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Abstract

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APPLICATION OF ION-EXCHANGE CHROMATOGRAPHY IN ACTIVATION ANALYSIS OF TRACE IMPURITIES IN SILICA*

(Presented by Academician I. V. Tananaev, 5 VI 1961)

One of the most sensitive methods for determining trace impurities in ultrapure materials is radioactivation analysis. Identification and quantitative determination of activated trace impurities are usually carried out either by decomposing the sample being analyzed with the addition of carriers and subsequent separation by ordinary analytical methods, or without decomposition (or with preliminary separation into groups)—by measuring the γ-spectrum of the irradiated sample. However, both of these methods have a number of shortcomings that limit their application. The method using the techniques of analytical chemistry is very laborious because of the necessity of carrying out operations of radiochemical purification and therefore, if isolation of a large number of elements is required, is very lengthy. The method of γ-spectrometry also has its limitations: it cannot be applied to the determination of pure β-emitters; the low resolving power of γ-spectrometers does not allow complex mixtures to be analyzed; because of the presence of Compton distribution, the sensitivity of determination of any trace impurity depends strongly on the presence of other impurities ([1,2]).

In the present work, devoted to the determination of trace impurities in silica by neutron activation, ion-exchange chromatography was used to separate the mixture of activated trace impurities; this method has a number of advantages over ordinary analytical methods. Ion-exchange chromatography makes it possible reliably and rapidly to isolate the elements being determined in radiochemically pure form from a complex mixture of activated impurities. With the proper choice of conditions for absorption and elution of elements on ion-exchange resins, the separation becomes quantitative. Microcolumns can be used for separating microquantities of elements, which considerably accelerates the separation process and reduces the consumption of reagents. In the present work, the quantities of the elements being separated were determined by the amount of carriers added, which are necessary to reduce losses of activated trace impurities during decomposition of the sample and during certain analytical operations.

Fig. 1. Scheme of separation of elements adsorbed on the anion exchanger in the F′ form

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Fig. 2. Scheme of separation of elements eluted together with 17 N HF

Figure 2: Fig. 2. Scheme of separation of elements eluted together with 17 N HF

For irradiation, the silica sample to be analyzed was sealed in a quartz ampoule. A solution of standards of the elements to be determined was placed in a polyethylene ampoule, dried in a vacuum desiccator at 60°, and then the ampoule was sealed. The sample and standards were irradiated simultaneously in an atomic reactor. After irradiation, the sample, in order to remove surface contaminants, was washed with aqua regia while heating. Then a solution of carriers, containing 10 μg of each of the elements to be determined, was added to it, and after this the sample was decomposed with a mixture of hydrofluoric and nitric acids. After decomposition, the solution was evaporated three times with HF to remove

* The work was begun at the initiative of Yu. V. Morachevskii.

excess HNO_3; the last time the solution was evaporated to a volume of one or two drops and then diluted with approximately an equal volume of water. The resulting solution was passed through a polyethylene column 2 mm in diameter, filled with the strongly basic anion exchanger AV-17 (divinylbenzene content 8-10%, resin grain size 30-40 μ, resin-bed height 5 cm) in the F′ form. In this process the elements forming negative fluoride complexes are adsorbed on the column: Sn^IV, Mo^VI, W^VI, As^V, Ta^V, Sb^V, and Au^III.

Fig. 1. Scheme of separation of elements adsorbed on the anion exchanger in the F′ form

According to Ferris ([3]), who studied in detail the adsorption of elements from hydrofluoric acid solutions, these elements are strongly adsorbed in dilute solutions, and as the concentration of HF increases their adsorption decreases. Therefore, in 17 N HF solution it is possible to elute Sn, Mo,

Fig. 2. Scheme of separation of elements eluted together with 17 N HF

W, and As successively, as shown in Fig. 1. However, good separation of these elements can be obtained when long columns are used and equilibrium separation conditions are maintained, which, however, greatly increases the separation time. Therefore these elements are eluted together and then separated on a column 50 × 2 mm in size, filled with AV-17 anion exchanger in the Cl′ form. Solutions of hydrochloric acid and mixed solutions of hydrochloric and hydrofluoric acids of various concentrations were used for elution. The separation

scheme is presented in Fig. 2.

The fluoride complex of tantalum is sorbed much more strongly, and it is difficult to displace it with 17 N HF; therefore, to accelerate elution, the NO'_3 ion was added to HF, since it is sorbed by the resin more strongly than the F' ion and displaces tantalum more rapidly. The fluoride complexes of antimony and gold are adsorbed very strongly. Antimony can be removed with great difficulty by 3 N $HClO_4$, while gold, which is not eluted by any of the eluents listed above, is eluted with thiourea, with which it forms a stable positive complex.

The mixture of elements not adsorbed in the hydrofluoric-acid medium is evaporated several times with hydrochloric acid and placed on a column 90 × 2 mm in size, filled with AV-17 anion exchanger in the Cl' form. On this column the elements forming negative chloride complexes are adsorbed: Cu^II, Co^II, In^III, Ga^III, Zn^II, Cd^II, and Hg^II ([4]). The scheme of separation of these elements is presented in Fig. 3. Elution of the elements was carried out mainly with HCl solutions of various concentrations.

It should be noted that the chloride complex of copper in 8–12 N HCl solutions has a constant and relatively small distribution coefficient. Washing the column with such solutions shifts the copper zone, and this may lead to poorer separation of cobalt and copper. Therefore, immediately after removal of the nonabsorbed elements with a minimal volume of 8 N HCl, cobalt and copper are eluted with 4 N HCl, and after this indium is washed out with 11.6 N HCl.

Fig. 3. Scheme for the separation of elements adsorbed on an anion exchanger in the Cl' form

Since the course of the absorption curves of gallium and iron is approximately the same, they are washed out together. But the sensitivity of the activation determination of iron is very low, especially with the comparatively short irradiation time used in this work; therefore iron does not interfere with the determination of gallium. If necessary, gallium and iron can easily be separated on a cation exchanger [5]. The developed scheme of chromatographic separation was used for determining microimpurities in silica samples. During the separation, fractions containing the corresponding elements were collected. These fractions were then dried, and their activity was measured on an end-window counter. The time required to carry out the complete separation cycle, not including the time for decomposition of the sample, is approximately 4 hours. Separation of standards was carried out by this same scheme and on the same columns.

Table 1

Element	Content, wt. %	Element	Content, wt. %
As	$5.2 \cdot 10^{-7}$	In	Not detected
Au	$4.1 \cdot 10^{-8}$	Mo	$1.8 \cdot 10^{-6}$
Cd	$2.6 \cdot 10^{-6}$	Sb	$2.8 \cdot 10^{-5}$
Co	$2.0 \cdot 10^{-6}$	Sn	$5.9 \cdot 10^{-5}$

Element	Content, wt. %	Element	Content, wt. %
Cu	$3.8 \cdot 10^{-7}$	Fe	$5.4 \cdot 10^{-6}$
Ga	$6.2 \cdot 10^{-7}$	W	$4.8 \cdot 10^{-8}$
Hg	$5.1 \cdot 10^{-8}$	Zn	$5.1 \cdot 10^{-6}$

The radiochemical purity of the isolated elements being determined was checked γ-spectrometrically and by measuring the half-life of the activated isotopes. Experience showed that most elements are isolated in radiochemically pure form.

Table 1 gives, as an example, the results of analysis of one of the silica samples irradiated for 10 hours in a flux of 10^{14} neutrons/cm$^2 \cdot$ sec.

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Note: Figure translations are in progress. See original paper for figures.