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SIMULTANEOUS DETERMINATION OF RUBIDIUM, CESIUM, CHROMIUM AND PHOSPHORUS IN ROCKS BY NEUTRON ACTIVATION AND A SIMPLE GROUP SEPARATION

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A neutron activation method is devised for the simultaneous determination of Rb, Cs, Cr and P in silicate rocks. After alkaline fusion and removal of the insoluble hydroxides, the filtrate is assayed for Rb, Cs and Cr by Ge(Li) γ-spectrometry and for P by β-counting. An additional hydroxide scavenging step permits the γ-spectrometric measurements to be performed by means of a sodium iodide detector. Results obtained on some standard rocks are in good agreement with previous neutron activation data obtained by methods based on more complicated radiochemical procedures.

Introduction

The use of simple radiochemical group separations in activation analysis has become increasingly important since the introduction of modern equipment for γ-spectrometry. The simplest possible group separation after alkaline fusion of an irradiated geological sample would be to separate by filtration the elements having insoluble hydroxides from those forming soluble species in strongly alkaline solution. In the soluble fraction of a decomposed irradiated silicate rock, after the decay of the major activities ^{24}Na and ^{42}K, the major contribution to the activity will in most cases be the γ-emitting nuclides ^{51}Cr, ^{86}Rb and ^{134}Cs, besides the pure β-emitter ^{32}P, provided that the removal of insoluble hydroxides has been efficient. GREENLAND[1] used this kind of separation to obtain a sample sufficiently pure for the measurement of ^{134}Cs by $\gamma\gamma$-coincidence spectrometry using two NaI(Tl) detectors. In the present work, Rb, Cs, Cr and P have been determined from the filtrate using either Ge(Li) γ-spectrometry or β-counting. If an additional hydroxide scavenging step is introduced, the filtered solution becomes sufficiently pure for the use of a NaI(Tl) detector in the γ-spectrometric measurements.

Preliminary experiments

The method described in this work was originally intended for determination of rubidium and cesium based on NaI(Tl) γ-spectrometry, and the irradiated samples were treated as follows: Fusion with sodium hydroxide pellets in an elec-

trothermal bunsen, quantitative transfer from the nickel crucible with water, removal of insoluble hydroxides by filtration, addition of iron(III) carrier, and another filtration. The filtrate, besides ^{86}Rb and [134]Cs, was also found to contain ^{51}Cr and ^{32}P in high and reproducible yield. For chromium the yield was improved by introduction of some sodium peroxide in the fusion step.

Initial tests with radioactive tracers showed a yield of 96 ± 2% for chromium and phosphorus, while the rubidium and cesium yields were only about 90% and less reproducible. It appeared that most of this loss took place during the fusion step. After introduction of an exactly fixed fusion time and cooling the crucible in air for 30 sec before removing the cover, the yield of rubidium and cesium also reached a value of about 96%.

Another series of tracer investigations was performed in order to study the efficiency of the double filtration procedure for some radionuclides which were likely to interfere with the determinations. The nuclides studied were [46]Sc, ^{59}Fe, ^{60}Co, [65]Zn, [124]Sb, [233]Pa and [160]Tb, the latter representing the rare-earth group. For all elements except iron the experiments were run with 1 mg carrier added, as well as without carrier addition, and the results are shown in Table 1. For scan-

Table 1

Decontamination factors for some interfering
nuclides after two hydroxide scavenging steps

| Nuclide | Decontamination factor | |
	1st run	2nd run*
[46]Sc	$2 \cdot 10^3$	$>5 \cdot 10^4$
	$3 \cdot 10^3$	
[59]Fe	$3 \cdot 10^4$	$1 \cdot 10^4$
	$4 \cdot 10^4$	$1 \cdot 10^4$
[60]Co	$1 \cdot 10^4$	$>5 \cdot 10^4$
	$4 \cdot 10^4$	
[65]Zn	$6 \cdot 10^2$	$1.3 \cdot 10^2$
	$4 \cdot 10^4$	$0.6 \cdot 10^2$
[124]Sb	$0.6 \cdot 10^2$	$1.9 \cdot 10^2$
	$2.3 \cdot 10^2$	$1.1 \cdot 10^2$
[160]Tb	$9 \cdot 10^4$	$>5 \cdot 10^4$
	$5 \cdot 10^4$	
[233]Pa	$4 \cdot 10^4$	$1 \cdot 10^4$
	$1 \cdot 10^4$	$2 \cdot 10^4$

* 1 mg carrier of Sb, Zn, Co, Sc added.

dium, carrier addition seemed to improve the decontamination. The decontamination factor observed should be satisfactory for work with most silicate rocks where the contents of the elements to be determined are not extremely low.

After Ge(Li) detectors became available, it appeared that the second filtration was unnecessary, and could be omitted.

In an investigation parallel to this work,[2] it was found that the number of nuclides causing significant interference with the determination of phosphorus in silicate rocks by neutron activation and direct β-counting is relatively small, provided a sensible use is made of absorbers. Of the potential interfering nuclides, ^{86}Rb is the only one that must be considered when ^{32}P is measured in an aliquot of the filtrate obtained by the present method.

Experimental

Apparatus

For the β-measurements a Geiger-Mueller counter was used. The window thickness of the tube was 10 mg/cm^2 and the effective diameter was 28 mm. The γ-activity measurements were based on a $3'' \times 3''$ NaI(Tl) detector coupled to a 400-channel analyzer. For some of the measurements, a 2000-channel γ-spectrometer with a 20 cm^3 Ge(Li) detector was used.

Reagents

Reagents of analytical reagent grade were used.

Carrier solutions: Stock solutions were prepared by dissolving in water corresponding amounts of Na_2CrO_4, KH_2PO_4 and the chlorides of the other elements to obtain the following concentrations: Cr, 10 mg/ml; P, 20 mg/ml; Rb, 5 mg/ml; Cs, 0.5 mg/ml; Fe, 20 mg/ml; Sc, 1 mg/ml.

Standard solutions: Stock solutions were prepared by dissolving the carbonates of Rb and Cs, and Cr metal, in dilute nitric acid to give the following concentrations: Cr, 500 μg/ml; Rb, 500 μg/ml; Cs, 40 μg/ml.

Irradiation

Finely-crushed rock samples of about 100 mg were accurately weighed and wrapped in aluminium foil. Standards of rubidium, cesium and chromium were prepared by evaporating 100 μl of the standard solutions on separate 3×3 cm sheets of aluminium foil. For a phosphorus standard, about 50 mg of KH_2PO_4 was dried for 20 min at 110 °C before weighing and wrapping in aluminium foil. Samples and 3 standards of each element were irradiated for 5 days in the JEEP-II reactor at a neutron flux of about $1 \cdot 10^{13}$ n $\cdot$ cm$^{-2} \cdot$ sec^{-1}, and stored for one week before starting the analysis. Possible contribution of rubidium, cesium and chromium from the aluminium foil was checked by irradiating 'blanks'.

Radiochemical procedure

Samples: 1.0 ml portions of Rb, Cs, P, Cr, Fe and Sc carrier solutions were pipetted into a nickel crucible and evaporated to dryness under a heating lamp. The aluminium foil was unwrapped and the sample poured quantitatively into

the crucible, whereafter fusion with 2 g of NaOH pellets and 0.5 g of Na_2O_2 was carried out with an electrothermal bunsen for exactly 5 min. Before removing the cover, the crucible was allowed to cool at room temperature for 30 sec. The contents were then released with water and transferred quantitatively to a 250-ml beaker. The solution was filtered through a blue ribbon filter paper in a funnel, the precipitate was washed with a few ml of water, and the combined solutions were transferred to a 100-ml volumetric flask and diluted to the mark. (If exceeding 100 ml, the volume was reduced by evaporation.) The sample was now ready for measurements on the Ge(Li) detector.

If a NaI(Tl) detector was to be used, 1 ml of iron carrier solution was added to the filtrate and mixed thoroughly with a glass rod. After 1 hr, filtration and transferring to a 100 ml-flask was carried out as described above.

For the β-activity measurements, 1.00 ml of the solution was withdrawn from the volumetric flask and evaporated to dryness in a small iron cup (diameter 20 mm) under the heating lamp. The iron cup was fixed to a cardboard sample holder and covered with Scotch Tape.

Standards: The standards were transferred to 25-ml volumetric flasks (for phosphorus, the aluminium foil was unwrapped), dissolved in dilute hydrochloric acid and diluted to the mark with water. From each solution 1.00 ml was withdrawn and transferred to a nickel crucible containing the same carrier solutions as described for the samples. Enough NaOH to make the mixture alkaline was added, and evaporation to dryness was performed under a heating lamp. Then 2 g of NaOH pellets and 0.5 g of Na_2O_2 were added, and further treatment was carried out as described above for the samples. For each rock series, three standards were run in this manner.

Activity measurements

The γ-spectrometric measurements for both detectors were based on the 320 keV, 795 keV and 1077 keV lines of ^{51}Cr, ^{134}Cs and ^{86}Rb, respectively. Peak areas were calculated according to the method of COVELL.[3] The β-counting was performed through two different aluminium absorbers of 210 mg/cm^2 and 650 mg/cm^2, respectively, the first one in order to eliminate possible contribution from low-energy β-emitters such as ^{35}S, the second one to correct for γ-rays recorded by the detector. The difference between the two count-rates was made the basis for the calculation of the phosphorus content. A correction factor for the ^{86}Rb contribution was established by counting samples prepared from the rubidium and phosphorus standard solutions. Correction for rubidium was then made according to the rubidium content determined for each sample from the γ-counting.

Results and discussion

The method was tested on a series of U. S. Geological Survey standard rocks, and the results are listed in Table 2. Five different series were run, of which three were based on measurements with the sodium iodide detector, while the Ge(Li) detector was used for the remaining two series. For rubidium and cesium there appeared to be no significant difference between the results obtained by either of the two modifications of the method. For chromium, the measurements with the NaI(Tl) detector appeared to give low results for samples with low chromium content, probably due to interference from the large bremsstrahlung 'ridge' in the γ-spectrum. In the Ge(Li) detector measurements, this effect was not important.

In Table 3, the results from the present work are compared with previous neutron activation data. The results are discussed separately for each element below.

Rubidium, cesium

Early neutron activation analyses for these elements had to be based on a fairly complicated radiochemical procedure.[4] More recently, a method[5] making use of Ge(Li) detectors was published, involving a separation sequence based on two iron hydroxide scavengings and a final precipitation of the tetraphenylborates. GORDON et al.[7] demonstrated that a purely instrumental determination using a Ge(Li) detector was possible for rubidium at concentrations exceeding 50 – 100 ppm and also for Cs at the 1 ppm level. Activation with epithermal neutrons[8,9] was shown to enhance the sensitivity by a factor of about 10 for both elements.

The present method should be favourable by involving less work than previous radiochemical methods for these two elements, and being more sensitive especially for rubidium than the instrumental methods.

The results from this work are in good agreement with those from the epithermal activation work[8] except for GSP-1, where the present values are about 8 % higher. Compared with the values of TOMURA et al.,[5] the present Cs values are in reasonable agreement, while the rubidium values differ by about 8 %. The rubidium values of GANGADHARAM and REDDY[6] lie between the two sets of data.

Chromium

The data obtained in this work are in good agreement with previous data from the author's laboratory.[10,11] The previous data for the standard rocks low in chromium were obtained by a radiochemical neutron activation method,[10] specifically designed for chromium. The present method, being considerably simpler, seems to give equally good results when a Ge(Li) detector is used, except perhaps for rocks with very low chromium contents. Determination of chromium by purely instrumental activation analysis[7] is difficult for concentrations at the 10 ppm level, mainly because of spectral interference from ^{233}Pa.

Table 2

Concentrations of rubidium, cesium, chromium and phosphorus

Rock	Rb, ppm					
	NaI(Tl)			Ge(Li)		Mean value
	I	II	III	IV	V	
Andesite AGV-1	71 71	67 68	68 60	63 63	61 64	66
Basalt BCR-1	50 51	50 46	52 49	44 46	50 52	49
Granite G-2	173 176	171 175	177 166	167 167	166 164	170
Granodiorite GSP-1	249 254	250 258	256 256	244 246	245 251	251
Diabase W-1	21.8 22.2	22.2 22.4	21.4 22.4	23.4 21.5	19.6 20.5	21.8
Dunite DTS-1						<0.2
Peridotite PCC-1						<0.2

* Not included in the calculation of the mean value.
** Corrected for interference from the $^{32}S(n, p)^{32}P$ reaction.

Phosphorus

The data from this work are in reasonable agreement with recent data by the author[2] obtained using a specific radiochemical procedure,[13] as well as with other neutron activation data, including samples with phosphorus contents of the order of 10 ppm.[12,13]

In routine work where somewhat less accurate results may be adequate, the chemical treatment of standards described in this paper may be omitted, and the chemical yield for all four elements may be taken as 96%. The method may also be used more specifically for the determination of phosphorus by adding sodium tetraphenylborate to the mixture after decomposition, thus removing rubidium and cesium along with the elements carried by the hydroxide precipitate. In this fashion, the method should be especially well suited for the determination of phosphorus in samples with low contents of this element.

in some U.S.G.S. standard rocks, determined by the present method

Cs, ppm						Cr, ppm			P₂O₅, %	
NaI(Tl)			Ge(Li)		Mean value	NaI(Tl)	Ge(Li)	Mean value	β-counting	Mean value
I	II	III	IV	V		I	V		I	
1.24	1.36	1.17	1.21	1.23	1.25	8.5*	8.9	9.3	0.473	0.470
1.26	1.33	1.20	1.22	1.25		8.1*	9.6		0.466	
0.98	1.01	0.93	0.81	0.97	0.95	11.3*	13.6	13.4	0.376	0.377
1.02	0.97	0.90	0.99	0.93		10.7*	13.2		0.378	
1.28	1.39	1.37	1.23	1.36	1.33	6.6*	7.8	7.8	0.141	0.140
1.32	1.48	1.26	1.28	1.28		7.0*	7.7		0.139	
0.95	1.26*	1.04	0.96	0.94	1.00	9.7*	11.2	10.9	0.269	0.280
0.94	1.32*	1.04	1.14	0.94		10.0*	10.6		0.291	
1.03	0.98	0.99	0.94	0.93	0.99	114	114	117	0.129	0.130
1.02	1.03	0.96	1.04	0.97		117	123		0.130	
					<0.03	4280	4040	4100	0.0025	0.0022
						4120	3960		0.0019	
					<0.03	2720	2580	2670	0.0016	0.0019**
						2630	2750		0.0027	

Conclusion

Some essential features of the present method may be summarized as follows:

1. The method appears to give good data for rubidium and caesium in silicate rocks. It is simpler than previous radiochemical methods and more sensitive than purely instrumental analysis.

2. The method should be very useful for the determination of low concentrations of chromium in rocks, when used in connection with a Ge(Li) detector.

3. Results for phosphorus may be obtained along with data for the other elements without much additional work. The method may be especially useful for rocks with low phosphorus contents.

4. The method seems well suited to serve as the first group of a multi-element analytical scheme for silicate rocks based on neutron activation.

Table 3

Comparison of present mean values with literature data obtained by neutron activation

Rock	Rb, ppm		Cs, ppm		Cr, ppm		P$_2$O$_5$, %		
	Present work	Literature data	Present work	Literature data	Present work	Literature data	Present work	Radio-chemical values[2]	Literature data
AGV-1	66	71,[5] 68,[6] 65[8]	1.25	1.22,[5] 1.10,[6] 1.27[8]	9.3	9.6[10]	0.470	0.481	0.50[12]
BCR-1	49	53,[5] 50,[6] 46[8]	0.95	1.08,[5] 0.96,[6] 0.99[8]	13.4	13.3[10]	0.377	0.347	0.34[12]
G-2	170	185,[5] 178,[6] 161[8]	1.33	1.27,[5] 1.15,[6] 1.33[8]	7.8	7.5[10]	0.140	0.133	0.13[12]
GSP-1	251	272,[5] 268,[6] 227[8]	1.00	1.07,[5] 0.95,[6] 0.92[8]	10.9	11.4[10]	0.280	0.273	0.25[12]
W-1	21.8	22,[5] 21.4,[6] 22.2[8]	0.99	1.06,[5] 0.9,[6] 0.95[8]	117	114[10]	0.130	0.130	0.12[12]
DTS-1	<0.2	<1,[5] 0.4[6]	<0.03	0.02,[5] 0.03,[6] 0.008[14]	4 100	4 190[11]	0.0022	—	0.0017[12] 0.0019[13]
PCC-1	<0.2	<1,[5] 0.2[6]	<0.03	0.03,[5] 0.04[6]	2 670	2 770[11]	0.0019	—	0.0016[12] 0.0016[13]

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