Determination of the content of impurity elements in a sample of high purity India by the method of radiochemical neutron activation analysis

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Abstract. The present article is devoted to the development of a method for neutron activation analysis of a microimpurity composition of high-purity indium with the radiochemical separation of indium radionuclides from radionuclides of the determined elements by extraction chromatography in the system tributyl phosphate (TBP) - solutions of hydrobromic acid (HBr).

Neutron activation analysis (NAA) has a special place among the physical methods for determining the trace composition of high-purity substances. Low detection limits, the possibility of simultaneous determination of a large number of impurity elements from one sample, no correction for the control experiment, the possibility of using inactive carriers in separating traces of radionuclides of impurity elements from matrix elements ensured the widespread use of NAA in the analysis of highly pure substances.

The developed technique allows separating matrix radionuclides from radionuclides of impurity elements with high efficiency and determination of 28 impurity elements in high-purity indium with detection limits of 0.7 ppm to 0.05 ppb.

Key words: neutron activation analysis, high purity indium, extraction chromatography, radiochemical separation

1. Introduction.
For a long time, indium has been used to produce low-melting alloys and solders in electronics. Since the 1980s, a significant part of the total indium production has been used to obtain semiconductor compounds of the $\text{A}^{\text{III}}\text{B}^{\text{V}}$ class, such as InAs, InP, InGaP, InGaAs, InSe, InSb, etc. Currently, up to 45% of all indium produced in the world is used for the production of mixed indium-tin oxide $\text{In}_{2-x}\text{Sn}_x\text{O}_3$, which is used in the production of solar panels and LCD-based displays [1–5].

The electrophysical and optical properties of semiconductor materials depend on their impurity composition. Therefore, special requirements are placed on the purity of the materials used to obtain semiconductors. A high level of purity also implies high requirements for the methods of their analysis.

This paper presents the results of studies on the development of a highly sensitive and multielement technique for radiochemical neutron activation analysis of high-purity indium.

2. Experimental technique
Reagents - hydrobromic acid (HBr) of analytical grade, nitric acid (HNO$_3$) of high purity grade, tri n-butyl phosphate (TBP) were used in the work. Before using, TBP was subjected to additional
purification from degradation products by three times washing with 5% Na₂CO₃ solution, followed by five times washing with water. The rest of the reagents were not further purified.

**Equipment** - research nuclear reactor VVR-SM with a capacity of 10 MW, gamma spectrometer with semiconductor detector HPGeGC-1518 and multichannel analyzer DSA-1000. The gamma spectra were processed using the Genie-2000 software package.

Radioactive tracers of the investigated elements were obtained by irradiation of pure metals or their suitable compounds in a nuclear reactor. As multi-element comparison samples, we used filter paper coated with a certain amount of determined elements. The manufacturing technique and the content of elements on the reference samples are given in [6].

The samples were irradiated in a vertical channel of a WWR-SM nuclear reactor (INP AN Ru) with a neutron flux density of 5-7×10¹³ cm⁻² s⁻¹.

**Analysis technique.** 0.2 g of indium was irradiated with neutrons from a WWR-SM nuclear reactor for 20 hours. One day after irradiation, the sample was dissolved in 10 ml of concentrated nitric acid. The solution was evaporated to wet salts and treated several times with 1–2 ml of concentrated hydrobromic acid. The residue was dissolved in 5 ml of 1M HBr, transferred to a chromatographic column with TBP, and eluted with 35 ml of 1M HBr at a rate of 0.5–0.7 ml / min, then 40 ml of 6M HBr at the same rate. The isolated fractions were separately evaporated to 5 ml, poured into vials for measurement, and their radioactivity was measured on a gamma spectrometer. Silver is determined from the second fraction, and all other elements from the first fraction (Figure 1).

![Figure 1. Curves of elution of the separated elements in the TBP-1M HBr system (d = 1 cm, h = 6 cm)](image)

The developed technique makes it possible to determine 28 impurity elements with detection limits 0.7 ppm-0.05 ppb. (Table 1). Chemical yields, established by the put-found method, are 88-96% at S_r≈ 0.15.

| №  | Element | C_{lim}. ppb | №  | Element | C_{lim}. ppb |
|----|---------|-------------|----|---------|-------------|
| 1  | Na      | 0.1         | 15 | Sb      | 0.5         |
| 2  | K       | 30.0        | 16 | Te      | 80.0        |
3. Results and discussion

Irradiation of indium with thermal neutrons with an activation cross section of 56 barn according to the \(^{113}\text{In}(n, \gamma)^{114m\text{In}}\) nuclear reaction with high activity produces the \(^{114m\text{In}}\) radionuclide with a half-life of 50.1 d. impurity elements. To determine impurity elements in indium samples with a mass of 0.2-0.3 g after 10 h of irradiation, it is necessary to separate the radionuclides of micro-components with a purification factor of \(F = 10^8\). Extraction chromatography (EC) was used for efficient separation of radionuclides.

One of the most efficient and selective SEC systems for the separation of indium is D2EHPA - solutions of hydrochloric acid (HCl) with a partition coefficient (\(D_{\text{In}}\)) up to \(2.5 \times 10^4\). At the same time, experiments have shown that, due to the low capacity of D2EHPA for indium, this EC system is unsuitable for separating its macro-quantity, and the well-studied systems TOA-HCl, TOPO-HCl, TBP-HCl are not sufficiently selective.

Scarce data on extraction and extraction chromatography \([7]\) suggest that the use of the TBP-HBr system for separating impurity elements from matrix elements in the case of indium NAA will expand the range of separated and also determined impurity elements respectively. Since the cited work determined the distribution coefficients of some elements only from concentrated HBr solutions, we determined the distribution coefficients of many elements during their extraction with TBP from HBr solutions, with a concentration from 0.1 M to 7 M (Figure 2).

![Figure 2](image-url)
Figure 2. Distribution coefficients of some elements during their extraction with TBP from HBr solutions

It was found that DIn in the entire range of HBr concentrations exceeds 1000, and only Cd, Ag, Zn, Sn, Au, and Hg are appreciably extracted; however, from 6 M HBr, the distribution coefficient of silver decreases to 2-3, and Ag can be separated. At the same time, Fe, Se, Mo, Ga, Te, Cu, Sb, W, Sc, Cr, Mn, Co, Ni, Zr, Hf, as well as all alkaline, alkaline earth and rare earth elements are practically not extracted by TBP from 0.1-1M HBr. The capacity of TBP for indium from 0.1-7 M HBr is 1.1 mmol / ml, which is important for the extraction of the macrocomponent.

To study the mechanism of extraction, the composition of the extracted complex was determined. It was found that, regardless of the acid concentration, indium is extracted in the form of HInBr₄, which explains the same capacity of TBP at different HBr concentrations. Despite an increase in DIn with increasing acidity, a further increase in the HBr concentration is impractical due to the fact that, together with DIn, the distribution coefficients of a number of other elements also increase. To prove this conclusion and select the optimal separation conditions, the profiles of the distribution of indium over the column were investigated at various concentrations of acids (Figure 3) [6].

Figure 3. Profile of the distribution of indium along the length of the chromatographic column in the TBP-HBr system (mIn = 0.2 g)

As can be seen from Figure 3, the TBF-1M HBr system is the most optimal. In this case, DIn is 4000 and In is adsorbed in the first 3 cm of the column, which fully meets the requirement for the factor of purification of impurities from matrix indium, F = 108. the column then 25 ml of 6 M HBr will allow the separation of silver as well (Figure 1).

4. Conclusion

The possibility of performing neutron activation analysis of high-purity indium by radiochemical neutron activation analysis was investigated. It is shown that for the highly sensitive determination of impurity elements in high-purity indium, it is necessary to separate the matrix radionuclides from the radionuclides of the analyzed elements with a purification factor F=1.10⁸.

It was found that the extraction-chromatographic separation in the TBP-HBr system allows separating indium radionuclides from radionuclides of about 30 impurity elements with high efficiency.
Based on the obtained results, a technique for radiochemical neutron activation analysis of high-purity indium and its compounds has been developed, which makes it possible to determine 28 impurity elements with a detection limit of 0.7 ppm – 0.05 ppb.

5. References

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