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THE USE OF MIXED ELECTROLYTES FOR THE POLAROGRAPHIC DETERMINATION OF THALLIUM

A. I. Zebreva and M. T. Kozlovskii

The Kazakh State University

We were given the task of finding a simple and rapid method of determining thallium in solutions, which also contained small amounts of lead, cadmium, zinc, and arsenic, and traces of selenium, antimony, bismuth, iron, and copper.

TABLE 1

Determination of Thallium in the Presence of Lead and Cadmium

Taken, mg			Supporting electrolyte	Tl found, mg
Tl	Pb	Cd		
1.00	51	56	2 N NaOH + 1.5 N NH_4Cl (equivalent to 0.5 N NaOH + 1.5 N NH_4OH + 1.5 N NaCl)	0.975
0.75	30	45		0.76
0.50	30	34		0.50
0.50	102	56		0.52
0.40	51	34		0.40
0.40	102	45		0.415
0.35	102	45		0.37
0.30	102	45		0.31
6.12	500	—	1.5 N NaOH + N NH_4Cl (equivalent to 0.5 N NaOH + N NH_4OH + N NaCl)	5.93
0.50	51	22		0.50
0.50	30	16		0.52
0.40	20	22		0.385
0.40	30	22		0.405

It is known that univalent thallium is only capable of forming complexes to a very slight extent, so that its half-wave potential alters very little when different complexing agents are added to the solution, or when the pH is varied.

Thallium can readily be determined polarographically in the presence of cadmium, by using an ammoniacal supporting electrolyte, in which the cadmium half-wave potential is more negative than that of thallium. In the presence of lead, polarography should be carried out with an alkaline supporting electrolyte, which shifts the lead half-wave potential in the negative direction.

In the presence of both cadmium and lead, we used a mixed alkaline–ammoniacal supporting electrolyte. No reference to such a supporting electrolyte was found in the literature. Vlcek's tables * mention a mixture of ammonia with ammonium salts, but not with alkali. Clearly, it was also possible to use a mixture of ammonium salts with caustic soda in different proportions. With these components in equivalent proportions, this mixture is equivalent to an ammonia solution, but differs in having a higher electrical conductivity and in being somewhat more convenient to use.

Table 1 shows some results for the determination of thallium in the presence of lead and cadmium, their relative proportions being similar to those observed under production conditions.

Polarography was carried out using a visual polarograph, with a galvanometer of sensitivity $1.7 \cdot 10^{-9}$ amp per scale division, and a 1 : 32 shunt. The supporting-electrolyte compositions are shown in Table 1; they also contained gelatine, and sodium sulfite to remove oxygen. The thallium half-wave potential was about −48 v (versus saturated calomel electrode) under these conditions; the thallium wave was recorded over the range −0.2 to −0.7 v. The total volume of the electrolyte was always 50 ml.

* A. A. Vlcek, Chem. Listy 50, 400 (1956).

TABLE 2

The Determination of Thallium in the Presence of Copper and Tellurium

Taken, mg			Tl found, mg
Tl	Cu	Te	
0.46	0.5	2.0	0.44
0.92	0.5	2.5	0.88
1.84	1.0	5.0	1.77
1.84	1.5	7.5	1.80
1.84	0.5	12.5	1.71
1.84	2.0	7.5	1.97
1.84	2.5	—	1.91
1.38	1.0	—	1.47
2.76	2.0	7.5	2.66
2.76	2.0	—	2.90

TABLE 3

The Determination of Thallium in the Presence of Large Amounts of Lead and Cadmium

Taken, mg					Tl found, mg
Tl	Cd	Pb	Bi	Sb	
0.46	270	1000	—	—	0.49
0.92	404	1000	—	—	1.04
1.84	1000	1000	—	—	1.76
4.08	500	1000	—	—	3.95
4.08	1000	1000	—	—	4.00
6.12	1000	1000	—	—	6.20
0.92	500	500	6.8	5.4	0.88
0.92	1000	800	8.0	5.0	0.88
1.84	500	1000	5.2	6.7	1.72
0.92	1000	500	—	25.0	0.55
1.84	1000	800	—	30.0	0.85
2.74	500	1000	—	25.0	1.62

We also investigated the effects of other elements on the polarographic determination of thallium. It was known from the literature that selenium and arsenic gave no polarographic waves in alkaline solutions. The presence of tellurium did not affect the determination, since the tellurium wave was at a more negative potential. Only in the presence of large quantities of tellurium (50-60 mg in 50 ml) was the upper step of the thallium wave found to be slightly shortened, because under these conditions the tellurium reduction wave began at −0.68 v.

The presence of up to 28 mg of antimony and up to 12 mg of bismuth in 50 ml of solution did not affect the thallium determination; the antimony potential (about −1.0 v); bismuth was nearly all precipitated, but the deposit hardly carried down any thallium.

Iron, in quantities of 3-4 mg per 50 ml of solution, did not affect the thallium determination, although it gave a precipitate of hydroxide. With larger quantities of iron, of the order of 10 mg, and when there was only about 1 mg of thallium, the latter was almost completely carried down in the precipitate.

The presence of zinc did not affect the thallium determination, since the zinc wave was at a considerably more negative potential.

The polarographic determination of thallium in an alkaline – ammoniacal supporting electrolyte was affected by copper, which, under these conditions, gave two waves, the second of which exactly coincided with the thallium reduction wave. But the determination could be carried out in the presence of small amounts of copper, not more than there was of thallium, by using the first copper wave to calculate a correction to be applied to the combined copper-thallium wave. In an alkaline – ammoniacal medium, the first copper wave fused with the anodic mercury oxygen wave, and therefore had no lower step; its height was found by measuring the height of its upper step above the residual current of the supporting electrolyte at the same potential.

Table 2 shows some results for thallium determination in the presence of copper; the solution also contained tellurium, whose wave began immediately after that of thallium.

Thus, the proposed supporting electrolyte was found to be completely satisfactory for determining thallium in solutions obtained by aqueous extraction of dust from lead production.

We also investigated the possibility of using an alkaline –ammoniacal supporting electrolyte for the analysis of materials containing large amounts of cadmium and lead. Depending on the relative proportions of these elements, it was found to be necessary to vary the composition of the supporting electrolyte in order to avoid the formation of a precipitate; with a large cadmium content, of the order of 1000 mg in 50 ml, it was necessary to increase the ammonia concentration, and, alternatively, to increase the alkali concentration for high lead content. When there were large amounts of both cadmium and lead, the high alkali concentration, required to keep the lead in solution, caused precipitation of cadmium hydroxide. Under these conditions it was necessary to remove the lead as sulfate, the thallium and cadmium were then extracted with water (3-4 portions of 3 ml), and the thallium was determined with an ammoniacal – alkaline supporting electrolyte. Since only a trace of lead then remained in the solution, we used a supporting electrolyte of the following composition: N NaOH + N NH_4Cl + + N NH_3 (equivalent to 2N NH_4OH + N NaCl).

Table 3 shows some results for the determination of thallium by this method.

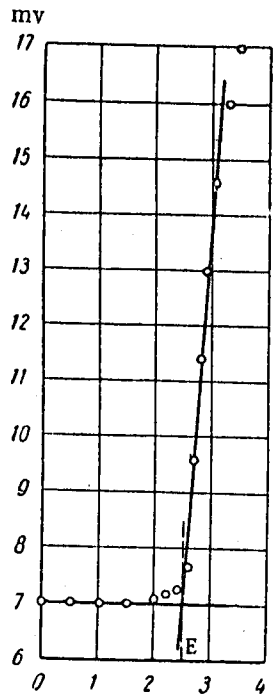
It is clear from the table that the method of removing large amounts of lead by evaporation with sulfuric acid gave satisfactory results, but not in the presence of large amounts of antimony, where the aqueous extraction of the residue from sulfuric acid evaporation gave rise to the formation of basic antimony salts which retained part of the thallium.

ELECTROMETRIC NONCOMPENSATION METHOD OF TITRATING BERYLLIUM

V. F. Barkovskii

(A. M. Gor'kii Ural State University)

The most interesting of the electrometric methods of determining beryllium described in the literature is the "indicator" method of amperometric titration proposed by Usatenko and Bekleshova [1]. The method is based on the formation of insoluble Na_2BeF_4 during titration. However, due to the complex preparation of the solution for titration, this method is difficult to apply to the analysis of large number of samples. According to Kleiner, Tananaev and Deichman's data [2, 3] in dilute aqueous solutions beryllium forms a quite stable monofluoride complex ion BeF^+ ($K_{inst.} = 1.3 \cdot 10^{-6}$) and soluble, undissociated beryllium fluoride, BeF_2 ($K_{inst.} = 1.11 \cdot 10^{-5}$).



Titration curve of beryllium chloride with ammonium fluoride solution.

The direct electrometric noncompensation method we proposed for titrating* the Be^{2+} cation with ammonium fluoride solution is based on the formation of normal beryllium fluoride, BeF_2, in aqueous solution. An aluminum metal electrode was used as the indicator electrode [4] and nichrome for the indifferent electrode. The apparatus described by S. K. Chirkov [5] was used for the titration.

During titration the electrode pair was connected through a needle galvanometer with a 17 mv scale and a resistance of 161.7 ohm, and through a constant resistance of 5000 ohm. The solution was mixed by rotating the beaker, fixed in the socket of an electric motor with a rotation rate of ~160 rev/min.

Beryllium may be titrated to give reproducible results in a base electrolyte of acetate buffer in the presence of sodium chloride.

A sample of beryllium carbonate was dissolved in hydrochloric acid; the titer was established gravimetrically. The ammonium fluoride solution was stored in a paraffin-waxed vessel; the titer was also established gravimetrically.

To study the relation between the ammonium fluoride consumed in beryllium titration and the acidity, 4.0 ml of beryllium was placed in a beaker, 10 ml of 20% sodium chloride solution added, the solution made up to 50 ml with a buffer solution of appropriate pH and the titration performed. The equivalence point was determined from the intersection of the tangents (see figure).

Table 1 gives the results of titrating beryllium at different acidities; the fluoride consumption increased with a decrease in the solution's acidity but in the range of pH values from 3.8 - 5.0 a constant amount of reagent was consumed. The ratio of beryllium to fluoride in this range corresponds to the formation of BeF_2 and not BeF^+ as would be expected from the values of the

* A. M. Blinova participated in the experimental work.