sulfur atom in a $\text{S}_2\text{O}_5^-$ 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 be-
because silver is comparatively rare in the Earth's crust,
being the 67th element in order of natural abundance. The
crustal abundance is estimated at 0.07 ppm (2).

Because of the low abundance levels of silver in rocks or
minerals, simple and rapid methods of analysis are re-
quired for its determination. Neutron activation analysis
(NAA), because of its inherent sensitivity, is one of the pre-
ferred methods for the determination of silver. Purely in-
strumental NAA is not feasible for determining silver in
common ore samples 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 ra-
diochemical procedures involving solvent extraction, ion-
exchange, and precipitation, usually combined together
(4–7).

Recently, we had proposed a method for the determina-
tion of gold and five platinum metals in geological ma-
terials 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–Srafion NMRR are de-
scribed in that paper (8). In continued work with this resin,
we found that silver(I) is also quantitatively adsorbed on
this resin. Since then Muzarelli 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 ref-
ence materials Syenite rock Sy-1 and sulfide ore SU-1. These
were all dried for 24 hours at 90 °C before weighing out for irradia-
tion. For tracer work $^{108}\text{Ag}$ (1.38 X $10^2$ 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" $\text{SiO}_2$
in high purity quartz vials and dried under a heat lamp, after
which they were sealed. The standards usually contained about 5
$\mu$g of silver. The silver carrier solution was prepared from AR grade
AgNO$_3$ and contained 1 mg Ag/ml.

Ion-Exchange Resin. Srafion-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
radius at which Hg$_2^{2+}$ and noble metals are adsorbed on this
in the central thimble facility of the Cornell TRIGA Mark II reac-
tor. 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)
Srafion NMRR ion-exchange column is washed till Cl$^- $ free before
using; 4) a 56-cm$^3$ coaxial Ge(Li) detector is used instead of a 30-
cm$^3$ 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 $^{106}\text{Ag}$ was 99.98% absorbed (six determina-
tions) on the resin column at pH 1.5–2. This is the same pH
range which at which Hg$^{2+}$ and noble metals are adsorbed on this
column. Once adsorbed, Ag$^+$ cannot be eluted with either
1M KSCN or 3N NH$_3$OH. In the case of NH$_3$OH, the column
turned brownish black because of silver oxide forma-
tion. 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 con-
sidered 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 proce-
dure with $^{109}\text{Ag}$. The yield of $^{109}\text{Ag}$ through the complete
procedure was 99.6% (average of triplicate determination).
In view of this quantitative adsorption, chemical yield de-
termination was considered unnecessary.
The only useful isotope of silver for radiochemical neutron activation analysis is $^{110m}\text{Ag}$ 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 $^{110}\text{Cd}(n,p)^{110m}\text{Ag}$ and $^{113}\text{In}(n,\alpha)^{110m}\text{Ag}$. However, in view of (a) low natural abundances of both $^{110}\text{Cd}$ and $^{113}\text{In}$, (b) poor cross-sections of both these reactions compared with the $^{109}\text{Ag}(n,\gamma)^{110m}\text{Ag}$ 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 1 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, PTO-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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**LITERATURE CITED**


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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 $C_{2-10}H_{2-22}O_{0-4}N_{0-2}$ is decomposed into linearly independent dimensions, whose...