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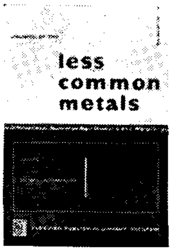

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A PRECISE MICROHETEROMETRIC DETERMINATION OF BISMUTH AS IODIDE WITH PYRAMIDON

A STUDY OF THE REACTION AND OF THE COMPOUNDS

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INTRODUCTION

Bismuth can be determined in the presence of potassium iodide by precipitation with alkaloids. Conversely, alkaloids can also be precipitated by the soluble bismuth iodide anion complex. The composition of the insoluble compound generally cited in the literature is $RN.BiI_4$. Analogous insoluble compounds are also obtained with the CNS^- ion instead of iodide. The use of this kind of compound for analytical purposes is very extensive[1]. Although the reactions concerned are very sensitive, they do not allow the determination of traces of metals in the presence of very large excesses of foreign metals. In addition, the insoluble compounds obtained are often influenced by foreign neutral salts present and the latter may even entirely prevent their precipitation. Some twenty years ago, SPACU and co-workers, as well as many other investigators, studied these compounds and their analytical applications extensively. Since then many organic reagents with specific properties have been found, and these are preferred to the above-mentioned methods. Although much work was carried out on the iodide and thiocyanate methods, the published information suffers from an excess of empirical detail and lacks a deeper insight into the formation and the structure of the compounds obtained. It is scarcely possible that these very insoluble compounds have structures as simple as presented for them in the literature.

The results of our studies are not limited to pyramidon, but concern many other complicated heterocyclic nitrogen compounds such as the alkaloids, etc., all of which act on the same basis.

Our aim was to make a more thorough investigation of the reactions concerned, to study the working conditions and to determine the various intermediate and final compounds which appear in the system. The following conclusions were reached as a result of our study: the reactions of iodo-complexes are very sensitive and specific for the determination of traces of certain metals, especially bismuth and mercury. The reactions always proceed quickly and the heterometric end-points obtained are accurate and unambiguous. The error was negligible, and the sensitivity of the reaction studied was of the same order of magnitude as with diethyldithiocarbamate[2-5].

As to the compounds which were obtained from the three components, their compositions depended on which of the components was used as titrant. Altogether more than ten compounds were traced and four final compounds were found. Each of these four could be used for the determination both of bismuth and of pyramidon.

Our investigation is being continued, and we are now testing different alkaloids as to the sensitivity and precision of their determination with a standard bismuth solution. The method may be of special interest for the determination of alkaloids, as in this case the question of interference by metals does not exist.

EXPERIMENTAL

The same apparatus and the same experimental conditions were observed as in previous heterometric investigations[2-5]. All titrations were carried out using a red filter. The reaction temperature was always 20°. The following reagents were used:

Pyramidon, Ph H, Dubeck and Dolder. A 0.02*M* stock solution was prepared in water and kept in a brown bottle in an ice box. More dilute solutions were obtained by diluting with water. These solutions were freshly prepared every three days. The 0.00125*M* solution was prepared twice a day.

Bismuth nitrate, $Bi(NO_3)_3 \cdot 5H_2O$, Baker's Analyzed. A stock solution of 0.05*M* was prepared by weighing the salt and diluting in nitric acid. The solution obtained was 1*N* in nitric acid. More dilute solutions were prepared from the stock solution and acidified water, so that in the final solutions the molar concentration of the nitric acid was twenty-two times that of the bismuth.

Potassium iodide, Baker's Analyzed. A 0.5*M* stock solution was prepared, from which more dilute solutions were always freshly prepared. All solutions were kept in dark brown bottles.

RESULTS

Many titrations were carried out in which either solutions of bismuth nitrate, or pyramidon, or potassium iodide were titrated into solutions containing the other two components. A selection of such experiments is compiled in three tables, while the courses of some titrations are presented in the figures. (The numeration is the same in the tables and in the figures.) It was found that the most suitable concentration for the analysis of bismuth was $\sim$0.0005*M* Bi. The same molar concentration was suitable for the determination of pyramidon. The concentration of potassium iodide in solution was not critical and there was no upper limit to its concentration. The concentration of potassium iodide in the titrated solution was 0.02*M*, but a 0.01*M* solution was sufficient. The molar ratio of bismuth to iodide was therefore 1 :40, and in some cases 1:20. The minimum amount of potassium iodide which was necessary for the reaction was found from titrations with potassium iodide as titrant. Evidently all three components acted stoichiometrically in all titrations. A minimum amount of nitric acid was also necessary to counteract the hydrolysis of bismuth. On the other hand, if more nitric acid was used, the sensitivity of the reaction was reduced and the end-point was no longer certain (see Table I, Expts. 13–15).

Pyramidon as titrant

In the absence of foreign metals

The compositions of the experiments and the results obtained are compiled in Table I and in Fig. 1. From the table the influence of neutral salts, various anions and halogenides can be seen.

Composition of precipitates. In almost all cases, heterometric curves with a critical maximum optical density point followed by a horizontal line were obtained. The critical point always occurred exactly at the molar ratio of 1 [Bi]: 1 [Py]. (The critical point was obtained at the intersection of the last part of the reaction curve with the horizontal line.) The error was mostly close to zero.

Supplements. The reaction studied was in general sensitive towards supplements and their amount was, therefore, restricted. In Table I the amounts cited are those which permitted the measurement of satisfactory titration curves. It was found that on the addition of small amounts of alcohol ($\leqslant$ 25–30%) the titration curve was steeper and the fixation of the end-point was generally easier. Therefore many titrations were repeated with some added alcohol. However, in a 50% alcohol solution (Expt. 5) no precipitation occurred at all. When the nitric acid was replaced by acetic acid (even in larger amount) the densities obtained were lower and no definite end-point was obtained. Acetic acid added to nitric acid had little influence (Expts. 17 and 18). The curve was also uninfluenced by moderate amounts of tartaric or citric acid added to the nitric acid (Expts. 29 and 31). However, in the presence of alcohol, citric and tartaric acid prevented precipitation (Expts. 30 and 32). Moderate amounts of orthophosphoric acid acted similarly to citric acid. But in the presence of larger amounts of phosphoric acid (0.5 ml M H_3PO_4) (Expts. 35–36) a *new final* critical point appeared at the molar ratio of 3 [Bi]:2 [Py]. As will be seen later, this point appeared in most of the regular titrations, but only as an *intermediate* point, further addition of Py

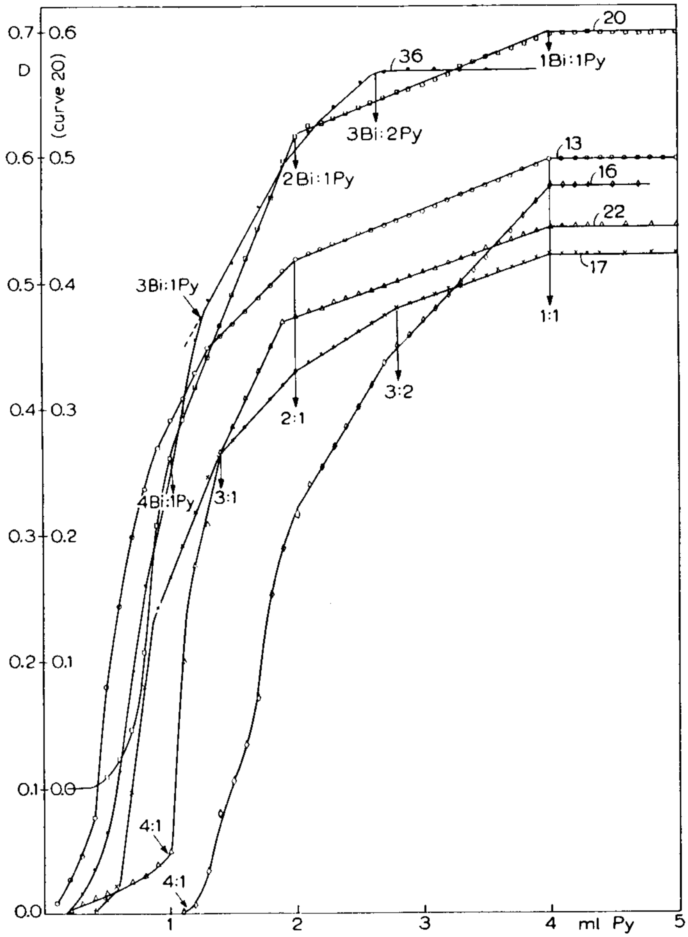


Fig. 1. Titrations of solutions of bismuth nitrate with pyramidon.

TABLE I

Composition: *a* ml $Bi(NO_3)_3$ + *b* ml KI + *c* ml supplements + water ad. 10 ml + *x* ml 0.00125*M* pyramidon (= titrant). Temp. = 20°. Fisher red filter.

Expt.	*Composition*	*Found* *Initial ppt. at ml*	*ml titrant at first max. p.*	*Max. optical density value*	*Titration time in min*	*% error*	*Remarks*
1.	4 ml 0.001*M* Bi + 1 ml *M* HNO_3 + 2 ml 0.05*M* KI	0.2	i 3.1 h	0.658	10	3.2	
2.	4 ml 0.001*M* Bi + 1 ml *M* HNO_3 + 2 ml 0.1*M* KI	0.4	i 3.20 h	0.565	12	0.0	
3.	4 ml 0.001*M* Bi + 1 ml *M* HNO_3 + 2 ml 0.05*M* KI + 3 ml alcohol	0.9	i 3.20 h	0.668	11	0.0	
4.	4 ml 0.001*M* Bi + 1 ml *M* HNO_3 + 2 ml 0.1 *M* KI + 3 ml alcohol	1.0	i 3.20 h	0.668	10	0.0	
5.	2 ml 0.002*M* Bi + 1 ml *M* HNO_3 + 2 ml 0.1 *M* KI + 5 ml alcohol						no ppt.
6.	4 ml 0.001*M* Bi + 1 ml *M* HNO_3 + 2 ml 0.3 *M* KI	2.6	3.3(?)h	0.163	11		
7.	4 ml 0.001*M* Bi + 1 ml *M* HNO_3 + 2 ml 0.05*M* KI + 1 ml alcohol	0.1	i 3.20 h	0.745	11	0.0	i.i.p. 1.8
8.	4 ml 0.001*M* Bi + 1 ml *M* HNO_3 + 2 ml 0.05*M* KI + 1 ml 0.1*M* NaCl	0.8	?	0.29	10		end-point uncertain
9.	4 ml 0.001*M* Bi + 1 ml *M* HNO_3 + 2 ml 0.05*M* KI + 1 ml 0.1*M* KBr	1.0	?	0.17	11		end-point uncertain
10.	4 ml 0.001*M* Bi + 1 ml *M* HNO_3 + 2 ml 0.05*M* KI + 2 ml 2*M* NH_4NO_3		?	0.09			
11.	4 ml 0.001*M* Bi + 1 ml *M* HNO_3 + 2 ml 0.05*M* KI + 1 ml 0.5*M* $(NH_4)_2SO_4$		?	0.05			
12.	4 ml 0.001*M* Bi + 1 ml *M* HNO_3 + 2 ml 0.05*M* KI + 2 ml *M* acetic acid	0.6	i 3.20 h	0.412	10	0.0	
13.	4 ml 0.00125*M* Bi + 1 ml *M* HNO_3 + 2 ml 0.1*M* KI	0.2	i 4.02 h	0.598	12	0.5	
14.	4 ml 0.00125*M* Bi + 3 ml *M* HNO_3 + 2 ml 0.1*M* KI	1.2	i 4.05 m	0.414	14	1.2	maximum point, then decrease
15.	4 ml 0.00125*M* Bi + 1.5 ml 2*M* HNO_3 + 0.4 ml 0.5*M* KI + 3 ml alcohol	$\sim$2.5	i 4.00 h	0.414	14	0.0	
16.	4 ml 0.00125*M* Bi + 1 ml *M* HNO_3 + 2 ml 0.1*M* KI + 3 ml alcohol	0.3	i 4.00 h	0.577	12	0.0	
17.	4 ml 0.00125*M* Bi + 1 ml *M* HNO_3 + 2 ml 0.1*M* KI + 2 ml *M* acetic acid	0.6	i 4.00 h	0.523	13	0.0	
18.	4 ml 0.00125*M* Bi + 1 ml *M* HNO_3 + 0.4 ml 0.5*M* KI + 1 ml 2*M* acetic acid + 3 ml alc.	1.7	i 4.00 h	0.553	12	0.0	
19.	4 ml 0.00125*M* Bi + 1 ml *M* HNO_3 + 0.4 ml 0.5*M* KI + 5 ml alcohol						no ppt.
20.	4 ml 0.00125*M* Bi + 1 ml *M* HNO_3 + 2 ml 0.1*M* KI + 0.5 ml *M* $(NH_4)_2SO_4$	0.6	i 4.02 h	0.598	12	0.5	

21.	4 ml 0.00125M Bi + 1 ml M HNO_3 + 0.4 ml 0.5M KI + 0.5 ml M $(NH_4)_2SO_4$ + 3 ml alcohol	2.3	i 4.00 h	0.475	12	0.0	
22.	4 ml 0.00125M Bi + 1 ml M HNO_3 + 2 ml 0.1M KI + 1 ml M NH_4NO_3	0.4	i 4.00 h	0.545	14	0.0	i.i.p. 2.1
23.	4 ml 0.00125M Bi + 1 ml M HNO_3 + 0.4 ml 0.5M KI + 1 ml 0.1M $(NH_4)_2SO_4$ + 3 ml alcohol	1.8	i 4.00 h	0.673	13	0.0	i.i.p. 2.6 and 3.4
24.	4 ml 0.00125M Bi + 1 ml M HNO_3 + 2 ml 0.1M KI + 1 ml 0.1M NaCl	0.4	i 4.00 h	0.648	12	0.0	
25.	4 ml 0.00125M Bi + 1 ml M HNO_3 + 0.4 ml 0.5M KI + 1 ml 0.1M NaCl + 3 ml alcohol	1.6	i 4.00 h	0.485	13	0.0	
26.	4 ml 0.00125M Bi + 1 ml M HNO_3 + 2 ml 0.1M KI + 1 ml 0.1M KBr	1.0	i 4.00 h	0.420	12	0.0	
27.	4 ml 0.00125M Bi + 1 ml M HNO_3 + 0.4 ml 0.5M KI + 1 ml 0.1M KBr + 3 ml alc.			0.097			
28.	4 ml 0.00125M Bi + 1 ml M HNO_3 + 0.4 ml 0.5M KI + 1 ml 0.05M KBr + 3 ml alc.	2	i 3.95 h	0.456	13	1.2	
29.	4 ml 0.00125M Bi + 1 ml M HNO_3 + 2 ml 0.1M KI + 3 ml 0.1M tartaric acid	0.8	i 4.00 h	0.553	12	0.0	
30.	4 ml 0.00125M Bi + 1 ml M HNO_3 + 0.4 ml 0.5M KI + 1.5 ml 0.2M tartaric acid + 3 ml alc.						no ppt.
31.	4 ml 0.00125M Bi + 1 ml M HNO_3 + 2 ml 0.1M KI + 3 ml 0.1M citric ac.	0.5	i 4.00 h	0.593	13	0.0	
32.	4 ml 0.00125M Bi + 1 ml M HNO_3 + 0.4 ml 0.5M KI + 1.5 ml 0.2M citric acid + 3 ml alc.						no ppt.
33.	4 ml 0.00125M Bi + 1 ml M HNO_3 + 1 ml 0.1M H_3PO_4 + 2 ml 0.1M KI	0.4	i 4.00 h	0.577	15	0.0	
34.	4 ml 0.00125M Bi + 1 ml M HNO_3 + 2 ml 0.1M H_3PO_4 + 2 ml 0.1M KI	0.3	i 4.00 h	0.745	13	0.0	
35.	4 ml 0.00125M Bi + 1 ml M HNO_3 + 2.5 ml 0.2M H_3PO_4 + 0.4 ml 0.5M KI	0.4	i 2.6 h	0.435	13		
36.	4 ml 0.00125M Bi + 2.5 ml 0.2M H_3PO_4 + 0.4 ml 0.5M KI	0.3	i 2.64 h	0.668	13		3 Bi:2 Py
37.	4 ml 0.00125M Bi + 1 ml M HNO_3 + 1 ml 0.2M H_3PO_4 + 0.4 ml 0.5M KI + 3 ml alc.	1.5	i 4.00 h	0.662	14	0.0	

Explanations: Py = Pyramidon; Bi = Bismuth nitrate; i.i.p. = intermediate intersection point at ml titrant; m.r. = molar ratio of [Bi]:[Py]; i = intersection point; h = horizontal maximum optical density line.

TABLE II

Composition: 4 ml 0.00125M Bi$(NO_3)_3$ + 1 ml M HNO_3 + a ml supplements + 2 ml 0.1M KI (or 0.4 ml 0.5M KI) + water ad. 10 ml + x ml 0.00125M pyramidon (= titrant). Temp. = 20°. Fisher red filter.

Expt. No.	*Supplements*	*% Bi*	*Found*					
			Initial ppt. at ml	*ml titrant at first max. p.*	*Max. optical density value*	*Titration time in min*	*% error*	*Remarks*
38.	1 ml 0.1M $Ca(NO_3)_2$	20.8	0.2	i 4.00 h	0.465	13	0.0	
39.	1 ml 0.1M $Ca(NO_3)_2$ + 3 ml alc.		1.6	i 4.00 h	0.409	13	0.0	
40.	1 ml 0.1M $Ba(NO_3)_2$	7	0.2	i 3.95 h	0.553	14	1.2	
41.	1 ml 0.1M $Mg(NO_3)_2$	30	0.3	i 4.00 h	0.423	13	0.0	
42.	1 ml 0.1M $Mg(NO_3)_2$ + 3 ml alc.		1.5	i 4.00 h	0.638		0.0	i 2.8; i 3.5
43.	1 ml 0.1M $Zn(NO_3)_2$	13.8	0.2	i 4.00 h	0.662	12	0.0	
44.	1 ml 0.1M $Zn(NO_3)_2$ + 3 ml alc.		1.4	i 4.02 h	0.770	13	0.5	
45.	1 ml 0.1M $Mn(NO_3)_2$	16	0.4	i 4.00 h	0.620	12	0.0	
46.	1 ml 0.1M $Mn(NO_3)_2$ + 3 ml alc.		1.6	i 4.00 h	0.561	12	0.0	
47.	1 ml 0.1M $Ni(NO_3)_2$	15.1	0.4	i 3.97 h	0.545	14	0.7	
48.	1 ml 0.1M $Ni(NO_3)_2$ + 3 ml alc.		1.6	i 4.00 h	0.585	14	0.0	
49.	1 ml 0.1M $Co(NO_3)_2$	15	0.5	i 4.00 h	0.557	12	0.0	
50.	1 ml 0.1M $Co(NO_3)_2$ + 3 ml alc.		1.5	i 4.00 h	0.502	12	0.0	i.i.p. 2.7
51.	1 ml 0.1M $Al(NO_3)_3$	28	0.4	i 4.00 h	0.678	13	0.0	
52.	1 ml 0.1M $Al(NO_3)_3$ + 3 ml alc.		1.6	i 4.00 h	0.577	13	0.0	
53.	1 ml 0.1M $Fe(NO_3)_3$ + 2 ml 0.1M H_3PO_4	15.9	0.3	i 4.00 h	0.516	13	0.0	i.i.p. 2.55
54.	1 ml 0.1M $Fe(NO_3)_3$ + 0.6 ml 0.33M H_3PO_4 + 3 ml alc.		2.1	i 4.00 h	0.42	13	0.0	i.i.p. 2.5
55.	1 ml 0.1M $Cr(NO_3)_3$	16.8	0.3	i 4.00 h	0.606	12	0.0	
56.	1 ml 0.1M $Cr(NO_3)_3$ + 3 ml alc.		1.45	i 4.00 h	0.620	12	0.0	
57.	1 ml 0.1M $Cd(NO_3)_2$	8.6	0.3	i 4.00 h	0.699	12	0.0	
58.	1 ml 0.1M $Cd(NO_3)_2$ + 3 ml alc.		1.8	i 4.00 h	0.745	12	0.0	

59.	1 ml 0.1*M* $UO_2(NO_3)_2$	4.2	0.3	i 4.00 h	0.782	12	0.0	
60.	1 ml 0.1*M* $UO_2(NO_3)_2$ + 3 ml alc.		1.8	i 4.00 h	0.763	12	0.0	
61.	1 ml 0.1*M* $CuSO_4$	14.1	0.2	i 4.00 h	0.776	12	0.0	
62.	1 ml 0.1*M* $Cu(NO_3)_2$		0.2	i 4.00 h	0.831	12	0.0	
63.	1 ml 0.05*M* $Hg(NO_3)_2$ (+ 4 ml 0.1*M* KI)	9.6	0.2	i 4.00 h	0.854	12	0.0	
64.	1 ml 0.05*M* $Hg(NO_3)_2$ + 3 ml alc.		1.8	i 4.00 h	0.678	13	0.0	
65.	1 ml 0.1*M* $ZrO(NO_3)_2$	10.2	1.0	i 4.00 h	0.585	28	0.0	
66.	1 ml 0.1*M* $ZrO(NO_3)_2$ + 3 ml alc.		1.8	c.i. 4.00 h	0.336	30	0.0	
67.	1 ml 0.1*M* $Ce(NO_3)_3$	7.0	0.2	i 4.00 h	0.745	11	0.0	
68.	1 ml 0.1*M* $Ce(NO_3)_3$ + 3 ml alc.		1.8	i 3.97 h	0.611	11	0.7	i.i.p. 2.45
69.	1 ml 0.1*M* $Th(NO_3)_4$	4.3	0.1	i 4.00 h	0.727	12	0.0	
70.	1 ml 0.1*M* $Th(NO_3)_4$ + 3 ml alc.		1.8	i 4.01 h	0.688	12	0.2	
71.	1 ml 0.1*M* $NaVO_3$	17.2	0.7	i 4.00 h	0.653	15	0.0	
72.	1 ml 0.1*M* $NaVO_3$ + 3 ml alc.		3.2	i 4.00 h	0.276	15	0.0	
73.	1 ml 0.05*M* Na_2MoO_4	18	0.8	i 4.03 h	0.553	13	0.7	
74.	1 ml 0.05*M* Na_2MoO_4 + 3 ml alc.		2.1	i 4.00 h	0.420	17	0.0	
75.	1 ml 0.05*M* Na_2WO_4	10.8	0.3	i 4.00 h	0.678	18	0.0	
76.	1 ml 0.05*M* Na_2WO_4 + 3 ml alc.		1.9	i 4.00 h	0.468	16	0.9	
77.	1 ml 0.05*M* $SnCl_2$	15.1	1.4	i 3.9 h	0.328	15	2.5	
78.	1 ml 0.05*M* $SnCl_2$ + 3 ml alc.							no ppt.

Explanations: i = intersection point; h = horizontal maximum optical density line; c = contact point; i.i.p = intermediate intersection point at ml titrant; Bi = Bismuth nitrate.

(= pyramidon) giving a final compound of composition 1:1. Evidently the phosphoric acid participated in the reaction through partial complex-formation with bismuth and stopped further reaction of bismuth with pyramidon. Whether a neutral salt or a specific anion in a given concentration disturbed the reaction, or even acted detrimentally or not, depended on the amount of bismuth being analyzed. This can be seen by comparing titrations with 4 ml $0.001M$ Bi (Expts. 8–11) and 5 ml $0.001M$ Bi (Expts. 20–28). Only in the latter case could titrations be carried out in the presence of nitrate, sulphate, chloride and bromide. *On increasing, even only slightly, the amount of bismuth in the titrated solution, it was possible to counteract the detrimental effect of neutral salts.* Thus, at the higher concentration of bismuth, chloride, present in a molar ratio of 1 Bi:20 Cl, was without influence (Expt. 24), while the bromide at this concentration reduced the maximum density value (Expt. 26). Large excesses of sulphate or nitrate also reduced the sensitivity.

Intermediates. On inspecting the titration curves of Fig. 1, it was interesting to establish that, in addition to the final critical point at 1 Bi:1 Py, more intermediate critical points were also obtained at definite molar ratios of bismuth to pyramidon. It must be emphasized that at all these points the ratios were always *higher* than 1 Bi:1 Py. In this investigation ratios less than 1:1 were never detected. It can, therefore, be concluded that such compounds do not exist. From the intermediate critical points it is evident that compounds of the following molar ratios of metal to pyramidon exist (in this work the ratios are always designated with the bismuth first).

$$4{:}1\uparrow\downarrow \xrightarrow{+\ \mathrm{Py}} 3{:}1\downarrow \xrightarrow{+\ \mathrm{Py}} 2{:}1\downarrow \xrightarrow{+\ \mathrm{Py}} 3{:}2\downarrow \xrightarrow{+\ \mathrm{Py}} 1{:}1\downarrow\downarrow$$

Probably the appearance of each of these points depended on the differences in solubility of the compounds concerned under the specific working conditions. Even intermediate compounds which were clear and certain depended on whether some alcohol was present or not. In the alcohol some of the intermediates were more soluble and therefore disappeared (compare Expts. 13 and 16). Thus the intermediate 4:1 was soluble in alcohol and ammonium nitrate. The compound 2:1 appeared in ordinary cases and in the absence of supplements (Expts. 13, 20 and 22). The existence of the above intermediates was also confirmed in the reverse titrations using bismuth nitrate as titrant (see below).

Foreign metals

There are probably no foreign metals which should be absent in the titrated solution, but in contrast to previous investigations their permitted concentrations were far lower. Generally the foreign cations could make up 80–90% of the total metal content in this investigation. In exceptional cases the percentage was even higher (see thorium). Probably it was not the foreign *metal* but the foreign *salt* which disturbed. The upper limits were not determined in each case, so that the percentage of bismuth may be much lower than that which is given in the table in special cases. Table II gives a compilation of such titrations. From the table it can be seen that *all titrations without exception were successful when the percentage of the foreign metal was* less *than 50%.* The error was always close to zero. In the presence of ferric iron the addition of phosphoric acid masked the iron entirely (Expts. 53 and 54). (In both experiments the intermediate 3 Bi:2 Py was also traced.) In all cases parallel titrations with some alcohol present were also carried out. These titrations are of special interest because they give the end-point of the final compound 1:1 directly as the solubility of the intermediates of compositions 4:1, 3:1 or 3:2 is increased in alcohol. However, in some cases the maximum optical density value was also reduced.

Bismuth nitrate as titrant

Working with similar compositions as in the basic experiments of Table I, reverse titrations were carried out using bismuth nitrate as titrant. These experiments are of special interest as similar titrations may be carried out in the presence of other complicated heterocyclic nitrogen compounds, alkaloids, etc. The results of such a study will be presented in a special report. The titrations of pyramidon with bismuth were very instructive because they provided a deep insight into the compositions of the intermediates which appeared in the system before the final compound was obtained. A compilation of selected experiments is presented in Table III and in Fig. 2. All titrations proceeded as smoothly as before. The titrations lasted 10–15 min and the end-point was always clear-cut with negligible errors. The numerical values of the intermediate critical points, as far as they could be safely taken from the titration curves, are also given in the table. The maximum optical density values obtained were proportional to the amount of pyramidon in solution. These titrations can therefore be used with the same success for the determination of the organic compound.

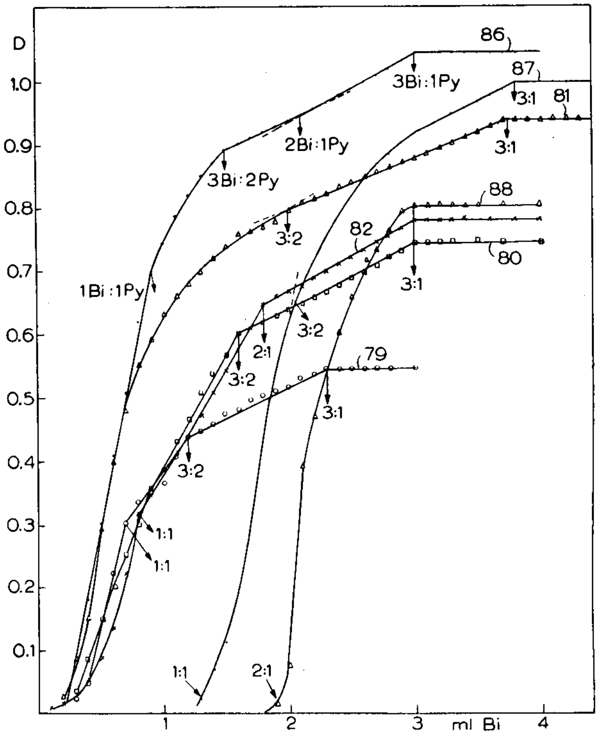


Fig. 2. Titrations of solutions of pyramidon with bismuth nitrate.

References p. 15

TABLE III

Composition: *a* ml *kM* Pyramidon (= Py) + 1 ml *M* HNO_3 + *b* ml *lM* KI [or *b* ml *mM* $Bi(NO_3)_3$ (= Bi)] + *c* ml alcohol + (9—*a*—*b*—*c*) ml H_2O + *x* ml *nM* titrant. Temp. = 20°. Filter: red. Titration time: 10–15 min.

Expt. No.	*Titrated solution contained*	*Titrant*		*Initial ppt. at ml titrant*	*Molar ratios of*	*Found*									
						1st critical point			*2nd critical point*			*Final crit. point*			*Error in final point*
		Name	*Molarity*			*At ml*	*Opt. density*	*Molar ratio*	*At ml*	*Opt. density*	*Molar ratio*	*At ml*	*Opt. density*	*Molar ratio*	
79.	3 ml 0.00125*M* Py + 2 ml 0.1*M* KI	Bi	0.005	0.2	Bi : Py	0.7	0.30	1:1	1.2	0.44	3:2	i 2.23 h	0.54	3:1	0.9
80.	4 ml 0.00125*M* Py + 2 ml 0.1*M* KI	Bi	0.005	0.1	Bi : Py							i 3.0 h	0.75	3:1	0.0
81.	5 ml 0.00125*M* Py + 2 ml 0.1*M* KI	Bi	0.005	0.2	Bi : Py				c 2.0	0.80	3:2	i 3.75 h	0.94	3:1	0.0
82.	4 ml 0.00125*M* Py + 4 ml 0.1*M* KI	Bi	0.005	0.2	Bi : Py				i 1.8	0.64	2:1	i 3.00 h	0.78	3:1	0.0
83.	5 ml 0.00125*M* Py + 1.2 ml 0.5*M* KI	Bi	0.005	0.1	Bi : Py				1.9	0.79	3:2	i 3.70 h	0.93	3:1	1.0
84.	6 ml 0.00125*M* Py + 0.8 ml 0.5*M* KI	Bi	0.005	0.1	Bi : Py				i 1.50	0.77	1:1	i 4.50 h	1.17	3:1	0.0
85.	4 ml 0.00125*M* Py + 2 ml 0.05*M* KI	Bi	0.005	0.2	Bi : Py	0.9	0.70	1:1	i 1.7	0.67	3:2	i 3.00 h	0.85	3:1	0.0
86.	4 ml 0.00125*M* Py + 2 ml 0.1*M* KI + 3 ml alc.	Bi	0.005	0	Bi : Py				c 1.50	0.89	3:2	i 3.00 h	1.05	3:1	0.0
87.	1.25 ml 0.005*M* Py + 2 ml 0.1*M* KI + 5 ml alc.	Bi	0.005	~1.3	Bi : Py	~1.3	i.ppt.p.	1:1	1.95	0.63	3:2	i 3.80 h	1.00	3:1	~1.0
88.	2 ml 0.0025*M* Py + 2 ml 0.1*M* KI + 5 ml alc.	Bi	0.005	~1.9	Bi : Py	~1.9	i.ppt.p.	2:1				i 2.95 h	0.80	3:1	~1.5
89.	2 ml 0.0025*M* Py + 1.6 ml 0.5*M* KI + 5 ml alc.	Bi	0.005									>5.0	0.0		
90.	2–4 ml 0.1*M* KI	Bi	0.005	>5.0								>5.0	0.0		
91.	4 ml 0.00125*M* Bi	KI	0.025	>5.0								>5.0	0.0		
92.	6 ml 0.0025*M* Bi	KI	0.04	>5.0								>5.0	0.0		
93.	4 ml 0.00125*M* Py + 4 ml 0.00125*M* Bi	KI	0.0166		Bi : I^-	1.2	i.ppt.p.	1:4				i 2.40 h	0.42	1:8	0.0
94.	2 ml 0.0016*M* Py + 4 ml 0.0025*M* Bi	KI	0.025	0.75	Bi : I^-	0.75	i.ppt.p.	1:2	c 1.6	0.72	1:4	i 3.20 h	0.83	1:8	0.0

95.	4 ml 0.00166*M* Py + 4 ml 0.0025*M* Bi	KI	0.025		Bi : I^-	0.55	i.ppt.p.	1:2				i 3.20 h	0.85	1:8	0.0
96.	3 ml 0.0033*M* Py + 4 ml 0.0025*M* Bi	KI	0.025		Bi : I^-	0.6	i.ppt.p.	1:2				i 3.20 h	0.72	1:8	0.0
97.	1 ml 0.01*M* Py + 4 ml 0.00125*M* Bi	KI	0.0166	0.6	Bi : I^-	0.6	i.ppt.p.	1:2				i 2.40 h	0.83	1:8	0.0
98.	2 ml 0.01*M* Py + 4 ml 0.00125*M* Bi	KI	0.0125	0.8	Bi : I^-	0.8	i.ppt.p.	1:2				i 3.20 h	0.88	1:8	0.0
99.	4 ml 0.01*M* Py + 4 ml 0.00125*M* Bi (+ 1.3 ml *M* HNO_3)	KI	0.0125	$\sim$0.8	Bi : I^-	$\sim$0.8	i.ppt.p.	1:2	$\sim$1.5	0.59	1:4	i 3.20 h	0.85	1:8	0.0
100.	3 ml 0.02*M* Py + 4 ml 0.00125*M* Bi (+ 1.5 ml *M* HNO_3)	KI	0.0125	$\sim$0.8	Bi : I^-	$\sim$0.8	i.ppt.p.	1:2	i$\geqslant$1.5	0.55	1:4	i 3.20 h	0.82	1:8	0.0
101.	4 ml 0.02*M* Py + 4 ml 0.00125*M* Bi (+ 1.5 ml *M* HNO_3)	KI	0.0125	0	Bi : I^-	0.75	i.ppt.p.	1:2				c 1.6 h	0.69	1:4	$\sim$0.0
102.	6 ml 0.02*M* Py + 2 ml 0.0025*M* Bi (+ 1.6 ml *M* HNO_3)	KI	0.0125	$\sim$0.7	Bi : I^-	$\sim$0.7	i.ppt.p.	1:2				i 1.55 h	0.68	1:4	
103.	4 ml 0.02*M* Py + 2 ml 0.0025*M* Bi (+ 0.5 ml 3*M* HNO_3) + 3 ml alc.	KI	0.0125		Bi : I^-	0.75	i.ppt.p.	1:2				c 1.6 h	0.68	1:4	$\sim$0.0
104.	4 ml 0.02*M* Py alc. + 4 ml 0.00125*M* Bi aq. (+ 0.5 ml 3*M* HNO_3) + 1 ml alc.	KI	0.0125	$\geqslant$1.5	Bi : I^-							i 1.6 h	0.50	1:4	
105.	4 ml 0.02*M* Py aq. + 4 ml 0.00125*M* Bi aq. (+ 1.5 ml *M* HNO_3)	KI	0.0063	$\sim$1.7	Bi : I^-	$\sim$1.7	i.ppt.p.	1:2				i 3.26 h	0.53	1:4	
106.	4 ml 0.02*M* Py aq. + 2 ml 0.0025*M* Bi (+ 0.5 ml 3*M* HNO_3) + 3 ml alc.	KI	0.0063	$\sim$1.7	Bi : I^-	$\sim$1.7	i.ppt.p.	1:2				i 3.20 h	0.63	1:4	
107.	4 ml 0.02*M* Py alc. + 4 ml 0.00125*M* Bi aq. (+ 0.5 ml 3*M* HNO_3) + 1 ml alc.	KI	0.0063	$\sim$2.6	Bi : I^-	$\sim$2.6						i 3.20 h	0.41	1:4	$\sim$0.0

Explanations: c = contact point; i = intersection point; h = horizontal maximum optical density line; i.ppt.p. = initial precipitation point; Bi = Bismuth nitrate; Py = Pyramidon.

Composition. It was interesting to establish that in these experiments the composition of the final compound (=↓↓) was always 3 Bi:1 Py. The critical point at the ratio of 1:1 was hardly observed at all in these experiments. The compounds which were normally deduced from the curves showed the following ratios of bismuth to pyramidon:

$$1:1\downarrow \xrightarrow{+\text{Bi}} 3:2\downarrow \xrightarrow{+\text{Bi}} (2:1)\downarrow \xrightarrow{+\text{Bi}} 3:1\downarrow\downarrow$$

The compound 2:1 appeared either in alcoholic solution or when more potassium iodide than usual was present (Expts. 82 and 88). The compound 3:2 was the most usual and clear intermediate.

Potassium iodide as titrant

At the beginning of this investigation an effort was made to find the optimum amount of potassium iodide necessary for the safe titration of bismuth. It was found that this amount was not critical as far as upper limits were concerned, as excesses of iodide were without influence. Therefore, most of our previous titrations were carried out with a constant amount of iodide. Here, our interest was to ascertain the minimum amount of iodide necessary for the reaction concerned, and to study the reaction with iodide in general. A selection of such titrations, their compositions and results are compiled in Table III and Fig. 3. Titrations with as high a concentration as 0.1*M* KI were carried out; the results of these experiments showed that in all cases after the formation of the final insoluble compound, a maximum horizontal density line was obtained and the end-point remained unchanged even upon the addition of a tenfold excess of iodide. The amount of bismuth which was present in the solutions was practically constant, while the molar ratio of [Bi]:[Py] was varied from 2:1 to 1:16.

The precision of the end-points of course depended on the concentration of potassium iodide used. Under our working conditions a minimum of 3 ml of titrant was necessary in order to obtain a precise end-point. Such titrations always gave end-points at the theoretically calculated ratio of either 1 Bi:4 I^- or 1 Bi:8 I^-. Therefore, *potassium iodide could be used with the same success as pyramidon for the titration of bismuth.* The sensitivity and the precision were of the same order with both titrants. It was interesting to establish that even when the molar amount of pyramidon was as low as $^1/_3$ of the molar amount of bismuth the end-point obtained was still normal (Expts. 94 and 95). The end-point occurred here, as in many other cases, exactly at the molar ratio of 1 Bi:8 I^-.

Composition. On varying the amount of pyramidon in the solutions between the limits of the ratio of [Bi]:[Py] from 3:1 to 1:12, the same end-point was always obtained at the ratio 1 Bi:8 I^- ↓↓. However, when the amount of pyramidon present was greater than the ratio of 1 Bi:12 Py, the final point of the titration occurred at the ratio 1 Bi:4 I^- (see Expts. 99, 102). The intermediate compounds obtained were at the following ratios of bismuth to iodide:

$$1:2\uparrow \xrightarrow{+I^-} 1:4\downarrow\downarrow$$

or:

$$1:2\uparrow \xrightarrow{+I^-} (1:4\downarrow) \xrightarrow{+I^-} 1:8\downarrow\downarrow$$

Sensitivity. With the same amount of bismuth, the maximum density values, and therefore the sensitivity of the reaction, were exceedingly high (at the ratio of 1 Bi : 8 I^-) when the molar amount of pyramidon in the titrated solutions was from twice to twelve times (critical concentration!) that of the bismuth. Within these concentrations the density was independent of the amount of pyramidon in solution. *It may, therefore, be concluded that these are the optimum conditions for a sensitive and precise titration of bismuth with potassium iodide.*

DISCUSSION

The impression gained from the results obtained is that the presentation of the insoluble compound concerned as $RN\cdot BiI_4$ only partly reflects the real structure and composition of the insoluble compounds studied by us. In gravimetric work the conditions are always uniform and therefore the above compound was always obtained. In contrast, in heterometry the working conditions were changed, as each of the three reacting components was used as titrant and studied separately. Altogether a series of intermediate compounds was obtained in addition to the *four* different *final* com-

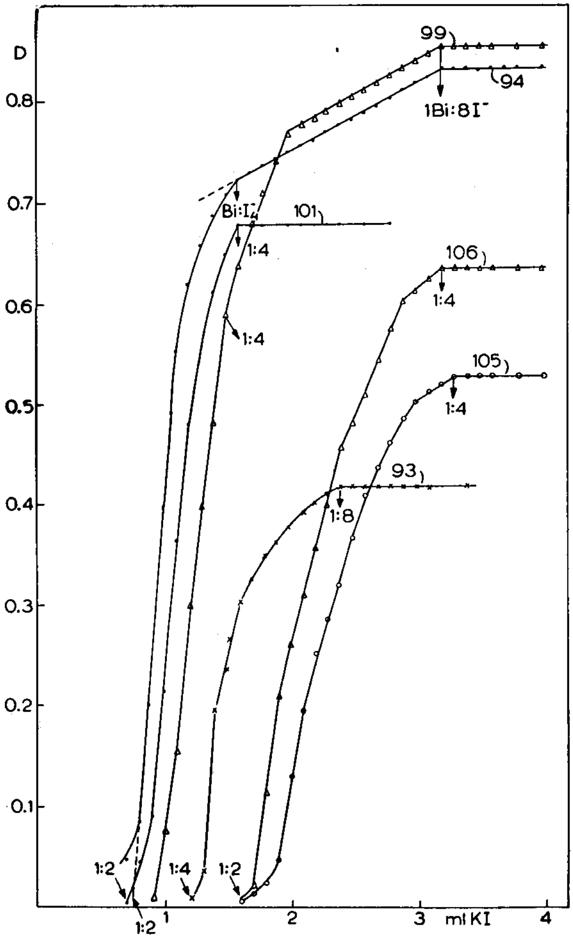
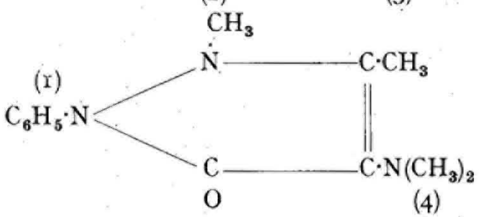


Fig. 3. Titrations of mixtures of pyramidon and bismuth nitrate with potassium iodide.

pounds which were studied. It was interesting to establish that the composition of all the final compounds was strictly constant and that each of them could be used with almost equal success for a precise determination of either bismuth or pyramidon. Amongst the intermediates traced a compound with the composition $Bi_3Py_2I_n$ was found. This compound must consist of at least two nuclei, each of which has the composition $PyBiI_m$, joined by a bismuth bridge. Therefore it may be deduced with certainty that the final compounds obtained are of quite complex structure. The same is the case with the anion $[BiI_8]^{-5}$ which was so often encountered by us. It is remarkable that the stoichiometry of the compounds is strictly maintained. On analyzing the conditions for the formation of the compounds having the compositions $PyBiI_n\downarrow\downarrow$ and $PyBi_3I_m\downarrow\downarrow$ it is seen (from the intermediates) that the latter was formed by the gradual addition of bismuth or better $[BiI_n]^{-(n-3)}$ to the former compound. Pyramidon which has the following structure



has three nitrogen atoms and it may well be that all three are saturated by the addition of $HBiI_n$. Conversely, on titrating with pyramidon, at the beginning of the titration there is a large excess of bismuth and only little pyramidon, and consequently the correct conditions for the formation of an intermediate $PyBi_3I_m$ exist. This intermediate as well as the other intermediates are finally transformed into the compound $PyBiI_n\downarrow\downarrow$. Therefore the results of titrations are compatible with the nitrogen content of the organic compound.

As to the composition of the bismuth-iodide complex, this may change with the organic base used. It is remarkable that, on titrating bismuth-pyramidon mixtures with a potassium iodide solution, the *final* compound only contained $[BiI_8]^{-5}$ anions even where the molar ratio was 1 Py to 3 Bi in solution. The anion complex $[BiI_8]^{-5}$ in which the coordination number of Bi^{+3} is 8 was often encountered in our work. Actually a high coordination number for bismuth is known although not satisfactorily explained. This high charge of the anion cannot be balanced solely by the organic base. It may, therefore, well be that H^+ ions coming from the mineral acid, which is present in the solution, participate in balancing the charge in the insoluble compound found. The question of whether an insoluble final compound with anion $[BiI_4]^-$ or $[BiI_8]^{-5}$ was formed depended (see Table III) on the excesses of pyramidon which were present in solution. If we accept that the anion $[BiI_8]^{-5}$ actually has the composition $[H_nBiI_8]^{-(5-n)}$, then it is plausible that high concentrations of organic base neutralize the H^+ ions and therefore destroy the above ion giving the more simple anion $[BiI_4]^-$. Another interesting fact is that no intermediate complexes between $[BiI_4]^-$ and $[BiI_8]^{-5}$ were found.

Analytical aspect

General

A red filter must be used. In each case the end-point of the titration coincides with the first maximum optical density point, after which a horizontal density line is obtained. The titration time is 10–15 minutes and the error is always close to zero.

Bismuth

Titration with pyramidon. Approximately *one* mg bismuth as nitrate in 10 ml solution can be determined by titration with a $\sim 0.00125M$ aqueous solution of pyramidon. The titrated solution must contain: 1 ml M nitric acid and 2 ml $0.1M$ potassium iodide. The analyzed solution may contain the following metals as cations or anions, which make up 80–90% of the total metal content: Ca^{+2}, Ba^{+2}, Mg^{+2}, Zn^{+2}, Mn^{+2}, Ni^{+2}, Co^{+2}, Al^{+3}, Fe^{+3}, Cr^{+3}, Cd^{+2}, $(UO_2)^{+2}$, Cu^{+2}, Hg^{+2}, $(ZrO)^{+2}$, Ce^{+3}, Th^{+4}, Sn^{+2}, VO_3^-, MoO_4^{-2} and WO_4^{-2}. The end-point lies exactly at the molar ratio of 1 Bi : 1 Py.

Titration with potassium iodide. Approximately *one* mg bismuth as nitrate in 10 ml solution can be determined by titrating with a $\sim 0.0125M$ aqueous solution of potassium iodide. The solution must contain 1–1.5 ml M nitric acid and 1–4 ml $0.01M$ pyramidon. The end-point lies exactly at the molar ratio of 1 Bi : 8 I^-.

Remark. If the amount of pyramidon is equal to 6 ml $0.01M$ pyramidon or more, the end-point lies exactly at the molar ratio of 1 Bi : 4 I^-. The first method is preferable.

Pyramidon

Titration with bismuth nitrate. Approximately 1.2 mg pyramidon in 10 ml solution which contains 1 ml M nitric acid and 2 ml $0.1M$ potassium iodide are titrated with a $\sim 0.005M$ aqueous bismuth nitrate solution. The end-point lies exactly at the molar ratio of 3 Bi : 1 Py.

SUMMARY

The reaction between iodide, bismuth and pyramidon and the composition of the compounds obtained were thoroughly studied.

At least four final insoluble compounds were obtained; each of them could be used with the same success for a precise determination of either bismuth or pyramidon. The molar ratios of bismuth to pyramidon found were 1 : 1 or 3 : 1; the ratios of bismuth to iodide were 1 : 4 or 1 : 8.

Analytical methods are presented for the determination of approximately *one* mg bismuth (or pyramidon) in the presence of 80–90% of the following cations or anions: Ca^{+2}, Ba^{+2}, Mg^{+2}, Zn^{+2}, Mn^{+2}, Ni^{+2}, Co^{+2}, Al^{+3}, Fe^{+3}, Cr^{+3}, Cd^{+2}, $(UO_2)^{+2}$, Cu^{+2}, Hg^{+2}, $(ZrO)^{+2}$, Ce^{+3}, Th^{+4}, Sn^{+2}, VO_3^-, MoO_4^{-2} and WO_4^{-2}.

The titrations always lasted 10–15 min and the error was practically negligible.

RÉSUMÉ

Les auteurs ont étudié la réaction entre un iodure, le bismuth et le pyramidon, ainsi que la constitution des composés obtenus. Par cette réaction, il est possible de doser avec précision soit le bismuth, soit le pyramidon.

ZUSAMMENFASSUNG

Es wird die Reaktion zwischen Jodid, Wismut und Pyramidon sowie die Zusammensetzung der Reaktionsprodukte untersucht. Mit Hilfe dieser Reaktion kann sowohl Wismut wie auch Pyramidon sehr genau bestimmt werden.

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THE DETERMINATION OF NITROGEN IN NITROCELLULOSE

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INTRODUCTION

The usual method of determining the nitrogen content of nitrocellulose involves the use of the nitrometer[1]. In this method the volume of nitric oxide liberated when a solution of nitrocellulose in sulphuric acid is shaken with mercury is correlated to the nitrogen content of the sample. Although capable of giving good results in the hands of an experienced operator, this method requires much practice and can be dangerous in the event of a nitrometer breaking during shaking.

In an effort to find an easier but equally accurate method, that of SHAEFER AND BECKER[2] was studied. This gave erratic results, however, and the source of error was not discovered. A procedure given by STALCUP AND WILLIAMS[3] was found to be more satisfactory, and after modification of the method, very precise results for both nitrocellulose and potassium nitrate were obtained. Moreover, the method was considerably more convenient for routine use than the nitrometer procedure.

EXPERIMENTAL

Briefly, STALCUP AND WILLIAMS' procedure[3] is as follows: The sample (about 0.3 g) is stirred with 10 ml of 98% sulphuric acid until dissolved. Within 20 min of the sulphuric acid addition, 10 ml of salicylic acid solution is added and the mixture allowed to stand for 10 min. Reduction is effected by refluxing for 1 min with 75 ml of $0.3N$ titanous chloride solution in an atmosphere of nitrogen. The solution is cooled and, while the inert atmosphere is maintained, the excess titanous ion is titrated with ferric ammonium sulphate using ammonium thiocyanate as indicator. A blank determination is run concurrently.

Using this procedure, the results obtained for a nitrocellulose sample containing 12.91% nitrogen (nitrometer) were unsatisfactory. Nine determinations gave a mean value of 12.99% nitrogen and a standard deviation of 0.11. In an attempt to locate the source of error, a homogeneous batch of nitrated salicylic acid was prepared and its nitrogen determined by reduction with titanous chloride. It was found that the time and temperature of the reduction were critical. When the STALCUP AND WILLIAMS' procedure was modified so that reduction was effected at room temperature for 30 min, the mean of 4 determinations was 9.68% nitrogen with a standard deviation of 0.021. Comparable figures for 12 determinations following the STALCUP AND WILLIAMS' method were 9.63 and 0.063.

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A fairly large excess of titanous chloride was required to obtain results agreeing with those of nitrometer determinations as shown in Table I.

TABLE I

EFFECT OF VOLUME OF TITANOUS CHLORIDE

Approximate excess of 0.4 N $TiCl_3$ (ml)	*No. of determination*	*Mean nitrogen content obtained (%*	*Standard deviation*
5	5	12.40	0.040
15	5	12.95	0.020
25	5	12.95	0.020

The nitrogen content according to nitrometer determinations was 12.94%.

As a result of this experiment the volume of titanous chloride (not less than 0.38*N*) was set at 50 ml and the weight of sample was reduced from 0.3 g to 0.20–0.22 g.

Factorial experiment

The errors in the method were finally assessed in a factorial experiment[4]. The factors investigated and their levels are summarized in Table II.

TABLE II

FACTORIAL EXPERIMENT

Factor	*Levels*	
A Amount of sulphuric acid added to sample	8 ml	12 ml
B Time of contact between sample and sulphuric acid	5 min	10 min
C Amount of salicylic acid solution added	8 ml	12 ml
D Time of standing with salicylic acid solution	10 min	20 min
E Reduction time with titanous chloride	15 min	30 min

The levels for factors A, C and D correspond approximately to STALCUP AND WILLIAMS' conditions and were chosen to determine how closely these conditions must be adhered to. The levels of factor E were based on the considerations mentioned above, while those for B were governed by the fact that low results were obtained in preliminary experiments if the nitrocellulose was allowed to remain in contact with sulphuric acid for as long as 20 min as indicated by STALCUP AND WILLIAMS.

The experiment, with a nitrocellulose sample of 12.90% nitrogen (nitrometer), showed that only factors B and E affected the result. The mean per cent nitrogen found was 12.853 and the significant factors had the following effects:

B. Increase in time of contact from 5–10 min resulted in a mean decrease of 0.073% nitrogen.

E. Increase in reduction time from 15–30 min resulted in a mean increase of 0.054% nitrogen.

A later experiment showed that it was necessary to increase the reduction time to 45 min in order to obtain accurate results.

In the method finally chosen, therefore, the levels of the non-significant factors (A, C and D) were set at the mean of the values shown in Table II, and the contact and reduction times were 5 and 45 min respectively. Under these conditions the mean result of 16 determinations, carried out on recrystallized reagent-grade potassium nitrate was 13.844% nitrogen, with a standard deviation of 0.012 (the theoretical value is 13.85% nitrogen). It was found to be necessary to dry the potassium nitrate for 2–3 h at 240° in order to remove last traces of water from the crystals.

To determine the suitability of the method for routine work, analyses were carried out by a different operator. A similar batch of potassium nitrate was used and ten determinations resulted in a mean of 13.830% nitrogen with a standard deviation of 0.014, showing that there is no significant operator bias.

Comparison with the nitrometer

To illustrate the reasonable agreement between the transnitration and the nitrometer methods, results using both methods are given in Table III.

TABLE III

COMPARISON OF NITROGEN CONTENTS OF NITROCELLULOSE SAMPLES OBTAINED BY THE NITROMETER AND TRANSNITRATION METHODS

Sample	*Nitrometer A (Operator A)*	*Nitrometer B (Operator B)*		*Transnitration (Operator C)*	
1	11.84	11.93	11.94	11.88	11.90
2	11.91	11.91	12.01	11.92	11.93
3	11.95			11.99	11.99
4	12.11			12.05	12.07

Precision of the method under routine conditions

Routine determinations of the nitrogen content of nitrocotton and guncotton were carried out in duplicate and the standard deviation was calculated from the differences between duplicates. The standard deviation of the results of an experienced operator was 0.012 (6 degrees of freedom) while for an operator who was new to the method the standard deviation was 0.023 (5 degrees of freedom). For comparison, the standard deviations of the results of two operators experienced in the nitrometer method were 0.025 (17 degrees of freedom) and 0.019 (10 degrees of freedom).

RECOMMENDED PROCEDURE

Reagents

Ferric ammonium sulphate (0.4*N*). 195 g analytical reagent-grade ferric ammonium sulphate and 25 ml 98% sulphuric acid per litre. Filter and standardise the solution by gravimetric determination of the iron content. Alternatively, standardise the solution by carrying out the determination with a material of known nitrogen content. A suitable material is analytical reagent-grade potassium nitrate which has been dried for 2–3 h at 240°.

Titanous chloride solution (0.4*N*). Mix 2500 g of B.D.H. titanous chloride solution (approximately 12.5%) and 250 ml of concentrated hydrochloric acid. Filter under a blanket of nitrogen, and make up to about 4 l in an aspirator which has been painted to protect the solution from light. Dispense the solution by means of a 50-ml burette, the aspirator, burette and a Kipp carbon dioxide apparatus being inter-connected so as to exclude all air. Adjust the strength of the solution to 0.39–0.41*N*, and standardise regularly by titration with ferric ammonium sulphate solution.

Ammonium thiocyanate solution. 200 g/l.

Salicylic acid solution. Dissolve 100 g of salicylic acid in a mixture of 900 ml 98% sulphuric acid and 100 ml glacial acetic acid. Although slight precipitation sometimes occurred on prolonged standing, the solution was still suitable for use.

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(It is stressed that the procedure given below must be rigidly adhered to in order to obtain precise results.)

Weigh accurately 0.2–0.22 g of sample into a dry 50-ml beaker. Add 10 ml of concentrated sulphuric acid and stir and crush the sample with a glass rod to aid solution. Exactly 5 min after the addition of the sulphuric acid, and even if the sample is not completely dissolved, add 8 ml of salicylic acid solution. Stir until solution is complete. Allow the solution to stand for 10–15 min and transfer into a 500-ml refluxing (reduction) flask fitted with gas inlet. Wash the solution remaining in the beaker into the reduction flask, using about 15-ml portions of distilled water. The total volume of water should be 45–50 ml. The water must be added very slowly otherwise darkening will occur. Cool the flask in running water and swirl carefully to mix the solution. Connect the gas inlet of the flask to a supply of nitrogen (*via* a wash bottle containing about 20 ml of water to act as a flow meter) and displace the air from the flask with nitrogen. Add exactly 50 ml of titanous chloride swirling occasionally during the addition. Allow the solution to stand for 45–50 min under a continuous flow of nitrogen. The nitrogen flow should produce a faint ripple on the surface. Add 1–2 ml of ammonium thiocyanate solution and titrate the excess titanous ion with ferric ammonium sulphate. Maintain the nitrogen flow continuously during the titration. Titrate slowly near the end-point. Wash down the walls of the flask and the tip of the burette with water and continue titrating until the first appearance of a permanent orange-red colour. Carry out a reagent blank under the same conditions as above. The nitrogen content of the sample is given by[3]:

$$\%\text{N} = \frac{\text{ml of TiCl}_3\text{ oxidised} \times \text{normality of TiCl}_3 \times 0.2335}{\text{weight of sample}}$$

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SUMMARY

A method for the determination of nitrogen in nitrocellulose has been developed. The sample is dissolved in concentrated sulphuric acid and a salicylic acid solution is added. The nitrosalicylic acid formed is reduced at room temperature with an excess of titanous chloride solution and the excess is estimated by titration with ferric alum. Statistically designed experiments were used to establish the conditions necessary for accurate results. The procedure is more rapid than the usual nitrometer method and gives results of high precision; *e.g.* on a mean result of about 13.8% nitrogen, the standard deviation is 0.014.

RÉSUMÉ

Une méthode est proposée pour le dosage de l'azote dans la nitrocellulose. L'échantillon à analyser est dissous dans l'acide sulfurique concentré. On ajoute une solution d'acide salicylique. L'acide nitrosalicylique formé est réduit par un excès de chlorure titaneux; cet excès est ensuite déterminé par titrage au moyen d'alun ferrique.

ZUSAMMENFASSUNG

Es wird eine Methode zur Bestimmung des Stickstoffs in Nitrocellulose beschrieben. Die Nitrocellulose wird in conc. Schwefelsäure gelöst und eine Lösung von Salicylsäure zugegeben. Die hierbei entstandene Nitrosalicylsäure wird mit einem Überschuss von Titan(III)chlorid reduziert und dieser Überschuss durch Titration mit einer Eisenalaunlösung bestimmt.

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SUR LA STABILITÉ THERMIQUE DES ÉTALONS ANALYTIQUES. VI*

CLÉMENT DUVAL

avec la collaboration technique de
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Poursuivant l'étude thermogravimétrique et spectrophotométrique des substances utilisables comme étalons en analyse volumétrique, nous présentons aujourd'hui nos résultats avec 12 nouvelles substances, à savoir: l'acide nitrilotriacétique, le thiosulfate de strontium, le nitrite de sodium, l'acide phosphomolybdique, le paraperiodate de sodium, le persulfate de potassium, le chlorure d'aluminium, le pyrosulfate de sodium, l'alun d'aluminium et d'ammonium, le sulfate de fer(II), le sel de Mohr, l'alun de fer ammoniacal.

Les courbes de thermolyse ont été réalisées comme d'habitude par voie photographique et par voie graphique, sur 200 mg environ de substance et avec une vitesse de chauffe de 300° par heure. Les spectres d'absorption infrarouge ont été enregistrés par la méthode des poudres (au besoin en les agglomérant avec un peu de vaseline) sur un spectromètre Perkin-Elmer 12C, équipé avec un prisme de sel gemme.

Acide nitrilotriacétique

L'acide nitrilotriacétique est parfaitement sec et se montre stable jusqu'à 286° (Fig. 1). La décomposition se produit subitement et le creuset est vidé complètement à 638°.

Le spectre infrarouge, à côté de la bande très forte du carboxyle à 1742 cm^{-1}, indique 722 (aF), 730 (aF), 745 (aF), 865 (F), 902 (TF), 966 (TF), 1010 (TF), 1074 (aF), 1206 (aF), 1238 (aF), 1335 (F) cm^{-1}.

Thiosulfate de strontium

Le produit qui nous a servi comme point de départ, cristallisé au-dessus de 50°, retient 1 molécule d'eau qui disparait très lentement entre 70 et 180° (Fig. 2), plus rapidement ensuite; il faut compter que le départ complet de l'eau n'est pas effectué avant 240° mais alors le sel se dissocie; du soufre se dégage et le palier sensiblement horizontal obtenu entre 350 et 507°, correspond à un mélange de sulfate, de sulfite et de sulfure en évolution. Au-dessus de cette dernière température, le gain d'oxygène devient important et l'on arrive au sulfate de strontium sans sulfure dès 700°. En conclusion, pour faire une liqueur titrée avec cet étalon, on ne dépassera pas 170° pour le séchage du sel.

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* Pour le cinquième mémoire de cette série, voir *Anal. Chim. Acta*, 16 (1957) 545.

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Le spectre infrarouge de ce sel avait déjà été examiné par DUVAL ET LECOMTE[1]. Dans la région de 6 à 15 μ, nous relevons les bandes très fortes: 1019, 1113 et 1166 cm^{-1}.

Nitrite de sodium

Le nitrite de sodium sec, blanc, non hygroscopique, extrait d'un flacon neuf, se montre rigoureusement stable jusqu'à 538°. Commence alors une décomposition lente se prolongeant jusque vers 750°, puis plus rapide entre 792 et 956° et vers 1000°, il reste l'oxyde Na_2O. Nous ne sommes donc pas d'accord avec OSWALD[2] qui indique 320° pour le début de la dissociation, ni avec RÂY[3] qui indique vers 500° une transformation en nitrate; le gain de poids correspondant n'est pas accusé sur notre courbe (Fig. 3).

Dans la région du sel gemme, ce sel donne une bande forte déjà connue pour 825 cm^{-1}; MILLER ET WILKINS[4] donnent 831 (m). Dans l'eau, nous trouvons la bande très forte 1240 et faible 1338 cm^{-1}.

Acide phosphomolybdique

L'acide phosphomolybdique (produit Merck) ne possède pas, comme l'on sait, un degré d'hydratation fixe quoique FINKENER[5] indique la composition $P_2O_5 \cdot 24MoO_3 \cdot 3H_2O + 58H_2O$. Le produit de départ contenait environ $36H_2O$. De son côté DUPUIS[6] a préparé un acide phosphomolybdique contenant 32 molécules d'eau. Parfois le produit de départ en contient un nombre supérieur à 58 molécules et sans aucun accident dans la courbe de thermolyse pour cette teneur en eau. Il en résulte que l'on ne peut pas peser cet acide tel qu'il sort du flacon. Toutefois, lorsqu'on le chauffe à 116°, on arrive à la composition $P_2O_5 \cdot 24MoO_3 \cdot 3H_2O$ qui se maintient jusqu'à 412°. Là commence la déshydratation et de 477 à 757° s'étend le palier du corps anhydre pour notre vitesse de chauffe. Alors commence la sublimation de l'anhydride molybdique qui s'effectue rapidement au-delà de 802°. On possède donc deux formes de pesée: produit à $3H_2O$ et produit anhydre, pour ce corps (Fig. 4).

Le spectre infrarouge réalisé sur poudre, avec le produit Merck à $36H_2O$ environ, nous montre une bande très large allant de 791 à 832 cm^{-1} et 5 bandes très fortes pour 899, 959, 982, 1061, 1626 cm^{-1}. L'interprétation en a déjà été donnée par DUVAL ET LECOMTE[7].

Paraperiodate de sodium

Ce sel de formule $Na_2H_3IO_6$, d'accord avec RAMMELSBERG[8], est anhydre et stable jusqu'à 207° où commence une décomposition lente donnant naissance à: de l'eau, de l'oxygène, de l'iodate, de l'iodure et de l'oxyde de sodium. Puis, au-dessus de 821°, l'iodate et l'iodure se subliment (Fig. 5).

Le spectre infrarouge ne nous a donné que des bandes faibles pour 761, 882, 916, 1150, 1206 et 1644 cm^{-1}.

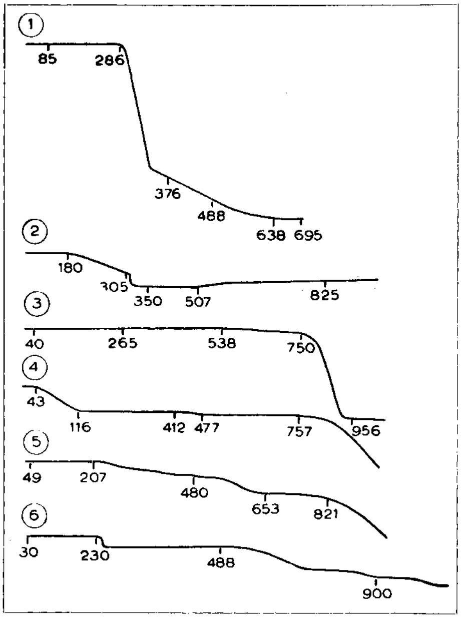
Persulfate de potassium

La décomposition thermique a été étudiée par LEVI ET MIGLIORINI[9]. Le persulfate de potassium anhydre ne change pas de poids jusqu'à 230°. Il se décompose alors brusquement avec perte d'oxygène en fournissant du pyrosulfate de potassium, stable à son tour jusqu'à 488°. Après quoi, une nouvelle décomposition a lieu en anhydride sulfurique et sulfate de potassium, décomposition qui s'achève vers 900° (Fig. 6).

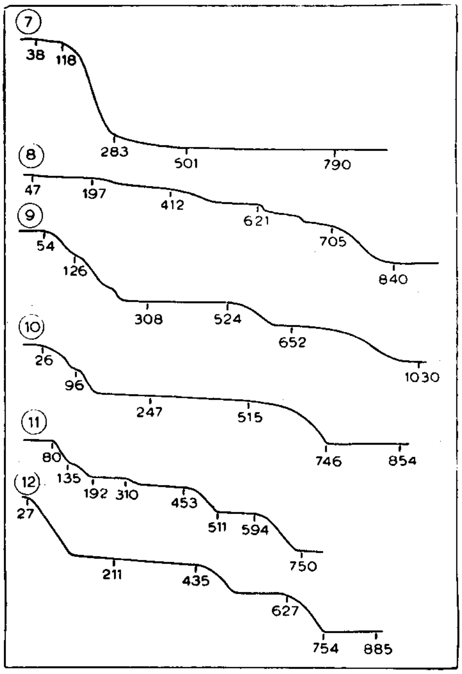
Le spectre infrarouge a déjà été fourni par Pascal, Duval, Lecomte et Pacault[10]; il donne les bandes: 900 (aF), 1059 (TF), 1254 (TF). Ces nombres sont d'accord avec ceux que nous avons reproduits plus récemment, à sec et en solution[11].

Chlorure d'aluminium

Le chlorure d'aluminium extrait d'un flacon neuf possède la formule $AlCl_3 \cdot 6H_2O$. Toutefois, la manipulation nécessaire pour le mettre dans le creuset lui fait gagner un peu d'humidité dont la perte jusqu'à 38° est signalée sur la courbe de thermolyse (Fig. 7). L'hexahydrate paraît stable entre 38 et 118°; après quoi, une hydrolyse et une déshydratation conduisent à l'oxyde Al_2O_3, assez rapidement jusqu'à 500°, puis excessivement lentement après. Vers 800° l'opération paraît terminée. Parravano et Montoro[12] indiquent que cette transformation est complète à 180°, mais il n'en est rien avec notre mode de chauffage.



Figs. 1–6.



Figs. 7–12.

Les six molécules d'eau sont assurément de constitution et conduisent à une bande extrêmement large entre 808 et 858 cm^{-1} et à une bande fine à 1626 cm^{-1} (qui est peut-être due à l'humidité captée par le corps au moment de confectionner la cuve).

Pyrosulfate de sodium

Le produit que nous avons eu entre les mains se présentait sous forme de plaques quelque peu hygroscopiques qu'il n'est pas recommandé de peser à la sortie du flacon.

La stabilité se manifeste jusque vers 197° (contrairement au sulfate acide de sodium $NaHSO_4$, qui n'est pas un étalon mais que nous avons examiné par comparaison; il perd de l'eau dès 43°). Le pyrosulfate, au-dessus de 197° perd de l'anhydride sulfurique jusque vers 800° et à partir de 840° apparaît le palier horizontal du sulfate neutre Na_2SO_4. L'équation:

$$Na_2S_2O_7 \rightarrow SO_3 + Na_2SO_4,$$

n'a pas été vérifiée d'une manière rigoureuse et le point de fusion mesuré sur un échantillon sorti d'un flacon neuf est 147° (en désaccord avec les nombres trouvés par CAMBI ET BOZZA[13], qui donnent 400.9° et qui indiquent aussi qu'à cette température le produit n'est pas dissocié) (Fig. 8).

Le spectre infrarouge dans la région du sel gemme, s'accorde assez bien avec celui des corps renfermant l'ion du type X_2O_7 et accuse les bandes: 856 (F), 895 (f), 1040 (aF), 1060 (aF), 1074 (f), 1166 (TF), 1245 (TF) cm^{-1}.

Alun d'aluminium et d'ammonium

Il est permis de lui supposer la formule $NH_4[Al(H_2O)_2(SO_6H_4)_2]\cdot 6H_2O$, par analogie avec la formule expérimentale donnée pour l'alun de chrome. Toutefois, il faut le remarquer, cet alun est assurément un complexe plus imparfait dans le cas de l'aluminium que dans le cas du chrome. La courbe de thermolyse est reproduite sur la Fig. 9 jusqu'à 1030° et nous en avons recommencé des fractions pour interpréter commodément la nature des produits apparus suivant les paliers. Ceci dit, l'alun à $12H_2O$ dont 6 à l'état d'eau de cristallisation, est stable jusqu'à 54°. Il perd la totalité de son eau jusque vers 310°, en 3 étapes qui ne sont d'ailleurs pas très nettement séparées avec notre vitesse de chauffe, c'est-à-dire d'abord la perte des 6 molécules d'eau de cristallisation jusque vers 126°, puis la perte de 4 molécules d'eau combinée à l'acide sulfurique jusque vers 170°, enfin la perte de 2 molécules d'eau disposées aux extrémités de l'axe quaternaire de l'octaèdre de Werner. Il faut noter tout de suite que le produit figurant suivant le palier presque horizontal entre 308 et 524°, n'est pas le sel double $(NH_4)_2SO_4 + Al_2(SO_4)_3$, mais plutôt un complexe du type $NH_4[Al(SO_4)_2]$. En effet, le sulfate d'ammonium, d'après des expériences précédentes, aurait déjà disparu par sublimation et dissociation; ainsi pour début de sa décomposition, CASPAR[14] indique 355° et JÄNECKE[15] 357°. Dans notre expérience, le sulfate d'ammonium, par suite de l'ouverture du complexe, s'échappe entre 524 et 620° environ. Il reste alors du sulfate d'aluminium, $Al_2(SO_4)_3$, qui commence à se dissocier progressivement vers 652° et l'alumine apparaît dès 1030°.

Nous avons soigneusement vérifié que cette alumine était exempte d'ion SO_4^{-2}, que le sulfate d'aluminium était exempt d'ammoniac et que ce corps contenu dans le sel anhydre et dans le sel dodécahydraté correspondait bien aux formules annoncées.

Le spectre infrarouge, qui est d'ailleurs le même pour tous les aluns à 12 molécules d'eau, montre deux bandes très fortes pour 918 et 1017 cm^{-1}, relatives au groupement SO_4.

Sulfate de fer bivalent cristallisé

Les échantillons parfaitement verts et provenant d'un flacon neuf, ne contiennent pas 7 molécules d'eau mais des quantités voisines de 6 et sur la courbe de thermolyse

(Fig. 10), on observe que la perte de poids se produit dès la température ordinaire. Les 6 ou 7 molécules d'eau ne partent pas d'un seul coup et l'allure de la courbe dépend beaucoup de la vitesse de chauffage. On peut dire, en gros, que 3 molécules d'eau partent entre 26 et 96°, déjà avec oxydation partielle, que 3 autres molécules disparaissent entre 100 et 140° (quelques auteurs avant nous avaient donné 110–120 ou 160°). Le départ de la dernière molécule se fait en même temps qu'une altération profonde ne conduisant ni au sulfate de fer(II) anhydre, ni à un sulfate de fer(III) anhydre, sans toutefois qu'il y ait de palier très net. SAITO[16], par chauffage linéaire de 1° par minute, avait donné 540-550° pour le domaine d'existence de ce sulfate basique, qui pourrait s'écrire $2SO_3 \cdot Fe_2O_3$, corps déjà signalé. Il perd alors l'anhydride sulfurique et au-dessus de 720° commence le palier qui correspond à l'oxyde salin Fe_3O_4 (Fig. 10).

Le spectre infrarouge montre naturellement la bande très forte pour 1103 cm^{-1}, correspondant à la triple dégénérée du groupement SO_4, une bande large entre 812 et 828 cm^{-1}, puis des bandes beaucoup plus faibles pour 887, 988, 1016 et 1150 cm^{-1}.

Sel de Mohr

Le sel de Mohr sorti du flacon ne montre pas de perte d'humidité sur aucun de nos enregistrements. Il ne faut pas dépasser 80° pour le sécher. La perte des 6 molécules d'eau est compliquée par un léger départ d'ammoniac et une oxydation du fer, de sorte qu'entre 192 et 310°, on aboutit à $NH_4[Fe(SO_4)_2]$ correspondant en quelque sorte à l'alun anhydre, triple opération qui s'effectue jusque vers 453°. Il est impossible d'obtenir des paliers rigoureusement horizontaux. Entre 453 et 511° et entre 2 molécules du corps $NH_4[Fe(SO_4)_2]$, s'échappe une molécule de sulfate d'ammonium; il reste alors, sur un nouveau palier s'étendant de 511 à 594°, du sulfate de fer(III) $Fe_2(SO_4)_3$, qui n'est jamais rigoureusement pur. Alors commence la dissociation bien connue:

$$Fe_2(SO_4)_3 \rightarrow Fe_2O_3 + 3SO_3,$$

mais comme on n'opère ni dans le vide, ni dans un milieu très réducteur mais dans l'air, le produit final, au-dessus de 750°, est l'oxyde Fe_3O_4.

Nous avons effectué des dosages répétés de fer correspondant à différentes températures de ce graphique (Fig. 11), mais il faut bien convenir que la thermolyse du sel de Mohr est une opération très compliquée et que les résultats manquent de netteté.

Le spectre infrarouge du sel de Mohr n'accuse pas la présence de la bande très forte de 1103 cm^{-1} correspondant au groupement SO_4, mais celle de 980 qui se retrouve chez les sulfates complexes. D'autre part, nous avons deux bandes fortes, l'une à 1385, l'autre à 1475 cm^{-1}, qui correspondent à l'ammoniac et à l'eau. C'est sans doute à cette dissimulation dans un complexe, que le sel de Mohr doit sa plus grande stabilité vis-à-vis de l'oxygène de l'air.

Alun de fer et d'ammonium

L'alun de fer et d'ammonium est un corps que l'on ne peut peser directement car il perd de l'eau dès la température ordinaire. Par suite, dans l'hypothèse de la formule $NH_4[Fe(H_2O)_2(SO_6H_4)_2] \cdot 6H_2O$, nous n'observons pas comme dans le cas de l'alun de chrome, trois paliers successifs pour le départ des 6 molécules d'eau de cristallisation, des 4 molécules d'eau combinée au soufre et des 2 molécules d'eau du complexe.

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Cette eau part d'une manière continue jusque vers 211°. Là commence un palier rectiligne mais non horizontal, s'accordant assez bien avec la formule de l'alun anhydre, $NH_4[Fe(SO_4)_2]$, puis au-dessus de 435°, ce nouveau complexe se détruit à son tour, perdant du sulfate d'ammonium et nous tombons, comme dans le cas précédent, sur le sulfate de fer(III), se dissociant pour conduire à l'oxyde Fe_3O_4 (Fig. 12). Nous avons d'ailleurs tracé par comparaison, la courbe de dissociation du sulfate de fer(III) et, dans ce dernier cas, si la dissociation commence bien vers 600°, elle ne s'achève que plus haut, à 770° au lieu de 750°, avec la même vitesse de chauffe.

Le spectre infrarouge montre encore nettement que ce sel est un complexe; d'ailleurs, sa couleur et les expériences de migration d'ions l'indiquaient déjà. La bande forte de 1103 cm^{-1} du groupement SO_4 a disparu; elle est remplacée par deux bandes fortes à 993 et 1063 cm^{-1}. Signalons encore d'autres bandes fortes à 1373 et 1450 dues à l'ammoniac et à l'eau et des bandes très faibles à 871, 887, 1137, 1174 et 1216 cm^{-1}.

RÉSUMÉ

Nous avons étudié 12 substances pouvant servir d'étalons en analyse volumétrique, en insistant surtout sur la pyrolyse de 3 sels de fer.

SUMMARY

Twelve substances, which can be used as standards in volumetric analysis were studied, special attention being paid to the pyrolysis of the three iron salts among these substances.

ZUSAMMENFASSUNG

Es werden 12 Substanzen beschrieben, die bei der Mass-analyse als Standarde verwendet werden können, darunter 3 Eisensalze, deren Veränderungen durch Pyrolyse besonders betrachtet werden.

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4-(2-PYRIDYLAZO)-RESORCINOL AS A POSSIBLE ANALYTICAL REAGENT FOR THE COLORIMETRIC ESTIMATION OF COBALT, LEAD, AND URANIUM

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INTRODUCTION

The development of chromatography for use in the quantitative analysis of inorganic substances has led to the need for the re-examination of many of the recommended organic reagents used for final determination of cations by spectrophotometry. Hitherto, reagents were selected for ordinary analytical purpose on the grounds that they were very specific for the particular cation being estimated, but now that cations can be so readily separated by chromatographic methods from possible interfering cations, specificity of the reagent is not quite so important. By and large, the main requirements for reagents which can be used for the determination of individual cations such as occur after paper chromatographic separation are (1) high sensitivity, (2) water solubility to avoid organic solvent extraction, (3) reproducibility.

Many colorimetric reagents have been produced by coupling reactions following the diazotisation of benzenoid or naphthalenic nuclei. Relatively few having a pyridine base have been investigated however[1–4], and further investigation of the coupling reactions of phenols with pyridine bases has led to the synthesis of the reagent 4-(2-pyridylazo)-resorcinol (hereafter called PAR-4).

TSCHITSCHIBABIN[1,2] investigated the coupling of *o*-hydroxy-phenols, and LIU[3] carried out a detailed investigation into one of these compounds, 1-(2-pyridylazo)-2-naphthol (PAN-2). This investigation, however, was directed at deducing the structures of the metal-chelate lakes formed, rather than at the colorimetric properties of the reagent. A similar, but much less detailed, investigation was made into the dyestuff produced by coupling with resorcinol.

CHENG AND BRAY[4] later investigated the analytical properties of PAN-2, and have suggested its use as an indicator in the complexiometric titration of zinc, copper and cadmium with ethylenediaminetetracetic acid (EDTA). FLASCHKE AND ABDINE[5] have recommended a modified procedure which leads to the use of PAN-2 as indicator in the complexiometric titration of iron, copper, nickel, cobalt, zinc, cadmium and gallium. CHENG[6] has suggested a further procedure for the complexiometric titration of indium.

BUSEV[7] has studied the complexiometric titration of Bi with EDTA, using PAN as indicator, and CHENG[8] has also studied a similar technique for titration of Cu, Zn, Cd and Ni with EDTA.

Our investigation has shown that PAR-4 has outstanding possibilities as a highly sensitive, water-soluble reagent for the colorimetric estimation of cobalt, lead and uranium.

EXPERIMENTAL

Preparation of dyestuffs

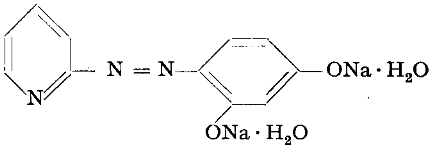
(*a*) *Preparation of diazotate*[2]. (All reagents used were of AnalaR quality.) A solution of sodium ethylate was obtained by dissolving metallic sodium (1.2 g) in absolute alcohol (18.5 ml). 2-Amino pyridine (5 g) was dissolved in the minimum quantity of absolute alcohol (5 ml), and isoamyl nitrite (6 g) was added. The solutions were mixed and refluxed gently for 2–2½ h, the diazotate forming as a brown solid. Coupling reactions were then carried out directly, without isolation of the very unstable diazotate.

(*b*) *Coupling reactions.* All the phenolic compounds with which coupling was attempted were dissolved in absolute alcohol and mixed with the alcoholic diazotate solution. Carbon dioxide was then passed into the solution, which was cooled in an ice bath.

No product was isolated from the attempted coupling of pyridyl diazotate with 2-naphthol-6-sulphonic acid (Schäffer's acid), 2-naphthol-6,8-disulphonic acid (G-acid), 2-naphthol-3,6-disulphonic acid (H-acid), and 1-nitroso-2-naphthol-3,6-disulphonic acid (Nitroso-R-salt).

Coupling with resorcinol (8 g) in absolute alcohol (5 ml) resulted in the isolation of the disodium salt of PAR-4, the outstanding colorimetric properties of which are described in the next section. It was found that a far greater yield of dyestuff could be obtained by coupling the diazotate with resorcinol dissolved in the minimum quantity of water, followed by cooling in a refrigerator. The passing of CO_2 was also dispensed with, since the sodium salt was being isolated.

The crude PAR-4 (sodium salt) was isolated by filtration and thoroughly washed with ether in which it is only slightly soluble. All other impurities (resorcinol, etc.) being soluble in ether, were removed, and on drying *in vacuo*, pure dyestuff in the form of a brown, amorphous, slightly hygroscopic powder was obtained. Analysis showed that this was the disodium salt of PAR-4, together with two molecules of water of crystallization:



Theory: C = 44.3%, H = 3.76%, N = 14.0%, Na = 14.1%.
Found: C = 44.7%, H = 3.73%, N = 14.2%, Na = 15.6%.

(The authors are indebted to Messrs. WEILER AND STRAUSS of Oxford for these analyses).

The disodium salt of the dyestuff is soluble in water to give an orange solution; it is also soluble to some extent in absolute alcohol.

Colorimetric properties

Samples of aqueous solutions of AnalaR salts containing 0.5, 0.05, 0.005, and 0.0005 g of metal per litre were used to determine those ions which formed coloured chelates with the dyestuff. The technique used was that of HEISIG AND POLLARD[9]. Table I shows those ions which were found to give a colour:

TABLE I

Ion	*Colour*	*Ion*	*Colour*
Fe^{II}	Brownish-red	Cd^{II}	Pink-red
Fe^{III}	Brown	Sn^{II}	Pink → yellow
Co^{II}	Red	V^{V}	Purple
Ni^{II}	Red	Pb^{II}	Red
Cu^{II}	Red	U^{VI}	Red
Zn^{II}	Pink-red	Ti^{IV}	Red
		Rare earths	Red

The following cations failed to give a colour: Na^+, K^+, Ca^{+2}, Sr^{+2}, Ba^{+2}.

The sensitivities of the coloured complexes formed with Co^{II}, U^{VI}, and Pb^{II} have been investigated in considerable detail, and lead to the conclusion that PAR-4 is an excellent colorimetric reagent for the estimation of these metals.

Cobalt complex. The pH at which the optical density of the cobalt-dyestuff complex is a maximum, and the position of the maximum, were first determined. All measurements were made using a "Unicam" S.P. 500 spectrophotometer fitted with 1-cm silica cells. Buffer solutions for pH 5.0, 6.0, 7.0, 8.0, 9.0, and 10.0 were obtained following the method of CLARK AND LUBS[10].

Aqueous solutions of the dyestuff (0.1 g in 100 ml, *i.e.* 1000 μg/ml) and AnalaR $CoCl_2 \cdot 6H_2O$ (12.38 μg Co/ml) were made up. Suitable proportions of the solutions were mixed, buffered to the requisite pH, and the optical density against a buffered dyestuff blank obtained over a range of wavelength from 450–620 mμ. Similarly the optical density of the aqueous dyestuff alone was obtained against a buffer blank in the range 330–520 mμ. The resulting spectra are shown in Fig. 1.

The dyestuff showed peak optical density at 410 mμ, over the pH range 7.0–9.0, and the complex showed peak optical density at 510 mμ over the same pH range. In all subsequent experiments on the cobalt complex the solutions were buffered at pH 8.0 for convenience.

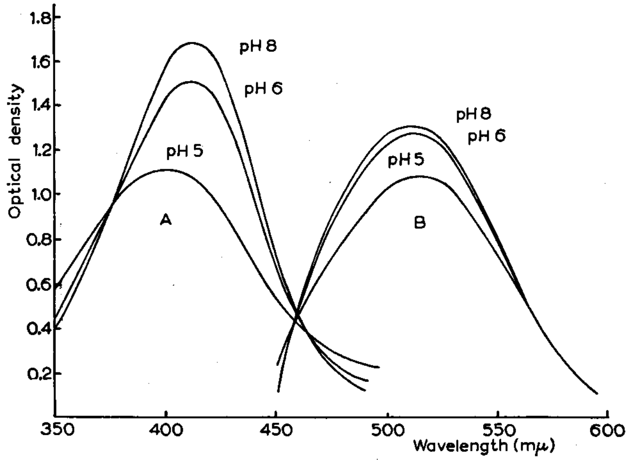


Fig. 1

A. Absorption spectrum of PAR-4. B. Absorption spectrum of cobalt complex.

The sensitivity of PAR-4 with cobalt was then determined as follows. A solution containing 10 μg/ml Co was obtained by dissolving 1.00935 g $CoCl_2 \cdot 6H_2O$ in 250 ml distilled water, and diluting a 10-ml aliquot to 1000 ml. A dyestuff solution of 1000 μg/ml was obtained by dissolving 0.25 g dyestuff in 250 ml distilled water. An optical blank was made up by mixing 1 ml of this dyestuff solution with 10 ml buffer pH 8.0, and diluting to 25 ml. Solutions of the coloured complex formed by mixing varying quantities of cobalt with a fixed quantity of dyestuff were obtained thus: x ml Co + 1 ml dyestuff + 10 ml buffer; diluted to 25 ml where:

$x=$	0.5	1.0	1.5	2.0	2.5	3.0	3.5	ml
i.e.	0.2	0.4	0.6	0.8	1.0	1.2	1.4	μg Co/ml

In all these cases the amount of the dyestuff present was greatly in excess of that required for complete complex formation. The optical density of the above solutions against the prepared blank was determined at 510 mμ (the peak complex height). The results are shown in Table II:

TABLE II

μg Co/ml	0.200	0.400	0.600	0.800	1.000	1.200	1.400
O.D.	0.190	0.382	0.570	0.760	0.940	1.120	1.310

The plot of optical density *versus* concentration of cobalt in μg/ml is linear over the range 0–1.4 μg Co/ml, from which the sensitivity of the dyestuff with cobalt is found to be 0.93 O.D. units/μg Co/ml at 510 mμ. This sensitivity is far in advance of that of any of the standard colorimetric reagents for cobalt. Nitroso-R-salt, the most sensitive so far reported[11,12], has a sensitivity of approximately 0.5.

Uranium complex. Upon the addition of a uranium salt to a slightly alkaline solution of the dyestuff, a red colour is immediately produced. The peak height of the uranium complex was determined exactly as for the cobalt complex and was found to occur at 530 mμ (pH = 8.0), the reagent giving maximum absorption at 410 mμ. The sensitivity of the dyestuff with uranium was determined precisely as with the cobalt complex, using the following solutions:

Standard solution of AnalaR uranium acetate containing 1000 μg/ml uranium (*i.e.* 17.81 g salt/1000 ml).

Standard solution of PAR-4 (500 μg/ml).

Buffer pH 8.0.

The optical blank contained 2 ml dyestuff solution + 10 ml buffer, diluted to 25 ml. The test solutions contained *x* ml uranium + 2 ml dyestuff solution + 10 ml buffer, diluted to 25. The uranium solutions were measured from an "Agla" micrometer syringe. The optical densities of these solutions were measured at 530 mμ against the above blank. The results are tabulated in Table III.

TABLE III

μg/ml uranium	10.0	8.0	6.0	4.0	2.0	1.0
ml soln. and diln.	0.25_{25}	0.20_{25}	0.15_{25}	0.10_{25}	0.10_{50}	0.05_{50}
O.D. at 530 mμ	1.565	1.270	0.965	0.640	0.320	0.155

The sensitivity from this data is 0.160 optical density units/μg U/ml at 530 mμ, over the range 0–6.0 μg U/ml.

Again, this places PAR-4 well ahead of the recognised colorimetric reagents, both as regards sensitivity and water solubility. The most sensitive colorimetric reagent for uranium, dibenzoylmethane[13], is not water-soluble, and the sensitivities of the water-soluble reagents (salicylamidoxime[14], sulphosalicylic acid[15]) are less than that of PAR-4.

Lead complex. Following the methods used for the cobalt and uranium complexes, the maximum absorbance for the lead complex was found to occur at 520 mμ. The colour of the complex was found to have maximum intensity when buffered to pH 10.0.

The sensitivity of PAR-4 with lead was found as in the previous cases. The following solutions were made up:

Standard solution of $Pb(NO_3)_2$ AnalaR, containing 1000 μg Pb/ml (*i.e.* 1.5990 g salt/1000 ml).

Standard solution of dyestuff containing 500 μg/ml.

Buffer solution pH 10.0.

To a 25-ml graduated flask was added a known amount of standard Pb solution (measured from an "Agla" micrometer syringe) + 2 ml dyestuff + 10 ml buffer. The mixture was diluted to 25 ml with distilled water, and the optical density measured at 530 mμ against a dyestuff + buffer blank. The results are tabulated in Table IV.

TABLE IV

μg Pb/ml	2.0	3.0	4.0	5.0	6.0	7.0
ml solution	0.10	0.15	0.20	0.25	0.30	0.35
O.D. at 520 mμ	0.348	0.514	0.684	0.860	1.020	1.196

This data gives the sensitivity as 0.171 optical density units/μg Pb/ml, over the range 0–5.0 μg Pb/ml.

A search of the literature has shown that no water-soluble colorimetric reagents for the estimation of lead have been reported, the most used method being estimation with dithizone following extraction with CCl_4.

GENERAL

Since PAR-4 gives coloured chelate compounds with many cations (see Table I) it is necessary to remove these ions before colorimetric estimation is possible. This may be achieved by several methods; in this laboratory interfering cations have been removed from lead solutions by paper chromatography, followed by determination of lead with PAR-4. Details of this procedure will be given in a later publication.

Investigations of the structures and stability constants of the metal chelate complexes of PAR-4 are at present in progress by spectrophotometric, polarographic and pH measurements. It is hoped to publish these results in a further paper.

The reagent 1-(2-pyridylazo)-4-phloroglucinol has also been synthesized, and its analytical properties are under investigation.

ACKNOWLEDGEMENTS

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SUMMARY

4-(2-Pyridylazo)-resorcinol has been synthesized, and its uses as an analytical reagent for the colorimetric estimation of cobalt, uranium and lead have been investigated. It has been shown to be the most sensitive reagent for the colorimetric estimation of cobalt, the most sensitive water-soluble reagent for the colorimetric estimation of uranium, and the first published water-soluble reagent for the colorimetric estimation of lead.

RÉSUMÉ

La pyridyle-2-azo-4-résorcine est proposée comme réactif analytique pour le dosage colorimétrique du cobalt, de l'uranium et du plomb. C'est un réactif particulièrement sensible.

ZUSAMMENFASSUNG

Es wurde gefunden, dass das Pyridyl-2-azo-4-resorcin ein äusserst empfindliches Reagens für die colorimetrische Bestimmung von Kobalt, Uran und Blei darstellt.

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THE ANALYSIS OF ZIRCONIUM-THORIUM BINARY ALLOYS

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INTRODUCTION

Complexometric titrations were considered for the analysis of this type of alloy because both zirconium and thorium can be determined individually by this technique. Experience with complexometric titrations for these elements has shown that the most satisfactory ones employ xylenol orange as indicator. The direct titration of zirconium is not very suitable because of hydrolysis difficulties, except in solutions approximately N in mineral acid. Under these conditions the determination of zirconium is possible directly in the presence of thorium since the thorium-EDTA complex is not formed. A back titration procedure is widely used for the determination of zirconium; this employs either bismuth or thorium as the titrant of the excess of ethylenediaminetetraacetic acid (EDTA) to the xylenol orange end-point[1]. With this procedure it may be possible to prevent interference from thorium by the use of a suitable masking agent. In the analysis of bismuth-thorium alloys, for example, BACON AND MILNER[2] succeeded in masking up to 100 mg of thorium with sulphate ions in the complexometric titration of bismuth. Both these approaches have been examined and the results are described in this paper.

EXPERIMENTAL

The direct titration of zirconium in the presence of thorium

KÖRBL AND PRIBIL[3] have reported the direct titration of zirconium with EDTA in hot normal nitric acid solutions using xylenol orange as indicator. Due to slight fading at the end-point, we obtained final titres slightly lower than the theoretical value. It was found that if, after titration to the end-point, sufficient ammonium hydroxide was added to neutralise about 80% of the nitric acid, the pink colour of the indicator was restored and a further small titration with EDTA could be carried out. The final titre was then correct for small amounts of zirconium, but slightly low for amounts greater than about 30 mg of zirconium. Under these less acid conditions, however, the tolerance for thorium proved much lower, amounts as low as 20–30 mg causing serious interference. Fluoride and sulphate ions interfered badly, no titration being possible in the presence of as little as 2–3 mg of fluoride and 100 mg of sulphate. Since the use of either hydrofluoric acid or sulphuric acid or both may be essential for the solution of alloy samples, further study of this direct titration method was discontinued.

Determination of zirconium and thorium with EDTA by back titration with bismuth

According to KÖRBL AND PRIBIL[3], bismuth can be titrated directly with EDTA in solutions between pH 1 and 3 using xylenol orange as indicator. At higher pH values, hydrolysis of bismuth causes difficulties. The reverse titration of EDTA with bismuth can be carried out in solutions up to pH 3.7, although the colour change of the indicator is sluggish at pH values greater than 3.5. Using bismuth for the titration of excess of EDTA, zirconium can be determined between pH 1.2 and 3.5, whereas the smaller pH range of 2.3 to 3.7 is applicable in the case of thorium. For quantitative results for zirconium, the excess of EDTA must be added to a fairly acid solution (*e.g.* $> 1.0N$ in nitric acid). In the thorium determination a slight positive error occurs at pH values less than 2.3, the sluggish colour change at the end-point possibly accounting for this error. The titration of known mixtures of thorium and zirconium resulted in the correct total being obtained when the titration was carried out between pH 2 and 3.

The behaviour of most other cations in this back titration procedure can be predicted from the stability constant data available in the literature. However, the behaviour of anions cannot be assessed with the same certainty and is best determined experimentally. The number of anions of direct interest in this work could be limited to about two, since the only useful solvents for zirconium metal and some of its alloys are a mixture of hydrofluoric and nitric acids or boiling concentrated sulphuric acid. Some knowledge of the effects of both sulphate and fluoride ions on the determination of thorium and zirconium was essential. From previous work the effect of sulphate ions on the determination of thorium was known to be serious[2]. Their effect on the determination of zirconium was found to depend on whether the sulphate was present before or after the addition of the EDTA. The addition of small amounts of sulphuric acid to a solution of zirconium in $2N$ nitric acid before the excess of EDTA caused low recoveries. However, large amounts of sulphate ions could be added after the complexation of the zirconium with EDTA with negligible effect on the recovery.

The complexation of thorium by sulphate ions proved to be of potential value for the direct determination of zirconium in the presence of thorium. Experiments showed, for example, that amounts of thorium up to at least 100 mg could be completely masked under favourable conditions. For the determination of zirconium under such conditions, solutions adjusted to the bottom of the previously reported pH range of 1.2 to 3.5 had to be employed. This low pH proved necessary because of difficulty in detecting the end-point visually at the higher values. An ammonium sulphate concentration of 2–3 g in 100 ml of solution proved very convenient and increasing it to greater values was found to serve no useful purpose.

Fluoride ions were found to affect adversely the determination of both thorium and zirconium, although they had little influence in the titration of EDTA with bismuth. As little as 1 mg of fluoride as sodium fluoride caused the masking of several milligrams of either thorium or zirconium. However, this effect could be nullified by the addition of beryllium to preferentially combine with the fluoride ions. The amount of beryllium needed to mask a certain amount of fluoride was found to depend on the pH of the solution. Thus in the determination of zirconium at pH 1.2, 1 ml of 50% w/v beryllium nitrate solution could mask 20 mg of fluoride, whilst at pH 3 it could mask at least 100 mg of fluoride, and similarly in the thorium determination.

Determination of thorium and zirconium in the same solution

From the results of the previous section it is possible to determine the total content of thorium plus zirconium and also the amount of EDTA combined with the thorium by preferential complexation with sulphate ions. Before these titrations could be applied in metallurgical analysis, however, it was necessary to prove them by analysing solutions of various compositions. Suitable mixtures of thorium and zirconium were prepared from $0.02M$ solutions of thorium nitrate and zirconium nitrate. Sufficient $0.02M$ EDTA was added to each solution to complex the thorium and zirconium and provide a small excess. After adjusting pH to 2.5–2.7, the EDTA in excess was determined by titration with $0.02M$ bismuth nitrate. Then 2–3 g of ammonium sulphate was dissolved in the solution, followed by the addition of nitric acid to lower pH to 1.2 to 1.3. The back titration with bismuth was then continued to determine the amount of EDTA liberated from the thorium complex. From these titres the composition of the thorium–zirconium mixture could be calculated and typical results are given in Table I.

TABLE I

THE ANALYSIS OF THORIUM–ZIRCONIUM MIXTURES
(all solutions were exactly $0.02M$)

Taken (ml)		*EDTA added*	*Back titraton with Bi (ml)*		*Found*		*Error*	
Th	*Zr*	*ml*	*pH 2.5*	*pH 1.3*	*Th*	*Zr*	*Th*	*Zr*
25.00	1.00	26.50	0.51	25.51	25.00	0.99	Nil	+0.01
25.00	1.00	26.50	0.49	25.48	24.99	1.02	−0.01	+0.02
20.00	5.00	25.50	0.51	10.50	19.99	5.00	−0.01	Nil
10.00	10.00	20.50	0.49	10.48	9.99	10.02	−0.01	+0.02
5.00	20.00	25.50	0.49	5.50	5.01	20.00	+0.01	Nil

It was shown that both thorium and zirconium determinations could be carried out directly at a 25/1 molar ratio of Th to Zr and Zr to Th respectively with a standard deviation of ±0.01 ml of 0.02*M* solution. Therefore, in order to obtain an accuracy of ±1%, it can be calculated that the lowest weight percentages of each metal are 10% thorium in zirconium-rich alloys and 1.6% zirconium in thorium-rich alloys. For the analysis of actual alloys it was considered preferable to increase these limits to about 20% for thorium and 5% for zirconium respectively. For other alloy compositions less direct methods involving some form of preliminary separation would have to be developed. The separation of thorium and zirconium need not be perfect, as long as the ratio of these constituents was reduced to a satisfactory value so that the EDTA procedures become applicable.

Separation and determination of small amounts of thorium

The available chemical methods for the separation of thorium from zirconium are very limited and that involving the precipitation of thorium as its insoluble fluoride proved to be the only approach applicable to this problem. In preliminary experiments the precipitation of thorium fluoride from nitric acid solutions was carried out by the addition of ammonium fluoride. With 5-mg amounts of thorium, the recovery was slightly low, but quantitative recoveries were obtained with larger amounts. Because of this behaviour, lanthanum was added to the solution to improve the recoveries at the lower levels. This procedure was tested on the recovery of thorium in the presence and absence of zirconium and full recoveries were obtained for 4.5- to 50-mg amounts of thorium in the presence of 500 mg of zirconium.

Separation and determination of small amounts of zirconium

Mandelic acid[4,5] and its derivatives are applicable to the precipitation of zirconium in the presence of thorium. The *p*-bromo derivative[6] is better than mandelic acid for the precipitation of small amounts of zirconium; it is also more satisfactory in the presence of sulphate ions. The application of this reagent was therefore studied because the presence of sulphuric acid in the sample solution was anticipated since the only effective way of removing fluoride ions from zirconium involves heating to strong fumes of sulphuric acid. Quantitative results were obtained for the determination of 0.5 to 2.5 mg amounts of zirconium in the presence of 100 mg amounts of thorium.

THE ANALYSIS OF ALLOYS

Solution procedure

A mixture of nitric and hydrofluoric acids was found to be a suitable solvent for the majority of alloys in this system. The best procedure consisted of the transference of a suitable weight of sample to a platinum dish, followed by the addition of 10 ml of nitric acid (sp. gr. 1.42) and 4 to 5 drops of 40% hydrofluoric acid and gentle warming of the dish and its contents. The use of a platinum lid to cover the dish was found to be essential to reduce losses of acid by evaporation and then only occasional additions of nitric acid were necessary to maintain the volume of this acid at the desired level. Most samples dissolved readily by this procedure but some difficulty was encountered with samples containing between 70 and 90% of zirconium. With these samples extreme caution was needed during the warming process, otherwise spontaneous combustion occurred with the formation of hard globules of oxide very resistant to solution. On completion of the solution of the sample in the nitric–hydrofluoric acid mixture, 20 ml of 60% perchloric acid was added to the platinum dish followed by evaporation to fumes of this acid. After cooling, the sample solution was quantitatively transferred to a 150-ml beaker with water washings and any small residue was dissolved in nitric acid. Then the solution was evaporated to fumes of perchloric acid again and the beaker was covered and the boiling of the acid continued to produce a clear solution. Next the beaker was uncovered and heating was continued to reduce the volume of perchloric acid to about 10 ml. After cooling, the solution was diluted with 25 ml of 5N nitric acid and finally made up to volume in a 100-ml volumetric flask.

Experience showed that the relative ease of solution depended on the zirconium content of the alloy. There was no difficulty with samples of low zirconium content. Moreover, the resultant perchloric acid solution could be evaporated to dryness and complete solution of the residue could be effected in 5N nitric acid. With alloys of high zirconium content, however, the position was less satisfactory and it was found to be necessary to limit the weight of sample to not more than about 250 mg. With greater sample weights a deposit was formed on fuming with perchloric acid and re-solution of this material proved extremely difficult unless it was heated with fuming sulphuric acid. This same type of deposit could also be formed on taking sample weights less than 250 mg by carelessness in the evaporation of perchloric acid and by removal of too much of this acid.

METHODS OF ANALYSIS

Reagents required

0.02M Bismuth nitrate solution. Dissolve 4.180 g of high purity bismuth metal in 100 ml 25% v/v nitric acid, boil the solution vigorously, cool and dilute to 1 l in a graduated flask.

0.02M EDTA solution. Dissolve 7.45 g of the di-sodium salt of the ethylenediaminetetraacetic acid di-hydrate in 1 l of water. Standardise against the 0.02M bismuth nitrate solution using xylenol orange indicator at pH 1.2–3.0.

2% p-Bromo-mandelic acid solution. Dissolve 10 g of the acid by warming with 500 ml of water, cool to room temperature and filter.

20% Ammonium fluoride solution. Dissolve 100 g of the A.R. salt in 500 ml of water, filter and keep in a polythene bottle.

1% Ammonium fluoride wash solution. Dilute 25 ml of 20% ammonium fluoride solution to 500 ml with 1% v/v nitric acid.

0.1% Xylenol orange solution. Dissolve 100 mg of the dye in 100 ml of water.

Ammonium sulphate, hydrofluoric acid and all other reagents of A.R. quality.

De-ionised water should be used throughout.

Apparatus required

Platinum dishes (50 ml capacity) with covers,
50-ml "Lusteroid", centrifuge tubes,
Polythene stirring rods,
M.S.E. Major centrifuge,
Burettes, pipettes and graduated flasks, all grade "A" quality.

Procedure

Solution of alloys (See above)

Preliminary examination. Take an aliquot to contain not more than 40 mg of zirconium-rich alloys or 100 mg of thorium-rich alloys and transfer to a 250-ml beaker. Add 25 to 30 ml of 0.02M EDTA solution and dilute to 150 ml. Introduce pH electrodes and a stirrer. Add 1 drop of 0.1% xylenol orange solution and adjust to pH 2 by the addition of ammonia. If the solution is pink, add enough 0.02*M* EDTA solution to turn the indicator yellow and provide a small excess. Finally adjust to pH 2.6–2.8 with dilute ammonia. Add 3 ml 50% w/v beryllium nitrate solution, readjust the pH and back titrate with 0.02*M* bismuth solution until the indicator turns pink. Next add 2–3 g ammonium sulphate and concentrated nitric acid dropwise until the solution is in the range pH 1.2–1.3. Continue to back titrate with 0.02*M* bismuth solution until the indicator again turns pink. Titrate slowly when approaching the end-point.

Calculate the thorium content from the difference in the bismuth titres and the zirconium content from the total EDTA added minus the total bismuth added.

1 ml 0.02*M* EDTA solution ≡ 4.642 mg Th or 1.824 mg Zr. If, from the preliminary examination, the alloy contains 20–95% thorium and 5–80% zirconium repeat the above procedure on more convenient aliquots of the sample solution to improve the accuracy of the results.

For alloys with < 20% thorium. Take an increased sample weight up to 500 mg and dissolve in nitric–hydrofluoric acid mixture. Transfer the solution to a 50-ml "Lusteroid" centrifuge tube and with washings make up to 25–30 ml. Add 20 mg of lanthanum carrier and 10 ml 20% ammonium fluoride solution. Stir with a polythene rod and spin in a centrifuge for 10 min. Discard the supernate, wash the precipitate with 20 ml of ammonium fluoride wash solution and again spin in a centrifuge for 5 min. Discard the supernate and transfer the precipitate into a 150-ml beaker with water washing. Rinse the centrifuge tube with 5 ml of concentrated nitric acid and more water. Add 5 ml 60% perchloric acid to the suspension in the beaker and evaporate to fumes of this acid. Continue the evaporation until the residue is almost dry. Dissolve the residue in dilute nitric acid, dilute to 100 ml with water, then add excess 0.02*M* EDTA solution and titrate as described in the preliminary examination.

For alloys with < 5% zirconium. Take an aliquot of the sample solution containing up to 100 mg of sample and add 1–2 ml of concentrated sulphuric acid. Evaporate carefully to dryness and gently heat the sides of the beaker with a bunsen flame to remove any condensed sulphuric acid. Cool the beaker, dissolve the residue in 20 ml 20% v/v hydrochloric acid by gentle heating and add 20 ml 2% *p*-bromo-mandelic acid solution. Cover with a watch glass, heat to boiling and then allow the solution to stand for 1 h at 90–95°. Filter the solution through a 9-cm Whatman No. 40 paper and wash the precipitate and beaker with water. Place the paper and precipitate back into the original beaker, cover it with a watch glass after adding 5 ml fuming nitric acid and heat. When the acid has nearly all evaporated, add a further 5 ml of nitric acid and 2–3 ml of perchloric acid and evaporate nearly to dryness. Dissolve the residue in 5 ml 5*N* nitric acid and dilute to 25 ml. Add excess 0.02*M* EDTA, 1 drop of 0.1% xylenol orange solution, 200–300 mg of ammonium sulphate and back titrate with 0.02*M* bismuth solution at pH 1.2–1.3.

RESULTS AND CONCLUSIONS

The methods for the analysis of binary alloys were tested by applying them to samples covering the complete composition range from 1–99% of thorium and of zirconium respectively. The results obtained together with some statistics on the reproducibility of the methods are given in Table II. The reproducibilities of the separation methods for alloys with less than 5% thorium and 20% zirconium respectively were found to be satisfactory on several samples and the methods proved to be very reliable. Only one sample was available for testing the direct method. However, the standard deviations obtained confirmed the suitability of this method.

TABLE II

RESULTS FOR THE ANALYSIS OF THORIUM–ZIRCONIUM BINARY ALLOYS

Nominal composition	*Method employed*		*Composition by analysis*	
			% Thorium	*% Zirconium*
1. 1% Zr	Fluoride pptn.		98.56	0.971 ± 0.006
2. 3% Zr	Fluoride pptn.		95.80	3.03 ± 0.04
3. 4% Zr	Fluoride pptn.		—	4.12 ± 0.011
4. 70% Zr	Direct	1)	30.18 ± 0.15	69.57 ± 0.012
		2)	30.11 ± 0.19	69.63 ± 0.08
5. 15% Th	*p*-Bromo-mandelate		15.34	84.44
6. 5% Th	*p*-Bromo-mandelate		4.99	—
7. 1% Th	*p*-Bromo-mandelate		1.03 ± 0.03	—

SUMMARY

Thorium–zirconium binary alloys are analysed by complexometric procedures. For alloys containing more than 20% thorium or 5% zirconium by weight, the sum of the constituents is obtained by a back titration procedure at pH 2.6–2.8 with bismuth nitrate using xylenol orange as indicator. Thorium is then masked with sulphate and the liberated EDTA is titrated with bismuth at pH 1.2–1.3. For alloys containing less than 20% of thorium, thorium fluoride is precipitated on lanthanum fluoride to effect its separation before titration. For alloys containing less than 5% of zirconium, the zirconium is separated by precipitation with *p*-bromo-mandelic acid.

RÉSUMÉ

On propose des méthodes complexométriques pour l'analyse d'alliages binaires thorium–zirconium. On peut obtenir la somme thorium + zirconium par titrage indirect au moyen de nitrate de bismuth, en présence d'orange de xylénol. On masque ensuite le thorium et on titre l'acide EDTA libéré. (Si < 20% de thorium: on le sépare préalablement comme fluorure. Si < 5% de zirconium: on le sépare préalablement à l'aide de l'acide *p*-bromo-mandélique.)

ZUSAMMENFASSUNG

Es wird eine komplexometrische Methode zur Analyse einer binären Legierung von Thorium–Zirkonium beschrieben. Man bestimmt zunächst die Summe Thorium–Zirkonium durch indirekte Titration mit einer Lösung von Wismutnitrat und Xylenol-Orange als Indikator. Thorium wird dann maskiert und die frei gewordene EDTA mit Wismut titriert. Bei weniger als 20% Thorium wird dieses vor der Titration als Thoriumfluorid abgeschieden. Bei weniger als 5% Zirkonium wird dieses mit *p*-Brommandelsäure abgetrennt.

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DIRECT FLAME-PHOTOMETRIC DETERMINATION OF CALCIUM IN SOIL AND PLANT EXTRACTS, WATER AND SERUM

WITH SPECIAL REFERENCE TO SODIUM, POTASSIUM AND PHOSPHATE INTERFERENCE

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The increasing use of flame photometry in recent years for the determination not only of the alkali metals, but also of calcium, justifies an investigation of the main interfering agents in the determination of the latter, with a view to exploring the possibilities of its application to the routine analysis of such common materials, as soils, plants, water and serum.

BARNES *et al.*[1] state that the presence of sodium causes an apparent increase in calcium content. EDGCOMBE AND HEWETT[2], investigating the determination of calcium in coal ash and coke ash, reported interference effects due to sodium, potassium and phosphate, among others, in the determination of calcium oxide. The interference effect of aluminium on calcium is of importance, especially with respect to soil analysis[3]. The presence of bicarbonate in natural waters is known to cause serious depression of calcium emission[4]. Since these effects at certain, not unusual, concentrations may be very significant, it is generally considered necessary for calcium determination with single-cell, filter flame photometers, to free it first from interfering agents by precipitation as oxalate. The precipitate is then dissolved in dilute perchloric acid and finally sprayed.

The aim of this work was to investigate the possibilities of calcium determination by direct spraying, without the preliminary precipitation as oxalate.

Physical sources of error, such as (a) fluctuation of the spraying rate, (b) changes of air and gas pressures, (c) variation of flame temperature, and (d) insufficiency of the filters, were considered to be outside the scope of this work. They have been discussed, among others, by FOX[5] and ROBINSON AND OVENSTON[6]. Impurities and the so-called "inert materials" which affect the viscosity of the test solutions have been dealt with by CATON AND BREMNER[7].

EXPERIMENTAL

Apparatus

An EEL flame photometer (Evans Electroselenium Ltd., Harlow, Essex, England) was used throughout this work[8]. The results, therefore, may not apply to other instruments, certainly not to those based on the internal standard technique. This is essentially a single-cell instrument using butane gas–air mixture. The optical sodium and potassium filters used are of gelatine cemented between glass, whereas the calcium filter is of the interference type. The relative over-all spectral

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responses of the filter–photo-cell combination for sodium and potassium have been reported by COLLINS AND POLKINHORNE[8], those for calcium are shown in Fig. 1.

All analyses were carried out in duplicate. To ascertain the reproducibility of the results, flame-photometric scale readings were first made serially and then repeated, the scale adjustment being re-checked against standard solutions during the repeat tests.

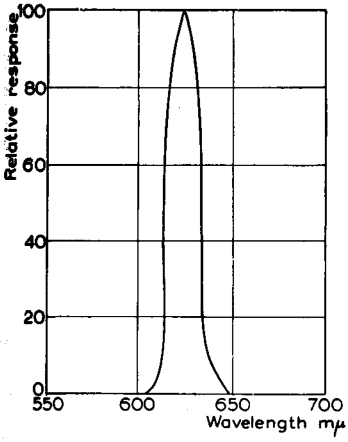

Fig. 1. Combined cell and filter response for calcium. (Courtesy of Evans Electroselenium Ltd., Harlow, Essex, Great Britain)

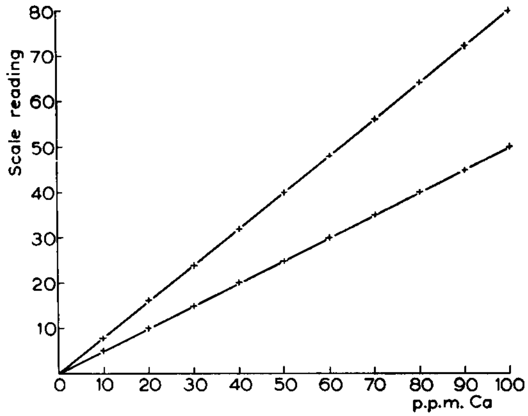

Fig. 2. Ca calibration curves at two different potentiometer settings.

Reagents

AnalaR reagents and demineralized water (containing about 0.5 p.p.m. of total salts as sodium chloride) were used throughout.

Standard solutions: A stock solution of 10,000 p.p.m. of calcium was made by dissolving 24.970 g of pure calcite (Iceland spar–$CaCO_3$) in a minimum of hydrochloric acid and making up to 1 l with water. Similarly the sodium and potassium stock solutions each containing 10,000 p.p.m. of the metal were prepared by drying their chlorides at 110° to constant weight, dissolving 25.422 g and 19.069 g respectively and making up to 1 l. For the preparation of a stock solution containing 1000 p.p.m. of phosphate, 1.400 g of ammonium monohydrogen phosphate, $(NH_4)_2HPO_4$, were dissolved in water and brought to 1 l.

Neutral N ammonium acetate solution[9]*:* Approx. 2*N* NH_4OH from conc. NH_4OH and 2*N* acetic acid from glacial acetic acid were prepared. The two solutions were mixed and the pH adjusted to 7.0 with a glass electrode. The solution should be kept in a stoppered bottle.

Calibration curve for Ca

Fig. 2 shows the instrument's two calibration curves for calcium made at two different potentiometer settings. Both lines are straight, which is evidence of the linear response of the photocell to the calcium emission in this range.

Effect of sodium on calcium

Using the calcium and the sodium stock solutions, a series of solutions was prepared containing from 0 to 5,000 p.p.m. of sodium, together with 100 p.p.m. of calcium. After adjusting the galvanometer spot to read zero for demineralized water and 50 for the sodium-free solution containing 100 p.p.m. of calcium, the series was sprayed and the amount of calcium thus found was recorded.

TABLE I

ERROR IN DETERMINING 100 p.p.m. OF CALCIUM IN THE PRESENCE OF SODIUM BY FLAME PHOTOMETER

Sodium present p.p.m.	*Calcium found p.p.m.*	*Error %*
50	102.0	+ 2.0
100	103.8	+ 3.8
200	106.8	+ 6.8
300	108.5	+ 8.5
500	113.0	+ 13.0
1,000	121.0	+ 21.0
2,000	136.7	+ 36.7
3,000	150.0	+ 50.0
4,000	163.5	+ 63.5
5,000	175.0	+ 75.0

It can be observed from Table I and Fig. 3 that the positive error caused by the presence of sodium is considerable, amounting to 75% for 5,000 p.p.m. of sodium.

Effect of potassium on calcium

A series of solutions containing from 0 to 5,000 p.p.m. of potassium together with 100 p.p.m. of calcium were likewise prepared from the stock solutions and similarly sprayed, adjusting the galvanometer spot to read 80 for the potassium-free solution containing 100 p.p.m. of calcium.

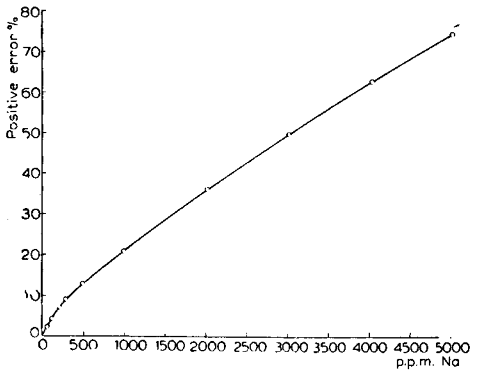

Fig. 3. Effect of sodium on 100 p.p.m. calcium.

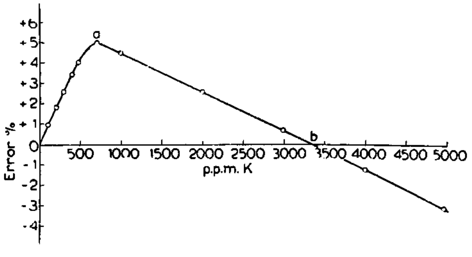

Fig. 4. Effect of potassium on 100 p.p.m. calcium.

Fig. 4 indicates that the error due to the effect of potassium on calcium differs radically in magnitude from that due to sodium and, above a certain concentration, in sign too. That the interference of sodium is relatively much greater in magnitude than that of potassium, may be explained, among other factors, by the following facts:

(a) The relative intensity of sodium measured at 5893 Å is 10,000, whereas it is 2,000 for potassium measured at 7670 Å[10]. The increment of flame background intensity due to sodium is, therefore, 5 times larger than that due to potassium. The relative

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intensity is defined as 100 divided by the number of p.p.m. of the element required to give a photometric response equal to 0.5% of the flame background.

(b) The sodium doublet (5890 and 5896 Å), being much closer to the calcium bands (6030, 6240 and 6480 Å) than the potassium doublet (7660 and 7690 Å), stands a greater chance of benefitting from the insufficiency of the calcium filter.

As an attempt to explain the unique behaviour of the potassium effect on calcium when it comes to the sign of the error, it may be assumed that, when potassium is sprayed together with calcium, two opposed factors come into play:

(i) an emission-intensifying effect due to the general increase in flame background, etc., and

(ii) an emission-suppressing effect caused by self-absorption of energy within the flame, anion interference, etc.

At low concentrations of potassium, effect (a) evidently becomes increasingly dominant, giving a maximum error of + 5% at 700 p.p.m. of potassium, after which the equilibrium turns more and more in favour of effect (b). At 3,350 p.p.m. of potassium, the two effects apparently just cancel each other out, and the same amount of calcium is read with or without this amount of potassium. Larger concentrations of potassium proved to give a negative error, indicating increasing dominance of effect (b).

The phenomenon of self-absorption of energy within the flame has been discussed by several authors. HARRISON *et al.*[11] point out that "an interesting situation arises when radiation emitted by an assemblage of atoms is divided into two regions, one at a higher and one at a lower temperature. Such a situation may exist . . . in which the atoms at the center . . . are at a higher temperature while the ones at the periphery are at lower temperatures. The spectral lines which originate at the higher energy levels will be emitted by the high temperature part of the assemblage with relatively higher intensities than the lower temperature part, but before this radiation can leave (the source) it must pass through the region of low-temperature atoms . . . and the radiation is absorbed."

"The diminution (of intensity) may be so great, that the lines actually are weaker than the continuous background."

The phenomenon is further discussed by HARVEY[12] who states that "as the concentration of the atoms in the discharge increases and the amount of atoms in the cold vapor correspondingly increases, the probability of absorption becomes greater . . . The absorption may occur partly in the discharge itself and partly in the cooler vapor

TABLE II

EFFECT OF WORKING AIR-PRESSURE ON THE POTASSIUM INTERFERENCE WITH 100 p.p.m. CALCIUM

Working air-pressure g/cm²	*Corresponding aspirat. rate ml/sec*	*Scale reading of K-free 100 p.p.m. Ca*	*Max. positive error %*	*p.p.m. K producing max. positive error **	*p.p.m. K producing zero error ***
562	0.0487	40.0	+ 4.5	625	3150
703	0.0550	50.0	+ 5.0	700	3350
844	0.0588	58.5	+ 5.3	760	3525
984	0.0621	63.3	+ 5.6	810	3670
1125	0.0653	70.8	+ 5.8	855	3780
1265	0.0684	77.5	+ 6.0	895	3875

* and ** are shown by points a and b respectively in Fig. 4.

surrounding the discharge. Hence the probability of absorption increases with the increasing concentration of the element"[13]. TWYMAN[14] gives a similar discussion.

It was felt to be of special interest to investigate further this phenomenon, which — so far as we know — has never been referred to yet, by inquiring to what extent changes in flame temperature would upset the equilibrium of the two assumed factors, and thereby cause a shift in points a and b (Fig. 4), if any. Abiding by the manufacturers' advice against using high-temperature gases, such as acetylene, without modification of the instrument, the only alternative left was to try repeating the measurements of potassium interference with the determination of 100 p.p.m. calcium at air-pressures other than the regularly used pressure of 562.5 g/cm². However, since any change in air-pressure automatically brings about a corresponding change in aspiration rate of the sprayed solution (Table II), it is clear that there will be two effects. On the one hand it is to be expected that a higher pressure, which allows the consumption of more fuel gas, will raise the flame temperature, while on the other the consequent increase in aspiration rate will tend to lower it. Further investigation of the phenomenon must, therefore, be left to other workers, whose instruments will allow separate control of flame temperature and aspiration rate.

However, it may not be wrong to draw certain tentative conclusions from Table II:

(1) Since increasing the working air-pressure requires the feeding of correspondingly more fuel gas, this seems to result in flames of relatively higher temperatures, as can be seen by comparing the scale readings of the K-free, 100 p.p.m. calcium solution obtained at the same potentiometric setting of the instrument.

(2) The net effect of such an increase in exciting energy on potassium-containing calcium solution seems to be in favour of the above-mentioned effect (a), thus shifting both points a and b in Fig. 4 to the right and raising the maximum positive error.

That the phenomenon may be due to self-absorption of energy within the flame seems to suggest that it is characteristic of the EEL flame source, since such a behaviour has not been reported by other workers using different sources. The EEL flame photometer utilizes a butane–air mixture which passes to a multi-jet burner, where it burns as a broad flat flame. On the other hand, the Lange instrument, for example, uses acetylene, a single jet burner, the resultant flame being long and thin. It is possible that the nature of the EEL flame might give rise to the regions of varying temperatures, at the high potassium concentrations reported here, fulfilling the conditions mentioned above (HARRISON, HARVEY, etc.[11–15]).

Effect of phosphate on calcium

This was studied by spraying a series of 100 p.p.m. calcium solutions containing from 0 to 400 p.p.m. of phosphate prepared from the stock solutions, and calculating the percentage error from the difference between the calcium introduced and the calcium found. Fig. 5 thus obtained in general confirms the results reported by EDGCOMBE AND HEWETT[2] except for two facts:

(a) We obtained the point of inflection at a somewhat higher potassium concentration.

(b) EDGCOMBE AND HEWETT did not point out that the error was *negative*, although it has been shown to be so by many other workers, *e.g.* LEYTON[16] in particular.

It must be mentioned here that this negative error is very considerable, amounting to —92.5% at a concentration as low as 400 p.p.m. of phosphate ion.

Mutual elimination of sodium and phosphate interferences with calcium

COLLINS AND POLKINHORNE[8] and PUFFELES AND NESSIM[17] both refer to the interference effect of phosphate on sodium in the absence of calcium. In order to find out to what extent these two main interfering agents with their opposite effects on calcium, can cancel each other's effects, solutions were prepared from the stock, containing amounts of these ions which were calculated on the basis of Figs. 3 and 5, to cause equal but opposite errors. The results are shown in Table III, indicating almost complete mutual elimination. The small differences observed are probably due to experimental errors.

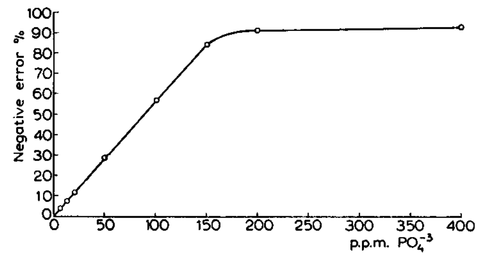

Fig. 5. Effect of PO_4^{-3} on 100 p.p.m. calcium.

TABLE III

MUTUAL ELIMINATION OF SODIUM AND PHOSPHATE INTERFERENCE EFFECTS ON CALCIUM

No.	*Ca^{+2} in soln. p.p.m.*	*PO_4^{-3} in soln. p.p.m.*	*PO_4^{-3} error %*	*Na^+ in soln. p.p.m.*	*Na^+ error %*	*Flame photometer scale reading*	*Ca^{+2} found p.p.m.*	*Deviation %*
1	100	0	0	0	0	80.0	100.0	0
2	100	100	−56	3475	+56	79.0	98.8	−1.2
3	100	50	−28	1500	+28	79.5	99.4	−0.6

APPLICATION TO CALCIUM DETERMINATION

(*a*) *Drinking and irrigation water*

Six samples of deep-well and river water were analysed for phosphate, sodium and potassium (Table IV). Calcium was determined by precipitation as oxalate and subsequent titration with permanganate. It is sufficient, for the purpose of this study to report the maximum and minimum results obtained. The water samples first had to be acidified and heated to remove the bicarbonate[4] which is known to have a serious depressing effect on calcium emission. In order to bring the calcium contents within the convenient range of flame-photometric scale reading (0–100 p.p.m. calcium) the water containing the max. amounts of 122 p.p.m. calcium should be diluted (conveniently, 1+1) with demineralized water.

It is obvious that the phosphate and potassium contents of the diluted water samples can cause only a negligible error when sprayed in order to determine calcium. Only the sodium content is significant and would give apparent calcium contents 4.5% higher than the actual ones, according to Fig. 3. A correction of —4.5% would consequently be necessary.

The water sample containing the minimum amount of calcium (34 p.p.m.) requires no dilution before spraying, and in this case the only correction necessary is —1.0% for the positive sodium interference.

It appears possible, therefore, to determine calcium in water directly with the flame photometer, without preliminary separation as oxalate, correcting only for the sodium interference and disregarding the potassium and phosphate errors.

(*b*) *Soil extracts*

Neutral ammonium acetate extracts of six local types of soils were prepared[9], evaporated to dryness and almost all the ammonium acetate sublimed in order to prevent its clogging effect on the capillary atomizer. The residues were then taken up in the minimum amount of 0.1N HCl, brought up to a definite volume, sprayed into the flame photometer and the max. and min. values obtained recorded as in the case of water samples (Table IV). The results show that here, too, direct flame-photometric determination is possible, correction only having to be applied for the phosphate contents, since the interferences due to sodium and potassium are negligible.

(*c*) *Plant-ash extracts*

Direct flame-photometric determination was, however, not possible when it came to the ten plant extracts (green and yellow citrus, eucalyptus, desert weed and tobacco leaves), which were found to differ very greatly in their phosphate, sodium and potassium contents (Table IV). The extracts were prepared by ashing about 5 g of the dried plant sample in a silica crucible at 550–600° and extracting the ash with 2.5 ml of conc. HCl and hot water. The extracts were then filtered, cooled and made up to 250 ml with water[18].

TABLE IV

INTERFERENCE ERRORS DUE TO PHOSPHATE, SODIUM AND POTASSIUM IN THE DETERMINATION OF CALCIUM IN WATER, SOIL, PLANTS AND SERUM

	Calcium		*Phosphate*		*Sodium*		*Potassium*	
	range p.p.m.	*dilution required* ×	*sprayed p.p.m.*	*error* %	*sprayed p.p.m.*	*error* %	*sprayed p.p.m.*	*error* %
Water								
Max.	122	2	0.22	0	118	4.5	7.0	0
Min.	34	0	0.15	0	23	1.0	0.8	0
Soil								
Max.	600	6	10	—6	10	0	14	0
Min.	82	0	16	—9	6	0	17	0
Plants								
Max.	1350	14	12	—7	2430	41.5	1643	3.3
Min.	274	3	32	—18	267	8.5	767	4.9
Serum (normal)								
Max.	120	4	35	—20	863	18	60	0.6
Min.	90	4	25	—14	787	16.5	40	0.4

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Although it is theoretically possible to calculate the net percentage error in calcium determination resulting from mutual elimination of interference, such a calculation would obviously be impossible unless an analysis is first undertaken to determine sodium, potassium and phosphate. This is not practical when such an analysis is otherwise not required. Clearly the tedious precipitation of calcium seems to be unavoidable in this case, in order to free the calcium from very significant and variable interferences.

(*d*) *Blood serum*

Even though the calcium contents of serum do not necessitate the dilution of 1+3 shown in Table IV, this is advisable because of the inconveniently high viscosity of the serum and the very small volume usually available. It is clear from the analysis of six normal sera (only the max. and min. are given in Table IV) that, in spite of the significant interferences of the individual ions, there is a good chance of mutual elimination, thus leaving only a small positive or negative net percentage error, which, considering the wide range of calcium in normal sera, may be clinically insignificant. It seems justifiable to conclude, therefore, that it appears possible to determine calcium in normal serum for clinical purposes, by spraying its 1+3 dilution directly, without running the risk of a significant error, since normal serum has a more or less stable composition within a certain range. Serum was considered "normal" for this purpose when it complied with the acceptable normal ranges (for adults) of: Na: 315–340, K: 16–22, Ca: 8.5–12 and phosphate 9–14, all in mg %[19].

In Table V a comparison is made of the results obtained by the direct spraying method and those obtained when preliminary precipitation as oxalate is carried out. Serum No. 1 is normal, No. 2 has high phosphate, normal sodium, No. 3 has low phosphate, high sodium, No. 4 has low sodium and phosphate, and No. 5 has high sodium and phosphate.

For normal serum, the agreement between the results of the two methods is good enough. The results of the other sera are influenced by the two main interfering agents: sodium and phosphate, the former tending to raise, and the latter to lower the calcium determined directly. In general, high calcium results are obtained, since the negative error due to phosphate is mostly over-compensated by the positive sodium effect.

It is suggested, therefore, for cases with abnormal serum sodium and phosphate, to be on the safe side and determine calcium by preliminary separation as oxalate, proceeding as follows: remove the supernatant liquid after centrifugation, dissolve the precipitate in 0.05N perchloric acid and finally read the solution with the flame photometer.

TABLE V

ANALYSIS OF SERUM SAMPLES

No.	*Sodium p.p.m.*	*Phosphate p.p.m.*	*Calcium p.p.m.*		
			By precipitation as oxalate	*By direct spraying*	*Difference %*
1	3300	100	110	112	+ 1.8
2	3250	140	105	102	— 2.8
3	3600	90	115	123	+ 7.0
4	3100	70	95	100	+ 5.3
5	3650	80	120	129	+ 7.0

SUMMARY

An investigation of the possibilities for the direct determination of calcium with a single-cell filter flame photometer, without preliminary separation as oxalate, led to the following conclusions:

Calibration curves for 100 p.p.m. of calcium are rectilinear.

Sodium causes an appreciable positive error.

The error due to potassium interference is relatively much smaller than that due to sodium. Up to a certain concentration it is positive and increases with the concentration, then the emission seems to be gradually depressed and the error finally becomes negative.

Phosphates cause a very significant negative error, which tends to be asymptotic. The "radiation buffer" method of correction is not practical here because the max. error is too high (—92.5%).

Except for extreme cases, calcium can be determined by direct spraying, without preliminary separation as oxalate:

(a) in drinking and irrigation water, correction being necessary only for sodium interference,
(b) in soil extracts, correcting only for phosphate effects,
(c) in normal blood sera, without clinically significant corrections at 1+3 dilution.

Owing to the large variations in the contents of Na, K and PO_4^{-3} in plants, calcium cannot be determined in plant-ash extracts without preliminary separation as oxalate. This applies also to abnormal sera, although there the variations in Na and PO_4^{-3} content are not so large.

RÉSUMÉ

Les auteurs ont examiné les possibilités d'un dosage direct du calcium dans des extraits de plantes et de sol, dans l'eau et dans le sérum, par photométrie de flamme, sans séparation préliminaire comme oxalate.

ZUSAMMENFASSUNG

Es wird die Möglichkeit untersucht, Calcium direkt in Pflanzen- oder Bodenextrakten, in Wasser oder Serum flammenphotometrisch zu bestimmen ohne vorherige Isolierung als Calciumoxalat.

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SPECTROPHOTOMETRIC DETERMINATION OF PYRIDOXAL-5-PHOSPHATE

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The existing enzymic method for the determination of pyridoxal-5-phosphate (Py5P), which is based on the activation of tyrosine apodecarboxylase[1], is highly specific for Py5P, but cumbersome and time-consuming. On the other hand, the existing colorimetric and spectrophotometric methods[1,2], though comparatively rapid and simple, are to a large extent unspecific.

The present paper describes a new and simple procedure for a spectrophotometric determination of Py5P, based on the optical properties of the reaction product which is formed when Py5P reacts with cyanide. The reaction itself, which has been described by us only recently[3], has been studied further and the results are also included in the present paper.

EXPERIMENTAL

Reagents

0.2M sodium phosphate buffer, pH 7.4.

0.03M potassium cyanide, in 0.2M sodium phosphate buffer, pH 7.4.

0.0001M solution of pyridoxal-5-phosphate (Hoffmann-La Roche, Switzerland), in 0.2M sodium phosphate buffer. This standard solution must be prepared just before use from a 0.001M stock solution, which should be kept frozen when not in use.

Procedure

The solution to be examined is diluted so that it contains not more than 25 μg Py5P/1 ml, and the pH is adjusted to 7.4. From this solution two 3 ml portions are taken, *A* and *B*. To the first, *A*, 0.1 ml of KCN is added and to the second, *B*, 0.1 ml sodium phosphate buffer. After incubation for 45 min at 50°, the optical density is measured at 385 mμ in a Beckman spectrophotometer model DU. The difference in optical density between *B* and *A* is compared with a calibration curve obtained with a range of Py5P standards.

RESULTS

Absorption spectra

When Py5P reacts with KCN in 0.2M sodium phosphate buffer, pH 7.4, profound changes in the ultraviolet absorption spectrum of the former occur, as shown in Fig. 1. The characteristic absorption maximum at 385 mμ is completely levelled off, while the maximum at 320 mμ is intensified, with a slight shift towards shorter wavelengths. A relationship exists between the spectral modifications and the amounts of KCN added, up to the molar ratio of 1:1 (Fig. 2), showing that the reaction between Py5P and KCN can be considered complete when the reactants are present in equimolecular concentrations. The complete disappearance of the 385 mμ maximum is probably due to the formation of an addition compound, namely a cyanohydrin, since this maximum is associated with the aldehyde group at C_4, which is the only one capable of reacting with cyanide. Completeness of the reaction is secured by the addition of excess KCN.

Paper electrophoresis

A further indication of the formation of an addition compound between Py5P and KCN is provided by the results illustrated in Fig. 3, which shows the difference of the mobilities between Py5P and its reaction product with cyanide.

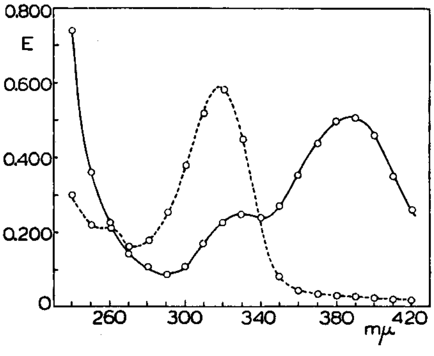


Fig. 1. Absorption spectra: Py5P, $10^{-4}M$, (solid line) and the same after addition of KCN (broken line) (see text).

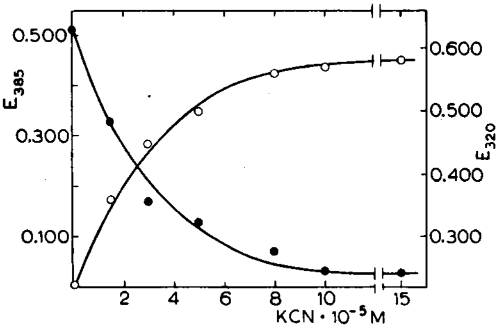


Fig. 2. Optical density changes at 320 mμ (o—o) and at 385 mμ (•—•) as a function of KCN concentration.

Influence of pH

The reaction between Py5P and KCN, as can be expected, is influenced by the hydrogen ion concentration. The rate of formation of the addition compound (cyanohydrin) at different pH values is illustrated in Fig. 4. The optimal pH appears to be near neutrality, on the alkaline side, where Py5P still has the structural formula (I)

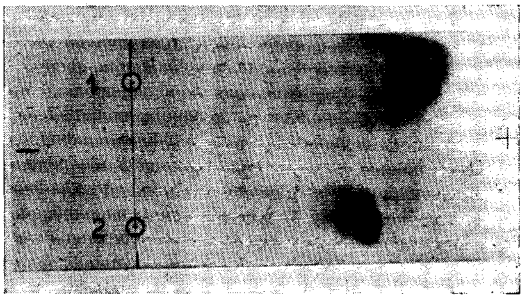


Fig. 3. Paper electrophoresis of Py5P cyanohydrin (1) and of Py5P (2). Experimental conditions according to SILIPRANDI, SILIPRANDI AND LIS[5].

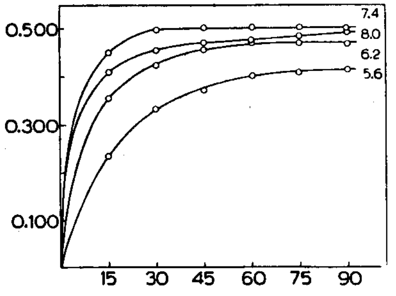
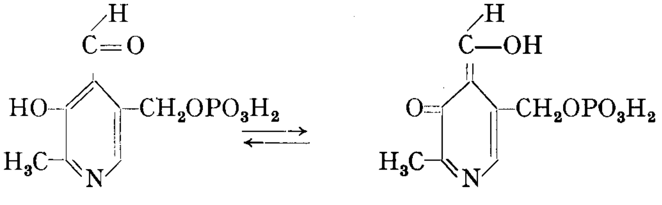


Fig. 4. Rate of interaction between Py5P and KCN at different pH values. Ordinate: decrease of the optical density at 385 mμ; abscissa: time in minutes.

which favours the interaction with KCN, and where KCN is not hydrolysed. At pH 9.0, Py5P does not react with KCN because structure (II) prevails[4].



(I) (II)

Linearity of the reaction

The optical density decrease at 385 mμ in the presence of a large excess of KCN is proportional to the concentration of Py5P present over a range of 0–25 μg, as shown in Fig. 5. The optical density increase at 320 mμ is also proportional to the concentration, but it has not been chosen to measure Py5P because almost every B_6 member has its characteristic maximum at this wavelength.

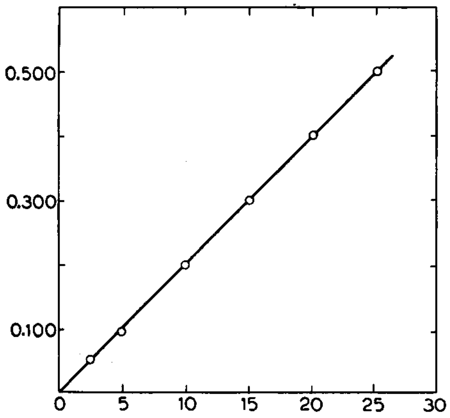


Fig. 5. Calibration curve. Abscissa: μg Py5P/1 ml; ordinate: decrease of the optical density at 385 mμ.

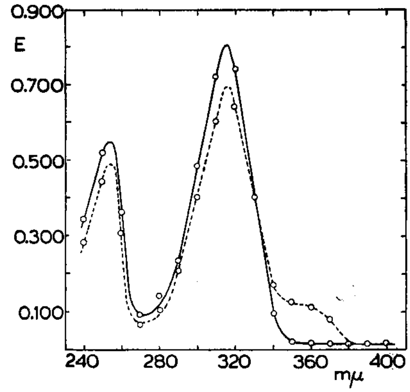


Fig. 6. Absorption spectra: pyridoxal hydrochloride, $10^{-4}M$ (solid line), and the same after addition of KCN (broken line).

Specificity of the reaction

The following structural analogues, belonging to the B_6 group, have been examined in order to test the specificity of the reaction with KCN and the possible interferences: pyridoxal hydrochloride (Bios Lab., U.S.A.), pyridoxine dihydrochloride (Italfarmaco, Italy), pyridoxamine phosphate (S.I.T.I., Italy), pyridoxal hydrochloride ethylacetal and pyridoxamine hydrochloride (Hoffmann-LaRoche, Switzerland). No changes appeared in the absorption spectra of the above-listed substances following the addition of KCN, except for pyridoxal hydrochloride, the spectrum of which is reported in Fig. 6. As can be seen, the addition of KCN produces an increase of the optical density in the region from 330 to 380 mμ, with a maximum at 360 mμ. At 385 mμ there is a very slight increase which can be neglected in practice.

DISCUSSION

The spectrophotometric procedure that has been described is very specific for Py5P and in this respect it is equalled only by the enzymic method of GUNSALUS AND SMITH[1]. The enzymic method, however, as pointed out already in the INTRODUCTION, is rather cumbersome and tedious, and is not suitable for occasional assays, such as those required to determine the purity of a Py5P preparation or the Py5P yield in artificial as well as in biological syntheses.

The colorimetric methods, on the other hand, are not specific unless a previous separation, chromatographic or electrophoretic, is made, but this eliminates the advantage offered by the simplicity and rapidity of the colorimetric methods themselves.

The spectrophotometric method suggested by SCHOTT AND CLARK[6], which is based on the decrease of optical density at 375 mμ and the increase at 327 mμ, following the addition of *m*-hydroxypropadrine, does not seem reliable.

The sensitivity of the present method, based on a spectral peculiarity of Py5P in presence of KCN, is comparable with that of colorimetric and spectrophotometric methods, but inferior to that of enzymic assay. The extreme simplicity both of reagents and procedure and the high specificity represent its main features.

We are studying the possible application of the present procedure to biological materials.

SUMMARY

A simple and specific spectrophotometric procedure for the estimation of pyridoxal-5-phosphate is described, based on the complete disappearance of the absorption maximum at 385 mμ following the incubation with potassium cyanide.

RÉSUMÉ

Une méthode simple et spécifique est proposée pour le dosage du pyridoxal-5-phosphate, par spectrophotométrie.

ZUSAMMENFASSUNG

Es wird eine einfache, spezifische spektrophotometrische Methode zur Bestimmung von Pyridoxal-5-phosphat beschrieben.

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MERCURY CHLORIDE FILM ANODE

I. STUDY OF THE CHARACTERISTICS OF A MERCURY CHLORIDE FILM ANODE BY CHRONOPOTENTIOMETRIC METHODS

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INTRODUCTION

The most common electrode materials for anodic oxidation are platinum, gold, or graphite. Reproducible results are obtained at these electrodes if they are either chemically or mechanically pre-treated prior to each run.

The mercury electrode is widely used for reductions due to its high hydrogen overvoltage and reproducible surface. It is severely limited as a practical working anode by the dissolution of mercury itself at low anode potentials.

Several workers have observed[1-3] that some unusual phenomena occur at the mercury surface when it is polarized anodically in the presence of halide solutions. The so-called anodic passivation of mercury in chloride media has been extensively studied[4-6] by constant current methods.

A similar effect has been observed in this laboratory where the passivation is characterized by a well defined potential rise to values of 1 V or more. This passivation is due to the formation of a film of mercury chloride that effectively limits the continued mercury oxidation. Such a Mercury Chloride Film Anode (MCFA) may be used for the oxidation of substances in the bulk of the solution. As reported earlier[7] several substances have been successfully oxidized using both conventional voltage-scan and chronopotentiometric techniques at a quiet MCFA.

In this paper the characteristics of the MCFA obtained through chronopotentiometric studies are discussed in detail. The MCFA is evaluated as an analytical tool and compared to the platinum electrode. The results obtained by the voltage-scan method will be reported in a separate paper.

EXPERIMENTAL

The chronopotentiometric equipment and circuit were conventional in all respects. Two electrolysis cells were constructed following the design illustrated by REILLEY, EVERETT AND JOHNS[8]. The lower and upper Lucite plugs (o.d. 50 mm) were machined and bevelled on a lathe to fit tightly a 50 mm length of pyrex tubing (i.d. 45 mm). One-quarter inch cavities were machined for the mercury pools in the lower plugs. The pool areas were calibrated through cadmium ion reductions[8] and found to be 1.47 and 1.60 cm^2. Because Lucite is not wetted by the solution or mercury, the interface is reproducible and constant. Contact with the mercury pool was made by a platinum wire which was inserted through a small hole in the bottom of the cavity and sealed with polystyrene. Polystyrene also served as a sealing agent between the lower plug and the pyrex tubing. The upper plug of Lucite had 4 holes drilled for inserting 2 saturated calomel electrodes (S.C.E.), a bubbling tube terminating in a sintered disk, and a nitrogen outflow. The saturated calomel electrodes were of the design described earlier[9]. The upper plug was permanently clamped to a supporting stand. The cell could be then inserted easily from the bottom and held into position with 2 rubber bands connected to small metal hooks drilled into the sides of the Lucite plugs.

Reagent-grade inorganic chemicals and Fisher triple-distilled instrument-grade mercury were used throughout the work without further purification. Stock solutions $2M$ in potassium chloride with pH adjusted to *ca.* 2.5 with hydrochloric acid were prepared fresh every three days. Erratic results were obtained with old potassium chloride solution which was probably due to formation of surface-active substances by bacterial growth.

Stock solutions of the organic substance to be oxidized in $0.01M$ concentration were prepared anew before each series of experiments. Appropriate amounts of stock organic solution and $2M$ potassium chloride were mixed to give final solutions for chronopotentiometry which were $0.2M$ in potassium chloride and about 10^{-3} to $10^{-4}M$ in organic constituent.

PROCEDURE

Approximately 0.5 ml of mercury was delivered from a 10-ml buret into the cavity of the cell. The sample solution with pH adjusted to *ca.* 2.5 was added to the cell. The solution was deaerated for 5 min to remove any dissolved oxygen. Oxygen reacts with mercury in the acidic chloride medium to form mercurous chloride, and more reproducible results are obtained after removal of oxygen. After deaeration the solution was allowed to quiet for *ca.* 1 min and then constant current of desired level was switched on for the chronopotentiogram.

FILM FORMATION

The theory of chronopotentiometry has been well established by the work of GIERST AND JULIARD[10], DELAHAY[11] and others.

Fig. 1, A shows the experimental potential-time pattern (chronopotentiogram) for the anodic polarization of a supporting electrolyte solution, $0.20M$ in potassium chloride and *ca.* $0.002M$ in hydrochloric acid (pH 2.7). A constant current of 240 μA/cm^2 was initiated at the point, $t = 0$, and the resulting chronopotentiogram displays four small potential hold-ups. The anodic potential of +1.4 V *vs.* S.C.E. is reached in less than 20 sec.

Fig. 1, B shows the chronopotentiogram of a $2 \cdot 10^{-3}M$ solution of N,N-dimethyl-*p*-phenylenediamine (DPP) in the same supporting electrolyte as that used for the

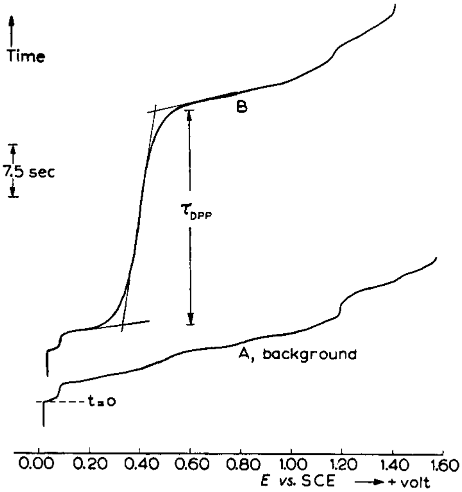

Fig. 1. Potential-time patterns.
A. Background, anodic polarization of mercury pool in $0.2M$ potassium chloride solution.
B. Oxidation of N,N-dimethyl-*p*-phenylenediamine (DPP).

chronopotentiogram of Fig. 1, A. The first wave is for formation of the mercurous chloride film followed by a clearly defined wave for the oxidation of DPP.

This phenomenon has not been observed previously in polarographic work at the dropping mercury electrode (D.M.E.) since the expanding mercury surface and the time interval between successive drops do not favor complete film formation. This is in agreement with the work of KOLTHOFF AND MILLER[12] who found from studies of current-voltage curves at the D.M.E. in the presence of chloride ion, that the diffusion current when corrected for residual current was proportional to the chloride concentration between $2 \cdot 10^{-3}$ and $10^{-5}M$. At higher chloride concentrations the C-V waves had an abnormal appearance which was caused by a film of calomel around the mercury drop.

A. Chloride concentration and current density

In Fig. 2 chronopotentiograms at a constant current of 167 μA/cm^2 are shown for potassium chloride concentrations varying from 0.04 to 0.90M in 0.002N hydrochloric acid. The initial wave is the formation of mercurous chloride that proceeds until the electrode becomes "passive". By the term "passive" it is meant that the electrode has become coated with a film of mercurous chloride. The filmed electrode, as will be discussed later, will now sustain oxidations of substances in the bulk of the solution, *i.e.*, it substantially operates as an inert working anode. This is seen in Fig. 1, B, where, following the small film wave, there is observed a typical chronopotentiogram for the oxidation of N,N-dimethyl-*p*-phenylenediamine (DPP).

The passivation time, T_1, refers to the first potential hold-up or wave. The time

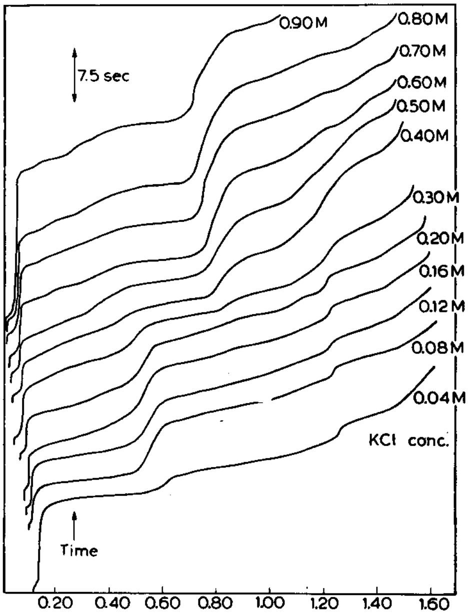

Fig. 2. Anodic potential-time patterns for varying potassium chloride concentrations.

required to deplete the chloride ion concentration at the electrode surface (in the usual sense of chronopotentiometry) is at least a factor of 100 times the value of T_1 observed experimentally.

The $E_{1/4}$ of the first wave follows closely the relationship

$$E_{1/4} = E^\circ - 0.0591 \log \frac{(\mathrm{Cl}^-)}{2} \quad \ldots\ldots\ldots \quad (1)$$

Where E° is the standard potential *vs.* S.C.E. for the reaction:

$$2\mathrm{Hg} + 2\mathrm{Cl}^- = \mathrm{Hg_2Cl_2} + 2\mathrm{e}^- \quad \ldots\ldots\ldots \quad (2)$$

The experimentally determined $E_{1/4}$'s are in good agreement with the calculated values with less than 10 mV deviation. The $E_{1/4}$ corresponding to the point $t = \tau/4$ on the first wave assumes that it is similar to the polarographic $E_{1/2}$. As pointed out by DELAHAY AND BERZINS[13] the potential $E_{1/4}$ corresponding to $t = \tau/4$ has no particular significance in cases of an irreversible wave.

The plot of the variation of $E_{1/4}$ with the log of $^1/_2$ chloride concentration in the bulk of the solution gives a slope of 0.064 in reasonable agreement with the theoretical value of 0.059. These data leave little doubt that the first wave corresponds to the formation of mercurous chloride.

From the chronopotentiogram of the 0.20*M* potassium chloride solution, two significant potential hold-ups may be seen above +0.30 V *vs.* S.C.E. At higher chloride concentrations, the T_1 increases followed by only one major potential hold-up prior to about +1.4 V *vs.* S.C.E. The $E_{1/4}$'s of all the waves are dependent on the chloride concentration which suggests not only further oxidation of mercurous chloride to mercuric chloride, but also oxidations involving mercury chloride complex ions. No systematic study has been made to determine the exact nature of these potential hold-ups.

In this paper further discussion of the background film waves will be devoted to the first and second potential hold-ups since they have the largest transition times and occur in the range of most interest for analytical purposes. They occur at *ca.* +0.080 and +0.55 V *vs.* S.C.E. for a solution 0.2*M* in KCl. The time for the second wave will be referred to henceforth as T_2.

T_1 and T_2 vary with the chloride concentration and the current density. The variation of $(T_1)^{1/2}$ with the chloride concentration is shown in Fig. 3. The pH of the solution was adjusted to *ca.* 2.7 with HCl. The constant current used was 167 μA/cm^2. The minimum of the curve is between 0.2 to 0.4*M* chloride. At lower than approximately $5 \cdot 10^{-3} M$ chloride the T_1 decreases due to the depletion of chloride at the surface of the mercury before film formation is complete. Therefore, in this region, $(T_1)^{1/2}$ changes linearly with the bulk chloride concentration as in the usual diffusion controlled chronopotentiograms.

The experimental variation of T_1 with current density follows the relationship:

$$i_0 T_1^K = 2.7 \quad \ldots\ldots\ldots\ldots \quad (3)$$

where i_0 is the current density in μA/cm^2, T_1 is the time in seconds. This equation can be used, if desired, to predict T_1 for any current density. The value of K found for 0.2*M* potassium chloride solutions at pH 2.5 was 0.60.

The variation of T_2 with current density and chloride concentration has been determined. The optimum conditions for analytical purposes are those which give minimum values of T_1 and T_2. These conditions are current densities between 100 and 400 μA/cm^2 and chloride concentrations of 0.2 to 0.3*M*.

B. Presence of other ions

Anions which form very stable complexes or salts with mercurous ion such as oxalate, sulfate, phosphate, and iodide ions can be tolerated in the 0.2*M* potassium chloride background solution only up to about 0.05*M* levels. Phosphate ion alone in the solution forms a film with mercury similar in behavior to chloride. The phosphate film is not satisfactory for analytical applications.

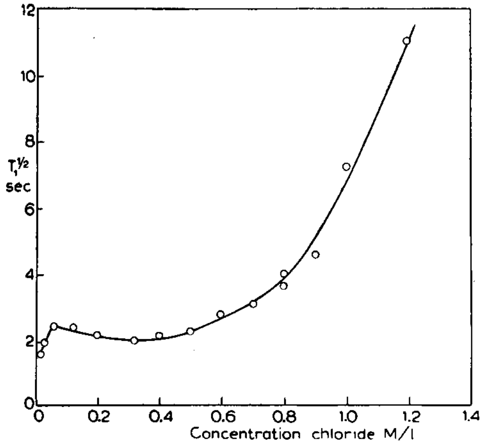

Fig. 3. Square root of passivation time, $T_1^{1/2}$, *vs.* chloride concentration.

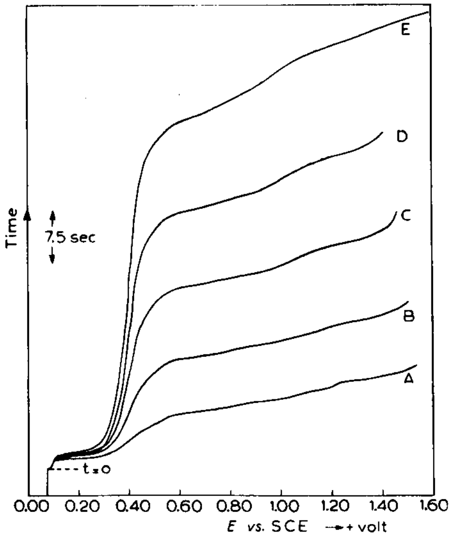

Fig. 4. Chronopotentiograms for oxidation of DPP. A to E, 1.0 to $5.0 \cdot 10^{-3}M$ solutions, respectively.

Indifferent anions, such as nitrate, acetate, fluoride, and perchlorate which do not form strong complexes may be tolerated to a concentration of *ca.* 0.10*M*. Higher concentrations of these anions weakens the film apparently due to incorporation in the film lattice. Their deleterious effect is obvious on the chronopotentiograms by the appearance of several sharp, saw-toothed patterns. These appear as the normally invisible film is ruptured. Small fissures and cracks are then visible on the surface of the electrode.

In basic solutions the background waves become erratic due to competition for formation of the oxide which also disrupts the film. The potential of the electrode under these conditions will remain constant at *ca.* +0.57 V *vs.* S.C.E. As the electrolysis continues, a mixture of a yellow and white precipitate is observed on the surface of the electrode. The precipitate is probably a mixture of mercuric oxide and mercury chloride.

C. Vibrations

Sharp vibrations tend to rupture the film. Small blips are observed on the chronopotentiograms. Vibrations were eliminated by placing the cell stand on a 4-inch thick piece of polyurethane padding.

ANALYTICAL APPLICATIONS

Oxidation of DPP

Fig. 4 shows chronopotentiograms for DPP in the background medium of 0.20*M* potassium chloride and 0.002*N* hydrochloric acid (hereafter called background electrolyte). The current density used in the electrolysis was 420 μA/cm^2. The concentrations of DPP were 1.0, 2.0, 3.0, 4.0 and 5.0 · 10^{-3}*M* for Figs. 4, A to 4, E, respectively. A well defined oxidation wave is observed for all these concentrations. A plot of the square root of the transition time, $\tau_{DPP}^{1/2}$, with concentration of DPP gives excellent linearity. The transition time, τ_{DPP}, is given by:

$$\tau_{DPP}^{1/2} = \frac{\pi^{1/2} n F C^b D^{1/2}}{2 i_o} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (4)$$

where n is the number of electrons involved in the electrode reaction; F is the Faraday; C^b is the bulk concentration of the electroactive species; i_o the current density; and D the diffusion coefficient of the electroactive species.

If the electrode reaction involves consecutive processes[13], the transition times τ_1 and τ_2 would be given by:

$$(\tau_1 + \tau_2)^{1/2} - \tau_1^{1/2} = \frac{\pi^{1/2} n_2 F D_2^{1/2} C_2^b}{2 i_o} \qquad (5)$$

TABLE I

OXIDATION OF DPP AT MCFA AND Pt ELECTRODES

Conc. DPP × *10*^{3}	*Conc.* KNO_3	T_1 *(sec)*	τ_{DPP} *(sec)*	$E_{1/4}$ *(V vs. S.C.E.)*
A. MCFA: (i_o = 205 μA/cm^2, background solution 0.20*M* KCl, pH = 3.2)				
2.5	0	9.37	59.2	0.340
2.5	0.005	14.2	57.0	0.340
2.5	0.010	13.9	62.0	0.340
2.5	0.05	7.50	63.0	0.338
2.5	0.10	8.25	60.0	0.335
2.5	0	7.50	60.0	0.340
			Average 60.2 ± 1.5	0.339 ± 0.002
			Average deviation 2.5%	0.6%
B. Pt electrode: (i_o = 245 μA/cm^2, background solution 0.20*M* KCl, pH = 3.2)				
2.5	0		34.1	0.334
2.5	0.005		32.3	0.340
2.5	0.010		33.0	0.342
2.5	0.050		33.0	0.350
2.5	0.10		33.5	0.350
2.5	0		31.1	0.341
			Average 32.8 ± 0.8	0.343 ± 0.005
			Average deviation 2.4%	1.5%

where n_2 is the number of electrons involved in the electrode reaction for the second substance; D_2, the diffusion coefficient for the second substance; and $C_2{}^b$, the bulk concentration of the second substance. If this were true in the present case under consideration, $[(\tau_1+\tau_2)^{1/2} - \tau_1{}^{1/2}]$ would be proportional to the concentration of DPP, where τ_1 and τ_2 refer to the transition time for the film formation and oxidation of DPP, respectively.

The data of Table I clearly show that τ_{DPP}, within experimental error, is independent of the variation of the transition time for film formation. This indicates that the oxidation of DPP proceeds independent of the film reaction. Table I also includes comparison data for the chronopotentiometric oxidation of DPP at a platinum foil electrode.

The calibration curves A, B and C for DPP in Fig. 5 are for current densities of 420, 240, and 167 μA/cm^2, respectively. The product $i_0\tau^{1/2}/C^b$ was not constant. The variation was less than 20% for these current levels. In a purely diffusion-controlled reaction with no complications, $i_0\tau^{1/2}/C^b$ is a constant.

The plots of log $\dfrac{\tau^{1/2}-t^{1/2}}{t^{1/2}}$ *vs.* potential of DPP at both types of electrodes show close similarity with a "break" appearing in the curve at *ca.* +0.38V *vs.* S.C.E. (Fig. 6). The DPP concentration is $2\cdot10^{-3}M$, current 167 μA/cm^2. The pH's of the solutions are 4.0 and 3.88 for the MCFA and Pt electrodes, respectively. The slopes of the curves for the MCFA are 0.135 and 0.064, and for the Pt electrode, 0.088 and 0.070. The reason for the "break" in the curve is not known although curves for such plots have been observed in instances of irreversible electrode reactions at the DME[14]. The similarities

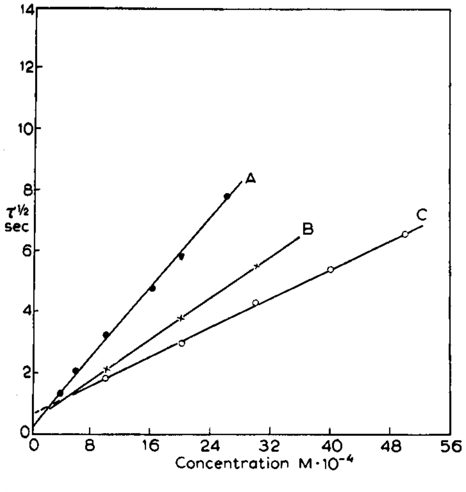

Fig. 5. Calibration curves for DPP oxidation at varying current densities. A. 420 μA/cm^2; B. 240 μA/cm^2; C. 167 μA/cm^2.

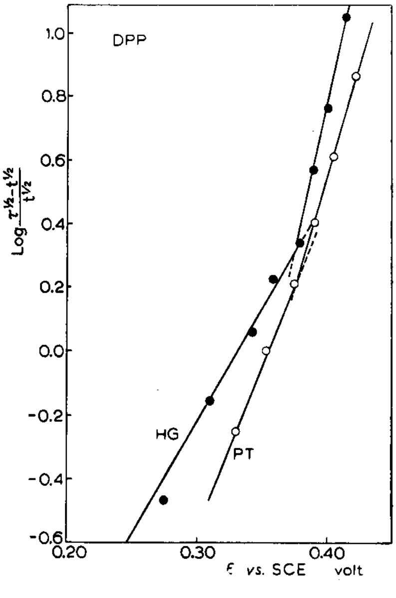

Fig. 6. Plot of log $\dfrac{\tau^{1/2}-t^{1/2}}{t^{1/2}}$ *vs.* electrode potential for oxidation of DPP at platinum and MCFA electrodes.

between the Pt electrode and MCFA for the oxidation of DPP suggests that the film on the surface of the mercury is functioning essentially as an "inert" electrode.

Oxidation of other compounds

The various organic molecules listed in Table II can be oxidized at the MCFA. In all cases except that of hydroquinone, the $E_{1/4}$'s at platinum and MCFA electrodes are in close agreement. Calibration curves for aniline, hydroquinone and 3,3′-dimethylbenzidine (*o*-tolidine) at a constant current level of 240 μA/cm^2 are shown in Fig. 7. The sensitivity for aniline is low. Linear calibration curves may be obtained for the other compounds with the exception of *o*-phenylenediamine and 8-amino-1,3,6-naphthalenetrisulfonic acid (Koch's Acid). Anomalous behavior is observed for *o*-phenylenediamine above a concentration of about $2.5 \cdot 10^{-3} M$ where the $\tau^{1/2}$ decreases markedly in the calibration plot. The reason for this behavior is not known.

TABLE II

COMPARISON OF OXIDATIONS AT PLATINUM AND MCFA

Compound	*pH*	$E_{1/4}$ *(Pt)* *V vs. S.C.E.*	$E_{1/4}$ *(MCFA)* *V vs. S.C.E.*
DPP	2.7	0.41	0.37
	4.3	0.33	0.33
Aniline	3.5	0.81	0.82
o-Phenylenediamine	4.0	0.38	0.43
p-Phenylenediamine	3.2	0.37	0.5
Hydroquinone	2.7	0.42	0.95
Ferrocyanide	2.7	0.40	—
1,10-*o*-Phenanthroline ferrous	3.5	1.10	0.96
8-Amino-1,3,6-naphthalenetrisulfonic acid (Koch's Acid)	3.1	0.76	0.80

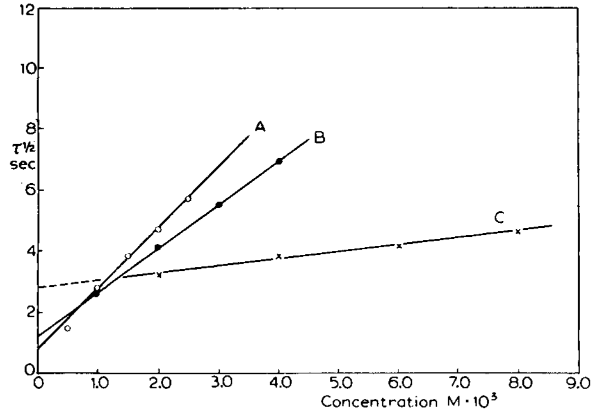

Fig. 7. Calibration curves. A. 3,3′-Dimethylbenzidine (*o*-tolidine). B. Hydroquinone. C. Aniline.

For Koch's Acid, a similar effect is found above a concentration of *ca.* $2 \cdot 10^{-3} M$.

In this case, the reason for the decrease in transition time is believed to be related to the surface-active nature of Koch's Acid. The strong absorption on the surface of mercury greatly enhances the passivation time, T_1, and consequently, the thickness of the film formed. The thick film hinders the oxidation of Koch's Acid and τ then decreases. Other surface-active agents such as gelatin, produce the same deleterious effect. Solid calomel has been observed frequently on the anode surface under these conditions.

Inorganic ions, such as Fe(II), U(IV), Co(II), ferrocyanide, bromide and iodide, do not exhibit oxidation at the MCFA. The last three ions interfere with the mercury chloride film formation due to competitive formation of insoluble mercury salts. T_1 is then large and solid precipitate is often observed on the electrode surface.

Re-use of MCFA

A possible advantage of this new electrode system is that it requires no special cleaning or pre-treatment procedures. After an oxidation run, the surface may be readily cleaned by cathodic stripping. Preliminary experiments indicate that successive determinations may be performed with the same mercury pool, using cathodic stripping to renew the electrode surface. A reproducibility of ±3% for 5 successive determinations of DPP has been obtained in this fashion.

ACKNOWLEDGEMENTS

We wish to express our appreciation to the Research Corporation of America for a grant in partial support of this work. Samples of Koch's Acid were kindly supplied by E. I. du Pont de Nemours and Company. The assistance of MARTHA KELLY in preparing the manuscript is gratefully acknowledged.

SUMMARY

The Mercury Chloride Film Anode (MCFA) is proposed as a new working anode which compares favorably with platinum or other inert metal electrodes.

Only organic compounds have been oxidized thus far at the MCFA. Since the oxidation of organic molecules is of considerable interest this is not a serious limitation. The use of this electrode is restricted to pH's less than 5. This, coupled with the interferences of high concentrations of certain anions like iodide, phosphate, and sulfate, represent the most serious restrictions to MCFA's analytical usage. A further interesting possibility of this electrode is its use as a working cathode or anode in solutions containing both reducible and oxidizable species.

RÉSUMÉ

L'anode à film de chlorure de mercure est proposée; elle peut être comparée avantageusement à l'électrode de platine ou à d'autres électrodes de métal inerte. D'autre part, elle peut fonctionner soit comme cathode, soit comme anode dans des solutions renfermant des substances oxydables ou réductrices.

ZUSAMMENFASSUNG

Es werden die Vorteile der ,,Quecksilberchloridfilm-Anode'' gegenüber der Platinelektrode oder solchen aus anderen inerten Metallen beschrieben. Sie kann in Lösungen, die reduzierbare oder oxydierbare Substanzen enthalten, sowohl als Kathode wie auch als Anode verwendet werden.

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MERCURY CHLORIDE FILM ANODE

II. INVESTIGATION OF THE CHARACTERISTICS OF THE MERCURY CHLORIDE FILM ANODE BY VOLTAGE-SCAN METHOD

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INTRODUCTION

An investigation of the anodic passivation phenomenon at the mercury pool electrode in the presence of chloride ion has led to the development of a Mercury Chloride Film Anode (MCFA). Its characteristics as applied to the oxidation of substances by the chronopotentiometric method were reported earlier[1].

In chronopotentiometry the film was formed in the presence of the substance to be oxidized in the background potassium chloride solution. This led to difficulties of non-reproducibility or no passivation in cases where the substance to be oxidized formed very stable salts with mercurous ion, or was strongly absorbed on the mercury surface. This difficulty may be eliminated by forming the film by voltage-scan prior to the introduction of the oxidizable substance.

The objectives of this paper were to evaluate the characteristics of the MCFA as a working anode for the oxidation of substances by the voltage-scan method. As a useful analytical tool, a method of reproducibly forming the film and applying it to oxidations will be discussed. The variation of peak current with concentration, sensitivity, and half-peak potentials obtained will be compared with the previously reported chronopotentiometry work.

APPARATUS AND REAGENTS

A Lucite cell described previously[1] was used throughout this work. The area of the mercury pool was 1.60 cm^2.

The polarizing unit was a 50-ohm $\pm 0.5\%$ linearity 10-turn Helipot. It was connected to a speed changer (Metron Instrument Co., Denver, Colo.) driven by a reversible, synchronous motor. By appropriate adjustment of the speed changer, scan rates from 200 to 5000 mV/min were possible. The polarizing voltage was obtained from four $1\frac{1}{2}$ V dry cells, connected in such a manner, that a voltage range from -3 to $+3$ V could be scanned.

The currents were determined by measuring the voltage drop across a calibrated decade resistance box in series with the circuit using a Varian recorder (10 mV full scale deflection). No damping was applied and the pen movement was limited only by the natural period of the recorder (1 second full scale). The chart speed of the recorder was 2 in./min.

The electrode potential *versus* an auxiliary saturated calomel reference electrode (S.C.E.) was also monitored by a Leeds and Northrup model 7664 pH meter which fed into a Leeds and Northrup Speedomax recorder adjusted for a 2.0-V full scale deflection. This system was used when it was desired to compare the applied voltage to the actual potential of the electrode. The L and N recorder operated at a chart speed of 2 in./min.

Bethlehem Apparatus Company instrument mercury was used without further purification.

Stock solution of 0.20M potassium chloride with pH adjusted by hydrochloric acid to about 2.5 (background electrolyte) was prepared fresh every 3 days for reasons previously described[1]. The 0.01M stock solutions of oxidizable substances were prepared containing 0.20M potassium chloride and pH adjusted to *ca.* 2.5 (hydrochloric acid or sodium hydroxide). They were prepared prior to each series of runs.

PROCEDURE

Approximately 0.5 ml of mercury was delivered to the cavity of the Lucite cell by a 5.0-ml buret. Care must be taken against stopcock grease or other contaminants coming in contact with the mercury. To the cell was added 30 ml of the background electrolyte. The cell was placed in position and the solution deaerated for ca. 5 min. After allowing the solution to quiet, 0.00 V *vs.* S.C.E. was applied (point C, Fig. 1) for approximately $^1/_2$ min, or until the potential of the mercury electrode *vs.* S.C.E., as measured independently, corresponded to the applied potential. The reason for applying this voltage is to reduce any mercurous chloride formed on the surface of the mercury through reaction with dissolved oxygen[2]. More reproducible results are obtained in this manner. The mercury pool was then polarized (see point D, Fig. 1) at the desired rate to an applied voltage of *ca.* +1.4 V *vs.* S.C.E. The mercury chloride film is formed during this voltage scan interval. After reaching the applied voltage of +1.4 V *vs.* S.C.E., the motor of the polarizing unit was reversed and the applied voltage returned to +0.10 V *vs.* S.C.E. At +0.10 V the film is not removed by cathodic reduction. Less than 5 μA of current was observed at this potential.

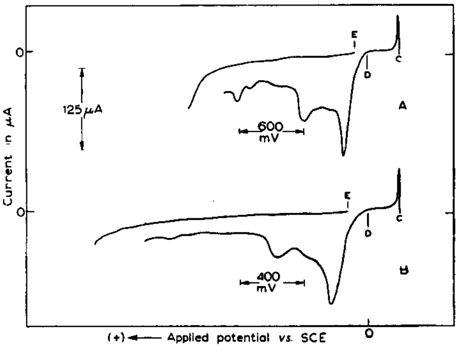

Fig. 1. Current–voltage curves for mercury chloride film formation and background re-scan. A. 600 mV/min. B. 400 mV/min.

The stock solution of the oxidizable substance was then added to the solution in the cell by a needle-tipped 10-ml buret which was inserted through a small hole in the top of the cell. Care must be taken during the addition to prevent any sharp jarring which may rupture the film surface. The solution was then stirred by nitrogen, allowed to quiet, and re-scanned from +0.10 V to +1.4 V *vs.* S.C.E. It is important that the applied voltage of +0.10 V *vs.* S.C.E. be maintained during the interval between the first and second scans.

RESULTS AND DISCUSSION

Fig. 1, B shows a typical current-voltage (C-V) curve for the anodic polarization of the mercury pool electrode in the supporting electrolyte solution at a scan rate of 400 mV/min. The first large wave of *ca.* 120μA peak anodic current is for the formation of mercurous chloride. Two other waves follow it whose half-peak potentials correspond closely to the quarter-wave potentials obtained by chronopotentiometry for the same chloride concentration and pH.

The peak current of the first wave is the point at which the freshly formed film first begins to limit the oxidation of mercury to mercurous chloride. The number of coulombs required to reach this state is reproducible from run to run within 5% and calculates to an initial film thickness of about 20 Å. The other waves which follow also contribute to the unique condition of passivation for the mercury electrode[3].

The re-scan of the electrode now called the Mercury Chloride Film Anode (MCFA) from +0.10 V *vs.* S.C.E., indicated in Fig. 1 by point E, to +1.4 V *vs.* S.C.E. gives a fairly flat "residual" current of *ca.* 5 μA. A background wave begins to appear at *ca.* 1.4 V *vs.* S.C.E. which is the useful limit of this electrode. The peak-type waves, representing film formation, are now absent on the re-scan. The potential of the MCFA *vs.* an auxiliary S.C.E. as measured independently follows the applied voltage within ±5 mV.

The level of the residual current varies between 5 and 10 μA from run to run depending on the polarization rate, the time required to return the applied voltage to +0.10 V *vs.* S.C.E. and the re-scan. The effect of the 600 mV/min scan rate on the film formation and re-scan waves may be seen in Fig. 1, A. Most work reported in this paper was performed at a scan rate of 400 mV/min.

The conditions of chloride concentration and pH favorable for film formation, and interferences from foreign ions and vibrations reported previously also apply here[1].

Oxidation of organic compounds

Curve B in Fig. 2 is for the oxidation of $3.8 \cdot 10^{-4} M$ solution of N,N-dimethyl-*p*-phenylenediamine (DPP) in the background electrolyte at a scan rate of 400 mV/min. The well defined peak-type wave (in an anodic direction) is similar to those obtained by STREULI AND COOKE[4] for voltage-scan polarography at a quiet mercury-pool electrode for the reduction of metal ions. Fig. 2, A shows the oxidation of 8-amino-1,3,6-naphthalenetrisulfonic acid (Koch's Acid).

Aniline, hydroquinone, and *p*-hydroxydiphenylamine gave similar peak-type waves as reproduced for 600 mV/min scan-rate in Fig. 3.

In this type of polarography the peak current is proportional to the concentration.

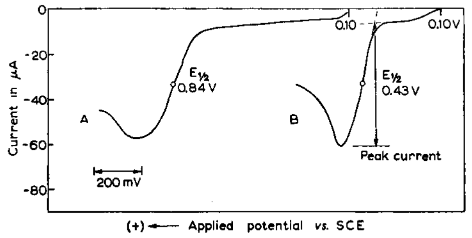

Fig. 2. Peak-type anodic C–V curves for oxidation at MCFA. A. $8.0 \cdot 10^{-4} M$ Koch's Acid. B. $3.8 \cdot 10^{-4} M$ DPP.

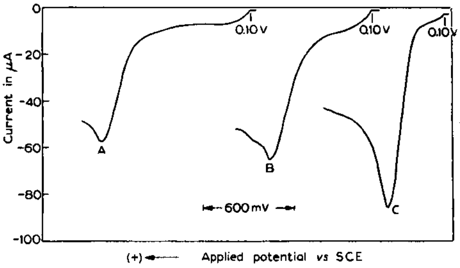

Fig. 3. Peak-type anodic C–V curves for oxidation at MCFA. A. $2.7 \cdot 10^{-4} M$ aniline. B. $4.1 \cdot 10^{-4} M$ hydroquinone. C. $6.0 \cdot 10^{-4} M$ *p*-hydroxydiphenylamine.

Aniline, hydroquinone, Koch's Acid, and DPP gave linear calibration curves in the concentration range of $10^{-4}M$ to $10^{-3}M$ solutions.

In conventional polarography at the dropping mercury electrode two procedures are generally used in correcting for the contribution of the residual current. One involves a subtraction of a previously recorded residual current. The other uses an extrapolation of the base line of the polarogram prior to the wave of the electroactive species. Since at the MCFA the residual current fluctuates a few μA from run to run, the latter method was selected. In applying this method, it was found empirically that more consistent results were obtained if the value of peak current (i_p) was determined as illustrated in Fig. 2, B. The variation of i_p/C was the least for this method of evaluating the peak current.

The values of i_p/C for DPP and Koch's Acid are summarized in Table I. The reproducibility is between 5 and 6%. There was a slight decrease in the value of i_p/C at higher concentrations.

TABLE I

VALUES OF CURRENT, HALF-PEAK POTENTIALS, AND NUMBER OF COULOMBS FOR FILM FORMATION

Concentration (mole/l)	i_p *(μA)*	i_p/C *(A/mole/l)*	E_p *(corrected)*[a]	*Coulombs*[b]
A. Koch's Acid: Background solution, 0.2*M* KCl, pH 2.7. Scanning rate 400 mV/min				
$2.51 \cdot 10^{-4}$	19.0	0.0757	+0.84	$7.9 \cdot 10^{-3}$
4.87	33.5	0.0687	0.85	7.1
7.10	47.2	0.0667	0.86	7.0
8.11	52.0	0.0640	0.88	7.1
9.20	58.0	0.0630	0.86	7.2
	Average	0.0676 ± 0.0037	0.86 ± 0.01	7.2 ± 0.2
	Deviation	5.5%	1%	3%
B. DPP: Background solution, 0.2*M* KCl, pH 2.4. Scanning rate 400 mV/min				
$1.96 \cdot 10^{-4}$	29.8	0.152	+0.49	$7.3 \cdot 10^{-3}$
3.23	43.5	0.138	0.46	7.2
5.06	68.0	0.134	0.45	7.4
6.83	87.2	0.128	0.45	8.0
8.00	99.2	0.124	0.46	8.2
	Average	0.135 ± 0.008	0.46 ± 0.01	7.6 ± 0.4
	Deviation	6%	2%	5%

[a] Corrected for *iR* drop. *R* as measured by AC bridge 620 ohms.

[b] Area under curve between 0.0 and 1.2 V *vs.* S.C.E. measured by planimeter. Number of coulombs calculated from area.

If the direction of the voltage-scan is reversed after the peak current is attained, and scanned in a less positive direction, a peak-type cathodic wave is observed for the reduction of the oxidized substance remaining near the electrode surface. Such a wave is shown for 3,3'-dimethylbenzidine (*o*-tolidine) in Fig. 4. Although no systematic study was undertaken to correlate these reverse waves, a general observation is that such waves only appear for compounds which behave in an approximately reversible manner at the platinum electrode. For compounds such as aniline and *o*-phenylenediamine which show irreversible behavior at the platinum electrode, no cathodic wave is observed prior to the reduction of the mercury chloride film.

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Oxidation of inorganic compounds

Oxidation of ferrocyanide ion was not possible by chronopotentiometry because of mercurous ferrocyanide formation which prevented the mercury chloride film formation. In voltage-scan where the film is formed prior to the introduction of ferrocyanide, a double wave was observed. The first wave at *ca.* +0.15 V *vs.* S.C.E. is believed to be for the formation of insoluble mercurous ferrocyanide[5]. The second wave has a half-peak potential that corresponds to that obtained at the platinum electrode and is probably the oxidation of ferrocyanide to ferricyanide. The peak height of the second wave is proportional to the concentration of ferrocyanide.

No oxidation was observed for $10^{-3}M$ solutions of Co(II), Fe(II), and U(IV). Iodide and bromide ions form more insoluble salts with mercurous ion than chloride and remove the film. Visible crystals of mercurous iodide or bromide then appear on the surface of the mercury pool.

Oxidation-reduction of p-nitroaniline

The oxidation of the amino group in *p*-nitroaniline is difficult at a Pt electrode. The wave occurs at such positive potentials that it is merged with the background. Well defined oxidation waves are observed at the MCFA at about 1.1 V *vs.* S.C.E. While no extensive survey has been made, it is possible that oxidations which are difficult at Pt and Au electrodes may be accomplished at the MCFA.

It is evident that the MCFA, when stripped of its film can be operated as a conventional mercury pool cathode. The interesting possibility exists of carrying out both oxidations and reductions on the same solution. *p*-Nitroaniline has a reducible nitro group as well as the oxidizable amino function. It was found possible to first oxidize the amino group, then, after stripping the mercurous chloride film, reduce the nitro group. The ratio of oxidation to reduction current observed was approximately 1 to 10. The nitro reduction under these conditions is a 6-electron process[6].

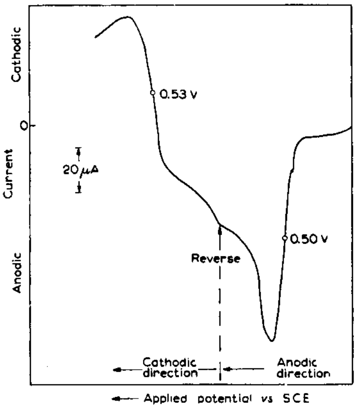

Fig. 4. Oxidation of 3,3'-dimethylbenzidine followed by reverse scan. Scanned anodically from right to left, reversed and scanned in a cathodic direction.

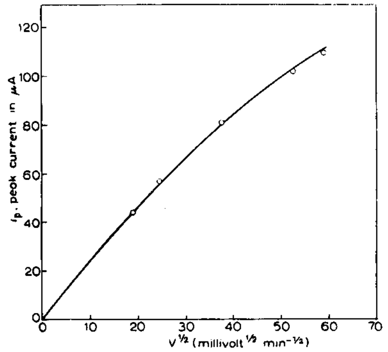

Fig. 5. Peak current *vs.* square root of scan rate. DPP concentration $3.2 \cdot 10^{-4}M$.

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Sensitivity

The sensitivity of the MCFA is about 10 fold greater by voltage-scan than chronopotentiometry. Further increase of sensitivity in conventional voltage-scan may be accomplished by increasing the area of the electrode, increasing the scanning rate, or by stirring the solution. The main limitation which determines the maximum sensitivity is still the ratio of the residual current to the peak oxidation current. A $10^{-4}M$ concentration of DPP gives approximately 14 μA current. This is about the lower limit of sensitivity where the residual current to the oxidation current approaches a 1:1 ratio.

In conventional quiet pool polarography[4] the peak currents are proportional to the square root of the scan-rate, $V^{1/2}$. This relationship also applies at the MCFA. Fig. 5 represents the experimentally determined curve of i_p *vs.* $V^{1/2}$ for $3.2 \cdot 10^{-4}M$ DPP in the background electrolyte. The value of i_p decreases at higher scan-rates. One possible reason for this decrease may be due to the larger iR drop which appears for the larger currents at higher scan-rates. The actual potential of the electrode then lags behind the applied potential.

Enhanced sensitivity may also be gained through stirring of the solution during the scan. Although sharp vibrations tend to rupture the film, mild stirring by nitrogen bubbling through a sintered glass deaerating tube can be tolerated. A preliminary experiment with stirring by nitrogen while oxidizing DPP indicates that at least a two fold increase in sensitivity is possible.

Reproducibility

The reproducibility of the peak current from day to day was checked for a period of a week at two scan-rates of 600 and 2800 mV/min. Fresh stock solutions of potassium chloride and DPP were prepared daily. The concentration of DPP was $3.2 \cdot 10^{-4}M$. The data are shown in Table II. In several instances, re-runs were made on the same MCFA and solution after stirring the solution by nitrogen and re-setting the applied voltage to +0.10 V *vs.* S.C.E. The day to day reproducibility for 9 runs is 4.4%. The reproducibility of 1–3 re-runs on the same MCFA and solution is between 2–4%.

The half-peak potential

The potential at the point where the current was one-half the peak value was designated as the half-peak potential, E_p.

The E_p values obtained at the MCFA for many organic compounds are in good agreement with $E_{1/2}$ values obtained at the Pt electrode under the same conditions of pH. The agreement of E_p values from run to run is *ca.* 2%. Table I gives the reproducibility of E_p values for changing concentrations of Koch's Acid and DPP. The values reported are corrected for iR drop of the circuit.

The E_p values determined at the MCFA are summarized in Table III. In the few cases where the agreement with the value obtained at the Pt electrode is poor, the E_p values are always shifted towards more positive potentials. Table III contains chronopotentiometric results at the MCFA and platinum electrodes for comparison.

Column 5 of Table I gives the total number of coulombs required for the formation of the film +0.00 to +1.2 V *vs.* S.C.E. prior to the oxidation of DPP and Koch's Acid.

TABLE II

REPRODUCIBILITY OF PEAK CURRENTS

Concentration of DPP $3.2 \cdot 10^{-4}M$. Background electrolyte $0.2M$ potassium chloride pH 2.5

i_p at 600 mV/min (μA)	*Re-runs*		*i_p at 2800 mV/min (μA)*	*Re-runs*		
	1	*2*		*1*	*2*	*3*
49.2			105.0	112.0	107.0	107.0
52.3			101.3	103.5		
54.0			101.4			
53.3	53.7		102.2	102.2	102.8	100.6
57.2						
58.0						
57.6						
52.7	56.9	59.0				
55.5	57.3	57.5				
Average 54.4 ± 2.4 Deviation 4.4%			Average 102.5 ± 1.3 Deviation 1.3%			

TABLE III

COMPARISON OF $E_{1/2}$ AND $E_{1/4}$ VALUES AT MCFA AND Pt ELECTRODE

Compound	*pH*	*Chronopotentiometry*		*Polarographic*	
		$E_{1/4}$ Pt	*$E_{1/4}$ MCFA*	*$E_{1/2}$ Pt*	*E_p MCFA*
DPP	2.7	0.41	0.37	—	0.43
	4.3	0.33	0.33	—	—
Aniline	2.7	0.85	—	—	0.85
	3.5	0.81	0.82	—	—
o-Phenylenediamine	4.0	—	0.43[a]	0.38[b]	—
	2.6	—	—	0.46[b]	0.70
p-Phenylenediamine	3.2	—	0.5	0.37[b]	0.63
Hydroquinone	2.7	0.42	0.95	—	0.61
p-Nitroaniline	2.6	N.P.[c]	—	—	1.1
p-Hydroxydiphenylamine	2.0	0.33	—	—	0.35
o-Tolidine	2.0	0.51	—	0.50	0.50
Koch's Acid	3.1	0.76	0.80	0.80[d]	0.78
H-Acid	2.7	—	—	0.73[e]	0.56
2,5-Dimercapto-1,3,4-thiadiazole	2.6	—	—	0.20	*ca.* 0.66[a]
1,10-*o*-Phenanthroline ferrous	3.5	1.10	0.96	1.05	—
Ferrocyanide	2.7	0.40	N.P.[f]	—	0.40
Ferrous ion			N.O.[g]		N.O.
Cobalt(II)			N.O.		N.O.
Uranium(IV)			N.O.		N.O.
Iodide ion			N.P.		N.P.

[a] Poorly defined wave.
[b] Data of PARKER AND ADAMS[7].
[c] Not Possible (N.P.): oxidation wave merges with background wave.
[d] Value at pH 9.0.
[e] Value at pH 1.2.
[f] Ferrocyanide interferes with film formation due to reaction with mercurous ion.
[g] No Oxidation Observed (N.O.).

It may be seen that the E_p's are independent of the number of coulombs required for the film.

Occasionally, perhaps one out of every 10 runs, the film formation waves were large. Since the E_p values become dependent on the film thickness above a certain maximum, an arbitrary upper limit of $10 \cdot 10^{-3}$ coulombs was set for the film formation wave. This corresponded to a maximum peak current for the first film wave of 200 μA using a scan-rate of 400 mV/min.

The presence of surface-active agents interfere markedly with the film formation waves. Gelatine, methyl red, Koch's Acid, and other surface-active agents may be introduced only after the film is formed. This was the reason why Koch's Acid could not be determined at higher concentrations by the chronopotentiometric method.

ACKNOWLEDGEMENTS

The authors are grateful to the Research Corporation of America for a grant in partial support of this work. The authors gratefully acknowledge the sample of pure *p*-hydroxydiphenylamine from John McCarty, samples of Koch's and H-Acid from E. I. du Pont de Nemours and Company, and the 2,5-dimercapto-1,3,4-thiadiazole from the B. F. Goodrich Company.

We are indebted to R. T. IWAMOTO for his helpful suggestions during the course of this work, and to MARTHA KELLY for assistance in preparing the manuscript.

SUMMARY

The Mercury Chloride Film Anode (MCFA) is proposed as a working anode which may have desirable properties for oxidation of organic molecules. For many organic molecules it shows characteristics comparable to the platinum electrode.

It has a higher background overvoltage than the platinum electrode. The polarographic wave of *p*-nitroaniline is not obtained at a platinum electrode. A well-defined wave is observed at the MCFA at *ca.* 1.1 V *vs.* saturated calomel electrode.

The sensitivity of the MCFA by voltage-scan is some 10 fold greater than that of chronopotentiometry. Preliminary experiments indicate that sensitivity may be enhanced by stirring of the solution.

RÉSUMÉ

Une anode à film de chlorure de mercure est proposée pour l'oxydation de molécules organiques. La sensibilité par „voltage-scan" est environ dix fois plus grande que celle obtenue par chronopotentiométrie. Des expériences préliminaires montrent que la sensibilité peut être améliorée par agitation de la solution.

ZUSAMMENFASSUNG

Die Quecksilberchloridfilm-Anode lässt sich zur anodischen Oxydation von organischen Substanzen verwenden. Die Empfindlichkeit durch „Voltage-Scan" ist ungefähr 10 mal grösser als die bei chronopotentiometrischen Messungen. Versuche haben gezeigt, dass die Empfindlichkeit durch Rühren der Lösung noch gesteigert werden kann.

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SEPARATIONS INVOLVING SULPHIDES

VIII. SEPARATION OF RUTHENIUM AND INDIUM FROM ALKALINE EARTH METALS

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Methods for the quantitative separation of alkaline earths from a number of elements forming thiosalts or sulphides, with 2*N* sodium sulphide reagent[1] have already been proposed in a previous publication[2]. In this paper similar procedures for estimating ruthenium or indium in the presence of alkaline earths are given.

EXPERIMENTAL

Separation of ruthenium from alkaline earths

Measured volumes of standard solutions of ruthenium chloride[3] (prepared with dilute hydrochloric acid) and barium chloride[4], strontium chloride[5], calcium chloride[6] or magnesium chloride[7] were mixed and treated with ammonium hydroxide till a slight turbidity appeared. The mixture was treated with 40–50 ml of 2*N* sodium sulphide reagent followed by enough 6*N* acetic acid to give an acidity of about 3*N* and then 10–15 g of ammonium acetate were added. The mixture was heated to boiling and allowed to cool to room temperature. The precipitate of ruthenium sulphide was filtered through a weighed sintered glass crucible (porosity 4), washed thoroughly with distilled water (the filtrate being reserved for the estimation of alkaline earths), alcohol and ether successively, dried in vacuum for half an hour and weighed as $Ru_2S_3 \cdot 2H_2O$.

The filtrate was boiled to expel hydrogen sulphide etc., the free acid neutralized with ammonia (sp.gr. 0.88), and diluted to 250 ml.

Barium or strontium were estimated as sulphate.

Calcium was precipitated as oxalate and estimated as $CaCO_3$.

Magnesium was precipitated as magnesium ammonium phosphate and estimated as $Mg_2P_2O_7$.

In the estimation of calcium or magnesium reprecipitation is essential to get satisfactory results.

28–36 mg of ruthenium could be separated from 55–70 mg of barium, 34–44 mg of strontium, 72–90 mg of calcium or 12–16 mg of magnesium. The metals were recovered with an accuracy of:

Ru +0.14 to —0.33% and Ba +0.1 to —0.16%;
Ru 0.0 to —0.24% and Sr 0.0 to —0.14%;
Ru 0.0 to —0.24% and Ca 0.0 to —0.12%;
Ru +0.14 to —0.24% and Mg 0.0 to —0.31%.

Separation of indium from alkaline earths

Standard solutions of indium chloride[8], barium chloride, strontium chloride, calcium chloride and magnesium chloride were used. The procedure given for the separation of ruthenium from alkaline earths was followed. The precipitate of indium sulphide was washed with hot 3*N* acetic acid (to prevent peptization) and then with alcohol and ether successively. Indium was estimated as In_2S_3.

In the filtrate barium or strontium was estimated as sulphate, calcium as carbonate and magnesium as pyrophosphate.

22–30 mg of indium could be separated from 57–72 mg of barium, 34–44 mg of strontium, 40–50 mg of calcium or 12–16 mg of magnesium. The metals were recovered with an accuracy of:

In 0.0 to —0.24%, Ba 0.0 to —0.23% and Sr 0.0 to —0.21%;
In +0.29 to —0.22% and Ca 0.0 to —0.32%;
In 0.0 to —0.22% and Mg 0.0 to —0.32%.

SUMMARY

It has been shown that 2*N* sodium sulphide reagent can be efficiently used for separating ruthenium or indium from alkaline earth metals.

RÉSUMÉ

On a utilisé avec succès le sulfure de sodium 2*N* pour la séparation du ruthénium ou de l'indium d'avec les métaux alcalino-terreux.

ZUSAMMENFASSUNG

Es wird gezeigt, dass eine 2*N* Natriumsulfidlösung zur Trennung von Ruthenium oder Indium von den Erdalkalimetallen verwendet werden kann.

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SEPARATIONS INVOLVING SULPHIDES

IX. SEPARATIONS OF ALKALINE EARTH METALS FROM SOME ELEMENTS THAT FORM THIOSALTS

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The work discussed in this series of papers, has been divided into three sections under the headings indicated in an earlier publication[1]. Some separations of alkaline earth metals coming under the first heading have been dealt with in two papers already published[1,2]. In this paper the remaining separations of alkaline earth metals from elements that form thiosalts are dealt with.

EXPERIMENTAL

Separation of arsenic, antimony, tellurium, selenium or molybdenum from strontium

Standard solutions of sodium arsenate, potassium antimony tartrate, potassium tellurite, selenious acid, ammonium molybdate and strontium chloride were used. Measured volumes of the two solutions were mixed together. The mixture was treated with 2*N* sodium sulphide reagent in excess. The solution containing the thiosalt was acidified with a measured quantity of hydrochloric acid. The mixture was heated to boiling and allowed to cool to room temperature. The precipitate was filtered through a weighed sintered glass crucible (porosity 4), and the metals were estimated as As_2S_5[3], Sb_2S_3[4], TeS_2[3], SeS_2[3] or $MoS_3 \cdot 2H_2O$[5] respectively.

The following points must be borne in mind when precipitating the different sulphides.

(1) If a white precipitate appears on mixing the two solutions, it should be dissolved in the minimum quantity of dilute hydrochloric acid.

(2) In the case of molybdenum sufficient acid should be present in the solution to which sodium sulphide is added and the reagent should be added dropwise with constant shaking, otherwise molybdenum blue may form and pass into the filtrate.

(3) The solution containing the thiosalt of arsenic should be acidified with a measured volume of concentrated hydrochloric acid, to produce an acidity of approximately 6*N* in the resulting mixture. In the case of other elements the solution containing the thiosalt is acidified with 2*N* hydrochloric acid to produce an acidity of approximately 1*N* in the resulting mixture.

(4) In the case of selenium a more easily filterable precipitate is obtained, if the concentration of the acid in the resulting mixture is about 4*N*. After acidification the mixture should not be boiled. It should be kept at a lower temperature (70°–80°), until the yellow precipitate becomes orange in colour.

(5) The caustic soda solution used in preparing the sodium sulphide reagent should be free from silica, which is sometimes extracted from the glass bottle in which it is preserved.

After filtering off the sulphide, the filtrate was evaporated to about 50 ml to remove hydrogen sulphide, the free acid neutralized with ammonia (sp.gr. 0.88), the solution diluted to about 250 ml and strontium estimated as $SrSO_4$[6].

39–40 mg of arsenic were separated from 45–47 mg of strontium.
59–61 mg of antimony were separated from 45–46 mg of strontium.
59–60 mg of tellurium were separated from 45–46 mg of strontium.
53–60 mg of selenium were separated from 45–50 mg of strontium.
51–53 mg of molybdenum were separated from 45–46 mg of strontium.

The metals were recovered with an accuracy of:

As —0.28% to +0.4%	Sr —0.2% to +0.4%
Sb —0.23% to +0.3%	Sr 0.0% to +0.4%
Te —0.21% to +0.08%	Sr ±0.39%
Se 0.0% to +0.29%	Sr —0.5% to 0.0%
Mo —0.19% to +0.17%	Sr —0.3% to 0.0%

Separation of arsenic, antimony, tellurium, selenium or molybdenum from calcium

Standard solutions of sodium arsenate, potassium antimony tartrate, potassium tellurite, selenious acid, ammonium molybdate and calcium chloride were used. Measured volumes of the two solutions were mixed together. The procedure given for the separation of these metals from strontium was followed. As, Sb, Te, Se or Mo were estimated as sulphides. After filtering off the sulphide the filtrate was evaporated to about 50 ml to remove hydrogen sulphide, the free acid neutralized with ammonia (sp.gr. 0.88), and the solution diluted to about 250 ml. Calcium was precipitated as oxalate. Reprecipitation was necessary to get satisfactory results. Calcium was estimated as $CaCO_3$[7].

39–40 mg of arsenic were separated from 45–46 mg of calcium.
59–60 mg of antimony were separated from 45–46 mg of calcium.
42–57 mg of tellurium were separated from 45–51 mg of calcium.
54–56 mg of selenium were separated from 45–46 mg of calcium.
39–53 mg of molybdenum were separated from 32–46 mg of calcium.

The metals were recovered with an accuracy of:

As —0.47% to +0.1%	Ca —0.42% to 0.0%
Sb —0.15% to +0.23%	Ca —0.35% to 0.0%
Te —0.33% to +0.35%	Ca —0.5% to 0.0%
Se 0.0% to +0.5%	Ca —0.5% to +0.2%
Mo —0.078% to +0.37%	Ca —0.5% to +0.27%

Separation of arsenic, antimony, tellurium, selenium or molybdenum from magnesium

Standard solutions of sodium arsenate, potassium antimony tartrate, potassium tellurite, selenious acid, ammonium molybdate and magnesium chloride were used. Measured volumes of the two solutions were mixed. The procedure given for the separation of these metals from strontium was followed. The metals were estimated as sulphides. After filtering off the sulphide the filtrate was evaporated to about 50 ml to

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remove hydrogen sulphide, the free acid neutralized with ammonia (sp.gr. 0.88), and the solution diluted to about 250 ml. Magnesium was precipitated as $MgNH_4PO_4 \cdot 6H_2O$. Reprecipitation was necessary to get satisfactory results. Magnesium was estimated as $Mg_2P_2O_7$[8].

32–63 mg of arsenic were separated from 21–22 mg of magnesium.

58–59 mg of antimony were separated from 21–22 mg of magnesium.

42–55 mg of tellurium were separated from 21–24 mg of magnesium.

53–60 mg of selenium were separated from 21–28 mg of magnesium.

40–50 mg of molybdenum were separated from 21–45 mg of magnesium.

The metals were recovered with an accuracy of:

As —0.5% to 0.0%	Mg —0.39% to 0.0%
Sb —0.39% to 0.0%	Mg —0.42% to +0.4%
Te —0.4% to 0.0%	Mg 0.0% to +0.7%
Se —0.4% to +0.18%	Mg —0.4% to 0.0%
Mo —0.15% to 0.0%	Mg —0.4% to +0.5%

Note: It has not been found possible to estimate tin in presence of alkaline earth metals by decomposing the thiosalt, owing to the tendency of stannic sulphide to peptize on washing.

SUMMARY

It has been shown that 2*N* sodium sulphide reagent can be used for separating strontium, calcium or magnesium from arsenic, antimony, tellurium, selenium or molybdenum.

RÉSUMÉ

Le sulfure de sodium 2*N* peut être utilisé pour la séparation du strontium, du calcium ou du magnésium d'avec l'arsenic, l'antimoine, le tellure, le sélénium ou le molybdène.

ZUSAMMENFASSUNG

Es wird gezeigt, dass eine 2*N* Natriumsulfidlösung zur Trennung von Strontium, Calzium oder Magnesium von Arsen, Antimon, Selen oder Molybdän verwendet werden kann.

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THE PALLADIUM ELECTRODE IN AQUEOUS AND NONAQUEOUS TITRIMETRY

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SCHWING AND ROGERS[1] have pointed out the uncertain state of the literature concerning the reliability of the palladium–hydrogen electrode. These workers studied the behavior of various forms of electrode and found the most satisfactory type to be one involving a palladium membrane on which hydrogen was generated continuously. They also made a few titrimetric studies in 75% ethanol. Earlier SANDVED AND HARANG[2] employed a concentration cell consisting of two palladium hydride electrodes for the potentiometric titration of a variety of bases dissolved in ethanol or acetone. The present work concerns our attempts to improve the design for the electrode recommended by SCHWING AND ROGERS and to develop a completely new form of "generation" electrode. This latter form is simple to construct, gives results of satisfactory reproducibility, responds rapidly, and was first tested in aqueous systems. Experiments in the field of nonaqueous titrimetry[3] gave useful results.

Reagents and apparatus

In much of the work, buffer solutions made from "pHydrion**" capsules were used. In other cases, McIlvaine buffers adjusted with potassium chloride to a constant ionic strength of 0.5M were employed[4]. All pH values were checked by a Leeds and Northrup Model 7664 pH Meter. Most of the organic solvents and reagents were "White Label" from Eastman Kodak Company, and were used without further treatment.

The palladizing solution used was 2% palladous chloride in 1N hydrochloric acid. A current density of 40–50 mA/cm^2 was employed in the deposition of the palladium black.

Potential measurements were made with a Beckman Model G pH Meter and saturated calomel electrode. All studies were carried out at room temperature, and with air-containing solutions.

RESULTS

Modifications of the Schwing and Rogers type electrode

To permit the easy interchange of different palladium diaphragms, the cement-mounting technique of SCHWING AND ROGERS was replaced by one in which the disc was gripped between two rubber "O"-rings. The arrangement is shown in Fig. 1. The electrode vessel, A, is a 25 × 80 mm screw-capped sample tube from which the bottom has been removed. The plastic cap, B, has a 15 mm central hole which permits palladium diaphragm, C, of thickness 0.12 mm, to come in contact with the test solution. To minimize the accumulation of gas bubbles on the underside of the diaphragm, two

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pairs of wide grooves are filed nearly through the thickness of the cap as shown at (a). Into a small hole in the side of the cap was cemented 1/8-inch diameter polyethylene tubing, D, which was bent upwards and allowed a platinum connecting wire, E, to be kept out of contact with the solution. The inner end of the wire was flattened so that it could be gripped between the upper rubber ring, F, and the palladium disc. Supported by a grooved stopper, auxiliary electrode, G, is a 5-cm length of 24-gauge platinum wire wound into a spiral. This platinum wire was sealed through the end of a length of glass tubing so that contact could be made to the copper connecting wire by means of a column of mercury. The electrode vessel contained decinormal sulfuric acid. The auxiliary electrode was connected through a milliammeter and a variable resistor to the positive pole of a dry battery. The negative pole of the battery was connected to platinum lead, E. The latter was also connected to the "glass electrode" pin of the pH meter while the other pin led to the saturated calomel reference electrode. The small voltage correction introduced by the resistance of the platinum lead was allowed for.

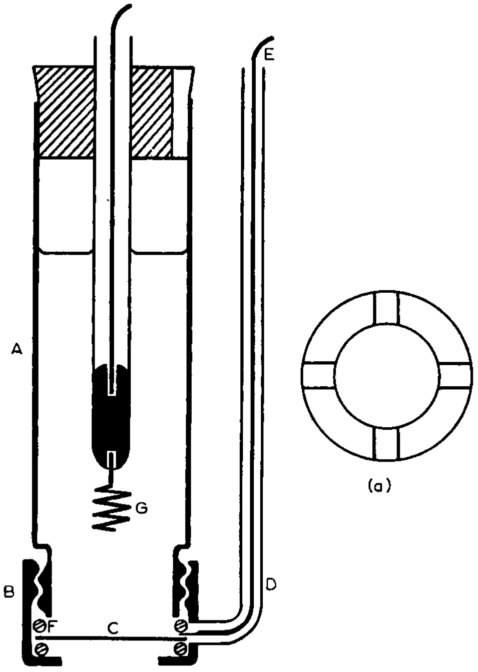

Fig. 1. Diaphragm-type palladium electrode.

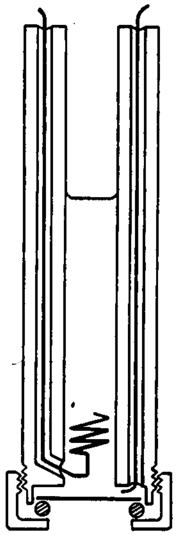

Fig. 2. Electrode constructed from Lucite rod.

A smaller form of electrode was constructed from a lucite rod. General details are shown in Fig. 2. The principal difference in design is that the leads to the disc and to the auxiliary electrode pass down holes drilled in the wall thickness. These holes were subsequently filled with liquid cement which was allowed to harden before the electrode was used.

Most of the experiments were, however, made with the electrode shown in Fig. 1. The results obtained in the measurement of the pH of aqueous buffers and in acid-base titrations closely paralleled those reported by Schwing and Rogers. A generating current of 5 mA, corresponding to a current density of about 2.5 mA/cm^2 on the inner side of the disc, was used initially. Numerous experiments in which the current density was varied between 0.5 and 10.0 mA/cm^2 indicated the desirability of operating at small values. This minimizes gas formation on the surface of the disc, appears to reduce the stabilization time, and gives steadier readings. The sensitivity of the e.m.f. measurements to stirring found by Schwing and Rogers was also noted.

The circulating palladium electrode

Owing to the uncertain readings obtained with palladium electrodes of the type described above, experiments were made to develop an electrode of radically different design. The desired features were (1) a vertical diaphragm to avoid entrapment of hydrogen bubbles (2) the elimination of joints which needed to be watertight, and (3) the introduction of powerful constant stirring which would give constant potentials. The last feature is essential for the plotting of potentiometric titration curves while the well-known changes in dimensions undergone by palladium when it absorbs or desorbs hydrogen cause the buckling of a tightly held disc.

These features are incorporated in the electrode shown in Fig. 3. Electrode tube, H,

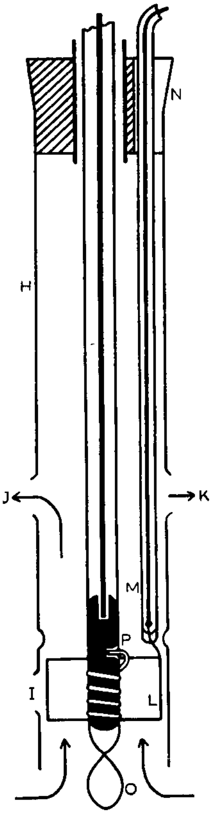

Fig. 3. Circulating-type palladium electrode.

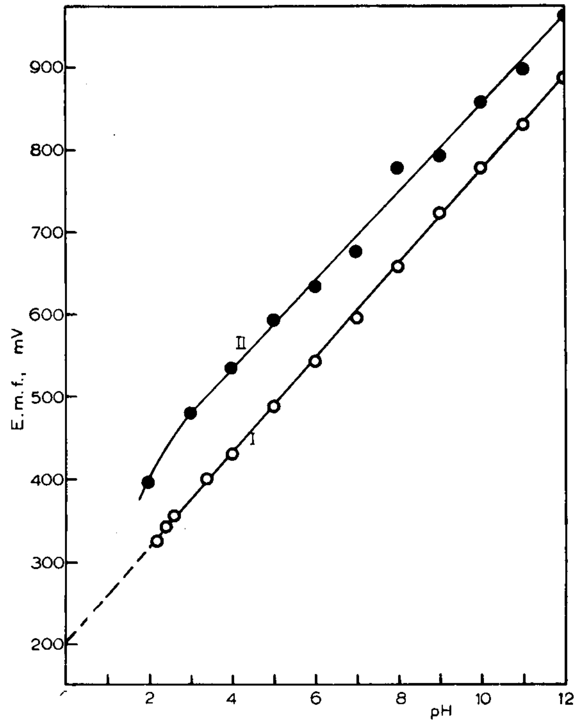

Fig. 4. E.m.f.-pH relationship: Curve I — generating current 1 mA, Curve II — generating current 5 mA.

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is 20 mm in diameter and 100 mm long. Three six-mm holes, I, J, and K, are blown in the wall as shown and the tube is crimped as shown about 20 mm from the lower end. The crimp serves to locate the palladium foil electrode, L, which is a rectangle 10×40 mm and has a small projecting tongue on one of the longer sides. A platinum connecting wire is welded to this tongue and a polyethylene-tubing sleeve, M, is slipped over the joint as shown, the lower end being closed by cementing. For studies in nonaqueous media, "Teflon" or glass tubing should replace polyethylene. After palladizing both sides of the rectangle, it is coiled up to form a nearly complete cylinder and sprung into the electrode tube from the bottom. The gap in the cylinder should be about diametrically opposite to hole I. The upper end of the polyethylene tubing is lightly gripped in grooved cork, N, which also carries a loosely-fitting glass guide cylinder for the rotating auxiliary electrode. This is constructed of 6-mm diameter glass tubing, carries at its lower end a spiral stirrer, O, and is driven by a Sargent Synchronous Rotator at a constant rate of 600 r.p.m. The auxiliary electrode proper consists of a close four-turn spiral of 24-gauge platinum wire, one end of which is sealed through the wall of the

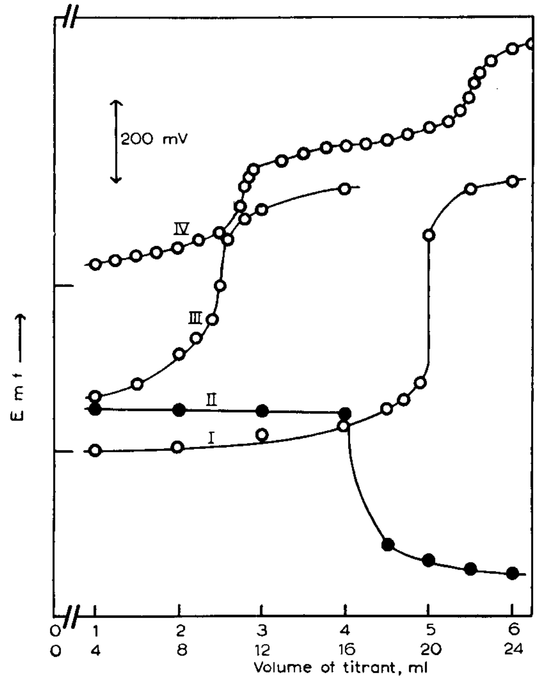

Fig. 5. Acid–base titration curves in aqueous medium: Curve I - 50 ml of $0.1N$ HCl with $1.0N$ NaOH, Curve II - as I, but generating circuit broken, Curve III - 25 ml of $0.01N$ CH_3COOH with $0.1N$ NaOH, Curve IV - 25 ml of $0.147M$ H_3PO_4 with $1N$ NaOH. The upper volume scale refers to curves I, II, III, the lower to curve IV.

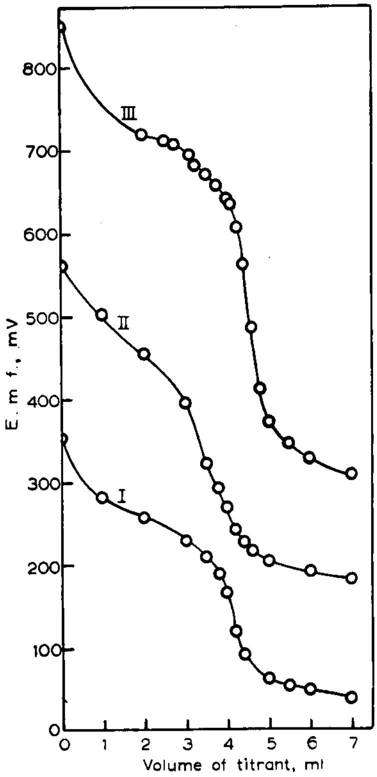

Fig. 6. The nonaqueous titration of 25 ml of approximately $0.02N$ triethylamine with $0.1N$ hydrochloric acid: Curve I - in acetonitrile, Curve II - in ethanol containing 5% of water, Curve III in dimethylformamide.

tube at P. Connection to this electrode is made in the usual way by means of a mercury column. The electrical connections are essentially the same as those described for the electrode shown in Fig. 1.

Studies in aqueous solutions

To assess the likely performance in titrimetry, the electrode assembly shown in Fig. 3 was immersed successively in a series of buffer solutions and the e.m.f. was measured 2 min later. After removal from one buffer, the system was rinsed with distilled water and introduced into the next buffer. As noted with the horizontal palladium diaphragm electrodes, use of a low current density is beneficial. This is illustrated in Fig. 4, which clearly shows the scattered results obtained with a generating current of 5 mA and the improvement effected by reducing the current to 1 mA. In the latter case, the slope, namely 57.6 mV per pH, approximates quite closely the theoretical value. On extrapolation to pH 0, the standard potential referred to the S. C. E. is 200 mV. Correcting to the hydrogen scale, this value agrees well with that found for saturated α-palladium in hydrogen stirred solutions[5,6].

Numerous acid–base titrations were then performed using a generating current of 1 mA. Typical titration curves are given in Fig. 5. It was found that e.m.f. readings could be taken within 1 min after each addition of reagent. When the generating current is cut off, the electrode soon fails to respond satisfactorily. This is clear from a comparison of curves I and II which both refer to the titration of 0.1*N* hydrochloric acid.

Studies in nonaqueous media

Titrations of a variety of weak and strong acids dissolved in 95% ethanol gave satisfactory curves when titrated with decinormal sodium methoxide in absolute methanol. A generating current of between 0.1 and 0.2 mA was found to be satisfactory in most of the nonaqueous titrimetry. The results were erratic with succinic acid and others which gave precipitates during the titration.

Titrations of organic bases were performed in a variety of solvents; of these, dimethylformamide appears to be the most satisfactory (Fig. 6). Attempts to titrate organic acids in ethylenediamine with sodium aminoethoxide solution have so far proved unsatisfactory. In some of these attempted titrations, a visible film formed on the palladium surface.

ACKNOWLEDGEMENT

The authors are indebted to the U. S. Atomic Energy Commission for partial support of this work.

SUMMARY

Two modifications of the palladium–hydrogen electrode of SCHWING AND ROGERS have been made and tested. A new form of "generation" electrode with a vertical palladium diaphragm and fast constant speed circulation has been devised. This form of electrode responds rapidly and has been used in a variety of acid–base titrations in aqueous and nonaqueous systems.

RÉSUMÉ

Deux modifications ont été apportées à l'électrode palladium–hydrogène de SCHWING ET ROGERS. Cette nouvelle forme d'électrode peut être utilisée pour de nombreux titrages acide–base en solutions aqueuses et non aqueuses.

ZUSAMMENFASSUNG

Es werden 2 Modifikationen der Palladium-Wasserstoff Elektrode nach SCHWING UND ROGERS beschrieben. Mit der neuen Elektrodenform können zahlreiche Säure-Basen Titrationen in wässrigem und nicht-wässrigem Medium ausgeführt werden.

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THE PHOTOMETRIC DETERMINATION OF SILICON AS α-SILICOMOLYBDIC ACID

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An accurate and at the same time rapid method for the determination of silicon has long been needed by the analysts. Accurate gravimetric methods are too laborious, and rapid gravimetric or titrimetric methods do not give satisfactory results. Therefore, in the last years, photometric methods have often been suggested.

The accuracy of photometric measurement is now so high that also the main components of a mixture can be determined with relative errors of a few tenths of a per cent or less. However, this accuracy is delusive if the method is not based on sound chemical principles. Above all, the color must be quite stable and reproducible.

Existing photometric methods for the determination of silicon are based on the utilization of either the yellow color of silicomolybdic acid or the blue color of reduced silicomolybdic acid. A critical examination of the procedures described in the literature does not give very encouraging results. (For references, see JEAN[1,2] where a list of papers is given.) The color always depends on the experimental conditions, particularly the acidity and the excess of the reagent, and a perfect reproducibility is difficult to attain. As a rule, the colors obtained are not stable; the intensity varies with time.

An explanation for this behavior was given by STRICKLAND[3], who in 1952 reported the results of a careful investigation of the formation of silicomolybdic acid. He showed that two modifications of this acid exist: an α acid formed at low acidities and a β form formed at high acidities. The α form is the stable form, and the β compound changes more or less rapidly into the α form. Using light with a wave-length of approximately 400 mμ, the absorbance index of the β form is about twice the index of the α form.

Reducing agents convert both forms into blue-colored products. However, the colors differ considerably; the α product is greenish blue whereas the β product is deep blue.

As far as we have found, all procedures given in the literature are based on reactions leading to the β form*, but since this form is not stable, smaller or larger amounts of the α form are always present. Therefore, it is not surprising that the colors — the yellow as well as the blue ones — are usually neither sufficiently stable nor sufficiently reproducible for the attainment of a high precision in analysis.

From the point of view of the analyst, it seems that the logical deduction from STRICKLAND's observations should be that the α form is superior as the basis of a photometric method. A procedure leading to this form seems to provide a solution of the problem of developing a rapid, precise method for the determination of silicon. The higher absorbance index of the β form is sometimes considered as a particular advantage. However, if silicon is one of the main components, the stability and reproducibility of the color is more important than a slightly higher sensitivity. Moreover, the absorbance index of the β form is greater than the index of the α form only at wave-lengths above 340 mμ, whereas at shorter wave-lengths the α form absorbs more light. In most analyses a reduction of the yellow form is unnecessary.

The results of some experimental investigations will be reported in the following.

EXPERIMENTAL CONDITIONS LEADING TO THE FORMATION OF THE α ACID

According to STRICKLAND, both silicomolybdic acids have the formula $H_4SiMo_{12}O_{40}$. STRICKLAND has also determined the absorption spectra of the two forms, and our results were in good agreement with his values. The two curves intersect at 340 mμ as can be seen in Fig. 1.

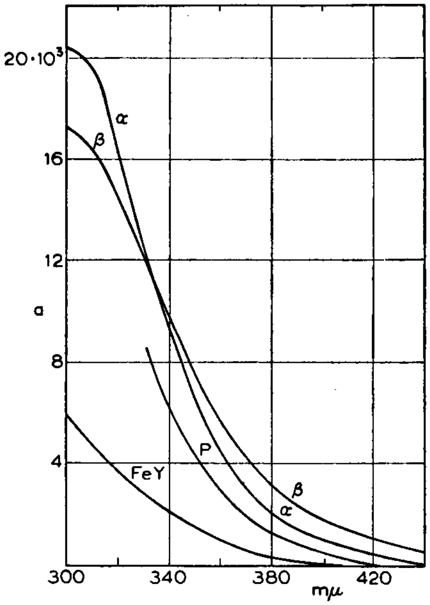

Fig. 1. Absorbance indices of α-silicomolybdic acid, β-silicomolybdic acid, phosphomolybdic acid, and Fe(III)-EDTA as functions of the wave-length.

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* Note added in proof: In a recent paper by ANDERSSON[6] also a method based on the color of the α acid is described.

The problem of the structure of the two forms will not be discussed in this paper. It may only be mentioned that the two modifications are probably derived from the two polynuclear molybdate ions formed on acidification. According to LINDQVIST[4] MoO_4^{-2} ions are stable at pH > 6.5. At pH ∿ 4.5, paramolybdate ions $Mo_7O_{24}^{-6}$ are formed, which are transformed into octamolybdate ions $Mo_8O_{26}^{-4}$ in the pH range 2.9–1.5. It seems likely that the α acid is formed from the paramolybdate and the β acid from the octamolybdate.

Systematic investigations of the formation of the yellow compounds led to the following results:

1. In very acid solutions (pH < 2.5) the reaction between silica and ammonium molybdate results in a yellow color, which gradually fades.

2. In very weakly acid solutions (pH > 4) a yellow color is produced which gradually becomes more intense.

3. At pH values between 2.3 and 3.9 a yellow color is formed which slowly changes in intensity — it usually decreases, but increases at the upper limit of the pH range — and attains a constant value after $^1/_2$ to 12 hours depending on the pH (Fig. 2). For a certain concentration of silicon the final absorbance value is always the same. The reaction is accelerated by a rise in temperature. Heating to 100° is usually enough for the rapid attainment of equilibrium. If the solution is made strongly acid after the equilibrium state has been reached, no change in the color will occur.

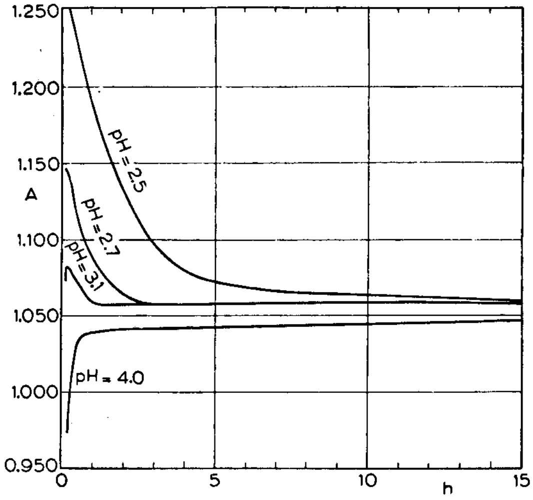

Fig. 2. Change of absorbance with time in hours at various pH values.

These results can easily be interpreted on the basis of STRICKLAND's investigations. At low acidities, the α acid is formed, but at pH values above 3.9, the reaction is incomplete. At pH values below 2.3, the β acid is formed, which very slowly goes over into the α form.

It seems clear that the most favorable conditions for a photometric method based on the color of the α form exist in the pH range 2.3–3.9. Various buffer substances have been tried. Formic acid–formiate was used in many experiments, but since this buffer exhibited reducing properties, a monochloracetic acid–monochloracetate buffer was later preferred. The dissociation constant of this acid is $10^{-2.9}$.

Fig. 3 illustrates the dependence of the reaction on pH.

The curve shows a plateau at pH 2.1–3.9.

The influence of the concentration of molybdate was also investigated. Twice the theoretically required amount is sufficient to produce the final absorbance value. However, the required minimum concentration of molybdate depends somewhat on the acidity. At low pH values, a larger excess of molybdate is required.

The absorbance values obtained when the given procedure is followed are stable and reproducible, but they depend on the temperature of the solution. Several series of experiments gave a rather high temperature coefficient of 0.39% per degree centigrade. It is therefore necessary either to determine the absorbance at a constant temperature or to apply a temperature correction.

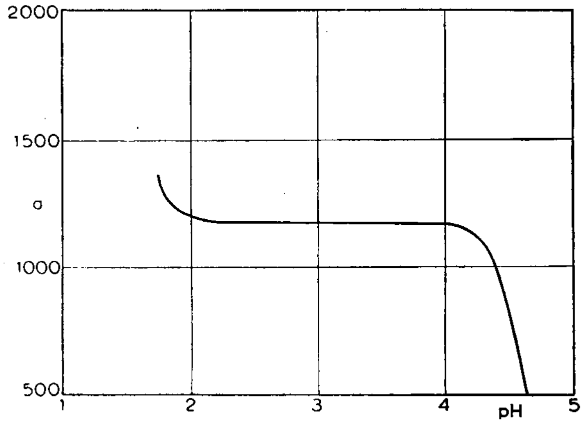

Fig. 3. Absorbance index (400 mμ) of silicomolybdic acid as a function of pH.

Even large amounts of neutral salts do not affect the absorbance values appreciably, but elements reacting like silicon may produce a yellow color. We have investigated the influence of phosphorus, arsenic and germanium. The absorbance index of phosphorus is plotted in Fig. 1.

The most interfering of these elements is phosphorus, and therefore a large number of masking agents were tried: oxalic acid, tartaric acid, citric acid, lactic acid, phthalic acid, ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA) and others. The best results were obtained with tartaric acid, but even then the phosphorus color was not completely masked, and also the color of the silicomolybdic acid faded slightly when this reagent was used. This fading was less when the tartaric acid was added after the silicomolybdic color had completely developed. As our samples usually contained very small amounts of phosphorus, we preferred not to use a masking agent but to apply a correction to the result. At 390 mμ the absorbance of one part of P_2O_5 corresponds to that of 0.43 part of SiO_2. For germanium the relationship is about the same, but the absorbance is very sensitive for small variations in pH. The absorbance due to arsenic can usually be neglected as one part of As_2O_5 corresponds to less than 0.01 part of SiO_2.

In dissolving silicate melts the formation of precipitates can be more or less completely avoided by the addition of EDTA. Since EDTA forms complex compounds with molybdenum, the influence of EDTA on the determination of silicon was investigated. Experiments showed that EDTA does not affect the results if the concentration of EDTA in the sample solution is less than 0.01*M*.

Rocks and other silicate materials often contain relatively large amounts of iron. The iron–EDTA complex formed when EDTA is present has an appreciable absorbance at the wave-length used, as can be seen in Fig. 1. The best way of eliminating this interference is to measure the absorbance of the unknown solution not against water but against a sample of the unknown solution to which no ammonium molybdate has been added.

THE ANALYSIS OF SILICATES

In analyzing insoluble silicates the procedure given below was followed.

Procedure

A suitable amount of the sample, usually 100–300 mg containing 20–70% SiO_2, is weighed and transferred to a nickel crucible containing 10 g of molten NaOH. After 5–10 minutes of heating the melt is cooled and dissolved in a plastic disk containing water and 40 ml of 0.05*M* EDTA (as the disodium salt). The solution is transferred to a tared plastic flask and diluted on a balance until the weight is 509.4 g, *i.e.* 500.0 ml at 20°. Some suitable aliquot of the solution (10–25 ml) is pipetted

TABLE I

Sample	*% SiO_2*	
	theoretical	*found*
Plastic clay No. 98, 0.08% P_2O_5	59.11 average value of 8 analyses of Bureau of Standards	58.99 59.19 59.09 59.17
Soda lime glass No. 80, 0.08% As_2O_5	73.98 average value of 13 analyses of B. of S.	74.10 74.24 74.08
Argillaceous limestone No. 1 A 0.15% P_2O_5	14.11 average value of 11 analyses of B. of S.	14.26 14.26
Standard sample 177 of Portland cement 0.05% P_2O_5	21.90 analysis of B. of S.	22.17 22.09 22.20 22.19 22.13

The theoretical values are average values of analyses reported by U.S. National Bureau of Standards, Washington, D.C. The agreement is satisfactory.

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into a 50-ml volumetric flask containing 10 ml of a suitable mixture of $2M$ monochloracetic acid and $2M$ ammonium monochloracetate and 10 ml of an ammonium molybdate solution containing 0.2 mole Mo per l (35.3 g $(NH_4)_6Mo_7O_{24}\cdot 4\ H_2O$/l). The composition of the buffer solution depends on how much of the alkaline (approx. $0.5M$) sample solution is used. The pH of the solution obtained must be between 3.0 and 3.7. The flask is immersed in boiling water and kept there for 5 to 10 min. The solution is then cooled to room temperature and diluted to 50 ml. The absorbance of the solution is measured at a wave-length of 390 mμ. The 100% transmittance value is adjusted using a solution prepared in the same way but omitting the addition of the ammonium molybdate solution and the heating.

The absorbance is corrected to 20° using the expression $\Delta A = (20-t)\ 0.004A$. The correction is thus negative for temperatures over 20° and positive for temperatures below 20°.

All solutions are prepared using redistilled water free from silica and kept in plastic bottles. The purity of the reagents is checked by a blank determination.

If a Beckman spectrophotometer (or any other one-cell instrument with a 1:10 sensitivity adjustment) is used, it is advantageous to choose the wave-length and silica concentration so that the absorbance is a little above 1.0. A higher sensitivity can then be used, *i.e.* one scale unit of the transmittance scale corresponds to a relative error of about 0.4%[5]. As the reproducibility of a measurement is usually about half a scale unit, the error in analyzing silicate rocks is, as a rule, about ± 0.1% SiO_2.

The absorbance index was determined according to the procedure given above using a solution of pure SiO_2 in NaOH, but since the absorbance curve is rather steep (Fig. 1), the value obtained may depend somewhat on the instrument used. We have used a value $a_{390} = 1.701\cdot 10^3$ (20°). It is advisable to adjust the wave-length very carefully using a magnifying glass. A Beckman DU spectrophotometer was used.

The colors were stable for nearly two days.

The results of some analyses of silicates are given in Table I.

ACKNOWLEDGEMENT

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SUMMARY

A photometric method for the determination of silicon based on the yellow color of α-silicomolybdic acid is described. The pH must be kept within the range 3.0–3.7, and the equilibrium state is established by heating the solution. Since the color of this modification is remarkably stable and reproducible, a high degree of precision can be attained.

RÉSUMÉ

Une méthode photométrique est proposée pour le dosage du silicium; elle est basée sur la coloration jaune de l'acide α-silicomolybdique. Cette coloration est très stable et reproductible et permet d'obtenir une très bonne précision.

ZUSAMMENFASSUNG

Es wird eine photometrische Methode zur Bestimmung von Silizium beschrieben, die auf der gelben Farbe der α-Silikomolybdänsäure beruht. Wegen der hohen Stabilität und guten Reproduzierbarkeit des Farbtons ist eine grosse Genauigkeit erreichbar.

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DROP-SCALE CHRONOPOTENTIOMETRY

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In recent times the analytical chemist has been confronted more and more with the analysis of trace amounts of substances. In many cases in which the concentrations of the components of mixtures are very small, the materials are first concentrated by evaporation, electrolysis, or other techniques. Even then, the ultimate concentration attainable is quite often too low for most analytical methods unless the volume is decreased to the size of a drop, a volume too small for most analytical techniques. Also it is not uncommon to start with only a drop or two of sample for analysis. SCHREIBER AND COOKE[1] recently described coulometric generation of titrant within a drop of solution. A physico-chemical method of great promise is chronopotentiometry. REILLEY, EVERETT AND JOHNS[2] have published an excellent experimental evaluation of this technique. They pointed out the successful analytical determination of electroactive substances in solutions as dilute as $5 \cdot 10^{-5}M$. The very nature of the technique makes it ideally suited for carrying out analysis on one drop (0.05 ml or less) of solution. This paper describes the application of rapid chronopotentiometry to single drops of dilute solutions of iodide, ferrocyanide, ferricyanide, and zinc ions. In the light of the excellent papers on chronopotentiometry, both theoretical and practical[2-5], that phase of the subject will not be discussed.

EXPERIMENTAL

Reagents

Reagent-grade chemicals were used throughout this investigation. Stock solutions of ferricyanide, ferrocyanide, iodide, and zinc ions were prepared by dissolving known amounts of potassium ferricyanide, potassium ferrocyanide, potassium iodide, and zinc nitrate to known volumes. In the cases of potassium ferrocyanide and potassium iodide solutions, dilutions of the stock solutions were made with deaerated dilute sulfuric acid. The solutions of ferricyanide and ferrocyanide were $0.05M$ in sulfuric acid. The potassium iodide solutions were $0.08M$ in sulfuric acid, and the zinc nitrate solutions were $0.1M$ in potassium nitrate. Sodium sulfite was added to the zinc nitrate solutions to rid the solutions of oxygen. Deaeration of the solutions with purified nitrogen was not satisfactory, due to the rapid absorption of oxygen on exposure to air. Upon electrolyzing deaerated solutions, there was a noticeable interval before the potential of the mercury pool attained that for the reduction of zinc. Such was not the case, however, when sodium sulfite was used to purge the solutions of oxygen.

Apparatus

The chronopotentiometric assemblies used in this experiment are shown in Fig. 1. The reference electrode and auxiliary electrode units in both assemblies were the same. The reference electrode was a Beckman Fiber Type 270 (supplied with the Model G pH meter). A platinum wire wound around the tip of the reference served as the auxiliary electrode. The working electrodes were platinum and mercury. The platinum electrode was prepared by placing a 1/4-inch diameter, stiff paper disc on a 1.5 × 2.5 cm piece of heavy platinum foil and spraying lightly with Krylon (Krylon, Inc., Norristown, Pa.). On drying, a light coating of plastic was left on the surface of the platinum foil except for the area covered by the disc.

The mercury working electrode unit consisted of a 2-inch length of heavy capillary glass tubing (0.25 cm I.D. and 0.9 cm O.D.) with a rubber tubing connected to one end. The top and inside of the capillary were coated with Desicote (Beckman Instruments Inc., South Pasadena, Calif.).

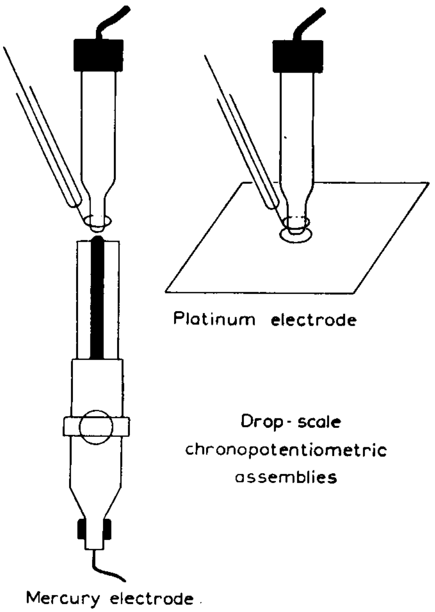

Fig. 1. Chronopotentiometric assemblies.

The end of the rubber tubing was clamped and the capillary and tubing were filled with mercury. The screw clamp attached between the capillary tubing and the clamp at the bottom was used to squeeze mercury out of the capillary to renew the mercury working electrode.

The constant current source was a bank of 45-V "B" batteries connected in series with a megohm resistor (1 to 22 megohms) and a three-way switch. When not being passed through the cell, the current was directed back to the batteries *via* a potentiometer whose resistance was adjusted to match that of the cell. Also in series with the dropping resistor and the batteries was a precision resistor (1% tolerance). The electrolysis current was determined by measuring the potential drop across the resistor with a Beckman Model G pH meter. The values of the precision resistors were sufficient for current measurements good to 1%.

The potential of the working electrode *versus* the reference S.C.E. was fed into a Leeds and Northrup pH Indicator whose output was recorded on a Varian Model G-10 Graphic recorder at a chart speed of 8 inches/min.

The potential of the working electrode *versus* the reference S.C.E. was also fed into a Sargent Malmstadt Automatic Titrator which actuated a timer through a relay. The potential change, however, was so small and gradual that the biasing voltage at the grid of the first thyratron tube in the Titrator had to be reduced to such a value that very erratic times were obtained. A three-electrode differential derivative technique was also studied. Here the potential difference between two working electrodes operating at different current densities was followed by the Titrator[6].

Procedure

1-2 drops (0.05-0.10 ml) of solution were placed on the platinum foil or the top of the capillary tube such that the uncoated section of the platinum foil or the mercury surface was completely covered. The reference electrode and the auxiliary electrode unit was then moved over and on top of the drop. The recorder was started and the solution was electrolyzed. After the chronopotentiogram was obtained, the electrode unit was moved aside and the platinum electrode and the reference electrode and auxiliary electrode unit were washed and blotted dry with filter paper. In the case of the mercury electrode, special care was taken to dry the capillary. The mercury electrode was renewed by tightening the screw clamp. Excess mercury was removed by running the edge of a filter paper across the top of the capillary.

Aside from the time involved in the electrolysis period, which never was longer than one minute, each run took only about one minute.

The same procedure was followed in the derivative studies with the Sargent Malmstadt Automatic Titrator. In the three-electrode differential derivative technique, the reference electrode was replaced with a small button-type platinum electrode, which served as a common auxiliary electrode.

PERFORMANCE

Figs. 2, 3 and 4 show the plot of $\tau^{1/2}$ *versus* concentration for the oxidation of ferrocyanide and iodide ions and the reduction of ferricyanide ions at the platinum working electrode. Fig. 5 shows a similar plot for the reduction of zinc ions at the mercury working electrode. The transition times were evaluated from conventional chronopotentiograms. In all cases, the curves do not pass through the origin, but cross the abscissa. In the case of zinc at a current of 3.3 μA, the curve (not shown) crossed the ordinate. The discrepancy is not due to the technique used in evaluating transition times, as several different methods gave virtually the same point of intersection. The important linear relationship of $\tau^{1/2}$ *versus* concentration, however, held in all cases.

Each point in the plots represents the average of four to six runs. The average deviation for each point was 1%. In the case of zinc, however, the average deviation was 2 to 6%. The large deviation was due to difficulty in reproducing the electrode area. When mercury is squeezed out of the capillary and the excess scraped off with the

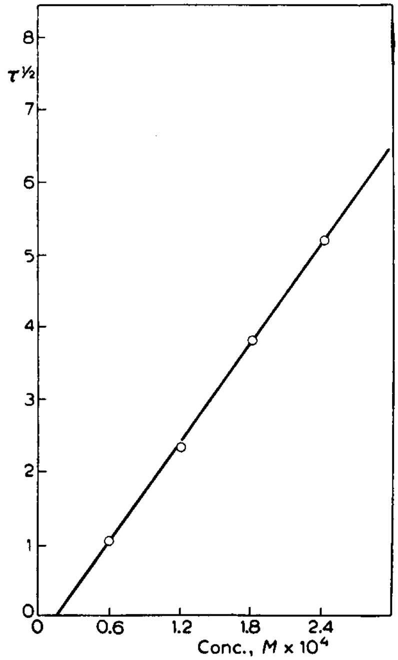

Fig. 2. Oxidation of iodide ions in 0.08M sulfuric acid at 6.8 μA.

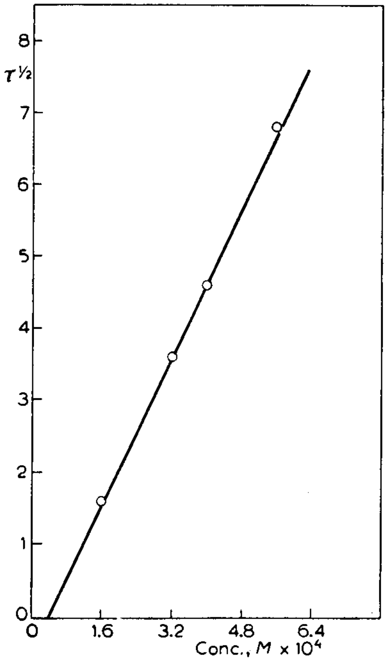

Fig. 3. Oxidation of ferrocyanide ions in 0.05M sulfuric acid at 6.4 μA.

edge of a filter paper, the mercury level could be slightly below or above the top of the capillary. The area in the latter case would be larger than in the former.

Fig. 6 shows the potential–time plots for the oxidation of iodide ions in $5 \cdot 10^{-6}M$ potassium iodide solution at 1.1 μA (A) and the background scan (B) obtained on 0.07 ml of solution. A potential holdup is clearly indicated for the oxidation of iodide ions. The amount of iodide ions in the drop was $3.5 \cdot 10^{-10}$ equivalents. The detection of much smaller amounts of electroactive substances is complicated by the foot of the decomposition wave of the supporting electrolyte solution being magnified with decreasing current densities. In chronopotentiometry, the detectable limit is not simply determined by the background scan as is the case in polarography.

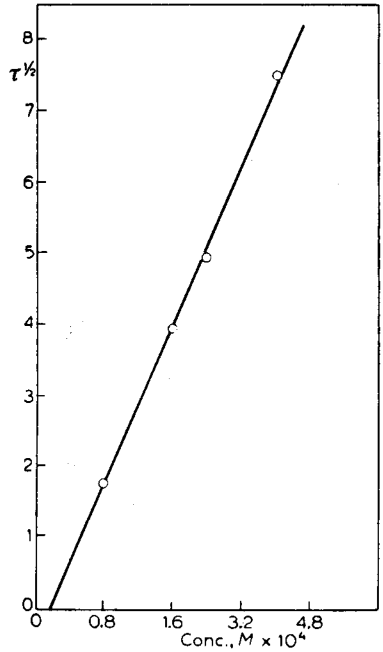

Fig. 4. Reduction of ferrocyanide ions in 0.05M sulfuric acid at 6.4 μA.

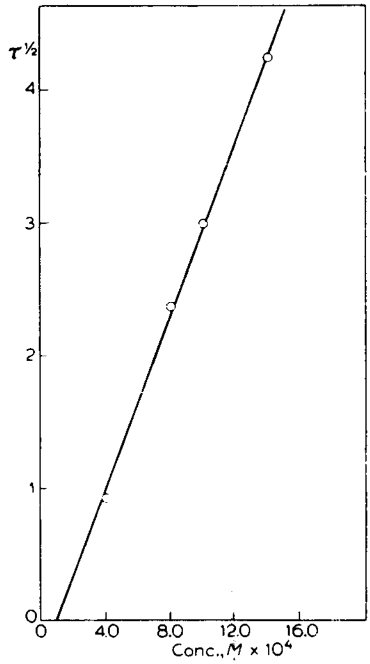

Fig. 5. Reduction of zinc ions in 0.1M potassium nitrate at 6.4 μA.

Transition times for the reduction of ferricyanide ions were also obtained by two derivative techniques. In one, the potential between the working electrode and the reference electrode was followed with the Sargent Malmstadt Automatic Titrator which fed a derivative of the potential into a recorder. In the other, a differential technique was used. The potential difference between two working electrodes operating at different current densities was followed by the Titrator, which fed the derivative of the potential difference into a recorder. Although both types of derivative chronopotentiograms, when evaluated, gave the same transition time as the conventional chronopotentiogram, the derivative signals of the differential technique were much sharper.

Use of the Titrator to turn off a timer by either of the two techniques was unsuccessful for the concentration range investigated due to the lack of sharp potential changes

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from one electrode process to the next. Decreasing the bias voltage resulted in the Titrator firing prematurely. Increasing the bias voltage to prevent premature firing invariably resulted in the Titrator not firing at all.

Obviously, much smaller volumes of solution can be handled by this technique by decreasing the area of the electrode. The reference electrode can be ground to a finer point so as to enable it to be placed in smaller volumes of solution.

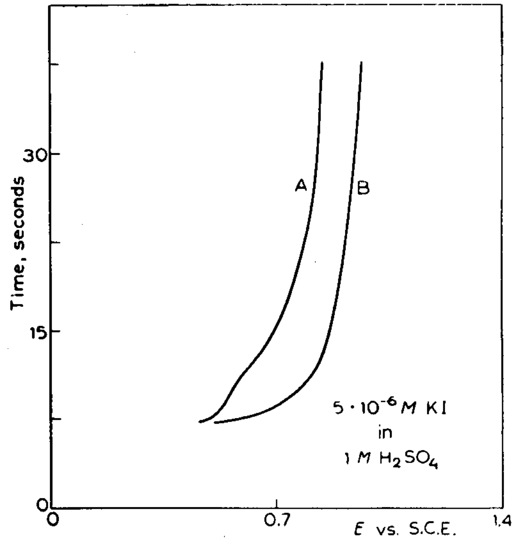

Fig. 6. Potential-time curves for the oxidation of iodide ions (A) and the supporting electrolyte solution (B). Current 1.1 μA.

SUMMARY

Chronopotentiometry has been successfully carried out on one drop of solution. A simple arrangement enabled determinations to be performed in one to two minutes. A potential holdup was clearly indicated for the oxidation of iodide ions on electrolyzing 0.07 ml of a $5 \cdot 10^{-6} M$ potassium iodide solution $1 M$ in sulfuric acid, a total of $3.5 \cdot 10^{-10}$ equivalents of iodide ions.

RÉSUMÉ

La chronopotentiométrie a été effectuée avec succès sur une goutte de solution. Un dispositif simple permet de faire des dosages en une à deux minutes.

ZUSAMMENFASSUNG

Chronopotentiometrische Messungen sind mit Erfolg bei einem Tropfen Lösung angewandt worden. Dauer einer Bestimmung: 1-2 Minuten.

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POLAROGRAPHIC REDUCTION OF HEXAVALENT URANIUM IN SODIUM TRIPOLYPHOSPHATE

I. GENERAL STUDIES

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FRANKENTHAL AND NEUBERG[1] were the first to report on the interesting masking effects of sodium tripolyphosphate. FEIGL[2] later observed that this reagent was far more effective in masking inorganic precipitations than any known at the time. Yet tripolyphosphate has not found many applications in analytical chemistry.

JANKOVITS[3] has recently used sodium tripolyphosphate in a manner similar to EDTA for the direct titration of calcium and magnesium. VAN WAZER AND CAMPANELLA[4] have shown that the condensed phosphates shift the half-wave potentials of barium and even of sodium by complex formation. An understanding of the polarographic behaviour of the tripolyphosphate complexes may lead to useful analytical applications, but literature on the subject is meagre. This paper describes some observations on the polarographic reduction of the tripolyphosphate complex of hexavalent uranium.

EXPERIMENTAL*

Reagents

All the reagents used were tested and found to be polarographically pure. The sodium tripolyphosphate was an anhydrous, granular material supplied on request by Blockson Chemical Co., Inc.

Standard uranyl sulphate was prepared by fuming uranyl nitrate with sulphuric acid to a paste, dissolving in water and making up to volume. Its uranyl content was estimated by reduction through Jones' reductor followed by titration with ceric solution.

Apparatus

(1) Tinsley Recording Polarograph.

(2) Doran glass electrode pH meter.

(3) Polarographic cell. An H-type cell carrying an S.C.E. as reference electrode. An agar bridge (4% agar saturated with potassium chloride) reinforced by a coarse-porosity sintered pyrex disc was used in the cross-member. The cell resistance was about 500 ohms.

Procedure

Polarograms were taken at 30.0 ± 0.1° unless otherwise stated. Oxygen was removed from the test solution by bubbling purified nitrogen for fifteen minutes. The capillary had an m value of 1.68 mg/sec, and the mean drop-time was 4.204 sec/drop at a potential of —1.3 V and h 36 cm.

Mixtures of penta- and hexa-valent uranium for the composite polarograms were prepared by controlled potential electrolysis[5] of a 2 mM uranyl perchlorate solution in 0.1 M sodium perchlorate. The pH was maintained at 2.7 and the cathode potential at —0.55 V *vs.* Ag/AgCl electrode. Electrolysis was carried out for 45 minutes in an atmosphere of nitrogen.

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* Abbreviations used in the text: UTP, uranyl tripolyphosphate complex; NaTP, sodium tripolyphosphate; h, mercury pressure corrected for back pressure; S.C.E., $E^1/_2$, id, i, m and t have their conventional significance.

RESULTS

Reduction of some common radicals in presence of NaTP

The $E^1/_2$ for the radicals examined are listed in Table I. Cr^{+3}, Co^{+2}, Ni^{+2}, Zn^{+2}, Ti^{+4}, WO_4^{-2}, MoO_4^{-2}, Sn^{+4}, Mn^{+2} gave no steps in the available potential range. Ceric cerium gave a drawn-out wave. Copper gave two waves, the height of the first wave being considerably less than that of the second. No waves except the first one for copper showed an apparent maximum.

The rest of the present paper deals exclusively with the polarographic behaviour of uranyl tripolyphosphate complex.

TABLE I

REDUCTION OF TRIPOLYPHOSPHATE COMPLEXES

Electrolyte composition: 1 m*M* depolarizer under test, 0.1*M* NaTP, 0.1*M* KCl, 0.02*M* borate buffer, pH 9. KCl replaced by K_2SO_4 in the case of ceric ion.

Depolarizer	$E^1/_2$ *vs. S.C.E. in V*	*Voltage span in V*	*Remarks*
—	—	—	Current rise at —1.81 V
Bi^{+3}	—0.53	—0.4 to —0.7	Well-developed wave
Pb^{+2}	—0.66	—0.6 to —0.75	Very well-developed
Fe^{+3}	—0.76	—0.55 to —0.95	Drawn-out wave
Cu^{+2}	—0.25	—0.2 to —0.35	Rounded maxima
	—1.18	—0.9 to —1.5	Drawn-out
VO_3^-	—1.32	—1.1 to —1.5	Well-developed
AsO_3^{-3}	—	—	Discharge at —1.4
Ce^{+4}	—	—0.8 to —1.5	Ill-defined, and drawn-out
Cd^{+2}	—1.2	—0.75 to —1.55	Appears to consist of two overlapping waves
UO_2^{+2}	—1.07	—0.8 to —1.25	Well-developed

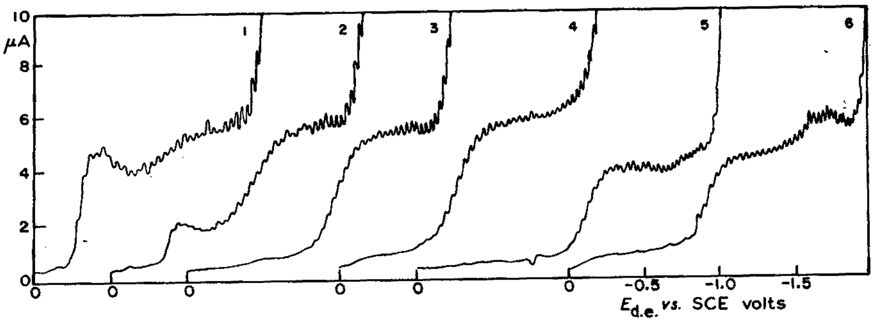

Fig. 1. Polarogram of 1 m*M* uranyl ion in 0.02*M* $Na_5P_3O_{10}$, 0.2*M* KCl and adjusted to: 1–pH 3; 2–pH 4; 3–pH 5; 5–pH 9; 4 and 6 were at pH 5 and pH 9 respectively but contained 1*M* KCl.

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Effect of pH

The polarograms of unbuffered solutions at different pH are recorded in Fig. 1. Both *id* as well as $E^1/_2$ change with pH (Table II). Buffered solutions behaved similarly except for a solution buffered to pH 5 with phthalate, in which case the polarogram appeared to consist of two waves, the first starting around —0.4 V and merging with the second at —0.7 V.

TABLE II (*cf*. Fig. 1)

EFFECT OF pH ON UTP WAVE

pH	$E^1/_2$ *vs. S.C.E.*	*id* (μA)
3	—0.86 [a]	1.0 [a]
4	—0.92 [a]	3.8 [a]
5	—1.00	4.5
9	—1.10	3.2

[a] Refers to the second wave corresponding to reduction of UTP.

Effect of variables on id

The temperature coefficient of *id* as measured between 30° and 40° were 1.7% and 1.0% per degree at pH 9 and pH 5 respectively. Any change in $E^1/_2$ between these temperatures was not appreciable. The effect of mercury pressure on the diffusion plateau is indicated in Fig. 2. The values for $id/\sqrt{h}$ at pH 9 and pH 5 are shown in Table III. The diffusion current constants at 30°, as obtained from the linear plot of *id vs. c* (Fig. 3), were 2.44 and 1.65 at pH 5 and pH 9 respectively. There was no noticeable change in $E^1/_2$ with change in uranyl ion concentration (0.1–5 mM) or with change in the concentration of NaTP (0.01M–0.2M).

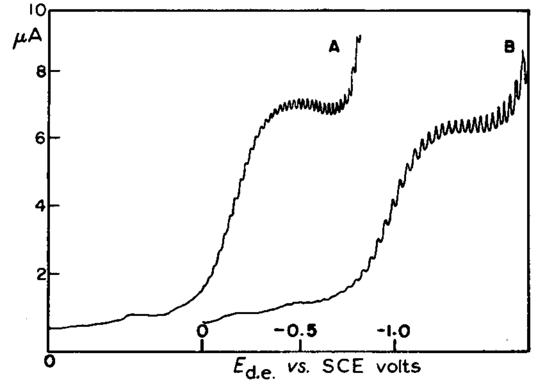

Fig. 2. Polarogram of 1 mM uranyl ion in 0.5M $Na_5P_3O_{10}$ and 0.1M KCl, pH 9. A – Hg ht. 49 cm; B – Hg ht. 36 cm.

TABLE III

UTP WAVE, *id vs. h*

pH 9		*pH 5*	
Mercury pressure (cm)	$id/\sqrt{h}$	*Mercury pressure (cm)*	$id/\sqrt{h}$
34.5	5.19	36	4.25
47.5	5.22	49	4.43
62.5	5.06	64	4.63

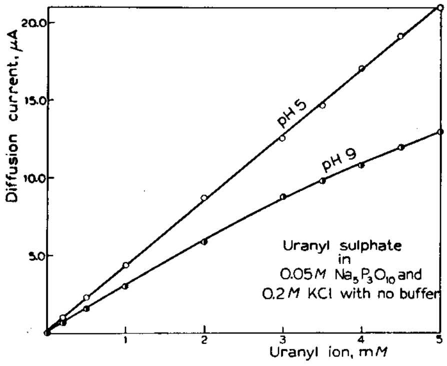

Fig. 3. Diffusion current *vs.* uranyl concentration at 30°.

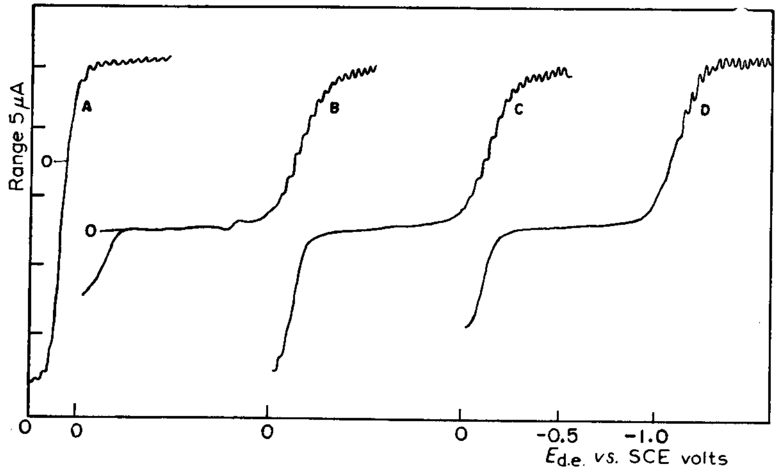

Fig. 4. Composite polarograms of U^{+5} + U^{+6} in sodium tripolyphosphate. A – Uncomplexed U^{+5} + U^{+6}, U = 2 m*M*, pH 2.5; B – U^{+5} + U^{+6}, (U = 1 m*M*) in 0.05*M* $Na_5P_3O_{10}$, pH 8.4; C – Electrolytically pre-reduced uranyl tripolyphosphate complex pH 9; D – Same as C after standing for 90 min without contact with air.

Composite polarograms of UTP

Fig. 4 is a record of the composite polarograms of a mixture of pentavalent and hexavalent uranium under the following conditions:

A. Perchlorate solution, pH 2.5, uranium 2 m*M*.

B. 1:1 (by vol.) mixture of solution A and 0.1M NaTP, final pH 8.43.

C. A UTP solution (2 mM uranyl perchlorate in 0.2M $KClO_4$ + equal volume 0.1M NaTP) electrolysed at pH 9 for 30 min under nitrogen at cathode potential —1.25 V *vs.* Ag/AgCl.

D. Solution C after being allowed to stand under nitrogen in the polarographic cell for 90 min.

Influence of indifferent electrolytes

When the electrolyte concentration is increased by the addition of salts including those which are not known to form complexes with the uranyl ion, the $E^1/_2$ was found to shift in all cases to more positive potentials. This effect is shown in Table IV (*cf.* Fig. 1).

TABLE IV

EFFECT OF INDIFFERENT ELECTROLYTES ON UTP WAVE

Electrolyte composition: 1 mM uranyl ion, 0.04M NaTP, indifferent electrolyte, pH 9, h = 51 cm.

Indifferent electrolyte	$E^1/_2$ *vs. S.C.E.*	*id (μA)*
Nil	—1.27	2.8
0.1M KCl	—1.15	3.6
0.6M KCl	—0.98	3.2
1.1M KCl	—0.92	3.0
1.6M KCl	—0.89	2.8
2.6M KCl	—0.86	2.8
0.1M $NaNO_3$	—1.20	3.0
1.0M $NaNO_3$	—1.02	2.8
0.1M $NaClO_4$	—1.20	3.1
1.0M $NaClO_4$	—1.02	3.0
0.1M K_2SO_4	—1.17	3.2
1.0M K_2SO_4	—0.97	2.9

Effect of capillary-active substances

Polarograms in presence of some common surface-active agents are recorded in Fig. 5. Their effect on *id* and $E^1/_2$ are listed in Table V.

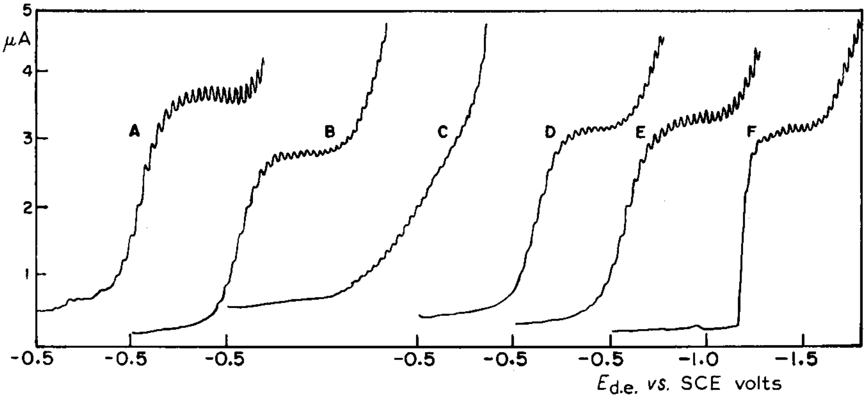

Fig. 5. Polarograms at pH 9 of 0.8 mM uranyl ion in 0.05M $Na_5P_3O_{10}$, 0.1M KCl, and A – no maximum suppressor, B – 0.001% gelatine, C – 0.01% gelatine, D – 0.01% gum arabic, E – 0.001% camphor, F – 0.01% camphor.

TABLE V

EFFECT OF MAXIMUM SUPPRESSORS ON UTP WAVE (*cf.* Fig. 5)

Electrolyte composition: 1 mM uranyl, 0.05M NaTP, 0.1M KCl, pH 9, mercury height (h) = 51 cm.

Maximum suppressor (%)	*id* (μA)	$E^1/_2$ *vs. S.C.E.*
Nil	2.9	—1.06
Gelatine		
0.001	2.5	—1.07
0.01 [a]	—	—
Gum arabic		
0.01	2.6	—1.12
0.10	2.5	—1.24
Camphor		
0.001	2.9	—1.08
0.01	2.8	—1.19
0.10	2.3	—1.42

[a] Wave badly deformed.

DISCUSSION

The polarogram of uranyl tripolyphosphate complex (UTP) shows a slight dip near the end of the diffusion current plateau. The dip becomes less pronounced at lower pH, longer drop-times (Fig. 2) and higher concentrations of indifferent electrolytes (Fig. 1). The departure from diffusion control is not considerable[6], as indicated by the normal temperature coefficient, the linear plot of *id vs. c* (Fig. 3), and the fairly constant value for $id/\sqrt{h}$ (Table III).

The irreversible nature of the wave is apparent from its large voltage span and the resulting high reciprocal slope (0.115 V at pH 9) of the plot E *vs.* log $i/(id - i)$. For this reason, the formula and the dissociation constant of the uranyl tripolyphosphate complex could not be determined polarographically.

The uranyl ion in presence of NaTP gives two waves in the pH range 3–4 (Fig. 1). The first wave with $E^1/_2$ around —0.3 V (Table II) is, in all probability, caused by the reduction of uncomplexed uranyl ion. Its disappearance seems to indicate that complexation of uranyl with NaTP is complete above pH 5. Greater stability of the complex in neutral to alkaline media is apparent from the increasingly negative values for $E^1/_2$ with rising pH. A steady decrease in *id* with increasing pH is also observed, the reason for which is not clear. A similar observation has been reported by SENISE AND DELAHAY[8] on the polarographic reduction of thallium in a pyrophosphate medium.

From the composite polarograms Figs. 4A and 4B, it will be seen that the anodic portions, caused in either case by the oxidation of pentavalent uranium, differ considerably from each other in their $E^1/_2$ values. The anodic wave (Fig. 4B) at $E^1/_2$ = approx. —0.1 very probably corresponds to the oxidation of pentavalent uranium in the complexed state. An anodic wave with the same $E^1/_2$ is given by a solution of UTP (Fig. 4C) provided it has been pre-reduced at a potential slightly more negative than the $E^1/_2$ of the uranyl complex. It, therefore, appears that the polarographic reduction of UTP complex proceeds essentially to the U^{+5} stage. Whether any U^{+4} is also formed in the process is difficult to say, since U^{+4} in presence of NaTP did not give an anodic wave.

The marked shift in the $E^1/_2$ to more positive values (Table IV) with increasing concentration of an indifferent electrolyte seems too high to be caused entirely by increased ionic strength. ORLEMANN AND KOLTHOFF[9] and, later, DELAHAY AND MATTAX[10] noted similar behaviour in the irreversible reductions of iodate and bromate. To explain the positive shift, the latter authors postulated the formation of a transitory collision complex between the cation and the iodate ion. The cation which functions as a bridge between the reducible anion and the cathode facilitates electron transfer.

Maximum suppressors shift $E^1/_2$, particularly of irreversible waves, to more negative potentials[7]. The effect of some of them on the UTP wave is set out in Table V (*cf.* Fig. 5). Gum arabic has a perceptible though not a pronounced effect, while gelatine in as low a concentration as 0.01% almost obliterates the wave. The gelatine effect resembles that observed by MEITES[11] on the polarogram of copper in alkaline tartrate medium. With camphor, however, the current rises abruptly, rendering the wave very steep[12,13]. When the solution is almost saturated with camphor (0.1%), the UTP wave starts only at —1.4 V which is nearly the desorption potential [12] of camphor. With a moderate concentration of camphor (0.01%), the steepening of the wave is not accompanied by a change in *id*. Advantage may be taken of this fact in the polarographic estimation of uranium.

SUMMARY

The behaviour of some tripolyphosphate complexes at the dropping mercury electrode has been examined, in particular that of the uranyl tripolyphosphate complex. The uranyl ion in alkaline tripolyphosphate medium undergoes an irreversible one-electron reduction with an $E^1/_2$ of —1.07 V *vs.* S.C.E. at pH 9. Indifferent salts shift the $E^1/_2$ to more positive potentials whereas maximum suppressors have an opposite effect. The wave obtained in presence of 0.01% camphor is well-defined and suitable for use in uranium analysis.

RÉSUMÉ

Les auteurs ont étudié le comportement des complexes formés avec le tripolyphosphate de sodium et divers cations, en particulier l'uranium. La vague obtenue en présence de camphre à 0.01% est bien définie et peut servir au dosage de l'uranium.

ZUSAMMENFASSUNG

Es wurde das Verhalten einer Tripolyphosphat-Komplexe, besonders der des Uranyl-Tripolyphosphates, untersucht. In Gegenwart von 0.01% Kampher ist der Verlauf der Kurve so eindeutig, dass die Methode zur Bestimmung des Urans geeignet erscheint.

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ANALYSIS OF SULPHONYL CHLORIDES BY POLAROVOLTRIC TITRATION WITH SODIUM SULPHIDE

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The usual method for analysis of sulphonyl chlorides depends on hydrolysis to hydrochloric acid and the corresponding sulphonic acid which are then titrated. Alternatively, hydrolysis can be carried out with a measured excess of standard alkali and the unused part back-titrated after complete reaction. In many cases, however, complete hydrolysis is slow and in the present work a faster method of analysis has been worked out.

Reaction of sulphonyl chlorides with sodium sulphide

This reaction has been used for many years in the industrial preparation of sulphinates and TRUCE AND MURPHY[1] quote numerous examples in their review. The first reaction is

$$R \cdot SO_2Cl + Na_2S \rightarrow R \cdot SO_2Na + NaCl + S.$$

GILMAN[2] gives a further reaction which takes place at higher temperature

$$R \cdot SO_2Na + S \rightarrow R \cdot SO_2SNa.$$

Although apparently not mentioned in the literature, the first reaction is evidently fast, even in dilute solution, and forms the basis of the titration method described in the present article. Two types of titration of sulphonyl chlorides with sodium sulphide solutions have been carried out:

(1) Visual titration, with the persistence of a yellow colour as end-point. This is evidently caused by the formation of yellow polysulphides between the reaction product sulphur (appearing as an almost colourless suspension) and the excess of the sodium sulphide titrant

$$Na_2S + xS \rightarrow Na_2S_{x+1}.$$

This end-point is arrived at only in more concentrated solutions (0.05–0.1M).

(2) Polarovoltric titration with the "Titravit" apparatus. The jump in potential taken as end-point is mainly caused by excess of sodium sulphide reagent.

It was observed in practice that the visual and instrumental end-points coincided. Further, in the concentration range studied in this work, end-point and equivalence-point appeared identical at least within the limits of titration error.

EXPERIMENTAL

Sulphonyl chlorides

Those used were:

methane sulphonyl chloride	–	Eastman Kodak, distilled
benzene sulphonyl chloride	–	Eastman Kodak, distilled
p-toluene sulphonyl chloride	–	B.D.H., not less than 98% pure

p-chlorobenzene-, *p*-bromobenzene-, *p*-methoxybenzene- and tetralin -sulphonyl chlorides
benzene *m*-disulphonyl chloride.

All were prepared according to the method of HUNTRESS AND CARTEN[3] and purified by repeated crystallisation from mixtures of petroleum ether, diethyl ether and chloroform. The benzene disulphonyl chloride proved most difficult to purify on account of its low solubility in available solvents.

Solutions

Sodium sulphide (Prolabo pour analyses) 0.5 and 0.1M in freshly distilled and boiled water (to expel dissolved oxygen as much as possible). The solutions were freshly prepared every few days and standardised with iodine solution just before use.

Sulphonyl chlorides in dry acetone, 0.5 and 0.1M with factor. These solutions maintained a sensibly constant titre for at least several days.

Apparatus

Commercially available Titravit apparatus. Electrodes each of about 15 mm platinum wire, 0.3 mm diameter, bent into spirals about 5 mm apart from each other.

Procedure

5 ml of sulphonyl chloride solution were measured into a 50 ml beaker, diluted with about 20 ml acetone–water mixture (1:1 by volume) and titrated with the sodium sulphide solution under magnetically operated stirring. The visual end-point was the persistence of a distinct yellow colour for 30–60 sec; this was found to be sharp to within a drop of titrating solution (error of less than 1%) in the 0.05–0.1M range of concentration.

The instrumental titration was carried out on the same quantities by the procedure previously described[4]. To eliminate the gradual change of electrode potential during the earlier part of the titration, which is brought about by the increase in electrolyte concentration from zero at the beginning, about 1 ml of approximately M aqueous sodium chloride solution was added to the sulphonyl chloride solution before titration.

The solvent composition and dilution was also varied.

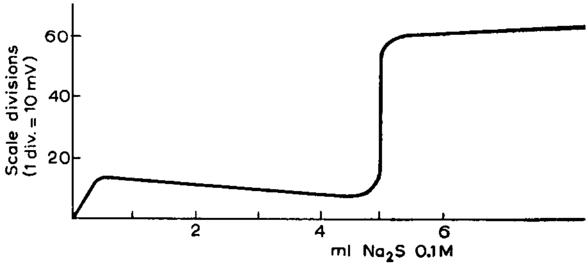

Fig. 1. Titration of 5.0 ml 0.1M *p*-toluene sulphonyl chloride + 20 ml acetone–water.

RESULTS

Sensitive and stoichiometric titration of all the sulphonyl chlorides was achieved, visually in 0.1M solution and instrumentally in 0.1 and 0.02M solution. Fig. 1 shows a typical titration with the Titravit.

The observed potential jumps in 0.1M solution were of the order of 0.5 V (from +1.6 to about +1.1 V).

The reaction speeds of the various sulphonyl chlorides varied slightly but were in all cases sufficiently high to permit convenient titration.

Under the reaction conditions used, both sulphonyl chloride groups of the benzene *m*-disulphonyl chloride were simultaneously titrated. A rather high result was obtained,

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probably because the compound contained a small amount of the trisulphonyl chloride. This high result was reduced a little by further recrystallisations.

Effect of different solvent mixtures

Acetone–water mixtures between about 95 :5 and 40 :60 (by volume as values at the end of titration) were all found to be equally satisfactory in trials with *p*-toluene sulphonyl chloride. Outside these limits one or other of the reactants was no longer soluble.

Amounts of over about 10% of dioxan led to over-titration with the visual end-point. The yellow polysulphide colour was much less persistent than in absence of dioxan. The polarovoltric end-point was also influenced. The sudden jump of potential was replaced by a series of smaller jumps for several successive dropwise additions of reagent. Up to about 20% dioxan, the middle of the overall potential change corresponded reasonably accurately with the expected titration, so that analysis was still possible, if rather less precise. This disturbing effect of dioxan was observed with all the sulphonyl chlorides studied here. At still higher dioxan concentrations, the interference was too large to permit even an approximate titration. This effect of dioxan has not been examined further in the present work.

Titration at low concentrations

This was not systematically studied, but on the basis of some trials at concentrations of about 0.01–0.005M, and from consideration of the Titravit titration curves, some forecasts can be made:

(1) A reasonably sharp end-point can be obtained down to about 0.001M concentration.

(2) In most cases, the speed of reaction should be adequate for titration at concentrations of 0.005M and in many cases, especially with gentle warming to about 30-40°, for titration of 0.001M sulphonyl chloride solutions.

(3) End-point and equivalence point should agree satisfactorily at these lower concentrations.

We hope to carry on our studies of these points, and of the kinetics of the reaction.

SUMMARY

A method has been developed for the rapid analysis of aliphatic and aromatic sulphonyl chlorides by polarovoltric titration with a standardised sodium sulphide solution. Visual end-point determination is also possible in more concentrated solution.

RÉSUMÉ

Une méthode est proposée pour l'analyse rapide des chlorures de sulfonyle aliphatiques et aromatiques, par titrage polarovoltrique au moyen d'une solution étalon de sulfure de sodium.

ZUSAMMENFASSUNG

Es wird eine Schnellmethode beschrieben für die Analyse aliphatischer und aromatischer Sulfochloride, welche auf der polaro-voltometrischen Titrierung mit einer Standard-Natriumsulfidlösung beruht.

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REVUES DE LIVRE

Die Methoden der Mikromassanalyse, JOSEF MIKA, Budapest, Zweite umgearbeitete Auflage, xv + 375 Seiten, 76 Abb. und 18 Tab. Geheftet DM 63.—. Ganzleinen DM 66.—. *Die chemische Analyse*, herausgegeben von GERHART JANDER, 42. Band, Ferdinand Enke Verlag, Stuttgart, 1958.

La collection ,,*Die chemische Analyse*'' compte dorénavant dans son actif une des monographies des plus complètes et des plus importantes qu'un microchimiste puisse désirer: ,,*Les méthodes de la microanalyse volumétrique*''.

Le volume que nous avons entre les mains constitue la deuxième édition, entièrement refondue et augmentée, du livre homonyme paru, pour la première fois, en 1939.

Le Professeur MIKA a su, d'une manière admirable, développer le sujet dans toute son ampleur. sans pour cela négliger les détails. Extrêmement systématique et rationel, l'auteur examine successivement les réactifs et instruments utilisés pour les microanalyses volumétriques, les différentes méthodes appliquées actuellement et les causes d'erreur inhérentes à chacune d'elles, la théorie étant partout suivie de nombreux exemples pratiques.

L'érudition et l'expérience personnelle de l'auteur (plus de 600 références bibliographiques) éblouissent littéralement le lecteur et confèrent à cet ouvrage une valeur très grande.

Vu le nombre considérable des sujets traités dans le livre en question, il ne nous est pas possible de donner ici même un bref aperçu des chapitres. Nous relèverons donc au hasard quelques titres: *Allgemeiner Teil:* Die indirekte Bestimmung des Äquivalenzpunktes. Die photometrischen Titrationen. Die potentiometrische Indikation. Die amperometrische Indikation der Mikrotitrationen. Die Mikrotitrationen mit Hochfrequenzindikation. Die Fehlerquellen der volumetrischen bzw. gravimetrischen Bestimmung von Lösungsmengen. Die verschiedenen Arten der Mikroburetten. Die coulometrischen Mikro- bzw. Ultramikrobestimmungen. Der Wirkungsgehalt der Masslösungen. Die Unterteilung der Probelösungen. Die Mikro- und Ultramikropipetten. *Spezieller Teil:* Neutralisationsanalytische Bestimmung von schwachen Basen in nicht wässrigen Lösungen. Alkalimetrische Bestimmung von Salzen mit Hilfe von Kationenaustauschern. Die Oxydation und Reduktion der Proben. Die wichtigsten Massflüssigkeiten der redoxymetrischen Mikrobestimmungen. Die Komplexbildungstitration. Die fällungsanalytischen Titrationen.

En conclusion, nous tenons à recommander chaudement cet ouvrage à tous les analystes, persuadés qu'il leur sera de toute utilité et leur rendra les services les plus grands.

I. KAPÉTANIDIS (Genève)

Proceedings of the Congress on Modern Analytical Chemistry in Industry, The Society for Analytical Chemistry, W. Heffer & Sons, Ltd., Cambridge, Great Britain, 1958, 244 p., 2 guineas.

Ce livre renferme les exposés présentés lors du Congrès organisé en juin 1957 par ,,The Scottish Section of the Society for Analytical Chemistry''. A la lecture de cet ouvrage, on se rend compte de l'importance que revêt pour l'industrie, la chimie analytique moderne. Elle dispose actuellement de tels moyens d'investigation que son domaine s'élargit sans cesse. Outre les dosages qui deviennent de plus en plus délicats, la chimie analytique a aussi pour objet la recherche des propriétés physico-chimiques des substances, de leur stabilité, des constantes acide - base, ox. - red., etc., connaissances indispensables à la bonne marche et au progrès de l'industrie chimique. C'est ce que nous apprend cet ouvrage. Il est divisé en trois sections, la première s'intitule: ,,L'analyse dans l'industrie moderne'' et comprend entre autres: les recherches analytiques et ses rapports avec l'industrie, les méthodes analytiques modernes dans l'industrie du fer et de l'acier, les problèmes chimiques dans l'industrie électrique, l'application des méthodes physiques d'analyse à l'industrie du gaz, les développements analytiques dans les laboratoires pharmaceutiques. La section II traite de quelques applications des nouvelles techniques analytiques dans l'industrie avec, comme chapitres essentiels: l'analyse et les aliments, les récents progrès dans la séparation des substances à hauts poids moléculaires, la spectroscopie d'émission dans l'analyse industrielle, l'analyse dans la recherche médicale, l'analyse et la spectroscopie infra-rouge. Il est aussi question des plastiques, des métaux rares, de la productivité et de l'automation. La dernière section s'occupe du développement de la chimie analytique et de ses applications à de nouveaux problèmes posés par l'industrie: nouveaux réactifs, utilisation des isotopes radioactifs, mesures analytiques automatiques, polarographie, chromatographie des gaz. Les divers exposés sont clairs, bien présentés, remarquablement documentés. En conclusion: un livre très instructif, à recommander.

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BUCHBESPRECHUNG

Fortschritte der pH-Messtechnik, von Kurt Schwabe, 2., überarbeitete und erweiterte Auflage, VEB Verlag Technik, Berlin, 1958, 280 S., 99 Abb., DM 18.—.

Es ist eine bekannte Tatsache, dass die Anzeigegenauigkeit moderner pH-Messgeräte häufig mit der Messgenauigkeit verwechselt wird. Das Verdienst des Verfassers ist es, auf diesen Umstand und die oft nicht genügend beachtete grundsätzliche Unsicherheit der praktischen pH-Messung in Lösungen unbekannter Zusammensetzung eindringlich hingewiesen zu haben. Das ganze Buch steht unter diesem Aspekt und ist gekennzeichnet durch eine sorgfältige Abschätzung der Messgenauigkeit und Fehlermöglichkeiten, so dass es auch einem Nichtfachmann, der pH-Messungen nur als Mittel zum Zweck durchführt, eine kritische Beurteilung seiner Messwerte ermöglicht.

Der Autor bringt zunächst einen ausgezeichneten Überblick über die verschiedenen Möglichkeiten zur Definition der pH-Skala. Relativ kurz werden dann die nichtelektrometrischen, die katalytischen und kolorimetrischen Methoden zur Bestimmung des pH-Wertes behandelt.

Entsprechend ihrer grossen Bedeutung ist im 3. Kapitel den elektrometrischen pH-Messmethoden der weitaus grösste Teil des Buches gewidmet. Zunächst wird die Wasserstoffelektrode als Grundbezugssystem für die gesamte pH-Messtechnik eingehend besprochen. Dann folgen andere, ebenfalls auf Wasserstoffionen ansprechende Elektroden: die Chinhydronelektrode als wichtigste Redoxelektrode, die Antimon- und Wismutelektrode als wichtigste Metall/Metalloxydelektroden. Besonders ausführlich wird auf die Glaselektrode eingegangen, der wegen ihrer universellen Anwendbarkeit in der praktischen pH-Messung heute wohl die grösste Bedeutung zukommt. Der Abschnitt umfasst Ausführungen über Elektrodenfunktion und Theorie der Glaselektrode, Angreifbarkeit, Temperaturbeständigkeit, elektrischen Widerstand und Polarisierbarkeit, Richtlinien für die Benutzung von Glaselektroden und Elektrodenformen. In einem weiteren Abschnitt werden die Bezugselektroden, insbesondere die Kalomel- und die Silber/Silberchlorid-Elektrode, sowie die Elektrolytschlüssel besprochen.

Erst dann folgt der Abschnitt über Messgeräte für elektrometrische pH-Messungen, unterteilt in Kompensationsinstrumente, stromverbrauchende Anzeigegeräte und elektrostatische Messinstrumente, insbesondere Röhrenvoltmeter. Ein abschliessender Abschnitt ist schliesslich dem Registrieren und Regulieren des pH-Wertes gewidmet.

Gegenüber der 1. Auflage sind Aufbau und Anordnung des Textes nur wenig verändert. Einige inzwischen überholte Tabellen und kleinere Absätze sind fortgefallen. Dafür sind an zahlreichen Stellen Erweiterungen vorgenommen worden, die die Fortschritte der pH-Messtechnik der letzten vier Jahre gebührend berücksichtigen. Wesentlich erweitert wurde der Anhang: Ausser der schon in der ersten Auflage vorhandenen Formelzusammenstellung für elektrometrische pH-Messungen wurden Formeln zur näherungsweisen Berechnung des pH-Wertes aus der Elektrolytkonzentration mit Rechenbeispielen neu aufgenommen. Die Tabellen zur pH-Messung mit Farbindikatoren und insbesondere die der pH-Werte von Puffergemischen wurden in erweiterter Form im Anhang zusammengestellt. Dadurch ist die Übersichtlichkeit sowohl des Textes als auch die der Tabellen verbessert worden. Jedoch sollten in der nächsten Auflage auch die Tabellen mit Hinweisen auf die zugehörigen Textstellen versehen werden.

Das kleine handliche Büchlein gibt trotz seiner Kürze nahezu erschöpfend auf alle Fragen des behandelten Gebietes Auskunft, wobei der Schwerpunkt auf der Behandlung der elektrometrischen Messmethoden liegt. Die Darstellung ist ausserordentlich gründlich und verzettelt sich doch nicht in Einzelheiten. Das Werk kann bestens empfohlen werden.

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