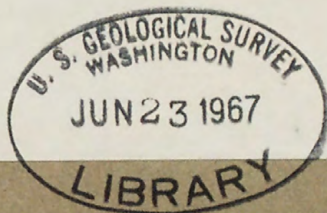


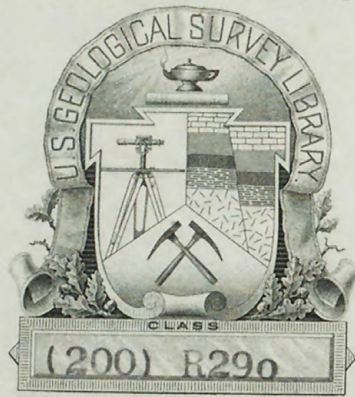
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A field method for the determination of silver
in soils and rocks

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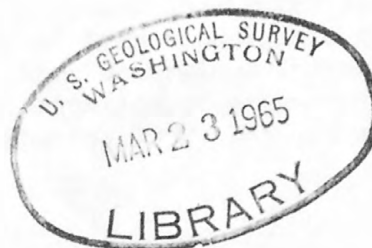
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H. M. Nakagawa and H. W. Lakin, *1923 - Robert Lakin* 1907-

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A field method for the determination of silver in soils and rocks

By H. M. Nakagawa and H. W. Lakin

Denver, Colo.

Abstract

A rapid, sensitive, and specific field method useful in geochemical exploration has been developed for the determination of silver in geologic materials. In this method the sample is digested with nitric acid and the silver is extracted with triisooctyl thiophosphate (TOTP) in benzene and stripped from the organic phase with dilute hydrochloric acid. Silver is then measured indirectly by its catalytic action on the persulfate oxidation of manganous ion to permanganate. The lower limit of sensitivity of the method is 0.01 ppm. Soils, rocks, oxides and sulfide ores have been analyzed, and the results agree favorably with assay and spectrographic analyses. About 80 determinations can be made per man-day.

Introduction

Several available colorimetric methods for the analysis of silver are adequate for many purposes and types of material (Sandell, 1959; Snell, Snell, and Snell, 1959; Kodama, 1963), but the need for a reliable, rapid, and sensitive method satisfactory for exploration purposes has led to the development of this procedure.

The most generally suitable reagents at the present time for the colorimetric determination of small amounts of silver are p-dimethyl-aminobenzilidenerhodanine and dithizone (Sandell, 1959). Neither reagent, however, is selective nor sensitive enough for the desired conditions and in order to isolate silver tedious precipitation or ion-exchange procedures are involved.

In the proposed method the sample is digested with nitric acid and silver is extracted with triisooctyl thiophosphate (TOTP) in benzene (Handley and Dean, 1960) and stripped from the organic phase with dilute hydrochloric acid. Silver is then determined indirectly by its catalytic action on the persulfate oxidation of manganous ion to permanganate (Underwood, Burrill, and Rogers, 1952; Lai and Weiss, 1962).

Although TOTP is not a specific extractant for silver it is highly selective, and according to Handley and Dean only Hg, Ta, and, to a lesser degree, V are extracted from a nitric acid solution containing 35 elements. These three elements are not considered as being interferences, as they do not catalyze the above reaction. Manganese does catalyze the oxidation but is not extracted by the TOTP. Palladium also catalyzes the oxidation, but is only partly stripped from the TOTP by 0.3N HCl. Because as much as 30% Pd merely doubles the effect of 0.1% of Ag, the procedure is nearly specific for Ag.

Procedure

Sample solution:

1. Place 1 g (or one 1-g scoopful) of the finely powdered sample in a 16- by 150-mm culture tube.
2. Add one teflon-covered magnet and 5 ml concentrated HNO_3 .
3. Place the tube, containing sample and HNO_3 , in the aluminum heating block over a magnetic stirrer and allow the acid to boil for 30 minutes. Adjust the heat so that the upper part of the culture tube serves as a condenser, thus conserving the HNO_3 .
4. Add 5 ml of demineralized water and again heat to boil.
5. Allow to cool.

Extraction:

1. Add 5 ml of the TOTP solution to the contents of the culture tube, stopper the tube with a cork, and shake the tube for 1 minute.
2. Allow the phases to separate and, with an automatic pipet, transfer the organic phase to a second 16- by 150-mm culture tube.
3. Add 10 ml 0.3N HCl to the second tube, stopper with a clean cork, and shake the tube for 1 minute.
4. Remove the organic phase with an automatic pipet and discard.

Oxidation of TOTP in 0.3N HCl extract:

1. Transfer 5 ml of the 0.3N HCl extract to an 18- by 150-mm culture tube. If a smaller aliquot is taken make the volume up to 5 ml with 0.3N HCl.
2. Add 1 g scoopful of $K_2S_2O_8$, place in a boiling water bath at 98-100°C and heat for 10 minutes.
3. Remove and cool the solution.

Estimation:

1. To the cool solution add 1 ml H_3PO_4 , 1 ml $MnSO_4$ solution, 5 ml demineralized water, and 5-6 1-g scoopful of $K_2S_2O_8$.
2. Mix thoroughly with glass stirring rod and again place in boiling water bath.
3. After heating for 10 minutes at 98-100°C, remove the sample solution from the boiling water bath and chill rapidly in an ice bath.
4. When cold, crush with a stirring rod the crystals of $K_2S_2O_8$ and K_2SO_4 that crystallized on cooling. Leave in ice bath until the upper inch or so of the permanganate solution is clear.
5. Compare the sample solution with standards prepared at the same time.

Preparation of standards:

Pipet 10 γ Ag into a tube containing 5 ml 1+1 HNO_3 . Add 5 ml TOTP and shake for 1 minute. Allow the phases to separate and transfer the organic layer to a second tube containing 10 ml 0.3N HCl. Shake for 1 minute and discard organic layer. Transfer appropriate aliquots

of the HCl solution, corresponding to 0, .005, .01, .05, .1, .2, .4, and 8 γ Ag, into tubes containing 5 ml 0.3N HCl. Add 1 g $K_2S_2O_8$ to each tube and heat in boiling water bath at 98-100°C for 10 minutes. Cool and add 1 ml H_3PO_4 , 1 ml $MnSO_4$, 5 ml demineralized water and approximately 5-6 g $K_2S_2O_8$. Place in boiling water bath and proceed as with sample. The acid permanganate solution slowly fades, so standards must be made with each group of samples. The samples and standards may be kept in an ice bath for about an hour without any noticeable fading.

Reagents and apparatus

Potassium persulfate, reagent-grade.

Nitric acid, concentrated, reagent-grade.

Nitric acid, 8N: Dilute 1 part concentrated nitric acid with 1 part demineralized water.

Triisooctyl thiophosphate in benzene: Dilute 300 ml TOTP with 700 ml benzene.

Hydrochloric acid, 0.3N: Dilute 25 ml concentrated HCl to 1 liter with demineralized water.

Phosphoric acid, reagent-grade: Dilute 1 to 1 with demineralized water.

Manganous sulfate: Dissolve 0.5 g $MnSO_4 \cdot H_2O$ in 500 ml demineralized water.

Silver standard solution, 0.01 percent in 0.1N nitric acid: Dissolve 0.158g $AgNO_3$ in 1,000 ml of 0.1N nitric acid solution.

Culture tubes, 16- by 150-mm: Calibrate at 5 and 10 ml.

Culture tubes, 18- by 150-mm: Calibrate at 5 ml.

Electric hot plate with magnetic stirrer.

Aluminum block, drilled to accommodate 16-mm culture tubes. Hot plate, magnetic stirrer and block with capacity of 13 tubes are available commercially.

Magnets: teflon-coated bars, 0.5 inch long.

Water bath, aluminum, 7 X 13 X 5 inches deep: The temperature of the water bath must be between 98 and 100°C. Add NaCl as necessary to raise boiling point at higher altitudes.

Test tube rack, to accommodate 18-mm culture tubes: A wire woven rack with handles to fit in water bath with capacity of 48 tubes.

Test tube rack, to accommodate 16-mm culture tubes, capacity 48 tubes.

2 automatic pipets 5 ml.

Pipets measuring 10 ml, calibrated in 0.1 ml.

Pipets, measuring, 1 ml, calibrated in 0.01 ml.

Pipets, micro, 0.005 ml.

4 scoops, 0.2g, 0.5g, and 2 of 1 g capacity.

Experimental

Sample solution:

Solution of silver in geologic materials is usually effected by digestion with boiling nitric acid followed by a sodium carbonate fusion of the insoluble residue (Hillebrand and others, 1953; Almond, Stevens, and Lakin, 1949). Potassium pyrosulfate fusion has also been used as a preliminary attack of the sample (Sandell, 1959). Samples of assayed materials were (1) digested with concentrated nitric acid, (2) fused with $K_2S_2O_7$ and digested with 8N nitric acid, and (3) fused with $K_2S_2O_7$ and digested with 8N sulfuric acid. Treatments (1) and (2) were followed by extraction from 8N nitric acid with 30 percent TOTP in benzene. Treatment (3) was followed by extraction from 8N sulfuric acid with 30 percent TOTP in benzene. Very little difference was observed between the three treatments and extractions. With Ag^{110} as a tracer 95 percent of the silver was extracted from the 8N H_2SO_4 as compared to 99 percent from 8N HNO_3 . The nitric acid digestion and extraction are favored for their simplicity and repeatability.

Extraction of silver from TOTP solutions:

The removal of silver from the organic phase into an aqueous medium is a necessary prelude to subsequent analytical steps. Handley and Dean (1960) stated that 93 percent of the Ag in TOTP solution can be extracted with an equal volume of dilute ammonium hydroxide. Attempts were made to strip the silver from the TOTP with dilute ammonium hydroxide; recovery of silver was inconsistent and incomplete, varying from 40 to 75 percent after 2 extractions. Sodium hydroxide was also tried, but it also yielded inconsistent and poor recoveries. The most effective stripping from the organic phase was accomplished by use of dilute hydrochloric acid. One wash with an equal volume of 0.3N hydrochloric acid removed 97-99 percent of the silver. Hydrochloric acid (0.3N) is the optimum concentration because it has maximum stripping ability without any adverse effects on the catalytic reaction used for estimation. According to Underwood, Burrill, and Rogers (1952), 7 mg of Cl^- gives an error of 1 standard deviation in the determination of $0.10\gamma \text{ Ag}$.

Silver ions tend to be adsorbed on the glass and this adsorption becomes the source of serious error in very dilute solutions. For this reason the analyses must be carried out with dispatch. Silver left in the 0.3N HCl may be partially lost from solution after standing overnight. This adsorption makes it necessary to carefully clean test tubes between analysis with dilute sodium cyanide solution and then several rinses with metal-free water.

Interferences:

Interferences are known for each phase of this procedure, but the method in its entirety is believed to be virtually specific for silver. Palladium is the only element besides silver extracted to an appreciable extent by TOTP, and the only one able to catalyze the oxidation reaction of manganous ion to permanganate. Mercury, tantalum, and, to a lesser degree, vanadium (Handley and Dean, 1960) are also extracted but none of these elements catalyzes the oxidation reaction. Large amounts of manganese prevent the formation of purple permanganate by producing brown manganous dioxide, but manganese is not extracted by TOTP. No interference was observed when the following salts and metals were dissolved with concentrated HNO_3 and subjected to the

proposed method of analysis for silver: 50 mg each of TeO_2 , Au° , KReO_4 , $(\text{NH}_4)_2\text{IrCl}_6$, $(\text{NH}_4)_3\text{RhCl}_6 \cdot \frac{1}{2}\text{H}_2\text{O}$, $(\text{NH}_4)_2[\text{Ru}(\text{H}_2\text{O})\text{Cl}_5]$, $(\text{NH}_4)_2\text{OsCl}_6$, $(\text{NH}_4)_2\text{PtCl}_6$ and Ta° ; 200 mg each of Bi_2O_3 , CoCl_2 , CrCl_3 , TlNO_3 , $\text{K}_2\text{TlO}(\text{C}_2\text{H}_4)_2 \cdot 2\text{H}_2\text{O}$, Nb_2O_5 , MoO_3 , CdCl_2 , SnCl_2 , Na_2WO_4 , $\text{K}(\text{SbO})\text{C}_4\text{H}_4\text{O}_6 \cdot \frac{1}{2}\text{H}_2\text{O}$, V_2O_5 , and HgCl_2 ; 500 mg each of PbCl_2 , NiCl_2 , ZnCl_2 and As_2O_3 ; 2 g each of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, CuSO_4 and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$. The tests indicated that these elements or compounds are tolerated in the quantities likely to be present in most samples. At first copper was thought to be an interference, since 2 g each of CuSO_4 and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ gave respective Ag values of 0.1 γ and 0.2 γ , although no test for copper could be obtained in the 0.3N HCl extract. We concluded that silver contamination in the salts used was responsible for the positive results because the interference was removed by the first extraction with TOTP. The second extraction of the same HNO_3 solution yielded excellent blanks without a trace of enhancement of the oxidation of manganese, indicating no interference from copper.

The chief interferences are Pd^{+2} , Cl^- and organic matter due to TOTP. Palladium becomes objectionable in quantities greater than 32 micrograms by increasing a 0.1 γ standard twofold, but such a concentration in a sample would be extremely rare and is therefore not too serious a consideration. Excess Cl^- leads to low results, but the quantity used in this method is tolerated without any loss of sensitivity. The most serious interference arises from incomplete separation of the organic and aqueous acid phases. Small amounts of TOTP remaining in the HCl extract form a yellow wax when heated with persulfate. The simultaneous formation of wax and purple permanganate leads to low results. This condition is remedied by a preliminary heating of the acid solution with $\text{K}_2\text{S}_2\text{O}_8$ prior to the taking of an aliquot for the catalytic procedure.

Discussion

Sensitivity:

The sensitivity of this method is due to the catalytic procedure. It has long been known that reactions of this type are extremely sensitive and involve primarily a rate measurement. Therefore time and temperature of such reactions and concentration of the reactants must be carefully controlled. For the proposed silver method the critical aspects of the catalytic phase are temperature of reaction and concentration of oxidant. A salt bath is used to keep the temperature at 98°-100°C and an excess of potassium persulfate is maintained to insure the dependency of rate of oxidation of manganous ion to permanganate upon the amount of silver present.

Reproducibility:

The reproducibility in the range 0.01-5 ppm is shown by replicate analyses of 8 samples presented in table 1. The large standard deviations of 63 percent, 46.8 percent and 47.9 percent obtained for 3 samples in table 1 are probably caused by lack of homogeneity of the sample. A relative standard deviation of 20 to 30 percent appears to be a reasonable measure of the precision of the method.

Table 1.--Replicate determinations of silver

| Sample no. | Silver (ppm) | | | | | | | Mean | Relative standard deviation (percent) |
|------------|--------------|-----|-----|-----|-----|-----|-----|------|---------------------------------------|
| | | | | | | | | | |
| 64-2730 | 5 | 5 | 4 | 3 | 3 | 3 | 3 | 3.7 | 25.7 |
| 64-2740 | 5 | 2.5 | 2.5 | 3 | --- | 3 | 4 | 3.3 | 29.5 |
| 114938 | 2 | 3 | 2 | 2.4 | 3.2 | 2 | 3 | 2.5 | 27.1 |
| 114939 | 1 | 1.5 | 1.5 | 1.2 | 1.2 | 1.2 | 1.6 | 1.3 | 16.6 |
| 64-2722 | .75 | .75 | .3 | .4 | .12 | .12 | .6 | .43 | 63.0 |
| 64-2733 | .3 | .12 | .28 | .4 | .14 | --- | --- | .25 | 46.8 |
| 64-2743 | .05 | .05 | .04 | .04 | .02 | .01 | .02 | .03 | 47.9 |
| 114933 | .05 | .02 | .02 | .04 | .02 | .01 | .02 | .03 | 21.5 |

Table 2.--Comparison of silver values (ppm) obtained by
analysis and assay

| Sample no. | Silver content (ppm) | | | | | |
|------------|----------------------|-------------------|-------------------|-------------------|-----------------------------|--------|
| | in 0.1g sample | in 0.2g sample | in 0.5g sample | in 1.0g sample | Average of 4 analyses | Assay* |
| 223188 | 60 | 50 | 60 | 30 | 50 | 50 |
| 91400 | 2 | 3.8 | 6 | 4 | 3.95 | 4.8 |
| 612953 | 5 | 3.5 | 4 | 7.5 | 5 | 7 |

*Converted from oz/ton; fire assay by D. W. Skinner, U.S. Geological
Survey, Denver, Colo.

Reliability:

The reliability of the method is based on analyzing samples having assayed values. Unfortunately samples of known silver contents in the range for which this method is intended are unavailable. Therefore, the accuracy of the method is determined on samples containing up to several parts per million silver as indicated in table 2. There is good agreement between various weights of the same sample. However, the precision of the method increases with the quantity of silver present, as shown in table 2. Another measure of reliability is given (table 3) by comparison with semiquantitative spectrographic results.

Table 3.--Comparison of silver content of diverse minerals obtained
by field and semiquantitative spectrographic methods

| Mineral constituting major component of sample | Silver content (ppm), determined by-- | |
|--|---------------------------------------|---|
| | Proposed field method | Semiquantitative spectrographic method* |
| Arsenopyrite | 30 | 30 |
| Allanite | 2 | 1.5 |
| Cervantite | .5 | 7 |
| Chalcopyrite | 150 | 300 |
| Cerussite | 100 | 300 |
| Descloizite | .7 | 1.5 |
| Galena | 600 | 700 |
| Gold quartz and pyrite | 7.5 | 7 |
| Glauconite | 10 | 7 |
| Hemimorphite | 3.5 | 7 |
| Hydrozincite | 30 | 15 |
| Molybdenite | 10 | 15 |
| Niccolite | 50 | 70 |
| Psilomelane | .5 | 1.5 |
| Pyrrhotite | 3.5 | 7 |
| Pyrite | 4 | 3 |
| Pentlandite | 4 | 3 |
| Smaltite | >1600 | 700 |
| Scheelite | 400 | 700 |
| Thorite | >8 | 1.5 |
| Tetrahedrite | 4000 | 7000 |
| Anglesite | 500 | 1500 |
| Antimony | 200 | 300 |

*Analyses by Pauline J. Dunton, U.S. Geological Survey, Denver, Colo.

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3. Preliminary surficial geologic map of the Danielson quadrangle, Connecticut, by A. D. Randall. 1 map, scale 1:24,000; 6 tables. Connecticut Geological and Natural History Survey, 303 Judd Hall, Wesleyan University, Middletown, Conn.; USGS, Room 1, 270 Dartmouth St., Boston, Mass. Copy from which reproduction can be made at private expense is available in the Boston office.

✓ 4. A field method for the determination of silver in soils and rocks, by H. M. Nakagawa and H. W. Lakin. 13 p., including 3 tables.

* * * * *

Following is the complete title of an open-file report announced on March 3, 1965:

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* * * * *



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