# THE POLAROGRAPHIC DETERMINATION OF INDIUM

A. T. Nizhnik and I. S. Chaus

Institute of General and Inorganic Chemistry. Acad. Sci. Ukrainian SSR, Kiev

Despite the fact that many methods have already been suggested for the quantitative determination of indium (spectrographic [1-3], titrimetric [4], colorimetric [5], polarographic [6], etc.), there is at the moment, no rapid and reliable method for the determination of this element; such a method is of particular importance for the technical production of indium, and for its determination in materials during the search for indium raw materials.*

The most widely used method is the polarographic method suggested by Aref'eva [7]; however, the chemical preparation of the solutions to be polarographed is very long, difficult, and incomplete.

In particular, according to Gurin's results [8], in order to achieve complete separation of cadmium from indium by means of ammonia, at least a threefold reprecipitation is necessary for ordinary industrial materials. At the same time it is essential to completely remove copper, and particularly cadmium, from the indium solution because of the nearness of their half-wave potential.

Various other methods have been suggested for preparing the solutions for polarographic determination of indium [9-11].

We should like to suggest an amalgam method for preparing the solutions for polarographing, for the determination of indium in production materials and wastes containing hundredth parts of a percent, and more, of indium. A characteristic feature of this technique is that during treatment of the original sulfuric acid solution of indium (at ordinary temperatures) with the zinc amalgam, all those elements which interfere with the polarographic determination of indium are removed, while the indium remains in solution. To the solution purified in this way is added 10% of its weight of sodium chloride and the indium then determined polarographically. Removal of indium from a number of elements, including tin and cadmium, in sulfuric acid solutions on a zinc amalgam, is based on the specific behavior of indium towards the sulfate ion.

In 1947, a study was made of the effect of chlorides on the value of the diffusion current for indium in sulfuric acid solutions [13]. It was established that addition of chloride ions until their concentration is 10% of the sulfuric acid solution, in which the polarographic wave for indium cannot be detected, ensures the normal reduction of indium ions and the appearance of its wave. Other research workers have observed the same phenomenon at various times: Kolthoff and Lingane [14], Babko, Polishchuk, and Volkova [15], Bukhman [16]. Seward [17] and Ensslin [18], in the system indium sulfate–sulfuric acid established that an acid sulfate of indium with the composition $In_2(SO_4)_3 \cdot H_2SO_4 \cdot 7H_2O$ is formed. Muzyka [19] while studying the same system by electroconductivity, cryoscopic, and transport-number methods established the existence of the anion $[In(SO_4)_2]^-$ in solution. Aksel'rud [20], using a polarographic method, confirmed the existence of the indium anion $[In(SO_4)_2]^-$ in acid solutions. Thus, the reason for the slow reduction of indium ions from sulfuric acid solutions is the formation of complex indium anions, and the changes in the value of the reduction potential of the latter arising from this. Under such conditions, as we have established, this process is essentially independent of the nature of the cation (hydrogen or metal) in the sulfates taken (Table 1).

*For a review of methods of determining indium, see [6a].

The half-wave potential of indium in a hydrochloric acid solution is equal to −0.597 volt (with respect to the saturated calomel electrode), while in sulfuric acid it is −1.06 volt; the half-wave potential of cadmium

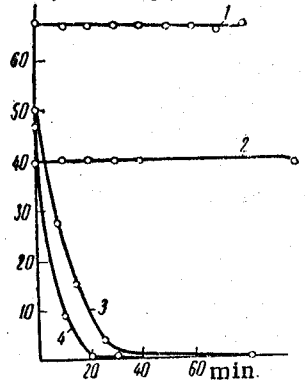
TABLE 1

Effect of the Concentration of $SO_4^{2-}$ Ions on the Extent of Reduction of Indium on a Zinc Amalgam

| In $H_2SO_4$ solutions | | In solutions of sulfates* | | |
|---|---|---|---|---|
| $H_2SO_4$ concentration, in % | Extent of the reduction of indium, in % | Sulfate taken | Concentration of $SO_4^{2-}$ ions, in % | Extent of the reduction of indium, in % |
| 3 | 12.1 | $(NH_4)_2SO_4$ | 20.0 | Not reduced |
| 6 | 9.5 | $MgSO_4$ | 19.9 | " |
| 10 | 5.8 | $MnSO_4$ | 20.2 | " |
| 15 | 2.4 | $ZnSO_4 \cdot 7H_2O$ | 21.0 | " |
| 20 | Not reduced | — | — | " |

*In order to avoid hydrolysis, about 1.5% of free sulfuric acid was added to the solution.

in sulfuric acid is equal to −0.642 volt. The large difference between the values of the potentials makes it comparatively simple to separate indium and cadmium completely in sulfuric acid solution by means of a zinc amalgam. The results obtained are shown in the diagram.




Separation of In and Cd by means of a zinc amalgam: 1,2) For indium; 3,4) for cadmium (curves 2 and 4 are enlarged 25 times along the ordinate).

Elements such as As, Sb, Bi, Cu, Tl, Se, Sn, Ma, Ti, Fe(III) and some others are vigorously reduced by the zinc amalgam. Under such conditions, some (Cd, Sn, Tl, and Cu) dissolve in the mercury, while others (As, Sb, Bi, Se, and Te) are deposited in the elemental state in the form of an insoluble, friable, deposit. Elements with higher valency are reduced to lower valency states ($Fe^{III}$, $V^{V}$, $Cr^{VI}$, and $Ti^{IV}$).

The technique developed has been checked on various samples of indium raw material.

The analytical procedure adopted for the polarographic determination of indium by the amalgam method is as follows. An aliquot of test material (1-3 g) is decomposed on heating in a mixture of nitric and sulfuric acid until the sample has been broken down completely, and until copious white fumes appear. After cooling, the sample is treated with hot water, and, in the event of the presence of an appreciable amount of precipitate in the solution, the latter is allowed to stand and then filtered. To the solutions thus obtained is added sulfuric acid (or an equivalent amount of some suitable sulfate), so that its final concentration is not less than 20%; the solution is then cemented with zinc amalgam* at room temperature. The zinc amalgam is prepared by dissolving zinc metal in mercury on heating in the presence of dilute sulfuric acid. Treatment of the solution with the amalgam, for a stirrer rate of 350-400 revolutions/minute, takes about 45 minutes. When cementation is complete, the solution is filtered, if necessary, and then about 10% of its weight of a soluble chloride (for example NaCl) added to it; indium is then determined in this solution polarographically.

*When sulfates are used it is essential to add some $H_2SO_4$ in order to avoid hydrolysis.

TABLE 2

Results for the Quantitative Determination of Indium in Various Types of Indium-Containing Raw Material

| Firms supplying test material \ Elements in % | Bi | Zn | Al | As | Fe | Pb | Sb | Cd | Cu | Sn | Indium content as found by the following methods: spectro. | Aref'eva | amalgam |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| ChETsZ | 0,1 | 20,0 | 10,0 | 0,05 | 0,5 | 0,3 | 0,05 | 0,02 | 0,05 | 0,01 | 5 | 5,00 | 5,01<br>5,00<br>5,00 |
| KMZ | 15,0 | 25,0 | — | 2,3 | 8,0 | 0,04 | 0,10 | 1,5 | 1,6 | 0,14 | 0,4 | 0,40 | 0,39<br>0,40<br>0,40 |
| Ukrtsink | 0,1 | 21,2 | 4,7 | 0,5 | 2,4 | 10,0 | — | 0,58 | 0,68 | — | 0,04 | 0,04 | 0,04<br>0,04<br>0,042 |

## SUMMARY

A new method has been developed for removing interfering elements prior to polarographic determination of indium in concentrates and in processed materials. The method consists of treating sulfuric acid indium solutions containing 20% free sulfuric acid (or the equivalent amount of other sulfates) with a zinc amalgam; the chloride of an alkali metal is then added to the solution purified in this way, the amount of chloride added being sufficient to bring its concentration up to 10% (with respect to the weight of the solution); indium is then determined polarographically.

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