

POLAROGRAPHIC DETERMINATION OF INDIUM IN METALLIC GALLIUM

S. I. Sinyakova, N. A. Rudnev, Shen Yu Ch'ih, and R. Dzhumaev

V. I. Vernadskii Institute of Geochemistry and Analytical Chemistry,

Academy of Sciences of the USSR, Moscow

Translated from *Zhurnal Analiticheskoi Khimii*, Vol. 16, No. 1, pp. 32-35,

January-February, 1961

Original article submitted February 23, 1960

Many papers have been devoted to the polarographic determination of indium [1-6]. However, these papers are devoted either to the mechanism of the electrode reaction, or to methods for the determination of indium in the presence of other elements, in particular cadmium, at the usual indium concentrations (10^{-3} - 10^{-4} M) for polarographic work. Polarographic methods have not been used for the determination of (10^{-5} - 10^{-7} %) indium in high purity metals. The work described here was devoted to establishing the requisite conditions for the polarographic determination of 10^{-5} - 10^{-6} % of indium, and also to methods for separating and concentrating indium during the analysis of metallic gallium.

In order to determine indium at a concentration of 10^{-6} M it was essential to choose a suitable supporting electrolyte. Very clearly defined indium waves are obtained in hydrochloric acid solutions, with $E_{1/2}$ equal to, for example in 1 M HCl, 0.60 v (relative to the saturated calomel electrode). With increasing HCl concentration, the half wave potential of indium is shifted to more negative values as a result of complex formation [7]. As our experiments showed, during polarographic examination of 10^{-6} - 10^{-7} M indium solutions the HCl concentration not only affects $E_{1/2}$, but also affects the shape of the indium reduction curve, the latter being distorted at HCl concentrations greater than 2 M, while in 6 M HCl the indium wave disappears. 0.2 M HCl was accordingly chosen as the supporting electrolyte. In this region the relation between the value of the diffusion current and the indium concentration is linear over the range 2×10^{-6} - 4×10^{-5} M (Fig. 1). The limiting concentration which can be determined is 2×10^{-6} M indium.

It was also demonstrated that indium can be determined on the GEOKhI oscillograph (Model 2) [8]. In Fig. 2 are shown oscillograms for indium in 0.2 M HCl, and also the curve relating indium peak height and its concentration in solution. As is evident from Fig. 2, the curve is linear from indium concentrations within the range 1×10^{-6} - 2×10^{-5} M. The limiting indium concentration which can be determined by the oscillographic method is 5×10^{-7} M. Thus, it is possible by means of the polarographic method to determine 1×10^{-5} % of indium on a sample weight of 2 g, while by means of oscillographic polarography it is possible to determine 2.5×10^{-6} % In, for a final volume of the solution of not more than 1 ml.

In order to determine indium in gallium it is necessary to carry out a preliminary concentration of the indium.

The method which we suggest for concentrating indium is based on its coprecipitation with cobalt sulfide,* with subsequent removal of indium from gallium** and sulfate ions by extraction of indium with dithizone in the presence of sulfosalicylic acid, or by extraction of indium or gallium with diisopropyl ether.

*Cobalt was chosen as the collector because of its very negative half wave potential.

**About 10% of gallium is coprecipitated with cobalt sulfide.

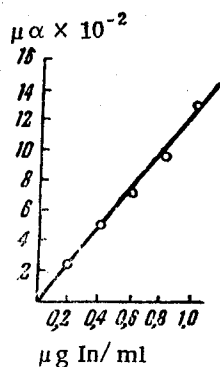


Fig. 1.

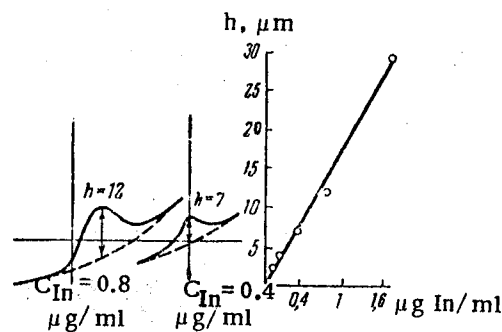


Fig. 2

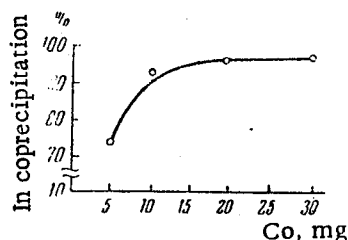


Fig. 3.

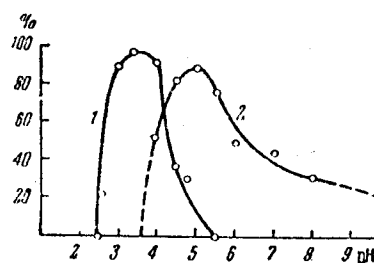


Fig. 4.

As experiments with the radioactive isotope In^{114} showed, by introducing sufficient amounts of cobalt chloride into the solution, indium is coprecipitated quantitatively with cobalt sulfide.

In Fig. 3 is shown the curve illustrating the coprecipitation of $1 \mu\text{g}$ of indium as a function of the amount of cobalt taken. For cobalt contents ranging from 15 mg upwards, the amount of indium coprecipitated amounts to 95% . In the case of $0.1 \mu\text{g}$ indium, the percentage coprecipitation is on an average 93% when $10\text{--}15 \text{ mg}$ cobalt is used.

Of a number of masking agents for gallium (citric, tartaric, malonic acids, etc.) sulfosalicylic acid [9] proved to be the most effective at $\text{pH } 4.8\text{--}5.2$. This pH range proved to be the optimum for the quantitative extraction of indium as its dithizonate in the presence of sulfosalicylic acid, as is clear from Fig. 4. The maximum extraction of indium dithizonate in the presence of sulfosalicylic acid is shifted towards higher pH values than occurs with an unbuffered 10^{-3} M solution of indium [10]. It was also established by means of the radioactive isotope In^{114} that indium is quantitatively separated (even $0.1 \mu\text{g In}$) from gallium (Ga about 0.1 g) by extracting it with diisopropyl ether from solutions containing HBr . Satisfactory separation of indium from gallium is also possible by extracting gallium with diisopropyl ether from a 6 N HCl solution (Table 1).

As a result of the work carried out, the following method is suggested for the determination of indium in gallium. A $2\text{--}5 \text{ g}$ aliquot of metallic gallium is dissolved on boiling in $25\text{--}30 \text{ ml}$ aqua-regia, the latter being added in portions of about 10 ml . ** The solution is evaporated to a volume of $3\text{--}5 \text{ ml}$, and, after cooling, 50 ml of distilled water is added. Ten- 25 g of tartaric acid is added, the solution is neutralized with a 25% ammonia solution, and the pH adjusted to $7\text{--}8$. Cobalt chloride solution (0.1 M) is added (1.7 ml per g of gallium ***), and the indium coprecipitated with cobalt sulfide by adding $10\text{--}25 \text{ ml}$ of 0.5 N sodium sulfide; the solution is allowed to stand for 30 min in order for the precipitate to coagulate. The sulfides are centrifuged, washed $3\text{--}4$ times with a 1% solution of ammonium nitrate. The precipitate is dissolved in concentrated HNO_3 (the latter being added gradually in $3\text{--}5 \text{ ml}$ lots) and the solution transferred to a 100 ml beaker of heat-resistant glass, in which it is evaporated to dryness. One of the following variants is then employed.

*The indium concentration was determined polarographically.

**Dissolution proceeds slowly.

***This corresponds to 10 mg cobalt.

TABLE 1

Separation of Indium from Gallium by Extracting the Latter with Diisopropyl Ether from 6 N HCl (0.1 g gallium taken)

In added, μg	In found, μg	Error (relative) %
5.0	4.75 *	-5.0
2.5	2.30 *	-8.0
1.0	0.90 *	-10.0

*Mean of three determinations.

TABLE 2

Determination of Indium in High Purity Gallium

In added μg	$i_d \cdot \mu\text{a} \times 10^{-2}$	In found μg	Error (relative), %
0,2	2,3	0,18	-10
0,4	4,8	0,39	-3
0,4	4,4	0,36	-10
0,6	6,3	0,51	-15
1,0	11,4	0,91	-9

The residue in the beaker is dissolved in 2-3 ml of concentrated hydrochloric acid, water is added to bring the volume up to 10 ml, 2 g of sulfosalicylic acid is added, * and the pH of the solution adjusted to 4.8-5.2.

The solution is transferred to a 50-100 ml separating funnel and the indium extracted twice with 3-5 ml of a 0.05% solution of dithizone in CCl_4 . The CCl_4 layer is removed to another separating funnel, and the collected extracts washed twice with distilled water. 3-5 ml of 2 M HCl is added to decompose the indium dithizonate, the CCl_4 layer is removed and discarded, while the hydrochloric acid solution is evaporated to dryness in a small quartz basin. To the dry residue is added a few drops of concentrated HClO_4 and the solution evaporated to dryness on a hot plate (in order to destroy organic matter). The residue is dissolved in exactly 1 ml of 0.2 M

HCl; the solution is placed in the electrolyzer and is purged with nitrogen (or hydrogen) for 5-10 min, and polarograms taken over the range 0.2 to 0.8 v at a high galvanometer sensitivity (1/2-1/3). The indium content is determined by means of a calibration curve (Fig. 1). The results given in Table 2 indicate the accuracy of the determination of indium in gallium. The relative experimental error for the determination of 0.2-1.0 μg of indium does not exceed 15%.

The solution obtained can also be analyzed by oscillographic polarography. In this case there is no need to remove the oxygen from the solution, and curves such as those shown in Fig. 2 are obtained. A calibration curve is constructed using solutions of an indium salt with a known concentration. The oscillograms of the standard and test solutions are obtained under the same operating parameters of the instrument [11].

The residue is dissolved in 2-3 ml of concentrated HNO_3 , 2-3 drops of bromine is added and the solution evaporated to dryness; after cooling, 10 ml of 5 N HBr is added, and the solution evaporated to dryness. The operation of evaporation with HBr is repeated.

The dry residue is treated three times with 3-4 ml of 5 N HBr and the solutions poured into a 25 ml separating funnel. Ten ml of diisopropyl ether is added and the mixture shaken for 2-3 min. After separating into two phases the aqueous layer is transferred to another 25 ml separating funnel, 10 ml of ether is added and the extraction repeated. The ethereal extracts are combined and washed twice with 5 ml of 5 N HBr. The ethereal solution is placed in a quartz crucible of about 25 ml capacity and is evaporated to dryness on a water bath. The residue is moistened with a few drops of perchloric acid, the crucible is then placed in a muffle and heated to 400-500° for 5-7 min to get a white residue. ** Some more drops of perchloric acid is added and the crucible carefully heated on a hot plate until white fumes of HClO_4 cease to come off. After cooling, the residue is dissolved in

*This amount of acid is sufficient to complex 0.1 g of gallium.

**If the residue is colored, this operation is repeated.

1 ml of 0.2 M HCl, the solution obtained is transferred to the electrolyzer, and the procedure outlined in the first variant then followed.

The residue is dissolved in 5 ml of 6 N hydrochloric acid and the solution transferred to a 20-25 ml separating funnel; the beaker is washed with 2-3 ml of 6 N HCl. Ten ml of diisopropyl ether is added and the mixture shaken for 2-3 min; after separating into two phases, the aqueous layer is transferred to another separating funnel and the operation of extracting gallium with the ether repeated twice again, 5 ml of ether being used each time. The ethereal extracts are discarded while the hydrochloric acid solution containing the indium is evaporated to dryness in a quartz basin, the residue is then twice evaporated to dryness with a few drops of perchloric acid (to remove organic matter). The dry residue is dissolved in 0.5-1.0 ml (exactly) of 0.2 N HCl, and either polarograms or oscillograms taken, as indicated in the first variant.

Note. All the reagents should be purified beforehand. The acids and organic solvents should be distilled 2-3 times in quartz apparatus. Chemically pure grade salts should be recrystallized 2-3 times, and then additionally purified by coprecipitation with cobalt sulfide or by extraction with a solution of dithizone in CCl_4 . The standard solutions of indium salts and others should be stored in quartz flasks.

The authors express their appreciation to I. P. Alimarin for his valuable assistance in conducting this work.

SUMMARY

Conditions have been developed for separating microgram amounts of indium from gallium by coprecipitating the indium with cobalt sulfide, followed by separation of indium from other components. Polarographic and oscillographic methods of determining indium in metallic gallium are suggested, which permit the determination of 10^{-5} - $10^{-6}\%$ of indium with an accuracy of $\pm 15\%$.

LITERATURE CITED

1. S. I. Sinyakova, Doklady Akad. Nauk SSSR 29, 375 (1940); Zhur. Anal. Khim. 1, 241 (1946).
2. M. Bulovová, Chem. listy 48, 655 (1954); Coll. Czechosl. Chem. Comm. 19, 1123 (1954).
3. N. V. Aksel'rud, Ukr. Khim. Zhur. 21, 457 (1955).
4. L. Treindl, Chem. listy 50, 534 (1956).
5. J. Doležal, Chem. listy 50, 54 (1956).
6. Z. S. Mukhina, Zavodskaya Lab. 14, 354 (1948).
7. D. Cozzi and S. Vivarelli, Z. Elektrochem. 57, 408 (1953); Ref. Zhur. Khim. No. 35,695 (1954).
8. Ya. P. Gokhshtein, A. F. Volkova, S. V. Kuz'min, and V. A. Yanchevskii, Zavodskaya Lab. 23, 988 (1957).
9. I. P. Alimarin and E. P. Tsintsevich, Zavodskaya Lab. 22, 1277 (1956).
10. K. E. Kleiner and L. V. Markova, Zhur. Anal. Khim. 8, 279 (1953). *
11. Ya. P. Gokhshtein and Yu. A. Surkov, Zhur. Anal. Khim. 8, 323 (1953); * 9, 319 (1954). *

*Original Russian pagination. See C. B. translation.