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Selective Microseparation and Estimation of Silver in Alloys and Minerals by Electro-Ring-Colorimetry as a Nondestructive Technique

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NOTE

Selective Microseparation and Estimation of Silver in Alloys and Minerals by Electro-Ring-Colorimetry as a Nondestructive Technique

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Abstract

Efficient analytical separation and an estimation of the microgram quantities of silver present in various alloys and minerals have been made possible by the Weisz ring-oven technique in combination with the nonsophisticated nondestructive technique of electrographic sampling. Silver is fixed selectively with IH-benzotriazole after masking interfering ions with EDTA or tartarate, and then it is estimated using PTC as a chromogenic spray reagent because the chelate of silver ions with 1,2,3-benzotriazole is white.

The new nondestructive technique of electro-ring colorimetry has been advantageously applied to various microanalytical studies by Johri et al. (*1*). This technique is a combined technique incorporating sampling of metallic objects without damaging them and their subsequent evaluation by ring colorimetry (*2*) based on the Weisz ring-oven.

Silver occurs native and with other ores in small amounts as an impurity, so it was felt necessary to separate and estimate silver in ultramicroregions. Scrutiny of literature (*3*) reveals that 1,2,3-benzotriazole can be used selectively for precipitating silver ions with the help of masking agents such as EDTA and tartarate. Kuang Lu Cheng (*4*) has determined macroamounts of silver gravimetrically and volumetrically. Microamounts of silver (0.1 to 0.2 mg) have been determined gravimetrically by Waldbolt Bassenheint (*5*) and potentiometrically by Havir (*6*). In the present communication, successful use has been made of this reagent for the selective separation of trace amounts of silver. Potassium thiocarbonate (PTC) has been used as a developer for the estimation of silver in rings by the standard scale procedure (*2*).

Electrograph. An electrograph unit as reported earlier (*1*) from these laboratories was used.

Weisz Ring-Oven. Procured from National Appliance Co., Portland, Oregon.

Standard Test Solutions. Aqueous solutions of (a) copper sulfate (0.1 mg/ml) (b) zinc sulfate (0.1 mg/ml) (c) silver nitrate (0.1 mg/ml), and (d) gold chloride (0.1 mg/ml) were used.

Double distilled water and analytical grade reagents were used throughout these studies.

ELECTROGRAPHIC PROCEDURE FOR SAMPLING OF METAL IONS

A paper disk was moistened with potassium nitrate (neutral electrolyte) solution and placed on a dry filter paper to disperse any undue excess of the electrolyte. The disk was placed on the clear surface of the alloy and inserted between the two electrodes. Sufficient pressure from the cathode side was applied to ensure good contact with the sample. A current of 10 to 20 mA was passed for 3 to 5 sec so that minute fragments from the surface of the sample were anodically dissolved and retained by the filter paper disk. The paper disk was then removed from the alloy and dried. The disk is hereafter referred to as Circle A.

ESTIMATION OF SILVER BY RING-COLORIMETRY

A standard scale of silver ions was prepared using potassium thiocarbonate (PTC) as the chromogenic reagent (*7*).

A circle of Whatman No. 40 filter paper of 55 mm diameter was placed on the ring-oven which was set at 100 to 110°C. A known volume of the standard sample solution of silver ions containing a number of diverse metal ions was transferred to the marked center of the filter paper circle with the help of a microsyringe. The filter paper was then dried and a solution comprised of a mixture of solutions of 1% ammoniacal ethylene-

TABLE 1

Limits of Identification

Amount of silver taken in (μg)	Amount of silver found in (μg)	Difference, %
0.5	0.49	−2.0
1.0	0.99	−1.0
2.0	2.00	±0.0
3.0	3.04	+1.3
4.0	4.03	+0.75
5.0	5.03	+0.6
6.0	6.09	+1.5
8.0	7.89	−1.3

diamine tetraacetic acid, and benzotriazole (E. Merck, India) (1:1) was applied at the center of the filter paper. Thus the silver ions were fixed as silver benzotriazole and the diverse ions were washed out with distilled water. The paper was then dried and the inner zone containing silver was removed by punching it out as a disk. This small filter paper disk (6 mm) was placed in the middle of another round filter paper (55 mm), which had been moistened with a drop of water, on the ring oven. The silver benzotriazole was brought into a soluble form by using sodium thiosulfate solution and collected in the ring zone by washing with distilled water. The filter paper was dried and the ring developed with PTC (*7*). The resulting rings were compared with "standard scale rings" to obtain the concentration of silver ions.

The same procedure was applied to the above-mentioned Circle "A" after the anodic dissolution of the metal ions from the alloy samples.

Typical results regarding the estimation of silver ions are given in Table 1.

The range of accurate determinations was found to be within 0.5 to 8.0 μg of silver in the ring. Visual comparison was difficult beyond this range.

DETERMINATION OF SILVER IN VARIOUS ALLOYS

For the microdetermination of silver in its alloys, the nondestructive technique of electrographic sampling was adopted. Some alloys were used for the purpose, but known mixed solutions of metal ions were also prepared as a substitute for alloys that could not be procured.

The other metal constituents in alloys (copper, gold, and zinc) were separated on the ring-oven itself. Copper was extracted in chloroform as its *N*-benzoylphenyl hydroxylamine (NBPHA) complex while gold was

TABLE 2
Representative Results of Determination

Alloy	Metals present	% Composition found: Ring oven electrographic method	% Composition found: Gravimetric method	% Error
Gold jewelery	Silver	2.48	2.50	−0.8
	Copper	10.5	10.54	−0.37
	Gold	86.8	86.03	+0.88
Silver jewelery	Silver	79.7	80.0	−0.37
	Copper	19.9	19.8	+0.5
Gold solder[a]	Silver	55.3	55.0	+0.54
	Copper	28.8	28.85	−0.17
	Gold	11.85	11.95	−0.83
	Zinc	5.9	5.85	+0.85

[a] Since this alloy could not be procured, synthetic mixtures were used as substitutes.

extracted as its chloro complex in ethyl acetate, leaving behind zinc (*8*). The rings for gold and copper were developed with PTC, while dithizone was used for zinc.

Typical results regarding the estimation of silver in its alloys are given in Table 2.

ESTIMATION OF SILVER IN MINERALS

Silver occurs both native and in combination with a wide range of materials in minerals. The larger part of the world's supply, however, is produced as a by-product in the treatment of lead, copper, zinc, and gold ores. Since in this method the above metals do not interfere, silver can be estimated with ease in the microregion. Because galenite contains silver in the microregion, it was used for estimation as a representative case: a known amount (0.7 g) of powdered galenite was chemically treated to obtain a test solution (10 ml) for making estimates of silver directly by ring colorimetry (Table 3).

TABLE 3
Representative Results of Determination

Mineral	% Range of silver expected	Silver found (%)
Galenite	0.35–0.55	0.44
		0.46
		0.40

DISCUSSIONS

As far as the use of 1,2,3-benzotriazole as a fixing agent is concerned, the range of its selectivity has been enhanced by using suitable masking agents to obviate the interference caused by various metal ions. As reported earlier (*4*), the interferences caused by metal ions such as Fe(III), Zn(II), Co(II), Cd(II), Cu(II), and Ni(II) are masked by using ammoniacal ethylenediamine tetraacetic acid (EDTA) because their EDTA complexes are more stable than the corresponding triazolates. Hg(I) and Fe(II) interefere, but their higher oxidation states do not. For ions such as Sn(II), Sb(III), Ti(IV), and Be(II), the hydroxides of which are soluble even in the presence of EDTA, it is necessary to add sufficient amounts of tartarate. Anions such as Cl^-, Br^-, F^-, SO_4^{2-}, NO_3^-, PO_4^{3-}, and acetate do not interfere, while CN^-, $S_2O_3^{2-}$, and I^- interfere because the complex is soluble in their presence.

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