

sulfur atom in a S_xO_y containing hydrocarbon has only a minor effect on the RMR.

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Determination of Silver in Rocks by Neutron Activation Analysis

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Silver is a major industrial metal in which a major world-wide imbalance of more than 100 million ounces per year exists between production and consumption (1). This is because silver is comparatively rare in the Earth's crust, being the 67th element in order of natural abundance. The crustal abundance is estimated as 0.07 ppm (2).

Because of the low abundance levels of silver in rocks or minerals, simple and rapid methods of analysis are required for its determination. Neutron activation analysis (NAA), because of its inherent sensitivity, is one of the preferred methods for the determination of silver. Purely instrumental NAA is not feasible for determining silver in common rocks because the presence of high activity of major and other minor-trace elements will swamp the small amounts of silver activity produced after irradiation. Hence, radiochemical separation has to be employed. There are several methods published for the determination of silver, only a few of which allow one-step separation of silver (3). Most others depend on tedious and elaborate radiochemical procedures involving solvent extraction, ion-exchange, and precipitation, usually combined together (4-7).

Recently, we had proposed a method for the determination of gold and five platinum metals in geological materials using NAA (8). The key aspect of the method was the use of an ion-exchange resin which was specific for noble metals. The details of this resin-Sraffion NMRR are described in that paper (8). In continued work with this resin, we found that silver(I) is also quantitatively adsorbed on this resin. Since then Muzzarelli and Rocchetti (9) have also studied this resin with 14 transition metal ions and found that, in addition, only Cr(VI), Mo(VI), Sb(tartrate), and Hg(II) approached quantitative adsorption. In this communication, we present our use of this resin for the determination of silver in rocks after neutron irradiation.

EXPERIMENTAL

Reagents. Samples. The rock samples analyzed included the USGS standards andesite AGV-1 and granodiorite GSP-1, South African platinum ore standard PTO-1, and Canadian standard reference materials Syenite rock Sy-1 and sulfide ore SU-1. These were all dried for 24 hours at 90 °C before weighing out for irradiation. For tracer work ^{108}Ag (1.38×10^2 years half-life) obtained from Oak Ridge National Laboratory, Oak Ridge, Tenn., was used after suitable dilution.

Standards. Irradiation standards were prepared by dissolving 5-9s pure silver metal in HNO_3 and diluting to the desired strength. Aliquots were weighed out on about 50 mg of "specpure"

SiO_2 in high purity quartz vials and dried under a heat lamp, after which they were sealed. The standards usually contained about 5 μg of silver. The silver carrier solution was prepared from AR grade AgNO_3 and contained 1 mg Ag/ml.

Ion-Exchange Resin. Sraffion-NMRR resin was obtained from the Ayalon Water Conditioning Co., Ltd., Haifa, Israel. The resin was packed in glass columns 10 cm in length and 1.5-cm inner diameter. To remove any chloride on the resin, the column was washed with 100 ml of 0.05N HNO_3 until the effluent did not give a positive test for chloride.

Irradiations. Geological samples (0.5-0.9 g) sealed in high-purity quartz vials along with ($\sim 5 \mu\text{g}$) Ag standards were irradiated either for 100 hours at a thermal neutron flux of $2 \times 10^{13} \text{n cm}^{-2} \text{sec}^{-1}$ in the GTRR reactor of the Georgia Institute of Technology, Atlanta, Ga., or for eight hours at a flux of $3.5 \times 10^{12} \text{n cm}^{-2} \text{sec}^{-1}$ in the central thimble facility of the Cornell TRIGA Mark II reactor. The samples were allowed to "cool" for several days before processing.

Radiochemical Procedure. This is practically identical with the method for other noble metals published by us earlier (8) with the following differences: 1) HNO_3 is used in place of HCl ; 2) 1 mg of Ag(I) carrier is used instead of noble metals carrier solution; 3) Sraffion NMRR ion-exchange column is washed till Cl^- free before using; 4) a 56-cm³ coaxial Ge(Li) detector is used instead of a 30-cm³ detector.

RESULTS AND DISCUSSION

Since it is possible that Ag^+ may be adsorbed on the resin column as AgCl , the resin was eluted with diluted HNO_3 until free of chloride ions. However, it was still found that $^{108}\text{Ag}^+$ was 99.98% adsorbed (six determinations) on the resin column at pH 1.5-2. This is the same pH range at which Hg^{2+} and noble metals are adsorbed on this column. Once adsorbed, Ag^+ cannot be eluted with either 1M KCNS or 3N NH_4OH . In the case of NH_4OH , the column turned brownish black because of silver oxide formation. The 1M KCN could elute up to 15% of the adsorbed Ag. A 5% thiourea solution could essentially quantitatively (90%) elute the adsorbed silver; however, in view of the quantitative adsorption of silver on the resin, elution and subsequent chemical yield determination steps were considered unnecessary. This adsorption and elution behavior is again similar to that observed in the case of noble metals (8).

In addition to the quantitative ion-exchange behavior of silver, we also carried out the entire radiochemical procedure with ^{108}Ag . The yield of ^{108}Ag through the complete procedure was 99.6% (average of triplicate determination). In view of this quantitative adsorption, chemical yield determination was considered unnecessary.

Table I. Determination of Silver in Rocks by RNAA

Sample	Found, ppm ^a	Literature values, ppm
SU-1	3.64 ± 0.85	4 (11), 4 (12)
PTO-1	0.405 ± 0.019	0.42 ± 0.04 (13)
SY-1	0.51 ± 0.07	0.4 (12)
AGV-1	0.21 ± 0.08	0.11 (11); 0.094 (6); 0.08 (7)
GSP-1	0.077 ± 0.046	0.10 (11); 0.084 (6); 0.075 (7)

^a All values are an average of three determinations. The error limits are estimates of one standard deviation on a single analysis.

The only useful isotope of silver for radiochemical neutron activation analysis is ^{110m}Ag with a half-life of 255 days and several gamma rays of which 0.658, 0.885, 0.937, 0.764, and 1.384 MeV are the most prominent (10). In this work, we have used the 0.658-MeV photopeak for abundance calculations. The possible interfering nuclear reactions are ¹¹⁰Cd(n,p)^{110m}Ag and ¹¹³In(n,α)^{110m}Ag. However, in view of (a) low natural abundances of both ¹¹⁰Cd and ¹¹³In, (b) poor cross-sections of both these reactions compared with the ¹⁰⁹Ag(n,γ)^{110m}Ag reaction, (c) high thermal-to-fast neutrons ratio in the irradiation positions used, and (d) equal if not lower abundance levels of Cd and In in rocks compared with Ag, it does not seem likely that these reactions can to any serious degree interfere with the determination of silver.

Self-adsorption and self-shielding problems were kept to a minimum by using standards and samples with roughly the same amount of silver (~5 μg).

Table I gives the results of analysis of three standard rocks and two standard ores distributed by American, Canadian, and South African geological organizations. Each value represents a mean of triplicate determinations. The absolute standard deviation for a single determination is included. Literature values, where available, are included for comparison. The agreement between our results and the cited values is fairly good. The first value given for SU-1, SY-1, AGV-1, and GSP-1 are either recommended, average, or approximate values given by Flanagan (11) and Sine et al. (12). The value given for the ore PTO-1 by Steele et al. (13) includes the techniques of emission spectrography, atomic absorption spectrometry, NAA, and spectrophotometry. The range of all results varies from 0.35 to 2 ppm with a mean value of 0.42 ± 0.04 ppm. The mean of NAA values averages 0.40 ppm which is in excellent agreement with our value of 0.41 ppm.

As mentioned before (8), part of the spread of results for silver and other noble metals may be due to their nonhomogeneous distribution in the rock samples and there may not be a "true" value for these elements because of the sampling problems. Lillie (7) also found the largest errors

in GSP-1 and G-2 in the determination of silver in a suite of rocks and attributes this to the sampling error or nonhomogeneous distribution of silver in these rocks. Brunfelt and Steinnes (6) analyzed SU-1 and SY-1 for silver, but did not report the results because the results indicated possible nonhomogeneous distribution of silver in these rocks; similar uneven distribution of gold in G-1 and W-1 rocks has been demonstrated by Fritze and Robertson (14). However, for AGV-1 and GSP-1, our results are in good agreement with those of Brunfelt and Steinnes (6), and Lillie (7). The precision of our results varies from better than 5% for PTO-1 to 60% for GSP-1. The experimental detection limit was found to be 0.01 ppm with a 100-hour irradiation of 0.5 g of the sample.

In combination with the earlier method (8) for the determination of gold and five platinum metals, silver also could be determined at the same time. However, some difficulty might arise because, in the case of silver, long irradiations are desirable to give enough sensitivity, and the resultant high radioactivity due to major and minor elements will pose a health physics problem in processing for the short-lived platinum metal isotopes immediately after irradiation.

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Factor Analysis of Mass Spectra

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Linear pattern recognizers have been used to predict structural features in mass spectra (1). Just how linear is the relationship between the mass spectra and the presence of various structural features has not been determined. To

study the relationship of functional group presence to linear variation of the data, a data set consisting of 630 mass spectra with elemental composition C₂₋₁₀H₂₋₂₂O₀₋₄N₀₋₂ is decomposed into linearly independent dimensions, whose