BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 253—255(1969)

Electrolytic Separation with Glassy-Carbon Electrodes Prior to Emission Spectrography: Determination of Traces of Silver in High-Purity Zinc

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(Received April 22, 1968)

In ultratrace analysis by emission spectrography, various chemical or physical separation methods are often used to remove matrix elements prior to the excitation step. These preconcentrations[1] are effective in improving sensitivity, precision and accuracy beyond those which direct excitation of the sample would achieve, provided that the separation loss and contamination due to reagents, vessels and the atmosphere are negligible. This paper describes electrolysis with glassy-carbon cathodes for concentrating 0.01 to a few ppm of silver in zinc metal prior to emission spectrography. Glassy-carbon,[2] a new form of carbon, has been employed in the electrodes for electrolytic separation[3,4] and emission spectrography,[5,6] because of its desirable properties compared with other carbonaceous electrode materials. In the proposed technique, traces of silver are electrodeposited on the end of a glassy-carbon rod from 0.5 to 1.5 N nitric acid solutions in greater than 90% yields, leaving about 99.999% of zinc in the electrolyte. The cathode is then used as an electrode for spark emission spectrography. After completion of the work, the authors found a report[7] describing a similar technique using high-purity graphite or pyrolytic graphite by Alvarez (presented at the 1st Materials Research Symposium held at the NBS, Gaithersburg, Md., in October 1966), although detailed information was not available.

Experimental

Apparatus. A Shimadzu quartz Littrow spectrograph QL-170 (Slit width used: 15μ). A Shimadzu universal excitation source SA-1 (The Feussner circuit was used at 10 kV, 0.0066μF, 0.08 mH and 10Ω). A Rigaku Denki microphotometer CM-1A.

Electrodes, Reagents, *etc.* Glassy-carbon electrodes: Tokai Electrode Manufacturing Co. GC-30S; $4\ \text{mm}\phi \times 40$ mm cathodes and $5\ \text{mm}\phi \times 50$ mm anodes, unless otherwise stated. They were polished with a series of emery papers of increasing fineness, then with a chromium oxide suspension ($0.5\ \mu$) on a rotary table polisher, and washed with nitric acid (1 : 1), followed by water. The cathode was inserted in open-ended polyvinyl chloride tubing (30 mm long) to limit the working area of the surface to the end (0.13 cm^2).

Counter electrodes: Hitachi spectroscopic graphite electrodes (regular, $6.15\ \text{mm}\phi$) were machined into a 60° cone.

Photographic plates: Fuji process panchromatic 101 mm × 252 mm plates.

Standard silver solutions: Prepared from silver nitrate.

$^{110\text{m}}$Ag solution: The Radiochemical Centre Amersham. $AgNO_3$ in HNO_3.

Purified zinc nitrate solution: A 25-*ml* solution containing 11.5 g of $Zn(NO_3)_2\cdot 6H_2O$ was electrolyzed with two glassy-carbon electrodes ($5\ \text{mm}\phi \times 100$ mm with no plastic sheath; working cathode area $\sim 5\ \text{cm}^2$) at the total applied voltage of 2.0 V for 24 hr to remove traces of silver. This solution was used to prepare synthetic samples. The Ag/Zn ratio in this solution was found to be 6×10^{-9}, or less than was found by a procedure described later.

All reagents used were of reagent grade. Water purified by distillation and ion exchange was used throughout the work.

Procedure. Place 5.0 g of zinc metal in a 100-*ml* beaker, add 44 *ml* of 6.5 N nitric acid and heat to dissolve. Cool the solution and dilute to 50 *ml* with water. Transfer an aliquot (1 to 5 *ml*) of the solution to an electrolysis cell (23 mm in diameter and 55 mm in height), and add water and 6.5 N nitric acid to give 8 *ml* of 1 N nitric acid solution. Insert two glassy-carbon electrodes into the cell, immersing them 5 mm into the solution. Cover the cell with a sheet of filter paper, stir the solution with a magnetic stirrer and apply 2.0 V *d. c.* between the electrodes using crocodile clips for electrical connections. After 20 hr of electrolysis, remove the cathode without breaking the current. Rinse the lower part of the cathode with water, remove

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1) A. Mizuike, "Trace Analysis: Physical Methods," ed. by G. H. Morrison, Interscience, New York (1965), p. 103.

2) S. Yamada and H. Sato, *Nature,* **193**, 261 (1962).

3) A. Mizuike and N. Mitsuya, *Bunseki Kagaku* (*Japan Analyst*), **17**, 1259 (1968).

4) A. Mizuike, K. Fukuda and N. Mitsuya, *Radioisotopes* (*Tokyo*), **17**, 199 (1968).

5) G. Dümecke and J. Wiegmann, *Silikattechnik,* **16**, 287 (1965).

6) K. Morita, H. Sunahara, T. Ishizuka, N. Nakayama and S. Yamada, *Bunko Kenkyu,* **16**, 169 (1967).

7) G. H. Morrison, "Trace Characterization: Chemical and Physical," ed. by W. W. Meinke and B. F. Scribner, (Natl. Bur. Std. Monograph 100)(1967), p. 417.

the plastic sheath, rinse with water again and allow to air-dry. Prepare calibration standards by electrolyzing 1 N nitric acid containing known amounts (0.003, 0.01, 0.03, 0.1, 0.3, 1, 3 μg) of silver by the same procedure as described above. Spark through a 3-mm gap between the silver-deposited and the counter (upper) electrode for 60 sec, and record the spectrum in the range of 2460 to 3480 Å on a photographic plate. Record the spectra of the calibration standards on the same plate. After photographic processing, measure the relative transmittance of the silver line 3280.683 Å against the background. Determine the amount of silver present by reference to a calibration curve (Seidel function *vs.* logarithm of quantity of silver) prepared from the calibration standards.

Results and Discussion

Electrolytic Separation of Silver. The conditions of electrolysis in the present work were developed from previous experiments.[3] In order to investigate the deposition rate and the recovery of silver, synthetic samples prepared from purified zinc nitrate, ^{110m}Ag and standard silver solutions were electrolyzed under conditions described previously. Aliquots (0.2 or 1 m*l*) were taken from the electrolyte during electrolysis, or from the 10-m*l* solution obtained by treating the cathode with 5 m*l* of hot nitric acid and water after electrolysis, and their gamma activities measured by means of a well-type scintillation counter. The results are shown in Fig. 1 and Table 1. Greater than 90% yields were achieved for 0.01 to a few μg of silver. About 2% of the total silver was adsorbed on the plastic sheath, and less than 1% deposited on the side of the cathode. Zinc accompanying silver was determined by square wave polarography, and found to be 4 μg when 500 mg of zinc was present before electrolysis.

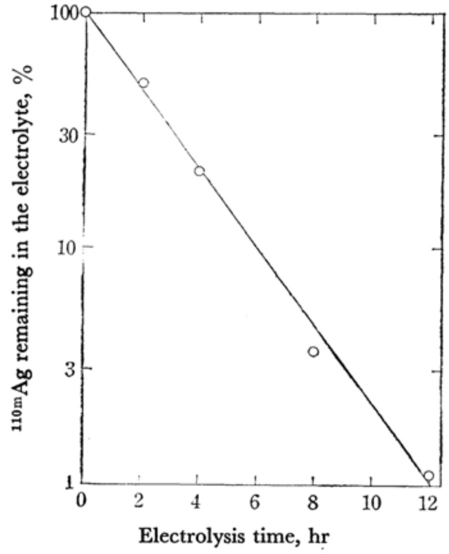

Fig. 1. Electrodeposition of silver on a glassy-carbon cathode from 8 m*l* of 1 N HNO_3 solution containing 0.05 μg of silver and 0.5 g of zinc.

TABLE 1. ELECTRODEPOSITION OF SILVER FROM NITRIC ACID SOLUTIONS

Free HNO_3 N	Zn present g	Ag present μg	Ag recovery* %
0.5	0	0.01	101
1	0	0.01	91
1.5	0	0.01	91
1	0	2	97
1	0.5	0.01	96
1	0.5	2	93

* By radioactivity measurement. error <3%.

TABLE 2. DETERMINATION OF SILVER IN SYNTHETIC SAMPLES

Zn present: 0.50 g. Analyses made on two separate days.

Ag added μg	Ag found μg
0	<0.003, 0.003
0.010	0.012
0.030	0.026
0.20	0.22
0.30	0.32*

* GC-20 grade glassy-carbon was used.

TABLE 3. DETERMINATION OF SILVER IN HIGH-PURITY ZINC METAL

Zinc metal	Sample taken, g	Ag found μg	Ag in sample, ppm
99.999% purity*	0.10	0.18	1.8
	0.10**	0.30	2.0
	0.20	0.42	2.1
	0.50	1.00	2.0
			(av. 2.0)***
99.9998% purity	0.10	0.019	0.19
	0.20	0.054	0.27
	0.50	0.12	0.24
			(av. 0.23)

* Analyses made on two separate days.
** 0.10 μg of Ag was added before electrolysis.
*** 2.1 ppm by the photometric *p*-dimethylaminobenzylidenerhodanine method.[3]

Determination of Silver in Zinc. Synthetic samples prepared from purified zinc nitrate and standard silver solutions, and two samples of commercial high-purity zinc metal were analyzed, with the results given in Tables 2 and 3. The blank value through the entire procedure was less than 0.003 μg of silver. The calibration curves were linear over the range 0.003 to 3 μg of silver, with a deviation of about ±10%. Although autoradiographs indicated that more silver electrodeposited near the circumference of the electrode, almost all the silver was evaporated from the electrode in the first 5-sec period of sparking. The lower limit of determination and the accuracy of the present method are about 0.01 ppm of silver in zinc, and about ±10% at the fractional to a few ppm level, respectively.

The authors are indebted to Dr. Kiyoshi Morita for help in part of the emission spectrography.