthogen produced in the above reaction remains in suspension since it is insoluble in water, and further oxidation does not take place with iodine. However, in the homogeneous medium produced by the addition of the alcohol, chloramine-T brings about further oxidation of dixanthogen. The chloramine-T method has therefore several advantages over the conventional methods.

Chloramine-T has been suggested<sup>8</sup> as a suitable oxidant for xanthates, the titrations with chloramine-T being taken to a bleached end-point, with methyl red as indicator for clear solutions and indigo carmine for coloured solutions. In this oxidation Afanasev observes that 1 equivalent of chloramine-T is consumed per mole of xanthate. In the light of the present observation it is more convenient to treat the xanthate with excess of chloramine-T and determine the excess iodimetrically than to use direct titration of xanthate against chloramine-T.

The determination of carbon disulphide in an aqueous solution can also be carried out as accurately as by the method described by Bang and Szybalski.<sup>9</sup> For instance the solubility of carbon disulphide at 25° in water was found to be 203 mg per 100 g of saturated solution by the chloramine-T method. This compares favourably with the value reported in literature<sup>10</sup> (217 mg/100 g of saturated solution at 20° and 195 mg/100 g of saturated solution at 30°). It should be noted that for carbon disulphide in aqueous medium it is necessary to add a fairly large amount of alcoholic potash to convert it into xanthate. In the present experiment 5 ml of a saturated solution of carbon disulphide in water were treated with 20 ml of alcoholic potash.

*Acknowledgement*—The authors wish to express their grateful thanks to Prof. M. R. A. Rao for his keen interest in this work.

*Dept. of Inorganic and Physical Chemistry*  
*Indian Institute of Science*  
*Bangalore 12, S. India*

V. R. SATYANARAYANA RAO  
 A. R. VASUDEVA MURTHY

**Summary**—Carbon disulphide, on treatment with alcoholic potash, can readily be oxidised quantitatively by chloramine-T, converting all the sulphur to sulphuric acid. Fourteen equivalents of the oxidant are consumed for every mole of carbon disulphide. Since excess of chloramine-T may be determined iodimetrically, this reaction may be used for the determination of carbon disulphide. It may also be applied to the determination of xanthates.

**Zusammenfassung**—Schwefelkohlenstoff, in alkoholischer Kalilauge, wird leicht durch Chloramin-T oxydiert. Die Oxydation ist quantitativ und führt zur Bildung von Schwefelsäure wobei 14 Äquivalente Oxydant per Mol Schwefelkohlenstoff verbraucht werden. Da ein Überschuss von Chloramin-T leicht iodometrisch bestimmt werden kann, ist die Reaktion eine geeignete Grundlage zur Titration von Schwefelkohlenstoff. Auch Xanthate können auf diesem Wege bestimmt werden.



**Résumé**—Le sulfure de carbone, traité avec la potasse alcoolique, peut être facilement oxydé de manière quantitative par la chloramine T, tout le soufre étant transformé en acide sulfurique. Quatorze équivalents de l'oxydant sont consommés par chaque mole de sulfure de carbone. Comme l'excès de chloramine T peut être déterminé par iodométrie, cette réaction peut être utilisée pour le dosage du sulfure de carbone. Elle peut aussi être appliquée au dosage des xanthates.

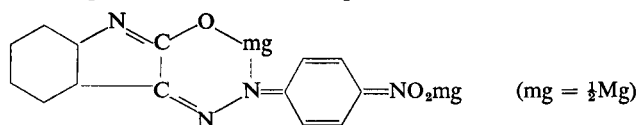
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## A selective spot test for isatin

(Received 11 April 1960)

It has been observed that a blue precipitate is formed by addition of the violet alkaline solution of isatin- $\beta$ -4-nitrophenylhydrazone to an aqueous solution of a magnesium salt. This reaction, which occurs also in ammoniacal medium, seems to be specific for magnesium ions.\* It is probable that the essential part of the blue product is the chelate compound where the enolised CO and NO<sub>2</sub> groups



of isatin and 4-nitrophenylhydrazine, respectively, react with magnesium. A chelate binding of this kind may also be established through chemical adsorption of the hydrazone on the surface of magnesium hydroxide or oxide leading to a colour lake. It is consonant with this assumption that moist Mg(OH)<sub>2</sub> or ignited MgO turns blue in contact with an alcoholic or ethereal solution of isatin- $\beta$ -4-nitrophenylhydrazone.

Due to the fact that this hydrazone reagent for magnesium is easily obtained by interaction of 4-nitrophenylhydrazine with isatin, a selective spot test for the latter can be based on the formation of the blue product. It may be expected that derivatives of isatin which condense with 4-nitrophenylhydrazone will behave like the parent compound.

**Procedure:** Heat, in a test tube, a small amount of the solid test material or a drop of its solution with 1 drop of an alcoholic solution of 4-nitrophenylhydrazine for 5–10 min. After cooling, add 1 drop of 10% sodium hydroxide and 1 drop of 1% magnesium nitrate solution. A positive response is indicated by the appearance of a blue precipitate. When the amount of isatin is less than 20  $\mu$ g, extraction with ether, to dissolve the excess nitrophenylhydrazine, is recommended.

**Limit of identification:** 0.5  $\mu$ g isatin.

The procedure given here also permits the detection of 2  $\mu$ g of 4-nitrophenylhydrazine after condensation with excess isatin.

**Acknowledgement**—We thank the Conselho Nacional de Pesquisas for financial support.

Laboratório da Produção Mineral  
Ministério da Agricultura  
Rio de Janeiro, Brazil

F. FEIGL  
D. GOLDSTEIN

**Summary**—Isatin may be detected by conversion to isatin- $\beta$ -4-nitrophenylhydrazone and reaction of the product with magnesium hydroxide to give a blue precipitate. The limit of identification of the test is 0.5  $\mu$ g isatin.

**Zusammenfassung**—Isatin kann nachgewiesen werden durch Überführung in Isatin- $\beta$ -4-nitrophenylhydrazon und Umsetzung dieses Produktes mit Magnesiumhydroxyd unter Bildung eines blauen Niederschlages. Die Nachweisgrenze ist 0.5  $\mu$ g Isatin.

**Résumé**—L'isatine peut être décelée par transformation en isatine-4- nitrophénylhydrazone et réaction du produit obtenu avec l'hydroxyde de magnésium pour donner un précipité bleu. La limite d'identification de l'essai est de 0,5  $\mu$ g d'isatine.

\* A paper on this subject will be presented by D.G. after finishing pertinent experiments.

## LETTERS TO THE EDITOR

### Quantitative oxidations by potassium ferricyanide

SIR:

WITH the enormous progress of analytical chemistry, reviews of its various fields become more and more important. It is very necessary, however, that these reviews should reflect correctly the progress in the branches of analytical chemistry with which they are concerned, and their present state. The paper by B. R. Sant and S. B. Sant in *Talanta*<sup>1</sup> repeatedly gives rise to misunderstandings, regarding which we feel it necessary to comment.

In the first part of the Review the authors mention that oxidations by ferricyanide are slow and incomplete, but that they can *generally* be accelerated by using osmium tetroxide as a catalyst. Here they refer to the work of K. Gleu. It is well known, however, that K. Gleu observed the catalysing effect of osmium tetroxide only in the case of the reaction between ferricyanide and arsenite. The general catalysing effect of osmium tetroxide was dealt with elsewhere<sup>2</sup> by the present author.

Determinations by ferricyanide are divided by Sant and Sant into two groups, direct and indirect measurements. They have erroneously classified methods recently developed for the determination of various inorganic sulphur compounds<sup>3,4</sup> within the group of indirect determinations, although from papers published on this subject it is quite obvious that these are direct procedures. The Reviewers' statement regarding simultaneous determination of sulphur compounds is somewhat surprising. They write: "It is not clear if the above sulphur compounds can be analysed when present together." But in the short communication referred to<sup>3</sup> there is a clear description of the method applied to simultaneous determination of a variety of sulphur compounds.

The section dealing with the arsenometric determination of ferricyanide also calls for comment. The present author has described<sup>5</sup> the arsenometric determination of ferricyanide in presence of OsO<sub>4</sub>. But one of the reviewers, B. Suseela Sant, while referring to our earlier paper, has again described the arsenometric determination of ferricyanide<sup>6</sup>, with the only "modifications" that titration of ferricyanide is carried out, not in 2-3*N* NaOH, but in 1-2*N* NaOH concentration, and at room temperature instead of at 50°-55°. (The citation of the original paper is not correct.<sup>6</sup>)

The question arises as to whether such slight changes in a procedure warrant a fresh scientific publication, when the only result of the modification is that the rate of the reaction between ferricyanide-arsenite becomes *slower* and the determination requires *a longer time* (instead of 5-6 min, 15-20 min!). And yet the Reviewers<sup>1</sup> write that S. B. Sant first applied the catalytic effect of OsO<sub>4</sub> to the arsenometric determination of ferricyanide and that this procedure is "*simpler and more rapid*".

In conclusion, it may be noted that the determination of selenite by ferricyanide was first published, not by the present author, as the Reviewers state,<sup>1</sup> but almost simultaneously and, in fact, a few months earlier, by their compatriots, G. S. Deshmukh and M. G. Bapat.<sup>7</sup>

*Institute for Inorganic and Analytical Chemistry*  
*University of Szeged*  
*Szeged, Hungary*  
8 April 1960

F. SOLYMOSSI

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- <sup>6</sup> S. B. Sant, *Z. Analyt. Chem.*, 1959, 168, 112.
- <sup>7</sup> G. S. Deshmukh and M. G. Bapat, *ibid.*, 1957, 156, 273.

### Quantitative oxidation by potassium ferricyanide

SIR,

In the first part of our article,<sup>1</sup> only Gleu's reference was cited in order to draw attention to the fact that he, in 1933, first observed the catalysing effect of osmium tetroxide in ferricyanide oxidation. All other references, based essentially upon this observation, were cited at relevant places when considered necessary. In 1955, B. Suseela<sup>2</sup> reported in detail the use of osmium tetroxide as a catalyst to initiate and catalyse the quantitative oxidation of thiocyanate by ferricyanide to sulphate and cyanate. After Gleu's observation, this was perhaps the first report on the application of osmium tetroxide as a catalyst in quantitative ferricyanide oxidation. It is surprising that this article is not referred to in a note<sup>3</sup> by F. Solymosi in 1957.

The short communication<sup>4</sup> suggesting analysis of sulphur compounds when present together does not contain any data in support of the suggestion.

The paper by S. B. Sant<sup>5</sup> in 1959 on electrometric titration of ferricyanide by hydrazine sulphate and arsenic<sup>III</sup> was a result of her independent investigations carried out during 1953–1956 and formed a part of her Ph.D. thesis. This fact is clearly mentioned as a footnote in the article.<sup>5</sup> Naturally, the above work is not a "modification" of an earlier procedure. Furthermore, nowhere in the article<sup>1</sup> is it written or even implied that "S. B. Sant first applied the catalytic effect of OsO<sub>4</sub> to the arsenometric determination of ferricyanide." In our opinion, an electrometric titration, and for that purpose any titration, is undoubtedly more convenient and easier to manipulate if it can be performed at room temperature (25–30°).

In addition to the question raised by F. Solymosi "whether slight changes in a procedure warrant a fresh publication", a further question arises, *viz.*, whether the same work by the same author need be published in two different journals.<sup>6,7</sup>

Department of Chemistry  
University of Toronto  
Toronto, Ontario, Canada  
31 May 1960

BHARAT R. SANT  
(MRS.) SUSEELA B. SANT

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## BOOK REVIEWS

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**Contributi Teorici E Sperimentale Di Polarografia:** Volume IV. Pp. 361. Italian National Research Council, Rome, 1959. Lire 2,500.

THIS is the fourth volume of collections of papers on theoretical and experimental polarography, relating to work in the Polarographic Centre of the Italian National Research Council at the University of Padua and to the papers read at courses organised, at Bressionone, by the Polarographic Centre.

The introduction to the volume is by Professor Giovanni Semerano, the Director of the Polarographic Centre and is given in four languages (Italian, French, English and German). Twenty-one papers are included of which ten are in Italian, five in English, four in French and two in German. Each paper is accompanied by adequate summaries in the four languages.

The first paper, by Semerano, is a report on the work of the Polarographic Centre, from 1952 to 1958. It includes details of the diverse subjects on which research has been carried out and lists the resulting publications. The work of the Research Institutes and laboratories in Italy in the field of polarography is also mentioned. The second paper describes the well-known summer courses at Bressionone and gives lists of lecturers, participants and subjects discussed. The third paper is concerned with the purposes and organisation of the specialist schools of analytical and nuclear chemistry in relation to the summer course. The other papers deal with polarographic methodology and instrumentation, theoretical and kinetic studies, the behaviour of inorganic and organic substances and analytical applications. Finally, a number of surveys of advances in the application of polarography to various fields of analytical chemistry are presented.

The high standard of the work is assured by the presence in the list of authors, among others, of authorities such as Delahay (U.S.A.), Milner (Great Britain), Tirouflet (France) and Berg (Germany). All the original papers are good and, although there is little new in the reviews, they form a comprehensive collection. The book will be valuable to polarographers and should also prove a useful source of information for the non-specialist.

G. F. REYNOLDS

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**Trace Techniques using the K-1000 Cathode Ray Polarograph.** Volume I, by J. HETMAN, F.R.I.C. Pp. 48. Southern Instruments Limited, Camberley, Surrey. 25s.

THIS book is a collection of thirty methods, developed by the author, for the determination of trace constituents and impurities in a wide variety of materials. Both inorganic and organic substances have received attention. Many of the methods contain novel features and will be of wide interest. They include a number of importance to food and public analysts, such as the determination of vitamin C in fruits and fruit juices, saccharin in non-alcoholic drinks, arsenic in plant materials, lead (in the presence of copper) in cocoa, cyanide in water and iron in blood serum and liver. Metallurgical methods include the simultaneous determination of copper, nickel and cobalt impurities in iron, of copper, lead and zinc in manganese brass, copper and lead in leaded steel, lead in brasses and bronzes and the simultaneous determination of beryllium, aluminium and lead. Those of interest to the Plastics Industry are the simultaneous determination of fumaric and maleic acids, the determination of *p*-chlorobenzyl cyanide in a polymerisation mixture and trace metal impurities in P.V.C. There are also methods connected with explosive and pyrotechnic materials. A bibliography, giving some background information and references to methods of allied interest, is appended.

The methods are in note form giving, in addition to brief details of procedure and interpretation of results, essential information such as preparation of sample, base electrolyte, reference electrode employed and instrumental settings. Specimen polarograms are included in each case.

The methods are easy to follow and contain sufficient details for direct application. Inevitably, however, they suffer in some cases from the brevity of the treatment and a number of errors are present. The most persistent is the use of "basic" instead of "base" electrolyte, which is an error sometimes encountered in papers in English in foreign journals. The heading "Basic Electrolyte" is itself sometimes misleading, since the materials listed under it in several methods do not have this function. It is also incorrect to refer to the current flowing at the peak of the wave as the diffusion current, since the current flowing at this point is not diffusion controlled. It is more usual to use the term "peak current".

The book would have been improved by the inclusion of an Introduction, setting out objectives and giving brief details of the principles and advantages of cathode ray polarography. The omission of this is not important to the specialist, but it would have helped non-specialist and potential users to realise that this is not concerned with a new method involving special and exclusive principles, but is an advance in polarographic instrumentation offering greatly increased sensitivity and rapidity of operation. The very low limits of detection that can be achieved in the determinations described have not been emphasised in the methods themselves and can only be inferred from the specimen polarograms and concentrations of the calibration solutions.

No previous collection of general methods for a single polarographic technique has been published in this way and the author is to be congratulated on his initiative. It makes an important contribution to the literature of the subject and he will undoubtedly receive the compliment of imitation. The book will be of great value, not only to the specialist, but also to polarographers and analytical chemists in general, who will find much of the information applicable outside the present field.

G. F. REYNOLDS

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**Instrumental Methods of Chemical Analysis:** GALEN W. EWING. Second Edition, McGraw-Hill Publishing Company Ltd., New York, Toronto, London, 1960. 69s. Pp. 437. Name and subject indexes.

THE first edition of this book appeared in 1954; that a second edition has been called for is an indication that it has fulfilled its author's aim—"To describe the important analytical methods with sufficient theory for their comprehension and to present significant design features of representative apparatus." The book has been generally brought up to date and sections on nuclear magnetic resonance, spectroscopy, gas chromatography, electro-chromatography (*i.e.* electrophoresis) and electronic circuitry are now included.

The book is not intended as a reference work on "instrumental analysis." It is planned for use in colleges by "upper level undergraduates or first year graduate classes." For this reason each chapter includes a series of questions, mostly numerical in nature, and any student who conscientiously reads the text, carries out the recommended practical exercises and finally works through some of the problems will acquire a firm grip on the principles involved. The bibliography to each chapter gives some general guidance to the best monographs and reviews as well as a selection of references to original papers. This is a most useful feature, particularly in a students' book.

Not all the chapters are equally good and this is inevitable, as no one man can be expert in every field of instrumental analysis. The chapters on chromatography and ion-exchange, on extraction analysis, on polarimetry and on refractivity and optical dispersion are not up to the level of some of the others and one would guess the author's real interest is in the more complex types of apparatus. An unusual and commendable feature is a chapter on "General considerations in analysis"; this gives diagrams showing the relative sensitivity of various methods for a number of inorganic elements and very rightly includes "personal preference" as a valid factor in deciding what method to employ. The author does not sufficiently emphasise the fact—well-known to practising analysts, and often ignored by instrument men and other enthusiasts—that most of the methods described require

calibration by known samples. This is implicit in many of the descriptions, but students seldom see implications and have to be taught by their tutors or by painful experience. A fruitful cause of error and dispute is to calibrate (for example) an infra-red spectrophotometer with a mixture of pure compounds and then to use it for real samples that contain unknown amounts of unidentified absorbing material.

The re-issue in U.S.A. of this undoubtedly successful book raises once again, in the mind of an English reviewer, the difficult query "How much instrumentation should be taught to university chemical students?" When one considers a modern research establishment, in which almost every laboratory seems to have its quota of electronic instruments, one is inclined to say that every graduate ought to have some knowledge of the subject; perhaps the proper place for teaching it is in the physics course. No doubt the physics curriculum is as over-loaded as the chemistry curriculum but it seems appropriate to teach the use of instruments that simply make physical measurements as part of physics, even though their applications are so largely chemical. This would raise great difficulties in co-ordinating chemistry and physics courses, and from a practical point of view it might seem that the chemistry course is the proper place. The tutor or the professor in either case will presumably say "Yes, we can arrange to teach the elements of instrumentation, but what would you like us to leave out? Qualitative analysis, perhaps, or preparative organic chemistry, or the phase rule, or even the quantum theory; after all very few chemists ever make any use of it. But we shall have to leave *something* out."

Chemistry is still an experimental science for most practising chemists. Few of them in the early stages of their career succeed in deserting the laboratory entirely, and nowadays, when physical instruments have become tools of the trade as important as the burette or the crucible, it seems desirable that the graduate should know something about them. The reviewer has not the temerity to suggest what should be left out so that this new subject can be carried by the already over-loaded curriculum. (It is, of course, arguable that it is the business of the university to teach fundamentals and to leave the practical aspect in a secondary position.) For the post-graduate student who proposes to become an analyst, some acquaintance with the physical instruments available to him seems essential and he should have a real appreciation of the potentialities of these devices before he leaves college. In fact, he is probably wasting his time if his post-graduate course is in "pure" analytical chemistry. The classical methods are certainly not obsolete, but inevitably occupy a much smaller percentage of the analyst's time and thoughts than they did twenty or even ten years ago and any system of training must take this into account. The number of useful non-specialised textbooks is quite small. Professor Ewing's work is certainly among the number; it is perhaps inevitable that at the present time it should be somewhat expensive. It would be desirable in the British part of the English-speaking world if a similar book were available in which the instruments described are those currently in use in this country.

H. N. WILSON

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**Proceedings of the International Symposium on Microchemistry:** Held at Birmingham University, August 1958. Symposium Publications Division, Pergamon Press, London and New York, 1960. Pp. xxvi + 583. 100s.

THIS substantial volume contains the material of sixty-one papers which were presented at the Birmingham Symposium. These have been arranged into groups, although, as is stated, many papers could be included in more than one group. The headings of these groups are, qualitative micro-analysis, the decomposition of organic matter, weighing, the determination of elements and groups in organic materials, the determination of physical constants, biochemical methods, chromatography and ion-exchange, polarography, radiochemical methods, spectrochemical methods, titrimetry, complexometry, industrial applications of microchemistry, teaching, apparatus, and Great Britain's contribution to microchemistry.

The contents of the majority of the papers are of a high standard, as is to be expected, since many were contributed by leading world authorities in their respective fields. For example, the plenary lectures were delivered by Feigl, Lieb, Benedetti-Pichler and Belcher.

Most of the papers are of the review-type and contain much useful information for the reader. A few papers contain only minor original contributions to knowledge using methods which are already well-established, and it would have been better if these had been published in one of the many journals already available for this purpose. The discussions which follow the papers are also recorded in detail, and in certain cases these contribute considerably to the value of the report.

Many items of "stop press" news at the time of the symposium have since appeared in other journals and it is unfortunate that the Proceedings could only now be published, eighteen months after the symposium. This delay detracts somewhat from the value of the book.

However it is well-produced and the format good. It is relatively free from errors, although in a book of this size some are to be expected, and do occur. Mistakes which require correction are formula C on p. 12 where there is a trivalent carbon atom, "pertitanic acid" on p. 44 (last paragraph) which presumably should be replaced by "pervanadic acid", and Fig. 1 on p. 480 where material mentioned in the text is not shown in the figure.

The price is rather high for the pockets of many chemists, but, for those who wish to acquaint themselves with recent developments in microchemistry, the book is certainly recommended. It should prove to be a popular acquisition for most scientific libraries.

J. B. HEADRIDGE

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**Separation and Identification of Food Colours Permitted by the Colouring Matters in Food Regulations 1957.** Association of Public Analysts, Bank Chambers, 16, Southwark Street, London S.E.1., England. Pp. vi + 31. 1960. 21s., postage 9d.

THE object of this monograph is to present the results of work carried out by a committee of Members of the Association of Public Analysts on the separation and identification of colours used in food-stuffs following the coming into force in Great Britain of the "Colouring Matter in Food Regulations 1957". Before the introduction of this legislation manufacturers were at liberty to use any colouring matter provided it was not prohibited by the Public Health (Preservatives etc. in Food) Regulations, 1925 to 1953 or contravened the provisions of sections 1 and 3 of the Food and Drugs Act, 1938. The new legislation restricts food manufacturers to a list of specified colours and thus imposes on Public Analysts and others the task of examining large numbers of samples of food containing single colours or mixtures of colours.

The general scheme of analysis proposed consists of extraction of the colour, separation of the colours if more than one is present, and finally, identification.

Although foods vary in nature it has been possible to divide them into four groups as far as the preliminary treatment to extract the colouring matter is concerned. A table containing the results of examining 368 foodstuffs shows that 49.7% contained one added colour, 42.7% two colours and 7.6% three or more colours. As the permitted water soluble colours are all acidic they are extracted on wool from acid solution. They are then stripped from the wool and finally separated by paper chromatography. Identification of the recovered colours is accomplished by chromatography, spectrophotometry, or chemical means.  $R_F$  values of the water soluble colours in a series of six solvents are given. Absorption curves of all the permitted colours are collected together at the end of the volume.

A separate section is devoted to the two oil-soluble colours: oil Yellow GG and oil Yellow XP.

This is a book which can be thoroughly recommended to all those concerned in the examination of colouring matter in food, and the methods outlined will no doubt rapidly become standard. The book is also likely to be of interest to a wider field of readers outside the food industry.

The standard of production is on the whole good, the illustrations and absorption curves are clear, but as the book will undoubtedly find its way to the laboratory bench it is unfortunate that the binding has not been made more robust to stand up to the hard wear it will receive.

A. J. HOWARD



**Automatic Titrators.** J. P. PHILLIPS. Academic Press Inc., New York, 1959. Pp. viii + 225. \$6.00.

AUTOMATIC analytical techniques for application in the laboratory and on the production plant, have made tremendous strides in the past 10 years. "Chemists of talent and originality can hardly fail to profit from the freedom from routine chores afforded by automatic instruments of all kinds." This quotation is from this excellent book on automatic titrators; it is a most readable review of their development up to 1958. The approach used is that of a chemist and the emphasis is on the performance and use of titrators and on instruments that are either simple or readily obtainable.

After a brief introduction, concerned mainly with the significance of automatic titration methods, the general considerations of titrator design are discussed in some detail. Backed by many references, this section of the book is factual and covers types of burette, instrumental indicators, recorders and controllers.

Sections then follow on potentiometric, amperometric, conductometric, photometric and coulometric titrators. Although the latter could have been placed in any of the other categories, according to which indication technique was used, the author has wisely treated them separately. Ideally suited to automation, coulometric titrators are now rapidly coming to the fore.

In dealing with fully automatic and continuous titrators the author is labouring under the disadvantage of the inadequacy of literature coverage. It is difficult to obtain practical evaluations of the majority of commercial titrators because they have not been in general use long enough. Thus, the Technican Auto-Analyser is dismissed in 9 lines of script. It is known in Great Britain that, particularly in biochemical laboratories, this instrument is proving a boon, saving both laboratory space and labour. This section, therefore, tends to be a recital of information published by the manufacturers, which the author rightly admits has obvious disadvantages.

A chapter describing commercially available titrators with a list of applications completes the survey.

The book provides a concise account of the subject and, being fully referenced, should find a ready market amongst forward-thinking analysts and those who employ them and have to "foot the bill." As the author points out, obsolescence in automatic titrators is exceedingly rapid at the present time, so that some parts of the book will soon be out-dated. Nevertheless, the book gives a worthwhile grounding on the subject.

R. M. PEARSON

## NOTICES

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### The following meetings have been arranged:

*Wednesday 22 June 1960: Society for Analytical Chemistry, Microchemistry Group. London Discussion Meeting on The Direct Determination of Oxygen. "The Feathers", Tudor Street, London, E.C.4. 6.30 p.m. Discussion will be opened by Mr. D. W. WILSON, M.Sc., F.R.I.C.*

*Wednesday-Friday 12-14 October 1960: Oak Ridge National Laboratory: Fourth Conference on Analytical Chemistry in Nuclear Reactor Technology and First Conference on Nuclear Reactor Chemistry.*

The Oak Ridge National Laboratory has announced that a combined meeting will be held at Gatlinburg, Tennessee, on October 12, 13 and 14, 1960, which will include the Fourth Conference on Analytical Chemistry in Nuclear Reactor Technology and the First Conference on Nuclear Reactor Chemistry.

The general theme of that portion of the meeting pertaining to analytical chemistry will be instrumentation and methods for the determination of minor and trace components in nuclear fuels, coolants, moderators or related materials. Specific sessions are planned on advances in methods for the analysis of  $UO_2$ -base fuels and on in-line instrumentation and methods for the analysis of gas and liquid streams in reactors and test devices.

The contribution of papers pertaining to these or closely related subjects is solicited. Improvements or new concepts in instrumentation or in methods of chemical analysis are especially sought. Theoretical or review papers on topics within the scope of the agenda may, however, be of equal interest and will be given careful consideration.

To facilitate the preparation and the distribution of the programme well in advance of the meeting and compilation of abstracts for use at the conference, authors are requested to submit abstracts of about 500 words not later than August 1, 1960, and to indicate the time, not to exceed 25 minutes, required for presentation of their paper.

The Proceedings of the Fourth Conference on Analytical Chemistry in Nuclear Reactor Technology will be published. Manuscripts must be submitted at the time of the conference in order to be included in the published Proceedings.

Enquiries concerning the meeting in general and communications relative to the analytical chemistry section, including the submission of abstracts, should be addressed to: C. D. SUSANO, Oak Ridge National Laboratory, P.O. Box Y, Oak Ridge, Tennessee.

For information concerning accommodation or for reservations, write to: Reservation Services, Chamber of Commerce, Gatlinburg, Tennessee.

The tentative programme for the analytical chemistry section of the conference is:

#### *Wednesday 12 October*

*Morning—Activation and Non-destructive Methods of Analysis*

*Afternoon—Radiochemical Analysis, including Applications of Tracers*

#### *Thursday 13 October*

*Morning—Continuous Analysis of Radioactive Liquid and Gas Streams*

*Afternoon—Non-radiochemical Methods for Trace Analysis of Reactor Materials*

#### *Friday 14 October*

*Morning—Analysis of Diverse Reactor Fuels and Fertile Materials*

*Afternoon—Application of Analytical Chemistry in Preparation, Evaluation and Use of  $UO_2$ -Base Fuels*

*Monday-Saturday 24-29 April 1961: Hungarian Chemical Society: Analytical Congress.*

The Analytical Section of the Hungarian Chemical Society, sponsored by the Hungarian Academy of Sciences, has arranged an Analytical Congress, with international participation, to be held from April 24 to 29, 1961, in Budapest.

The lectures will comprise the whole field of analytical chemistry. Plenary and section lectures will be delivered for 4 days. The sections will be organized according to papers received. Papers in any language will be accepted, although it is desirable to use English, Russian, German or Hungarian. Registration of plenary and short papers with the Organising Committee is requested not later than September 15, 1960.

In order to proceed with arrangements for the Congress, the Organising Committee requests registration of attendance—without any obligation—to be made not later than July 1, 1960.

A more detailed programme of the Congress will be available probably in October, together with details of accommodation, excursions, social events. After the Congress visitors will have the opportunity of touring Budapest and its surroundings and of visiting Lake Balaton.

All correspondence should be addressed to the Secretariat of the Hungarian Chemical Society, Budapest, V., Szabadsag ter 17, Hungary.

The B.S.I. News announces the following new British Standards:

*B.S. 1016: The analysis and testing of coal and coke: Part 14 (preliminary statement). The analysis of coal ash and coke ash. (Ref. PD 3714). Included in all copies of B.S. 1016: Part 15. (Gratis)*

*B.S. 1016: The analysis and testing of coal and coke: Part 15: 1960. Fusibility of coal ash and coke ash. This deals with the determination of the deformation temperature, the hemisphere temperature and the flow temperature on samples of coal ash and coke ash. (Price 4s. 6d.)*

*B.S. 1428: Microchemical apparatus: Part D3: 1960. Micro-nitrometer (Pregl type). The micro-nitrometer specified is intended for use with the micro-Dumas nitrogen combustion train specified in B.S. 1428: Part A2. Full dimensions are specified, with tolerances given in some cases and "normal working tolerances" specified for the remainder. A porcelain stand and a potassium hydroxide leveling vessel with a porcelain support suitable for use with the nitrometer are described in one appendix: a stopcock leakage test procedure and notes on the method of use of the apparatus are given in other appendices. Detailed diagrams are provided for the nitrometer and ancillary equipment. (Price 4s.)*

*B.S. 1428: Microchemical apparatus: Part HI: 1960. Weighing vessels for microchemical analysis. This specifies five types of glass vessel: three sizes of weighing bottles with ground stopper, a weighing pig with ground cap, long-handled weighing tubes with and without ground cap, and a weighing tube with two ground caps. Details are given of construction (fully dimensioned drawings), finish and maximum weights. (Price 3s.)*

*B.S. 1728: Methods for the analysis of aluminium and aluminum alloys: Part II: 1960. Method for the determination of silicon (perchloric acid method). This specifies reagents required, recommended methods of samplings, and analytical procedure, for the determination of silicon in alloys having a silicon content from 0.1% to 24% or over. (Price 3s.)*

## PAPERS RECEIVED

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- A critical review of methods of isolating and separating the six platinum metals.** F. E. BEAMISH. (2 April 1960).
- New redox systems—III: Indirect cerimetric determination of cobalt.** FRANTIŠEK VYDRA and RUDOLF PŘIBIL. (4 April 1960).
- Analytical uses of bromine chloride: Determination of hydroxylamine: Contributions to the bromic acid-hydrochloric acid reaction.** K. BURGER, F. GAIZER and E. SCHULEK. (4 April 1960).
- Cation-exchange studies of lead<sup>II</sup> on Dowex 50W-X8: Separation from mixtures.** SHRIPAD M. KHOPKAR and ANIL K. DE. (5 April 1960).
- Quantitative oxidations by potassium ferricyanide:** F. SOLYMOŠI. (8 April 1960).
- A specific spot test for isatin.** F. FEIGL and D. GOLDSTEIN. (11 April 1960).
- Estimation of carbon disulphide by chloramine-T.** V. R. SATYANARAYANA RAO and A. R. VASUDEVA MURTHY (12 April 1960).
- Simply designed safety pipette.** TSUTOMU MOMOSE. (19 April 1960).
- Scintillation radioautography of tritium-labelled compounds on paper chromatograms.** E. V. PARUPS, L. HOFFMAN and H. R. JACKSON. (23 April 1960).
- The sequential analysis of long-range fallout debris.** GEORGE A. WELFORD, WILLIAM R. COLLINS JR, ROBERT S. MORSE and DORIS C. SUTTON. (21 April 1960).
- Die chelatometrische Titration des Titans in Gegenwart von Niob und Tantal.** E. LASSNER und R. SCHARF. (23 April 1960).
- Chlorite as an oxidising agent in titrimetric analysis.** JERZY MINCZEWSKI and URSZULA GLABISZ. (23 April 1960).
- A new reducing agent: Reduction of vanadium<sup>IV</sup> and uranium<sup>VI</sup> with ferrous ion in catechol solution.** JOHN W. MILLER. (25 April 1960).
- Contributions au problème de la détermination du point d'équivalence—I: Une nouvelle méthode de calcul du point d'équivalence dans la titration linéaire.** CANDIN LITEANU et DUMITRU CÖRMÖŠ. (30 April 1960).
- Contributions au problème de la détermination du point d'équivalence—II: Une nouvelle méthode pour déterminer le coefficient réel d'asymétrie dans la titration potentiométrique.** CANDIN LITEANU et DUMITRU CÖRMÖŠ. (30 April 1960).
- Contributions au problème de la détermination du point d'équivalence—III: Une nouvelle méthode pour le calcul du point d'équivalence dans la titration potentiométrique.** CANDIN LITEANU et DUMITRU CÖRMÖŠ. (30 April 1960).
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## PUBLICATIONS RECEIVED

- The Radiochemistry of Cadmium.** JAMES R. DEVOE, U.S. Atomic Energy Commission, NAS-NS 3001, Jan. 1960. Pp. vi + 57. \$0.75.
- The Radiochemistry of Arsenic.** Harold C. Beard. U.S. Atomic Energy Commission, NAS-NS 3002, Jan. 1960. Pp. vi + 27. \$0.50.
- The Radiochemistry of Francium.** EARL K. HYDE. U.S. Atomic Energy Commission, NAS-NS 3003, Jan. 1960. Pp. vi + 34. \$0.50.
- Chromatographic Reviews, Vol. II.** Editor M. LEDERER. D. Van Nostrand Company, Ltd., London: Elsevier Publishing Company, Amsterdam, 1960. Pp. viii + 195. 46s.
- Oxidation-Reduction Potentials of Organic Systems.** W. MANSFIELD CLARK. 1960.

## 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. The essential contents of each paper should be briefly recapitulated in a summary at the beginning of the paper. This should be in the language of the paper,

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

4. Illustrations should be separated from the typescript of the paper and legends should also be typed on a separate sheet. Line drawings which require 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 lettering should be sufficiently large and bold to permit this reduction. The following standard symbols should be used on line drawings, since they are easily available to the printers:



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

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

<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.

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