USE OF SILICA GEL AS A CARRIER OF STANDARDS IN THE NEUTRON ACTIVATION ANALYSIS

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The optimum method of silica gel purification is described that makes possible its use as a carrier of standards in the neutron activation analysis. The achieved purity was checked by the instrumental neutron activation analysis. Silica gel was used as the carrier of Na, Br, Ba, Ca, Fe, Zn, Co, Cr, Sb, and Ni standards. The contribution of the carrier activity to the activity of the standard was less than 0·5%.

The standards for the long-period neutron activation (*i.e.*, longer than 5 h) are usually prepared by the evaporation of the corresponding volume of the standard solution of the element under study in a quartz ampoule that is then sealed. The purity of quartz from which the ampoules are usually made does not permit the direct measurement of standards so that it is necessary to wash out the elements under study into the measuring ampoules. Diluted mineral acids or acidic solutions of carriers with a high concentration of the washed-out element are used as washing-out solutions. Drying and washing out is made at a higher temperature so that there is a danger of losses of volatile elements or their compounds (As, Sb, Hg, Cr, and others). Some elements (Sb) are difficult to wash out from the ampoule.

The shortcomings of this procedure can be overcome by fixation of the standard solution on a solid carrier that could be after the activation quantitatively shaken out of the ampoule and the activity of which could not interfere with the measurement of radionuclides under study. At the same time the problem of the different geometry of the standard and sample at the activation is successfully solved. For this purpose Haldar[1] and Tanner[2] used silicon dioxide of high purity for the determination of trace elements by the neutron activation analysis of biological samples. Known volumes of standard solutions of elements were poured by drops on 20 mg of SiO_2 (Specpure) in quartz ampoules and dried at a higher temperature. After the irradiation the carrier with the standards was shaken out of the ampoule and measured. Due to the high purity of the Specpure or Suprasil[3] preparations of SiO_2 used in these experiments the background activity induced in the carrier is negligible at about 20 h after the irradiation and cannot interfere in the measurement of the standard amounts of elements. (The main radionuclide formed is ^{31}Si with the half-life of 2·62 h, which is a β and γ (0·07%) emitter with the saturation activity of $7{\cdot}96 \,.\, 10^8$ Bq g^{-1} at the thermal neutron flux density 10^{13} s^{-1}. Other radionuclides formed by the reactions $^{28}Si(n,p)^{28}Al$ and $^{30}Si(n,\alpha)^{27}Mg$ have shorter half-lives[4,5]).

This method solves successfully the removal of standards from the quartz ampoule but there still remains a delicate operation of the drying of the carrier with standards prior to irradiation. The use of dry silica gel instead of silicon dioxide seems more advantageous for this purpose. It remains loose even after wetting with a sufficiently small amount of an aqueous solution and can be quantitatively shaken out of the ampoule without preliminary drying before irradiation. The purity of the commonly available silica gel presents the only problem.

In this study various methods of the purification of silica gel used for the preparation of chromatographic columns were tested, particularly the treatment with hydrochloric acid or nitric acid in both static and dynamic regimes and at various temperatures. Both methods were combined with heating up to 800°C. The most effective method of purification was chosen and the use of the purified silica gel as the carrier of standards in the activation analysis was verified.

EXPERIMENTAL

Reagents

Water used for the preparation of diluted solutions and for washing out silica gel was purified by triple distillation (conductivity about 1·6 μS at 25°C). 37% HCl (purity for semiconductors) and 65% HNO_3 (analytical grade) were used in the experiments. In certain cases HCl (purity for semiconductors) was further purified by the isothermal distillation into water for about 21 days so that about 6M-HCl solution was obtained.

The standard solutions of the elements under study, *i.e.*, Na, Br, Ba, Ca, Fe, Zn, Co, Cr, Sb, and Ni were prepared by dissolving the analytical grade reagents in water or diluted HCl.

Silica Gel Treatment

The following procedures were used for the treatment of silica gel G (Merck): Drying (A): Silica gel was dried for 24 hours at 120°C and cooled down in an exsiccator. Heating (B): silica gel was heated up for 10 h to 800°C and cooled down in an exsiccator. Treatment with hydrochloric acid (C): 50 g of silica gel was boiled for 8 h in 500 ml of diluted HCl (1 : 1). After cooling down the acid was poured away and silica gel washed on a glass sinter until a neutral reaction. The washed silica gel was again boiled for 8 h in 500 ml of diluted HCl (1 : 5) and after cooling down the mixture was filtered through a glass sinter and silica gel washed with water until a neutral reaction. Treatment with nitric acid (D): 50 g of silica gel was boiled in 500 ml of concentrated HNO_3 and washed on a glass sinter until a neutral reaction. The dynamic treatment with the hydrochloric acid (E): silica gel was washed at the room temperature on a column (column height 15 cm, diameter 1·2 cm) for 60 h by 500 ml of isothermally distilled HCl. Finally the column was washed with water until neutral reaction.

A series of silica gel samples was prepared for the activation analysis in which various purification procedures were combined as given in Table I together with the sequence of the procedures.

Standards

The standards were prepared by pipetting aliquots of the standard solutions into the quartz ampoules with 0·8—1·2 g of silica gel No 3. The ampoules were sealed and their contents carefully shaken.

Activation and the Treatment of Irradiated Samples

Samples No 1—7 with 0·8—1·2 g of silica gel in sealed quartz ampoules were activated together with the standards in the active zone of the VVR-S reactor of the Nuclear Research Institute in Řež for 20 h at the neutron flux density of 2—6 . 10^{17} m^{-2} s^{-1}. The samples and standards were unpacked 5 days after the activation and the contents of ampoules were transferred into the measuring polyethylene ampoules.

Measurement

The activity of samples was measured using a coaxial Ge(Li) semiconductor detector (FWHM, 2·4 keV/1 332 keV, efficiency 6·4% of the standard NaI(Tl) scintillation crystal) connected with an electronic amplifier Canberra and with the multichannel analyzer Canberra 8180.

The samples were analyzed 6, 16, and 40 days after the irradiation and the following radionuclides were measured: ^{24}Na, ^{76}As, ^{82}Br, ^{140}La, ^{153}Sm, ^{239}Np, ^{47}Sc, ^{95}Zr, ^{160}Tb, ^{131}Ba, ^{233}Pa, ^{51}Cr, ^{141}Ce, ^{181}Hf, ^{59}Fe, ^{124}Sb, ^{85}Sr, ^{58}Co, ^{46}Sc, ^{182}Ta, ^{177}Lu, ^{65}Zn, and ^{60}Co.

RESULTS

The Effect of Purification on the Silica Gel Purity

In the silica gel samples No 1 – 7 the content of all elements, the radionuclides of which can be followed 6 – 40 days after irradiation, was determined. The relative contents (relatively to silica gel No 1) are given in Table II (the results are mean values from 3 analyses). As expected, heating decreased the content of volatile elements and of elements forming volatile compounds (As, Br, Sb, and Na). This effect was most conspicuous in the case of As and Br.

The treatment with hydrochloric acid mostly decreased the content of elements under study. The only exceptions were Br and Ta that are probably concentrated on silica gel from the hydrochloric acid. The higher efficiency of the purification was achieved in the static arrangement but at a higher temperature than in the

TABLE I

Various Combinations of Silica Gel Treatment

Sample	Treatment[a]	Sample	Treatment
1	A — —	5	C D A B
2	A B —	6	E A — —
3	C A B	7	E A B —
4	C D A		

[a] *Cf.* p. 87.

TABLE II

The Effect of Silica Gel Treatment on The Relative Content of Impurities

Element	Relative content in the sample						
	1	2	3	4	5	6	7
As	100	—	—	>2 000	>500	—	—
Br	100	42	32	430	14	190	0·5
Ba	100	100	53	510	480	8·8	10
Ca	100	100	2·3	2·1	2·1	3·1	3·0
Cr	100	96	18	17	17	29	30
Co	100	98	39	38	38	48	46
Fe	100	94	33	31	34	43	39
Hf	100	98	52	39	39	42	42
La	100	98	39	35	39	42	39
Ce	100	100	39	38	39	44	42
Sm	100	95	55	52	55	68	68
Tb	100	100	17	13	21	17	25
Lu	100	100	67	67	67	100	100
Na	100	87	1·4	11	6·9	2·1	2·1
Ni	100	100	<0·5	<0·5	<0·5	<0·5	<0·5
Sb	100	90	51	47	41	86	79
Sc	100	96	43	41	45	51	52
Sr	100	99	<0·5	<0·5	<0·5	<0·5	<0·5
Ta	100	99	140	140	140	160	170
Th	100	97	47	47	46	62	56
U	100	92	26	46	48	68	57
Zr	100	88	40	37	37	49	50

TABLE III

Results of the Silica Gel Sample No 3 Analysis

Element	Concentration ppm[a]	Element	Concentration ppm[a]
Na	11	Zn	<0·1
Br	2·1	Co	0·069
Ca	1 900	Cr	0·90
Ba	8·7	Sb	0·067
Fe	91	Ni	<1

[a] A mean value from 6 analyses.

dynamic arrangement. The exception in the case of Ba can be explained by the lower concentration of this element in the isothermally distilled HCl.

The treatment with nitric acid had a reverse effect in the case of As, Ba, and partly also in the case of Na and U. This procedure would be therefore more suitable for the removal of these elements from the concentrated HNO_3. The subsequent treatment with nitric acid after the treatment with hydrochloric acid does not render positive results with most of the elements under study. Hf and Sb are the only exceptions. The lower Br concentration on silica gel No 5 in comparison with silica gel No 3 cannot be unambiguously ascribed to the effect of nitric acid but more likely to the irregularities in Br loss during the heating.

From the obtained results it is evident that the double boiling with hydrochloric acid, drying and heating up to 800°C (*cf.* silica gel sample No 3) is the most effective method for the silica gel purification. This procedure decreases the content of Na, Ca, Ni, and Sr by about one order of magnitude, the content of Br, Cr, Co, Fe, La, Ce, Tb, Sc, U, and Zr in average by one third, and the content of Ba, Hf, Sm, Lu, Sb, and Th approximately by one half. Silica gel samples purified by all the described procedures are partly contaminated by Ta.

Analysis of the Purified Silica Gel

The contents of Na, Br, Ca, Ba, Fe, Zn, Co, Cr, Sb, and Ni in silica gel were determined by the instrumental neutron activation analysis. The concentrations of elements were calculated from the standard addition of the elements under study to the analyzed material. The mean results from 6 analyses are given in Table III.

The concentrations of impurities are comparable with the values given for the high purity silicon dioxide (Fe: 0·1 – 1·6 ppm, Co: 0·005 – 0·04 ppm, Cr: 0·005 – 2·2 ppm; *cf.* ref.[3]) with the exception of Fe. In order to decrease the contribution of the carrier activity under one per cent of the activity of the standard, the mass of the standard must be at least 100 times higher than the mass of the element under study in about 50 mg of the carrier. In the case of the purified silica gel No 3 this condition is fulfilled for the following masses of standards: Na 55 μg, Br 11 μg, Ca 9500 μg, Ba 44 μg, Fe 460 μg, Zn 0·5 μg, Co 0·35 μg, Cr 4·5 μg, Sb 0·34 μg, Ni 5 μg.

The commonly used amounts of standards of the given elements are minimum twice higher in the case of the measurement 5 – 50 days after the irradiation for 10 – 20 h at a reactor neutron flux density of about 10^{17} m^{-2} s^{-1}.

From the obtained results it is evident that silica gel G (Merck) purified by double boiling with hydrochloric acid, drying, and heating up to 800°C can be used as the carrier for the Na, Ba, Br, Ca, Fe, Zn, Co, Sb, Cr, and Ni standards in the neutron activation analysis. Under the above-mentioned conditions the contribution of the carrier activity to the activity of the standard will not be greater than 0·5%.

The described method of the standard fixation on a purified silica gel was successfully used for the instrumental neutron activation determination of the elements under study in biological materials[6].

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