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A Rapid Neutron-activation Method for the Simultaneous Determination of Arsenic and Antimony in Rocks

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A simple, rapid, radiochemical neutron-activation method for the determination of arsenic and antimony in rocks is described. After fusion with alkali and separation of the insoluble hydroxides, arsenic and antimony are determined in the filtrate and in the hydroxide fraction, respectively, by a single precipitation of the sulphides after acidifying each fraction with hydrochloric acid. Chemical yields are determined by re-activation. The precision of the method is high for both elements, as demonstrated by the analysis of some standard rocks, and the sensitivity is adequate for most geochemical studies.

NEUTRON-ACTIVATION analysis appears at present to be the most useful technique for the determination of arsenic and antimony in silicate rocks.¹ Several investigators²⁻⁶ have described radiochemical separation schemes for the simultaneous determination of a number of elements, including arsenic and antimony, by neutron activation. Methods based on two or more separation techniques, such as distillation, precipitation, solvent extraction or ion exchange, were used for the isolation of the two elements from complex mixtures as well as for their mutual separation.

After the advent of high-resolution solid-state detectors, the use of purely instrumental activation analysis has also been attempted for the determination of these elements. Gordon *et al.*⁷ demonstrated that abundances of antimony higher than about 1 p.p.m. could be determined in standard silicate rocks by using the 1691-keV γ -ray of antimony-124. Brunfelt and Steinnes⁸ showed that activation with epithermal neutrons facilitated the determination of antimony in the same standard rocks down to a concentration of about 0.1 p.p.m. via the 564-keV line of antimony-122 as well as the 602-keV line of antimony-124. Epithermal activation is advantageous also for arsenic,⁹ but the high sodium-24 activity induced in most silicate rocks prohibits the determination of arsenic concentrations below a few parts per million. An additional difficulty is that the 559-keV line of arsenic-76 is difficult to resolve from the 564-keV line of antimony-122, even with the most sensitive detectors available.

The method described in this paper takes advantage of two important chemical properties of arsenic and antimony—after fusion with alkali, arsenic is found quantitatively in the water-soluble fraction of the fusion "cake", while most of the antimony is precipitated with the hydroxides; and both elements can be precipitated as sulphides from solutions in concentrated hydrochloric acid, whereas most other elements are not precipitated under the same conditions.

For these reasons, a very simple method can be used to obtain fractions of sufficient radiochemical purity for the determination of arsenic-76 and antimony-122. After fusion with alkali, the soluble and insoluble fractions are separated. Both fractions are acidified with hydrochloric acid, and arsenic and antimony are precipitated as sulphides in their respective fractions. The samples thus obtained are of sufficient radiochemical purity to be measured with a γ -ray spectrometer based on a sodium iodide detector.

EXPERIMENTAL

APPARATUS—

A 400-channel γ -spectrometer with a well-type, 3×3 -inch, sodium iodide (thallium) crystal was used for the activity measurements.

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REAGENTS—

The reagents used were of analytical-reagent grade.

Arsenic carrier solution—Prepare a stock solution by dissolving arsenic(III) oxide in M ammonia solution to give a solution containing 5 mg ml⁻¹ of arsenic.

Arsenic standard solution—Dilute one volume of the arsenic carrier solution to one hundred volumes with M ammonia solution.

Antimony carrier solution—Prepare a stock solution by dissolving antimony(III) chloride in 3 M hydrochloric acid to give a solution containing 5 mg ml⁻¹ of antimony.

Antimony standard solution—Prepare a stock solution by dissolving antimony metal in a few millilitres of aqua regia and diluting the mixture with a solution of 0.1 M citric acid and M hydrochloric acid to give a concentration of 50 µg ml⁻¹ of antimony.

IRRADIATION—

Finely crushed rock samples, each of about 100 mg, were accurately weighed and wrapped in aluminium foil. Standards of arsenic and antimony were prepared by evaporating 100 µl of the standard solution on separate 3 × 3-cm sheets of aluminium foil. In the case of antimony, the aliquot should be neutralised with ammonia solution before evaporation. The arsenic and antimony contents of the aluminium foil were found to be negligible. Samples and standards were irradiated for 20 hours in the JEEP-II reactor (Kjeller, Norway) at a thermal neutron flux of about 1.5 × 10¹³ neutrons cm⁻² s⁻¹. The irradiated samples were stored for 4 days before starting the analyses so as to allow the short-lived activities to decay.

RADIOCHEMICAL PROCEDURE—

Transfer 1.00 ml of arsenic and antimony carrier solutions with a pipette into a nickel crucible containing enough sodium hydroxide solution to make the resulting mixture alkaline, and carefully evaporate the mixture to dryness under a heating lamp. Unwrap the aluminium foil and pour the rock sample quantitatively into the crucible, add 2 g of sodium hydroxide pellets and 0.5 g of sodium peroxide and fuse the mixture by heating it with an electrothermal heater. Release the fusion "cake" with 10 ml of water and transfer it to a 50-ml centrifuge tube. Centrifuge, decant the clear solution, wash the centrifuged solid with 10 ml of water, and add the washings to the previous clear solution in a beaker. Add water to make a volume of 75 ml, then add 75 ml of concentrated hydrochloric acid. Add about 100 mg of thioacetamide, and heat the mixture until precipitation of sulphide occurs. Filter the precipitate on to a membrane filter and wash it several times with 6 M hydrochloric acid. Dissolve the precipitate in a small volume of aqua regia, transfer the solution to a counting vial and dilute it with water to a volume of about 5 ml.

Dissolve the washed precipitate containing antimony with 10 ml of 3 M hydrochloric acid and centrifuge the solution in order to remove any undissolved matter present. Transfer the solution to a beaker, add about 100 mg of thioacetamide and heat. If precipitation of sulphide does not occur, add a few millilitres of water. Filter the precipitate on to a membrane filter and wash it several times with 2 M hydrochloric acid. Dissolve the precipitate in 5 ml of concentrated hydrochloric acid and transfer the solution to a counting vial. Dissolve the aluminium foils containing the standards in 6 M hydrochloric acid in separate 100-ml calibrated flasks, dilute to the mark with 6 M hydrochloric acid, and transfer 5.00 ml of the solution to counting vials.

ACTIVITY MEASUREMENTS—

The samples and standards were counted inside the well of the scintillation crystal, and the determinations were based on the photopeaks corresponding to the 559-keV γ-ray of arsenic-76 and the 564-keV γ-ray of antimony-122, respectively, the latter containing also a small contribution from the 602-keV γ-ray of antimony-124. Peak areas were calculated according to the method of Covell.¹⁰ The arsenic fraction was counted at the end of the radiochemical separation, while the measurements on the antimony fraction were postponed until 7 days after the irradiation in order to eliminate possible interference from the 511-keV line of copper-64 carried down with the antimony precipitate. The radiochemical purity was checked by re-counting the fractions after 3 days.

DETERMINATION OF CHEMICAL YIELDS—

After the γ -activity measurements had been completed, the chemical yields were determined by re-activation.

Arsenic—The samples were diluted to 100 ml with water. Aliquots of 1.00 ml were sealed in polythene tubes and irradiated for 10 minutes at a thermal neutron flux of about 1.5×10^{13} neutrons $\text{cm}^{-2} \text{s}^{-1}$, together with aliquots of the arsenic carrier solution that were treated in the same way. After a delay of 1 day the activity of the 559-keV γ -ray of arsenic-76 was recorded without the tubes being opened.

Antimony—The samples were treated in the same way as described under *Arsenic*, except that 0.4 M citric acid solution was used for the dilution. The measurements were based on the 564-keV γ -ray of antimony-122.

RESULTS AND DISCUSSION

The present method was applied to a series of U.S. Geological Survey standard rocks, and the results are given in Table I together with previous neutron-activation data for the same rocks. The precision of the method evident from duplicate analyses appears to be satisfactory for both elements even at very low concentrations.

TABLE I

ABUNDANCES OF ARSENIC AND ANTIMONY IN SOME U.S. GEOLOGICAL SURVEY STANDARD ROCKS

Rock	Arsenic, p.p.m.		Antimony, p.p.m.			
			Brunfelt and Steinnes			
	Present work (single values in parentheses)	Literature values	Present work (single values in parentheses)	Epi- thermal neutron activation ⁸	Radio- chemical separation method ^{11,12}	Other literature values
Andesite AGV-1	1.07 (1.09, 1.04)	1.0 ⁸ 0.68 ⁶	4.07 (3.97, 4.16)	4.18	4.35	4.12 ⁶ 4.6 ¹⁵
Basalt BCR-1 ..	0.67 (0.68, 0.66)	1.0 ⁸ 0.58 ⁶	0.63 (0.62, 0.64)	0.52	0.58	0.93 ⁸
Dunite DTS-1 ..	0.040 (0.038, 0.041)	0.03 ⁶	0.47 (0.44, 0.49)	—	0.50	0.44 ⁶
Granite G-2 ..	0.26 (0.28, 0.24)	0.33 ⁶ 0.2 ⁶	0.054 (0.048, 0.060)	<0.07	0.063	0.12 ⁶ 0.040 ¹⁵
Granodiorite GSP-1 ..	0.093 (0.090, 0.095)	0.092 ⁶	3.20 (3.29, 3.11)	3.01	3.09	3.0 ⁶ 3.35 ¹⁵
Periodotite PCC-1 ..	0.057 (0.060, 0.054)	0.05 ⁶	1.40 (1.36, 1.43)	—	1.39	1.56 ⁶ 1.37 ¹⁵
Diabase W-1 ..	2.22 (2.23, 2.20)	1.7 ⁴ 1.43 ⁶ 2.38 ¹³ 2.79 ¹⁴	0.94 (0.86, 1.02)	0.89	0.90	0.98 ⁴ 1.2 ⁶ 1.03 ¹³ 1.20 ¹⁴ 1.12 ¹⁵

The results in the literature for arsenic in diabase W-1 have quite a large scatter. The present value of 2.22 p.p.m. is fairly close to the mean value of the previous data. For the other six standard rocks, the present arsenic values are in agreement with the values obtained in previous work.^{5,6}

Antimony has previously been determined in this laboratory by using non-destructive analysis with epithermal neutrons⁸ as well as by using a radiochemical neutron-activation method based on extraction of antimony(V) chloride with diisopropyl ether as the principal separation step.¹¹ The present values are in good agreement with the results obtained in the previous investigation. The agreement with other results in the literature also appears to be reasonably good.

The chemical yields observed in this work were 91 ± 4 per cent. for arsenic and 50 to 72 per cent. for antimony. These results indicate that the determination of chemical yield for arsenic can be omitted in the routine application of the method. The yield for antimony

can be increased by carrying out the sulphide precipitation with hydrochloric acid of lower concentration, but this would probably result in greater contamination by copper-64 and possibly other radionuclides also.

The present method requires considerably less manual effort than previously published procedures for these elements, and should be attractive for the simultaneous study of both elements as well as for investigations on the individual elements. In spite of its simplicity, the method gives samples that are sufficiently pure to enable counting to be carried out with a γ -ray spectrometer equipped with a sodium iodide detector. No activities interfering with the arsenic determination were inferred from the decay measurements and, for antimony, only copper-64 is likely to interfere. This interference is easily eliminated by counting with a germanium (lithium) detector system, or by waiting for a further 3 days before counting the antimony fraction as indicated above.

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