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**POLAROGRAPHIC DETERMINATION OF  
BISMUTH, LEAD, TIN, CADMIUM,  
ZINC, AND TELLURIUM IN S. S. C.  
COPPER STANDARDS**

by

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**MINERAL SCIENCES DIVISION**

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C. H. McMaster\*

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SUMMARY

Analytical procedures are described for the separation and polarographic determination of bismuth, lead, tin, cadmium, zinc, and tellurium in high-purity copper.

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## INTRODUCTION

The Non-Ferrous Standards Committee of The Spectroscopy Society of Canada prepared four copper standards by the addition of various impurities in controlled amounts to high-purity electrolytic copper. The metal was fabricated into bars 5/16 inch diameter by 12 inches long. After homogeneity tests the samples were distributed to participating laboratories for certification analysis. The results presented in this report were obtained using polarographic techniques.

The polarographic determination of impurities in copper cannot be carried out directly as copper is reduced at a more positive potential than most other metallic species. It is necessary to perform chemical separations to eliminate most of the copper prior to the polarographic determination of the trace elements.

This report describes analytical procedures for the separation and polarographic determination of bismuth, lead, tin, cadmium, zinc, and tellurium in high-purity copper.

## EXPERIMENTAL

### 1. Apparatus

- Polarograph: K-1000 Cathode Ray Polarograph (Southern Instruments Ltd., Camberley, Surrey, England).
- Cells: Polarographic cells of conventional design, using mercury pool anodes and capable of holding 2-5 ml of solution, were employed.
- pH Meter: Leeds and Northrup.

### 2. Sampling

The copper bars were cut into 5-g pieces; one piece was used for each determination. After weighing, the sample was treated with hot 1:2 hydrochloric acid to remove surface contamination, and washed with water.

### 3. Procedure

#### a) Bismuth:

Transfer the sample to a 400-ml beaker and dissolve in 30 ml of 1:1 nitric acid. Dilute to about 100 ml with water, add 5 g ammonium chloride, 5 ml of 0.05% ferric iron solution, and adjust the pH to 9 with ammonium hydroxide. Add 1 g celite analytical filter-aid (Johns-Manville) and allow to stand for one hour with occasional stirring. Filter, using light suction, through a glass fiber filter disc supported in a porcelain filtering crucible. Wash 3 to 4 times with 1:5 ammonium hydroxide and twice with water. Dissolve the hydroxides from the filter with 20 ml of warm 1:3 nitric acid, catching the filtrate in a 100-ml beaker. Wash the filter twice with water and evaporate the filtrate to dryness.

Dissolve the residue in 10 ml of 1:5 hydrochloric acid. Add 20 ml of 10% ammonium citrate solution, adjust the pH to 10 with ammonium hydroxide, and add 10 ml of 5% potassium cyanide solution. Transfer to a 125-ml separatory funnel, add 20 ml of 0.1% sodium diethyldithiocarbamate solution and mix. Add 10 ml chloroform, shake for 1 minute, allow the layers to separate, and transfer the chloroform layer to the original beaker. Carry out a total of three extractions in identical fashion, and evaporate the extracts to dryness. Add 5 ml nitric acid, 3 ml perchloric acid, and evaporate to dryness.

Dissolve the residue in exactly 5 ml of a supporting electrolyte composed of 0.1 molar perchloric acid and 1 molar nitric acid. Transfer a portion to a polarographic cell, flush with nitrogen gas, and electrolyze using a start potential of -0.10 volt. The peak due to the reduction of bismuth occurs at -0.37 volt.

#### b) Lead

The procedure for the separation of lead is identical with the bismuth separation except the residue, after evaporation to dryness with nitric and perchloric acids, is dissolved in 10 to 50 ml (depending on the lead content) of a supporting electrolyte composed of 1 molar perchloric acid and 1% ascorbic acid. Transfer a portion to a polarographic cell and electrolyze using a start potential of -0.25 volt. The reduction peak due to lead occurs at -0.60 volt.

c) Tin

Dissolve the sample, precipitate the hydroxides, and wash as described in the bismuth procedure. Dissolve the hydroxides with 25 ml of warm 1:3 hydrochloric acid, catching the filtrate in a 100-ml beaker, and wash with water. Evaporate to 20-25 ml, cool, add 20 ml of 10% ammonium citrate solution, and adjust the pH to 9.5 with ammonium hydroxide. Transfer to a 125-ml separatory funnel, add 10 ml of 0.2% ammonium pyrrolidine dithiocarbamate solution, and mix. Extract for 1 minute with 10 ml of chloroform, allow the layers to separate, and discard the chloroform extract. Repeat three times or until all of the copper and lead are extracted.

Add 5 ml of 10% ascorbic acid solution (freshly prepared) and immediately add 20 ml of hydrochloric acid. Mix carefully and cool to room temperature with cold water. Add 5 ml of 0.2% ammonium pyrrolidine dithiocarbamate solution and extract with 10 ml of chloroform. Repeat the extraction three times, collect the extracts in a 100-ml beaker, and evaporate to dryness. Dissolve the residue in 4 ml nitric acid and 3 ml sulphuric acid, and evaporate to dryness.

Add 5 ml of 1:1 hydrochloric acid and warm to dissolve the residue. Transfer to a 25-ml volumetric flask containing 0.3 g ascorbic acid and 5.3 g ammonium chloride. Dilute to volume with water and transfer a portion to a polarographic cell. Electrolyze using a start potential of -0.20 volt. Tin exhibits a peak at -0.46 volt.

d) Cadmium and Zinc

Dissolve the sample in 20 ml water, 30 ml hydrochloric acid, and 6 ml nitric acid. Boil for 10 minutes, cool, and dilute to exactly 100 ml with water. Transfer a 20-ml aliquot to a 400-ml beaker, add 2 g hydrazine dihydrochloride, and dilute to about 200 ml with water.

Electrolyze the solution between platinum electrodes at a potential of -0.25 volt (vs S.C.E.) using a potentiostat to control the voltage. As the electrolysis proceeds, increase the voltage by increments until a potential of -0.45 volt is attained. After 30 minutes of electrolysis, wash the cover plate and the sides of the beaker with a stream of water and continue the electrolysis for a further 30 minutes. Filter the solution through a fast paper and collect the filtrate in a 400-ml beaker. Add 7 ml nitric acid and evaporate the solution to dryness. Dissolve the residue in 5 ml hydrochloric acid, transfer to a 100-ml beaker, and evaporate to dryness.

Dissolve the residue in exactly 10 ml of a supporting electrolyte composed of 1 molar ammonium hydroxide, 1 molar ammonium chloride, and 1% sodium sulphite. Electrolyze at the dropping mercury electrode using a start potential of -0.45 volt. Cadmium exhibits a peak at -0.65 volt. After recording the cadmium peak height, increase the start potential to -0.90 volt and read the zinc peak at -1.17 volts.

e) Tellurium

Transfer the sample to a 300-ml conical flask and dissolve in 20 ml perchloric acid, 10 ml nitric acid, and 10 ml water. Evaporate the solution to fumes. Cool, wash the sides of the flask with water, and evaporate again to fumes. Cool, and dissolve the residue in 50 ml of 1:1 hydrochloric acid. Filter to remove any insoluble residue and wash with 50 ml of 1:1 hydrochloric acid. Add 2 ml of arsenic solution (0.15%  $\text{As}_2\text{O}_3$  solution), and 25 ml hypophosphorous acid (50% solution). Heat to boiling and allow to simmer for 15-20 minutes to coagulate the precipitate. Filter the hot solution through a medium porosity fritted glass funnel using suction. Wash three times with 15-ml portions of 1:1 hydrochloric acid. Dissolve the precipitated metals from the filter with 10 ml hydrobromic acid containing 10% bromine, and wash with water. Dilute to about 50 ml with water, add 50 ml hydrochloric acid, and 20 ml hypophosphorous acid. Heat to boiling as before, allow the precipitate to coagulate, filter, and wash with 1:1 hydrochloric acid. Dissolve the precipitate from the filter with 10 ml nitric acid, catching the filtrate in a 100-ml beaker, and wash with water. Add 3 ml perchloric acid and evaporate to dryness. Dissolve the residue in exactly 10 ml of 1 molar ammonium sulphite solution containing 0.001% triton X-100 and adjust to a pH of 8.6.

Transfer a portion of the solution to a polarographic cell and electrolyze using a start potential of -0.20 volt. Measure the tellurium peak height at -0.52 volt.

## RESULTS AND DISCUSSION

Table 1 shows the results obtained for the determination of the six elements in the four standard samples. The statistical analysis of the results is shown in Table 2, in which

n	=	number of determinations,
$\bar{x}$	=	arithmetic mean (ppm),
s	=	standard deviation (ppm),
c.v.	=	coefficient of variance (%).

Bismuth and lead can be separated from copper, as the diethyldithiocarbamates, and determined simultaneously using polarographic techniques (1). In the present case it was considered advisable to determine the two elements separately as the lead content of three of the standards was much greater than bismuth.

A comparison between polarographic and spectrographic results for tin in the four standards is shown in Table 3. The spectrographic figures were obtained during homogeneity studies and represent the averages of large numbers of tests (2). The polarographic results are lower than the spectrographic values in standards 1, 2, and 3, but show complete recovery of tin in standard 4. The reason for the low results is not known but may be due to the presence of part of the tin as the refractory oxide,  $\text{SnO}_2$ , formed during fabrication of the samples by the interaction of tin and oxygen (3). Stannic oxide, formed under these conditions, is insoluble in acids and remains as a residue after dissolution of the sample (4). A test was carried out in which a 5-g sample of standard 1 was dissolved in 30 ml of 1:1 nitric acid, diluted to about 100 ml with water, and filtered. The filter paper was washed with water, placed in a platinum crucible, and ashed in a furnace. The residue was submitted for analysis to the Mineral Sciences Division Spectrographic Laboratory. The spectrographic report (Report No. SL-67-089) showed that tin, silicon, and copper were the major constituents of the ash. This indicates that some of the tin is present in a form that is not soluble in 1:1 nitric acid. To obtain a value for total tin, it is necessary to perform a fusion on the insoluble portion of the sample, and add this to the main solution.

After discussion of the results with Dr. A.H. Gillieson of the Non-Ferrous Standards Committee, it was decided to discontinue further work with tin at that time. However, it is hoped that the investigation can be resumed at a later date.

TABLE 1

Determination of Trace Elements in S.S.C. Copper Standards

Trace Element	Standard 1		Standard 2		Standard 3		Standard 4	
Bismuth (ppm)	1.12		0.10		0.50		0.22	
	1.10		0.10		0.52		0.24	
	1.14		0.09		0.53		0.26	
	1.14		0.12		0.55		0.28	
	1.18		0.11		0.59		0.25	
Lead (ppm)	71.2		5.6		3.9		17.4	
	72.1		5.2		4.0		15.4	
	72.7		5.4		4.1		16.5	
	69.2		4.9		3.4		15.6	
	68.3		4.7		3.5		14.6	
Tin (ppm)	13.0		3.5	4.2	5.7	4.8	19.3	21.7
	12.8		3.4	4.1	5.2		21.1	
	12.8		3.9	3.8	5.0		20.6	
	13.4		3.8	3.3	5.6		22.2	
	12.6		3.7		5.6		21.6	
Cadmium (ppm)	<1	<1	9.9	9.4	<1	<1	18.2	17.6
	<1	<1	9.4	9.0	<1	<1	18.0	17.6
	<1	<1	9.6	9.4	<1	<1	17.6	17.8
	<1		9.2		<1		17.6	
	<1		8.8		<1		17.8	
Zinc (ppm)	31.0	32.4	16.1	17.4	11.6	12.6	30.0	28.6
	30.6	31.6	15.0	17.4	12.6	13.4	29.2	29.6
	30.6	32.0	15.2	16.0	12.8	12.6	31.0	29.6
	30.6		16.4		12.0		29.6	
	32.0		14.6		12.0		31.0	
Tellurium (ppm)	4.5	4.8	0.84	0.82	2.9	2.8	0.96	1.00
	4.6	4.7	0.88	0.87	2.5	2.1	0.96	1.07
	4.6	4.7	0.80	0.88	2.4	2.2	0.98	1.01
	4.6		0.81		2.2		0.96	
	4.7		0.83		2.5		1.06	



TABLE 2  
Statistical Analysis of Polarographic Results

Trace Element	Statistical Symbol	Standard 1	Standard 2	Standard 3	Standard 4
Bismuth	n	5	5	5	5
	$\bar{x}$	1.14	0.10	0.54	0.25
	s	0.03	0.01	0.03	0.02
	c.v.	2.63	10	5.6	8
Lead	n	5	5	5	5
	$\bar{x}$	70.7	5.2	3.8	15.9
	s	1.9	0.4	0.3	1.1
	c.v.	2.7	7.7	7.9	6.9
Tin	n	5	9	6	6
	$\bar{x}$	13.0	3.7	5.3	21.1
	s	0.32	0.31	0.37	0.73
	c.v.	2.4	8.3	7.1	3.5
Cadmium	n	8	8	8	8
	$\bar{x}$	-	9.3	-	17.8
	s	-	0.3	-	0.2
	c.v.	-	3.2	-	1.1
Zinc	n	8	8	8	8
	$\bar{x}$	31.2	16.0	12.4	29.8
	s	0.7	1.0	0.6	0.8
	c.v.	2.2	6.2	4.8	2.7
Tellurium	n	8	8	8	8
	$\bar{x}$	4.6	0.84	2.4	1.0
	s	0.33	0.03	0.28	0.04
	c.v.	7.2	3.6	11	4.5

TABLE 3  
Comparison of Tin Results by Spectrographic and  
Polarographic Techniques

<u>Standard</u>	<u>Tin (ppm)</u>	
	<u>Spectrographic</u>	<u>Polarographic</u>
1	50	13.0
2	12	3.7
3	13	5.3
4	20	21.1

The electrolytic technique used in the separation of cadmium and zinc from copper is not practical for samples weighing more than 1 g. The small sample weight limits the amounts of cadmium and zinc that can be detected. Nickel exhibits a reduction peak midway between cadmium and zinc, and can be determined on the same polarogram.

An investigation was carried out to develop a method for the simultaneous separation and determination of tellurium and selenium. The two metals can be determined on the same polarogram using ammonium sulphite as the supporting electrolyte. Attempts to separate the two metals from copper by reduction with hypophosphorous acid were unsuccessful as only tellurium was recovered completely.

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