Radiochemical Neutron-Activation Analysis of High Purity Gallium

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Abstract: *The work is devoted to neutron activation analysis (NAA) of high-purity gallium, with the radiochemical separation of radionuclides of the determined elements from gallium radionuclides using extraction chromatography. To increase the number of elements separated from gallium, we used the effect of suppressing the extraction of trace amounts of elements by a macro amount of tellurium. This made it possible to increase the number of determined elements to determine an additional 11 elements. The developed method of radiochemical NAA (RNAA) of high-purity gallium allows to find out 28 elements with limits of determination from 0.5 ppm to 0.02 ppb.*
Key words: *High-purity substances, gallium, extractive chromatography, neutron activation analysis*

I.   Introduction.
Today, it is hard to imagine modern electronic technology without semiconductor materials. Gallium and its compounds of the $A^{III}B^{V}$ type are widely used as a starting material for the production of various detectors and infrared sensors. A significant part of the total production of gallium is used to obtain semiconductor compounds of class $A^{III}B^{V}$, such as GaAs, GaP, InGaP, InGaAs, GaSe, etc. [1-3]. The optical and electrical properties of these semiconductors depend on the impurity composition of the manufactured material. There are several works in the literature on the analysis of high-purity gallium by ICP-MS, ICP-AES, EAA, NAA, etc. [4-9]. However, these techniques are laborious, time-consuming and do not meet modern requirements either in terms of the number of elements to be determined or in terms of their detection limits.

Therefore, the aim of this work is to develop a procedure for the NAA of gallium of special purity with the radiochemical separation of radionuclides of impurity elements from the matrix using extraction chromatography.

II.   Material And Methods
Reagents and reference materials. In this experiment, we used: tributyl phosphate (TBP) qualification - high purity, nitric and hydrochloric acids - chemically pure, hydrochloric hydrazine - analytical grade, metallic tellurium - high purity, and tetrafluoroethylene powder (Teflon). Used reagents were not subjected to additional purification.

Radioactive tracers of the investigated elements were obtained by irradiation of pure metals or suitable compounds in a nuclear reactor. Multi-element reference samples were prepared by applying an aliquot (10 μL) of solutions of elements on strips of filter paper. Elements for one sample were chosen so as to exclude mutual overlapping of analytical γ-lines. The concentration of the elements was chosen so that the content of the element could provide a low (<5) measurement error and, at the same time, would not overload the measuring path. After drying under an IR lamp, the reference samples were placed in a plastic bag and wrapped in aluminum foil.

The samples were irradiated in the vertical channel of the WWR-SM nuclear reactor (INP AN RUz) with a neutron flux density of 1.10^{14}neutron.cm^{-2}.s^{-1}.

Equipment. Gamma activity was measured using an HPGe detector (detection efficiency 15%, energy resolution 1.7 keV along the 1332.5 keV line of ^{60}Co radionuclide) and a DSA-1000 multichannel analyzer (Canberra, USA). During the measurement of the gamma activity of the samples, the same conditions were observed (the volume of the measured solution in the vials, the distance between the sample and the detector, etc.) to ensure an identical "counting geometry". The spectra were processed using the Genie-2000 software package.

Chromatography. 3 ml of tributyl phosphate was poured dropwise onto 10 g of Teflon powder with constant and thorough stirring. Then the sorbent was converted into the CI-form by treatment with 0.1 M HCl solution. To remove adsorbed air, degassing was carried out by heating in a water bath to boiling under the discharge of a water jet pump. The study of the behavior of matrix and determined elements was carried out in

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glass columns with a glass filter sealed from below. The internal diameter of the columns is 0.7-1 cm, the length is 20-25 cm. The columns were filled with the suspension method [4].

Technique of Analysis. 0.1 g of gallium was sealed in a quartz ampoule with a diameter of 4-5 mm and, in turn, together with reference samples of the determined elements (standards), were sealed in a quartz ampoule with a diameter of 12-15 mm. The sample was irradiated in the vertical channel of the WWR-SM reactor for 10 h. A day after the irradiation, the sample was unpacked, dissolved in 5 ml of a mixture of HCl + HNO$_3$ acids with a ratio of 3: 1, evaporated to a minimum volume, and treated several times to remove traces of the NO$_3^-$ ion. 2-3 ml concentric HCl. The residue was dissolved in 5 ml of 4M HCl and introduced into a chromatographic column pre-saturated with tellurium. Then the elements to be determined were eluted with 45-50 ml of 4M HCl solution at a rate of 0.7-1 ml/min. The eluate was evaporated to 10-15 ml, transferred to a polyethylene vial for measurement, and the gamma activity was measured on a gamma spectrometer. The analysis scheme is shown in Figure no 1.
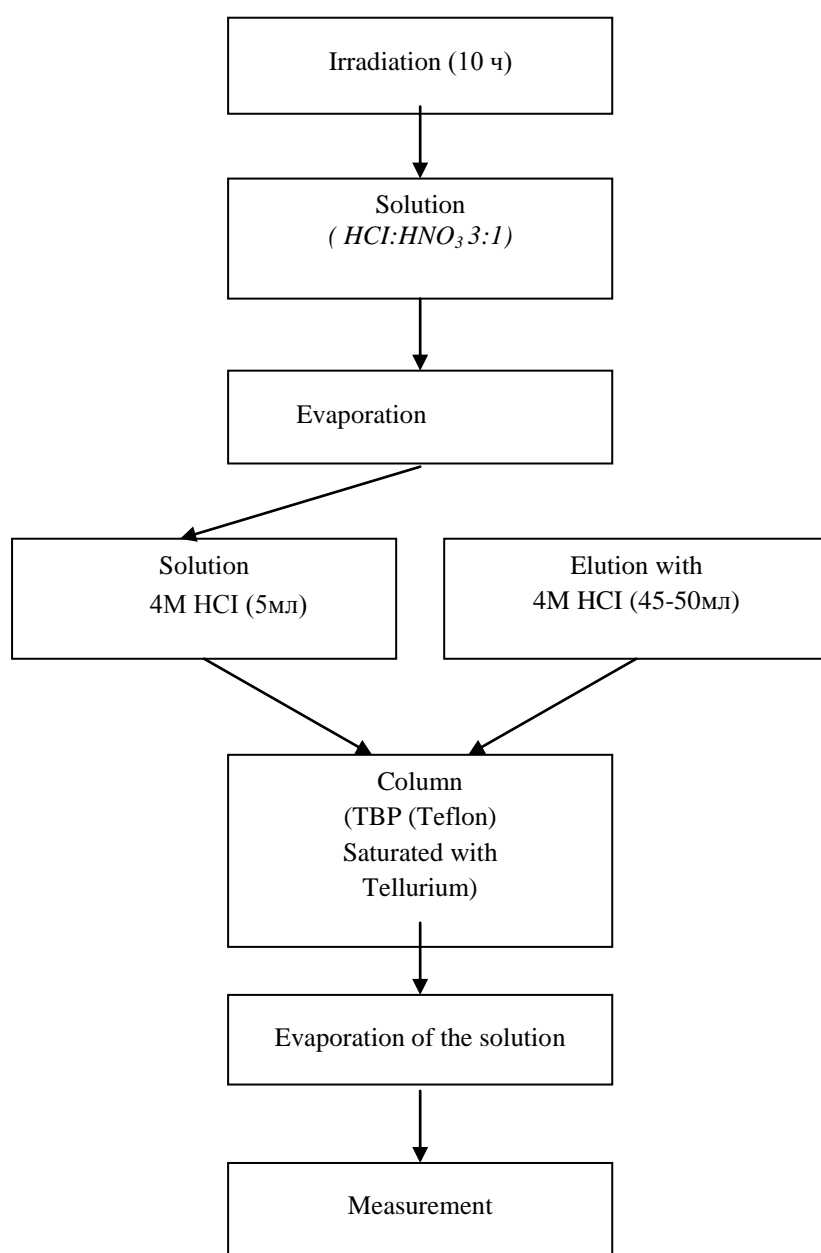

Figure no1: Flow chart of the analysis of gallium of high purity

III.   Results and discussion.

The study of the nuclear-physical characteristics of gallium showed that when 0.1 g of gallium was irradiated in a neutron flux of 5.10^{13} neutron.cm^{-2}.s^{-1} for 5 h, the radioactivity of the sample was more than 10^8 Bq, primarily due to the ^{72}Ga radionuclide with $T_{1/2}$ = 14.1 h and hard gamma radiation with energies from 600 keV to 2.5 MeV. Therefore, the instrumental version of NAA is either not acceptable, or is associated with long cooling of the sample for 10-15 days, which leads to a decrease in the sensitivity of the determination of elements by $T_{1/2}$ radionuclides of which are less than 2-3 days.

Radiochemical neutron activation analysis is possible only if the strongly activating base is sufficiently completely separated from the impurity elements. Therefore, the technique used should provide a highly efficient separation of gallium from impurities. Gallium extraction with alcohols, ethers or esters, organic acids is most often used for these purposes [6-9]. Study of the distribution coefficients (D) of gallium and a large number of other elements in various systems (TOPO-HCl, TBP-HCl, D$_2$EHPA-HCl, HNO$_3$) showed that the highest distribution coefficient and capacity for gallium is achieved in the TBP-HCl system [10-12]. However, during extraction, to ensure the required purification factor (F not less than 10^6), it is necessary to carry out the extraction several times, working with a highly active sample directly by hand. In addition, a number of elements are partially or completely extracted together with the base, which leads to a decrease in the separation selectivity. Therefore, to increase the separation efficiency, the chromatographic version of extraction was used, and to increase the separation selectivity, the suppression of the extraction of micro amounts of impurity elements, a macro amount of tellurium was used.

Measurement of D_{Ga} and D_i of micro amounts of determined elements in the TBP-HCl system under static conditions showed that D_{Ga} strongly depends on the HCl concentration and passes through a maximum that corresponds to the HCl concentration of 4-9 M (Figure no 2).
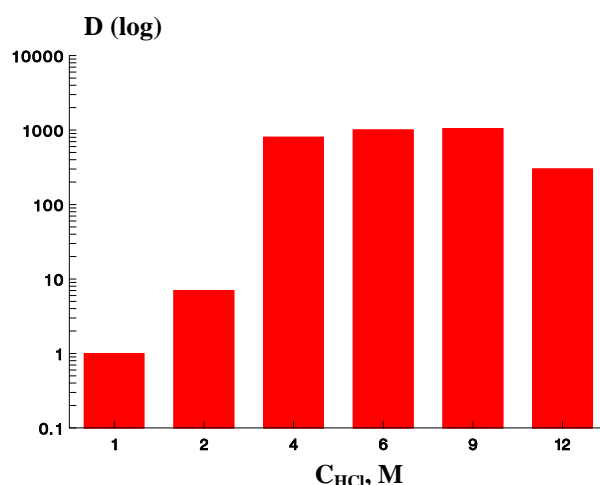

Figure no2: Coefficient of distribution of gallium in the TBP-HCl system.

However, D_i of more than 10 elements is higher than 10 and does not separate from gallium. To separate these elements from gallium, we used the suppression of their extraction by a macro amount of tellurium, the distribution coefficient of which is 800. According to the results of our studies, the largest number of determined elements in this system was achieved from 4 M HCl (Figure no2).

To optimize the size of the chromatographic column and the volume of the eluate, the profile of the distribution of matrix radionuclides along the length of the column and the elution curves of the determined elements in the selected system were measured. It was found that for the effective separation of impurity and matrix radionuclides, a chromatographic column with a diameter of 1 cm and a sorbent layer height of 6 cm is sufficient.

The elution curves of the determined elements showed that even indium, whose distribution coefficient is more than 700 due to the suppression of its extraction with tellurium (D_{Te} = 800), is eluted completely. For complete elution of more than 25 elements, 45-50 ml of eluent is required (Figure no 3).
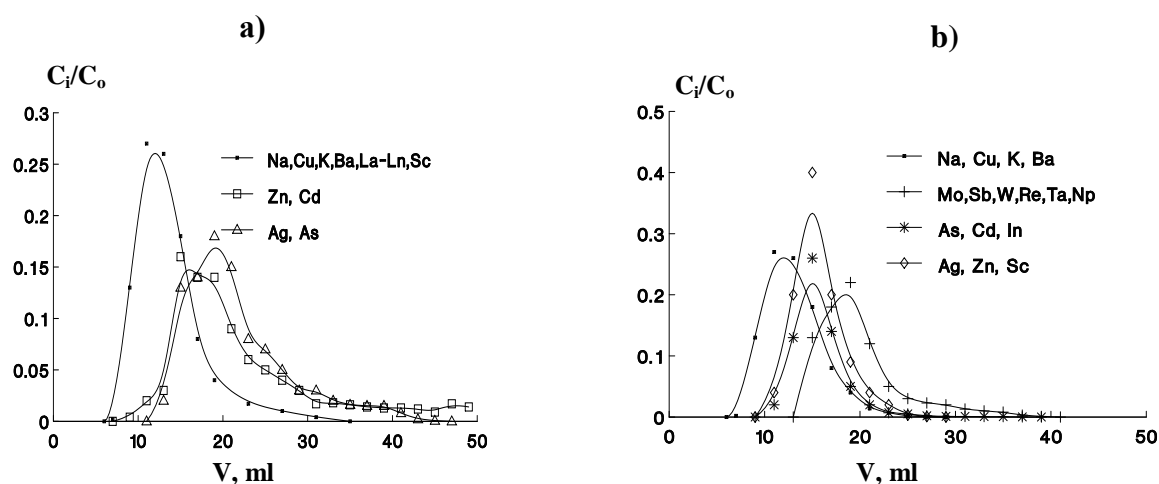
Figure no3. Curves of elution of the determined elements in the TBP - 4M HCl system,
a)   before saturation with tellurium b) after saturation with tellurium.

The chemical yields of the determined radionuclides, established by the "added-found" method, are shown in Table 1.

Table no1: Chemical yields of the determined elements during their extraction-chromatographic separation from gallium, system (TBP-4M HCl (Te))

Elements	Chem.yields, %	Sr	Elements	Chem.yields, %	Sr
Na	>98	0,02	In	95	0,03
K	96	0,03	Cd	97	0,02
Cr	>99	0,03	Sb	61	0,06
Sc	>99	0,03	Ba	>98	0,03
Cu	>98	0,04	La	>99	0,01
Zn	>93	0,02	Eu	>98	0,04
Co (Ni)	>99	0,02	Sm	>99	0,04
Cu	>98	0,02	Hf	96	0,04
As	>98	0,02	Ta	68	0,05
Rb	>99	0,02	W	65	0,05
Sr	>98	0,02	Re	66	0,05
Mo	62	0,13	Np (U)	68	0,05
Ag	94	0,03			

The detection limits for 28 elements with Sr 0.15-0.2 are presented in Table 2.

Table no2: The detection limits of the determined elements in PHAA of high purity gallium.

№	Elements	Ppm (µg/g)	№	Elements	Ppm (µg/g)
1.	Ag	0.02	15.	La	0.0008
2.	As	0.001	16.	Mo	0.03
3.	Ba	0.5	17.	Na	0.006
4.	Cd	0.05	18.	Ni	0.9
5.	Co	0.05	19.	Rb	0.4
6.	Cr	0.03	20.	Sc	0.0004
7.	Cs	0.1	21.	Sm	0.00002
8.	Cu	0.004	22.	Sr	0.2
9.	Eu	0.00004	23.	Ta	0.02
10.	Gd	0.005	24.	Tb	0.007
11.	Hf	0.005	25.	U	0.008
12.	Ho	0.02	26.	W	0.007
13.	In	0.04	27.	Yb	0.005
14.	K	0.3	28.	Zn	0.4

IV.   Conclusions

A technique has been developed for radiochemical neutron activation analysis of high purity gallium using the extraction chromatographic separation of macro and microcomponents in the TBP-4 M HCl system, which allows the determination of 28 elements with a detection limit of $0.09\text{-}0.2 . 10^{-4}$ ppm.

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