FTD-MT-66-142

AD 662383

FOREIGN TECHNOLOGY DIVISION

RADIOACTIVATION ANALYSIS OF SILICON DIOXIDE USING ION-EXCHANGE CHROMATOGRAPHY

By

A. I. Kalinin, R. A. Kuznetsov, V. V. Moiseyev
and V. E. Tsepurnek

Reproduced by the
CLEARINGHOUSE
for Federal Scientific & Technical
Information Springfield Va 22151

16

This document is a machine translation of Russian text which has been processed by the AN/GSQ-16(XW-2) Machine Translator, owned and operated by the United States Air Force. The machine output has been post-edited to correct for major ambiguities of meaning, words missing from the machine's dictionary, and words out of the context of meaning. The sentence word order has been partially rearranged for readability. The content of this translation does not indicate editorial accuracy, nor does it indicate USAF approval or disapproval of the material translated.

FTD-MT-66-142

EDITED MACHINE TRANSLATION

RADIOACTIVATION ANALYSIS OF SILICON DIOXIDE USING ION-EXCHANGE CHROMATOGRAPHY

By: A. I. Kalinin, R. A. Kuznetsov, V. V. Moiseyev and V. E. Tsepurnek

English Pages. 13

SOURCE: AN SSSR. Otdeleniye Obshchey i Tekhnicheskoy Khimii. Radiokhimicheskiye Metody Opredeleniya Mikroelementov (Academy of Sciences of USSR. Methods of Determining Trace Elements) Moscow-Leningrad, 1965, pp. 161-167.

TT7[illegible]

PREPARED BY:

TRANSLATION DIVISION
FOREIGN TECHNOLOGY DIVISION
WP-AFB, OHIO.

Date 24 Apr. 19[illegible]

ITIS INDEX CONTROL FORM

01 Acc Nr TT7500425	**68 Translation Nr** MT6600142	**65 X Ref Acc Nr** AT5013651	**76 Reel/Frame Nr** 0897 0919

97 Header Clas UNCL	**63 Clas** UNCL, 0	**64 Control Markings** 0	**94 Expansion**	**40 Ctry Info** UR

02 Ctry UR	**03 Ref** 0000	**04 Yr** 65	**05 Vol** 000	**06 Iss** 000	**07 B. Pg.** 0161	**45 E. Pg.** 0167	**10 Date** NONE

Transliterated Title RADIOAKTIVATSIONNYY ANALIZ DVOUKISI KREMNIYA S PRIMENENIYEM IONOOBMENNOY KHROMATOGRAFII

09 English Title RADIOACTIVATION ANALYSIS OF SILICON DIOXIDE USING ION-EXCHANGE CHROMATOGRAPHY

43 Source AN SSSR. OTDELENIYE OBSHCHEY I TEKHNICHESKOY KHIMII. RADIOKHIMICHESKIYE METODY OPREDELENIYA MIKROELEMENTOV (RUSSIAN)

42 Author KALININ, A. I.	**98 Document Location**
16 Co-Author KUZNETSOV, R. A.	**47 Subject Codes** 20, 07, 06
16 Co-Author MOISEYEV, V. V.	**39 Topic Tags:** chromatographic analysis, chromatography, ion exchange chromatography, gamma spectroscopy, silica, silicon dioxide, radioactivity effect
16 Co-Author TSEPURNEK, V. E.	
16 Co-Author NONE	

ABSTRACT: The authors propose a method for the rapid chromatographic separation of elements activated by activation analysis into groups; this is followed by a γ-spectrometric analysis of the isolated fractions. The method was applied to the radioactivation determination of trace impurities in silicon dioxide of high purity. Resins AV-17 and KU-2 were used for the separation. The following elements were determined: K, Na, Rb, Cs, Ca, Sr, Ba, Cu, Co, Ga, Zn, In, Cd, Sb, Ta, Mo, Sn, As, P, W, Ni, Cr, Au. The method has several advantages: (1) the separation is made in small volumes (0.1-0.5 ml) and with small chromatographic columns, so that the duration of the analysis is considerably reduced; (2) since the final determination is γ-spectrometric, no thorough radiochemical purification of the separated fractions is required; (3) the method permits the determination of a large number of elements as compared to the γ-spectrometric method involving no decomposition of the sample; the elements in the separated groups are selected in such a way that the interfering influence of some radioisotopes on others is eliminated during the recording of the γ-spectra; (4) the group chromatographic separation permits the separation of elements which, upon irradiation, yield isotopes with pure b-radiation or isotopes having a low determination sensitivity when a γ-spectrometer is used, so that the radioactivity of such isotopes can then be measured with a b-counter. A description of the entire analytical procedure is given. Orig. art. has: 7 figures and 1 table. English Translation: 12 pages.

FTD Form Feb 67 0-90

U. S. BOARD ON GEOGRAPHIC NAMES TRANSLITERATION SYSTEM

Block	Italic	Transliteration	Block	Italic	Transliteration
А а	*А а*	A, a	Р р	*Р р*	R, r
Б б	*Б б*	B, b	С с	*С с*	S, s
В в	*В в*	V, v	Т т	*Т т*	T, t
Г г	*Г г*	G, g	У у	*У у*	U, u
Д д	*Д д*	D, d	Ф ф	*Ф ф*	F, f
Е е	*Е е*	Ye, ye; E, e*	Х х	*Х х*	Kh, kh
Ж ж	*Ж ж*	Zh, zh	Ц ц	*Ц ц*	Ts, ts
З з	*З з*	Z, z	Ч ч	*Ч ч*	Ch, ch
И и	*И и*	I, i	Ш ш	*Ш ш*	Sh, sh
Й й	*Й й*	Y, y	Щ щ	*Щ щ*	Shch, shch
К к	*К к*	K, k	Ъ ъ	*Ъ ъ*	"
Л л	*Л л*	L, l	Ы ы	*Ы ы*	Y, y
М м	*М м*	M, m	Ь ь	*Ь ь*	'
Н н	*Н н*	N, n	Э э	*Э э*	E, e
О о	*О о*	O, o	Ю ю	*Ю ю*	Yu, yu
П п	*П п*	P, p	Я я	*Я я*	Ya, ya

* ye initially, after vowels, and after ъ, ь; e elsewhere. When written as ё in Russian, transliterate as yё or ё. The use of diacritical marks is preferred, but such marks may be omitted when expediency dictates.

RADIOACTIVATION ANALYSIS OF SILICON DIOXIDE USING ION-EXCHANGE CHROMATOGRAPHY

A. I. Kalinin, R. A. Kuznetsov,
V. V. Moiseyev and
V. E. Tsepurnek

1. Group Separation of Microimpurities with Subsequent γ-Spectrometric Determination

Radioactivation analysis is at present one of the most promising methods of determining microimpurities in hyperpure substances. The development of this method tends toward the raising of the accuracy and sensitivity of analysis and towards its simplification.

Success in both directions in many respects depends on the degree of improvement of the basic methods of radioactivation analysis: radiochemical (analysis), based on decomposition of the sample and on the isolation of activated microimpurities in the radiochemically pure form and γ-spectrometric (analysis), which allows one to conduct identification and quantitative determination of the elements by the energy and the intensity of the characteristic γ-radiation of the radioactive isotopes produced.

Until recently there was a tendency to contrast these methods and to conduct analysis either only γ-spectrometrically or only radiochemically, although in reality a reasonable combination of both methods in a number of cases opens great possibilities for the acceleration of analysis.

This was confirmed, for instance, in the work of Makasheva, Maslov and Obukhov [1], where the γ-spectrometric method was used for measurement of the activated impurities separated by the method of precipitation. Inasmuch as measurement of the radioactivity was based on the characteristic γ-radiation, for the majority of the elements a thorough radiochemical purification was no longer necessary, which considerably reduced analysis time.

A good example of the combination of the γ-spectrometric and radiochemical methods is the work of Samsahl [2] (developing a method of chromatographic separation of the activated impurities into 8 groups suitable for γ-spectrometry) for the activation checking of reactor materials and for the analysis of biological samples. According to the method suggested by the author, the solution obtained after decomposition of the sample was passed through a series of chromatographic columns filled with various ion-exchange resins on which sorption of the respective elements occurred. The activity of the columns and of some of the solutions was then measured on a multichannel γ-spectrometer. The time spent on conducting one analysis was one and a half to two hours.

For determination of 13 impurities in aluminum by activation analysis Girardi and Pietra [3] applied group separation of the elements with the help of coprecipitation and ion and isotope exchange. The separated fractions were then analyzed on a γ-spectrometer.

In this work we suggest the method of fast chromatographic separation of the activated elements into groups with the subsequent γ-spectroscopy of the separated fractions. This method was applied for the radioactivation determination of microimpurities in hyperpure silicon dioxide. The method developed possesses a number of advantages. In the first place, separation is made from small volumes (0.1-0.5 ml) and in small chromatographic columns and therefore the time expended on analysis is considerably reduced. Secondly, since the final determination is γ-spectrometric, thorough radiochemical purification of the separated fractions is not required. In the third place the method suggested permits one to determine a larger number of elements as compared to the γ-spectrometric method without decomposition of the sample, due to the fact that the elements in the separated groups are selected so as to exclude the disturbing influence of some radioactive isotopes on others when filming γ-spectra.

By no means the least merit of the suggested scheme for group chromatographic separation is the additional possibility of isolating the elements which during irradiation yield isotopes with pure β-radiation or the isotopes which have a low sensitivity of determination on a γ-spectrometer. The radioactivity of such isotopes can be measured on a β-counter.

Process of analysis (Fig. 1). Preparation of samples for analysis was conducted as usual [4]. After irradiation in a flux of $0.5\text{-}1 \cdot 10^{14}$ neutrons/cm^2·sec. For 24 hours the samples were mordanted by aqua regia, carriers of the elements being determined were added in a quantity of ~10 micrograms each, and decomposition was achieved by a mixture of hydrofluoric and nitric acids (1:1). fter full decomposition of the silicon dioxide the solution was evaporated until dry, the residue was dissolved in a mixture of hydrofluoric and perchloric acids (1:1) and the solution obtained was put in a polyethylene column filled with the resin [AV-17] (AB-17) in the ClO^{-}_{4}-form (the diameter of column was 2 mm; the height of the resin layer was 20 mm). The solution was pressed to the level of the resin and the column was washed with 3.3 $\underline{N}$ $HClO_4$. Under these conditions only the gold was sorbed on the colunm, after which it was washed out by a solution of thiourea. Preliminary isolation of the gold is necessary since during subsequent stages of separation significant losses of it are observed.

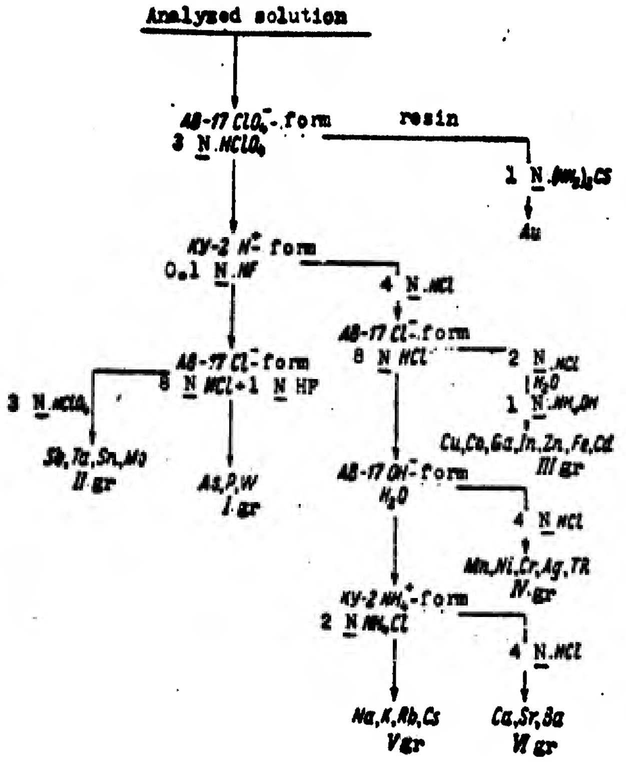

Fig. 1. Diagram of group chromatographic separation of activated microimpurities.

The solution, having passed through the first column, was evaporated until dry and the residue was dissolved in 3 to 4 drops of 1 $\underline{N}$ HNO_3 + 0.5 $\underline{N}$ HF and put in a polyethylene column filled with the cation exchange resin [KU-2x16] (KY-2x16) in the H^{+}-form (the diameter of the column is 2 mm and the height of the resin layer is 60 mm). After pressing of the solution to the level of the resin the column was washed with 0.1 $\underline{N}$ HF. On this column the cations are sorbed and all the elements pass which form the fluoride complexes (Sb, Sn, Ta, W, Mo, As) as do the elements in anion form. The solution was gathered in a teflon cup, sulfuric acid (2 drops) was added to it, and it was boiled until the sulfuric acid vaporized; then 10 to 20 milligrams of sublimed sulfur was added to the solution for reduction of $Sb^{(V)}$ to $Sb^{(III)}$. The reduction of antimony to a trivalent state is necessary in order to avoid the difficulties arising in the further course of the separation of elements of this group and caused by the behavior $Sb^{(V)}$ on the anionite in hydrochloric acid solutions [5]. Reduction was conducted with heating on a plate for 10 minutes. Then to the cooled solution there were added 2 to 3 drops of 8 N HCl + 1 N HF and the solution was placed in a polyethylene column with the resin AV-17 in the Cl^--form (the diameter of the column was 2 mm and the length was 60 mm). The column was washed with a solution of 8 N HCl + 1 N HF, which removes the tungsten, arsenic, and phosphorus. These elements form the first group. The tantalum, antimony, tin, and molybdenum sorbed on the column were washed out with 3 N $HClO_4$. These elements form the second group.

The elements which were sorbed on the cationite were washed out with 4 N HCl, the solution obtained was evaporated until dry, and the residue was dissolved in 8 N HCl and put in a glass column with the anionite AV-17 in the Cl^--form (column was 2 mm in diameter and 100 mm in length). On this column these elements are sorbed which form negatively charged chloride complexes (Co, Cu, Ga, Fe, In, Cd, Zn). These elements may be washed out consecutively by 2 N HCl, H_2O and 1 N NH_4OH, and they form the third group.

The solution of unabsorbed elements was evaporated until dry, and the residue was dissolved in 3 to 4 drops of water and was put in a glass column with the anionite AV-17 in the OH^--form (diameter 2 mm, length 20 mm). On this column those elements are precipitated which form the difficultly soluble hydroxides (Ni, Mn, Cr, Ag, TR); they were washed out with 4 N HCl. These elements compose a fourth group.

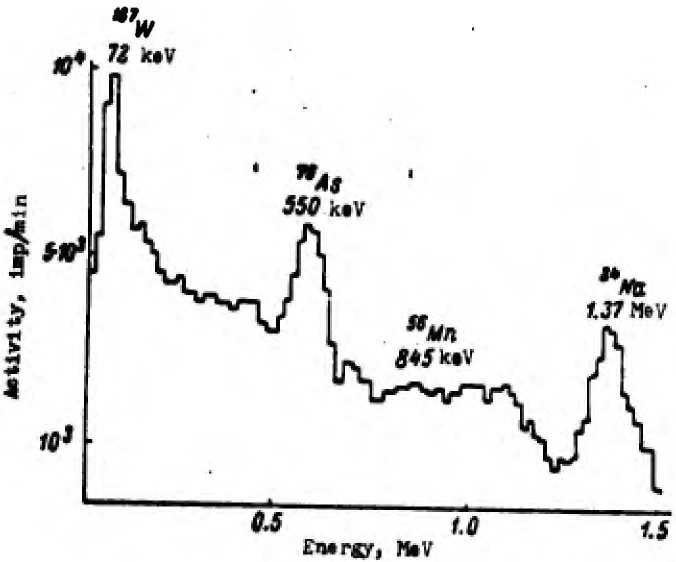

Fig. 2. γ-Spectrum of sample of silica after decomposition and removal of silicon.

The elements not precipitated on the column were washed out with water, and the solution was evaporated to 3 to 4 drops and put in a column with the cationite KU-2x16 in the NH_4^+-form. Then the alkali metals which form the fifth group were washed out with 2 N NH_4Cl. On the column there remain the alkali earth metals which can be washed out with a solution of 0.01 N [EDTA] (ЭДТА) (pH = 10). They form the sixth group.

All operations connected with the decomposition of the samples and with the evaporation of intermediate fractions were conducted in teflon cups; for the introduction of solutions into the columns polyethylene pipettes were used.

Solutions of corresponding groups of the elements were gathered in small glass boxes, evaporated until dry, and measured on a scintillation γ-spectrometer. In the work we used a γ-spectrometer with the crystal NaI(Tl) with dimensions of 40 × 40 mm and a 100-channel amplitude analyzer of [AI-100] (АИ-100) type. The spectrum registered by the analyzer was recorded with help of a special device in the form of a histogram on the tape of a [EPPV-60] (ЭППВ-60) recorder. The time of recording of the spectrum was about 5 minutes. Resolution of the spectrometer along the line ^{137}Cs was equal to 10%. Identification of the elements was made by the energy of the characteristic peaks and the quantitative determination was made by the area of the peak. Inasmuch as the elements in the groups were selected so that their radioactive isotopes did not give off γ-rays which are sufficiently close to the energies which can not be resolved by a γ-spectrometer, and inasmuch as the number of elements in the groups is small, the deciphering of the spectra was considerably facilitated, and the sensitivity, accuracy, and reliability of the analysis was increased.

Figure 2 shows the γ-spectrum of SiO_2 sample after decomposition and the removal of silicon. In the spectrum are distinctly seen only lines E_γ = 1.73 MeV (^{24}Na; the line with E_γ = 2.75 MeV is not shown in the figure), E_γ = 550 keV (^{76}As) and the X-radiation of 60 keV (^{187}W). Against the background of the Compton distribution from the γ-radiation of ^{24}Na the line with energy of 845 keV (^{56}Mn) is hardly noticeable. There are no other clearly defined lines in the spectrum.

This sample was subjected to group separation and the corresponding fractions were then measured on a γ-spectrometer. In Figs. 3-7 the γ-spectra of separated groups are given.

In the γ-spectrum of the fourth group (Fig. 3) the line with E_γ = 845 keV, which belongs to ^{56}Mn, can be clearly distinguished. In the γ-spectrum of the third group (Fig. 4) distinctly appeared lines with E_γ = 510 keV (^{64}Cu) and 440 keV (^{69m}Zn), which in the

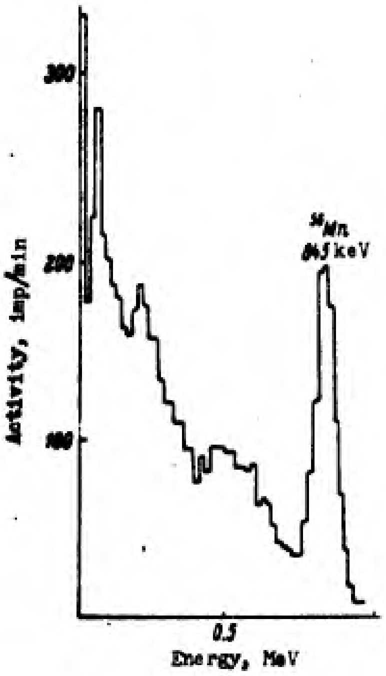

Fig. 3. γ-Spectrum of fourth group.

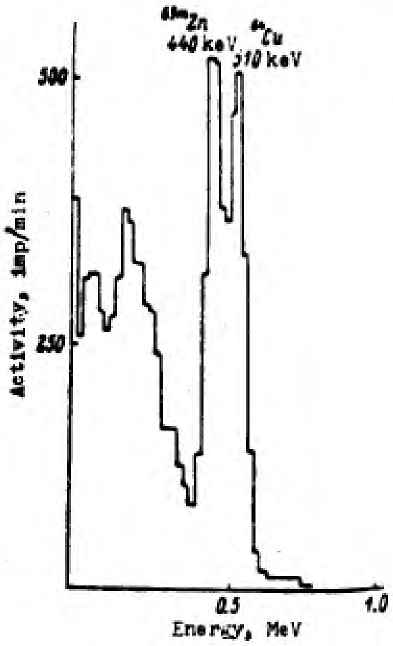

Fig. 4. γ-Spectrum of the third group.

overall spectrum in Fig. 2 are not seen because of interferences on the part of ^{76}As, ^{24}Na, and ^{187}W.

In Fig. 5 is presented the γ-spectrum of the first group, in which the lines with E_γ = 550 keV and 1.2 MeV (^{76}As) and E_γ = 130 and 60 keV (^{187}W) are easily seen.

The spectrum of second group (Fig. 7) is dominated by the line with the energy 560 keV (^{122}Sb), which is not conspicuous in the overall spectrum because it is concealed by the more intense line of ^{76}As (6550 keV).

In the γ-spectrum of the group of alkali metals (Fig. 6) there is only the line with E_γ = 1.37 MeV (^{24}Na). In the fraction of the alkali earth metals (sixth group) no activity was observed.

The quantities of the elements being determined in the sample were calculated by means of a comparison of the activity of separated

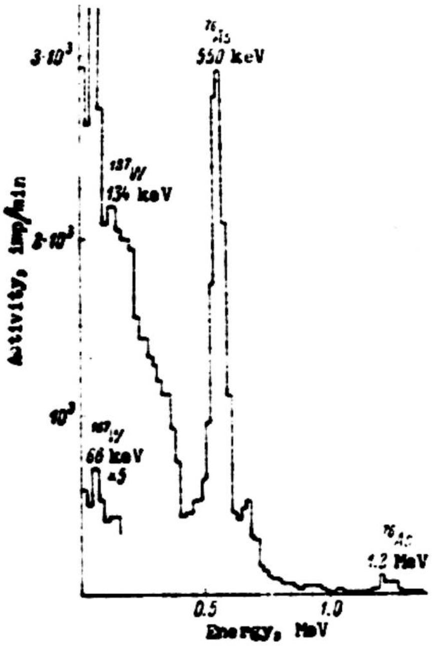

Fig. 5. γ-Spectrum of the first group.

groups with the activities of the standards. The standards were prepared from chemically pure metals or their compounds and were united in 6 groups in accordance with the scheme of analysis. In every group of standards the quantities of the elements were selected with the consideration that after irradiation for elements whose radioactive isotopes yield harder γ-radiation a small, but clearly recorded activity could be obtained, and for elements yielding isotopes with softer γ-radiation somewhat larger quantities were taken in order to obtain a higher level of activity. This measure allows one to avoid the difficulties connected with continuous Compton distribution from hard γ-radiation and to conduct exact measurements of the areas of the peaks of the respective standards.

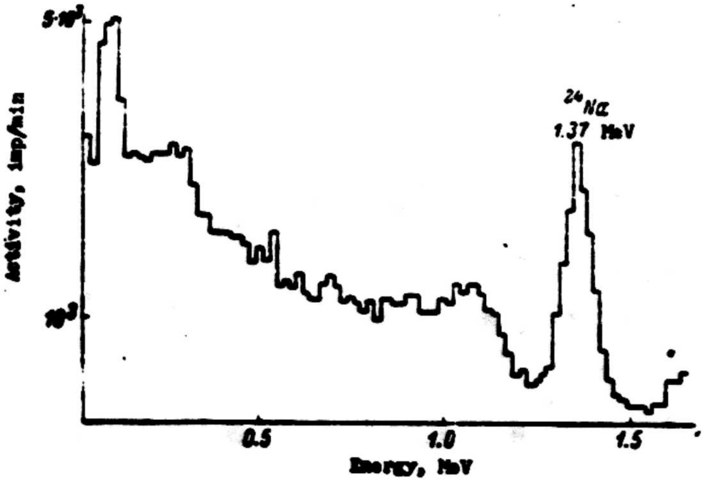

Fig. 6. γ-Spectrum of the fifth group.

Solutions of the standards were drawn off by a gravity method into small polyethylene ampules and were dried in a vacuum exsiccator at 60°. The ampules

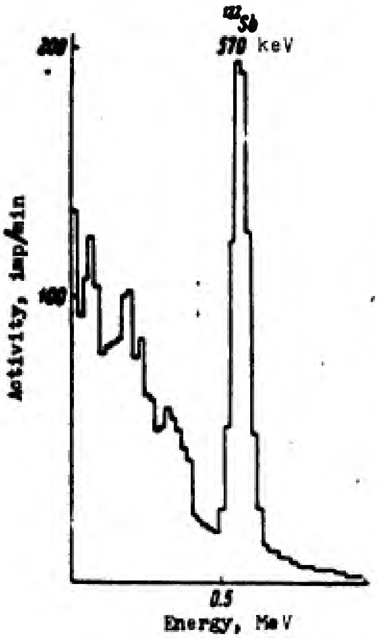

Fig. 7. γ-Spectrum of the second group.

were then soldered and were irradiated along with the samples. After irradiation the contents of the ampules were transferred to teflon cups by solutions of various acids (depending upon the group), to each of which was added 10 μg of the carriers of corresponding groups of the elements, and the solutions were evaporated until dry. Then in certain cases a small radiochemical purification of groups of the standards was conducted, mainly of sodium. After purification the solutions of the standards were evaporated until dry and were measured on a γ-spectrometer under the same geometric conditions as were the fractions which were separated from the samples.

With help of the radioactive tracers it was established that the yield of elements in the respective groups, which were separated by the suggested scheme of analysis, is 95-100%.

It is necessary to note that during group separation with measurement on a γ-spectrometer no determination of elements yielding the pure β-radiators (^{32}P, ^{45}Ca and others) during activation was accomplished. These elements were determined only when using full scheme of the systematic chromatographic analysis of impurities, which was based on the method of group separation suggested here.

In the table are given the results of analysis of a sample of silica which were obtained by the method of group separation with measurement on a γ-spectrometer and by means of complete

Element	Content (in %)		Element	Content (in %)	
	chromatographic separation with measurement on a β-counter	group γ-spectrometric determination		chromatographic separation with measurement on a β-counter	group γ-spectrometric determination
K	$3.3 \cdot 10^{-5}$	$3 \cdot 10^{-5}$	Sb	$4.1 \cdot 10^{-7}$	$4.5 \cdot 10^{-7}$
Na	$1.5 \cdot 10^{-6}$		Ta	$5.8 \cdot 10^{-8}$	
Rb	$2 \cdot 10^{-6}$		Mo	$5.7 \cdot 10^{-7}$	
Cs	$8 \cdot 10^{-6}$		Sn	$4 \cdot 10^{-6}$	
Ca	$<10^{-5}$	—	As	$3.5 \cdot 10^{-5}$	$4.2 \cdot 10^{-6}$
Sr	$<10^{-5}$		P	$2.3 \cdot 10^{-4}$	
Ba	$<10^{-5}$		W	$1.6 \cdot 10^{-7}$	$2 \cdot 10^{-7}$
Cu	$3.8 \cdot 10^{-6}$	$5 \cdot 10^{-6}$	Ni	$<5 \cdot 10^{-5}$	
Co	$<2 \cdot 10^{-7}$		Cr	$<5 \cdot 10^{-6}$	
Ga	$9 \cdot 10^{-7}$		Au	$3.2 \cdot 10^{-8}$	
Zn	$8.8 \cdot 10^{-5}$	$11 \cdot 10^{-5}$			
In	$<1 \cdot 10^{-7}$				
Cd	$8.7 \cdot 10^{-7}$				

chromatographic separation of the activated elements with measurement on a β-counter.

The time spent on separation, without taking into account the time for the decomposition of the sample, is 1.5 to 2 hours.

Conclusions

1. A method is developed for the chromatographic separation of elements into groups suitable for γ-spectrometric determination in reference to the activation analysis of hyperpure silicon dioxide.

2. Preliminary separation of activated elements into groups suitable for γ-spectrometric determination allows one to accelerate the analysis and to raise the sensitivity and accuracy of γ-spectrometric determination.

Literature

1. Makasheva, I. Ye., I. A. Maslov, and A. P. Obukhov. ZhAKh, 15, 3, 329, (1960).

2. Samsahl, K. A. "AE-Repts," No. 54, Actibolaget Atomenergi Stockholm, Sweden (1961).

3. Girardi, F. and R. Pietra. Anal. Chem., 35, 2, 173 (1963).

4. Kalinin, A. I., R. A. Kuznetsov, and V. V. Moiseyev. <u>Radiokhimiya</u> 4, 5, 575 (1962).

5. Nelson, Fr., K. M. Rush, and K. A. Kraus. J. Am. Chem. Soc., 82, 2, 339 (1960).

Submitted
19 April 1963