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J. Hole

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**DETERMINATION OF MERCURY IN A
TETRAHEDRITE-BEARING ORE**

by

J. C. HOLE

MINERAL SCIENCES DIVISION

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SUMMARY

A number of methods for the determination of mercury in a tetrahedrite ore and its products have been investigated. A procedure of slowly leaching the ore with hydrochloric and nitric acids, followed by the spectrophotometric determination of mercury with diphenylthiocarbazone (dithizone), proved to be the most reliable of these methods.

The method is described in detail, and applied to a number of ore products and other samples. A more rapid but less accurate method for the determination of mercury is also described.

* Scientific Officer, Analytical Chemistry Section, Mineral Sciences Division, Mines Branch, Department of Energy, Mines and Resources, Ottawa, Canada.

INTRODUCTION

An ore deposit located in Ontario is currently under investigation as a possible source of mercury production. This ore body contains mercury as a substitute for part of the copper content of the mineral tetrahedrite $3\text{Cu}_2\text{S}\cdot\text{Sb}_2\text{S}_3$, whereas most mercury ores of commercial interest contain mercury in the form of cinnabar HgS . Other elements found in the tetrahedrite are iron, silver, zinc and arsenic. The tetrahedrite is in turn found in a matrix of bornite Cu_5FeS_4 , and barite BaSO_4 . The Mineral Sciences Division of the Mines Branch has been asked to suggest an accurate and reliable method for the determination of mercury in this ore and its products.

Previous work in these laboratories (1) has resulted in a suitable method for the determination of mercury occurring as cinnabar in a zinc concentrate. The method, requiring finely-ground samples, involves a lengthy acid leach, followed by a spectrophotometric determination of the dissolved mercury. It is well-known (2, 3) that mercury may readily be lost by volatilization from acid solutions. In addition, mercury may be lost when a sample undergoes grinding, and it would be advantageous to have a method which required only preliminary crushing of the sample.

It was thought that these objections could be overcome by use of a method involving combustion of a sample followed by distillation of the mercury. The analytical methods for the recovery of mercury from ores, mentioned in the literature (3, 4) as the most reliable, are based on some modification of a distillation technique. Such a technique would eliminate the need for acid treatment to dissolve the sample, and would possibly be effective on a coarse sample.

Therefore a number of distillation techniques were attempted, but none were found satisfactory. However a fusion procedure was used which gave results of an accuracy sufficient to warrant its use as a rapid method for estimating mercury content. In addition, the leaching method mentioned above was tried and found to give accurate, reproducible results. This method has been recommended for use with the ore and its products, and is described in detail. The investigations of the various approaches are discussed in this report.

A number of techniques for completing an analysis after the mercury has been dissolved by a suitable method have also been investigated. A spectrophotometric determination using diphenylthiocarbazone has been recommended and described.

In the absence of suitable mercury standards, weighed portions of analytical grade mercuric oxide were employed in the investigation. In addition, two samples marked "A" and "B" from the orebody were used. These samples were very coarse, ranging in size from 1/4" in diameter down to -65 mesh. Portions of these samples were removed and ground slowly by hand in an agate mortar to -65 mesh.

The mercury contents of an ore sample, several mill products of the ore, and a sample of pure tetrahedrite, were determined by the recommended procedure.

DETERMINATION OF MERCURY IN SOLUTION

Previous workers have used titrimetric and spectrophotometric methods to determine the mercury content of a solution, and some of these were evaluated in the present investigation. In addition, an atomic absorption procedure was attempted in order to take advantage of the inherent speed and simplicity of this technique.

The method of Seamon (2) involves the titration of mercury with standard potassium iodate solution, with starch as the indicator, after the addition of "aged" nitric acid to oxidize the mercury. It was found that the end-point of the determination was not well defined, due to the formation of insoluble red mercury iodide crystals, and thus the results were erratic. The silver content of the tetrahedrite also interferes with this titration.

Another titrimetric method (4) provides for the titration of mercury with potassium thiocyanate. This method was found to be insensitive to the small quantities of mercury to be found in the tetrahedrite ores and, again, silver interferes.

The mercury content of several standard mercury solutions was determined by atomic absorption. However, the sensitivity of mercury by this technique is low, and the method was not suitable for the small amounts of mercury to be found in the tetrahedrite ore. The sensitivity might be increased by extraction of the mercury from its aqueous solution, but this would sacrifice the speed and simplicity of the technique.

It was finally decided to use the spectrophotometric procedure with diphenylthiocarbazon described by Ripley (1) to determine mercury in the sample solutions. This procedure was found to have the required sensitivity, and gave reproducible results. Beer's Law is obeyed up to a concentration of 300 micrograms of mercury. The only interferences are gold and the

platinum-group metals, which are unlikely to occur in tetrahedrite and its ores. The method is described in detail later in this report.

PRELIMINARY TESTS AND DISCUSSION

A. A distillation procedure for the recovery of mercury was followed exactly as described in the literature (4). The ore, mixed with a lime-cupric oxide flux as recommended for sulphide materials, was placed in a glass tube sealed at one end, and heated at 500°C. The mercury, which should have condensed in the cool, open end of the tube, was dissolved in hot nitric acid and determined spectrophotometrically. The mercury content of six portions of Sample A, ground to -65 mesh, was found to be 0.017, 0.033, 0.027, 0.033, 0.027, 0.033%. It was decided to modify the equipment in an effort to increase the efficiency of the distillation.

B. The distillation technique described by Hillebrand (3) was followed with various modifications. In this method the sample was placed in a boat, with or without the lime-cupric oxide flux, and inserted in a combustion tube in a furnace. Oxygen was passed through the tube while the tube and contents were heated to 900°C. The oxygen emerging from the tube was passed through various combinations and designs of air and nitric acid traps. The mercury was then rinsed from the traps with hot nitric acid and determined spectrophotometrically.

The mercury recovery from weighed amounts of mercuric oxide treated in this manner was found to range from 47 to 84%. Coarse (-1/4") portions of Sample A were found to contain from 0.003 to 0.017% mercury. Such erratic and incomplete recoveries indicated that the quantitative distillation of small amounts of mercury is more difficult than expected. It was decided to devote no further time to these distillation techniques.

C. Samples of ore, mixed with the lime-cupric oxide flux, were heated at 700°C in an iron retort. The design of the classical iron retort was modified to allow a stream of oxygen to be passed through the retort while being heated. The emerging oxygen was bubbled through a nitric acid trap. No mercury was found in the acid solution. This apparatus was designed for the distillation of relatively large amounts of mercury; apparently it is not suited for the smaller amounts contained in these ore samples.

D. A fusion technique for dissolving the mercury ore was investigated. It was thought that an oxidizing fusion would convert mercury to mercuric oxide which would not be volatilized from the fusion melt. In this procedure, a sample was dissolved by fusing with sodium peroxide in a zirconium

crucible. The melt was dissolved in water, the solution acidified with nitric acid, and then warmed until clear. Mercury was determined spectrophotometrically.

Using this technique, the mercury recovered from weighed amounts of mercuric oxide ranged from 84 to 92%. Furthermore, this treatment dissolved samples A and B completely, even in the coarse (-1/4") state. Table 1 shows the results of analyzing ore samples by this method.

TABLE 1

Analysis of Ore by Fusion Technique

<u>Sample and Grind</u>		<u>% Hg</u>
A	-1/4"	0.034, 0.021
A	-65 m	0.037, 0.035, 0.063, 0.034
B	-1/4"	0.078, 0.097, 0.080, 0.086
B	-65 m	0.115, 0.111, 0.141, 0.119

It is expected that losses of mercury occurred during heating of the acid solution of the fusion melt, and that these losses were responsible for the lack of precision of the results in Table 1. However, the results were much better than those obtained by the distillation techniques.

E. It was then decided to investigate the leaching technique (1) mentioned previously. In this method, a sample was very slowly leached, without heating, in both hydrochloric and nitric acids. The resulting solution was then filtered and the mercury determined spectrophotometrically.

The mercury recovered in this manner from four mercuric oxide samples was 100%, 100%, 101% and 100% respectively of the amount of mercury taken.

The mercury values obtained from ore samples by this method are shown in Table 2. Since antimony is a major constituent of tetrahedrite, the amount of tetrahedrite in the ore will be proportional to the antimony content. In an effort to relate the mercury content of the ore to the amount of tetrahedrite in the ore, the antimony determination is also shown in Table 2.

TABLE 2

Analysis of Ore by Leaching Technique

<u>Sample and Grind</u>		<u>% Sb</u>	<u>% Hg</u>	<u>Mean[†] Standard Deviation</u> <u>% Hg</u>
A	-1/4"	-	0.031, 0.039, 0.118, 0.024	- -
A	-65 m	0.29	(0.037, 0.038, 0.040 0.040, 0.038, 0.034 0.037, 0.037, 0.036	0.037 [±] 0.002

The results of the leaching tests show that the technique is capable of accurate and precise determinations of mercury in the ore, provided the sample is first ground to -65 m.

The completeness of the mercury recovery by this leaching procedure was investigated by using it to analyze ore samples, and then independently using the fusion technique mentioned above to analyze the insoluble residues from the leach. These results, four for each sample, are shown in Table 3 and are termed "Soluble" and "Insoluble" respectively. For one sample the mean and standard deviation of the results are also shown. Again, the antimony analysis is given.

TABLE 3

Determination of Mercury in Ore

<u>Sample B -1/4"</u>			<u>Sample B -65 m</u>			
<u>%Sol. Hg</u>	<u>%Insol. Hg</u>	<u>%Total Hg</u>	<u>%Sb</u>	<u>%Sol. Hg</u>	<u>%Insol. Hg</u>	<u>%Total Hg</u>
0.123	0.002	0.125	0.72	0.132	<0.001	0.132
0.112	0.001	0.113		0.130	<0.001	0.130
0.094	0.002	0.096		0.131	0.001	0.132
0.092	0.002	0.094		0.133	<0.001	0.133
						0.132 [±] 0.001

The results in Table 3 show that the leaching procedure is capable of recovering virtually all of the mercury in this ore providing the sample is first ground

to -65 m. The lack of precision of the results from the coarse sample is likely due to the difficulty of obtaining representative samples from the material.

The antimony contents of ores A and B given in Tables 2 and 3 show that, as expected, the amounts of antimony (and therefore of tetrahedrite) in the ores increase as the mercury contents of the ores increase.

As a result of these investigations, the leaching procedure has been chosen for the determination of mercury in this tetrahedrite ore and its products. The fusion technique may be used for a more rapid estimation of mercury. It is necessary to grind the ore to -65 m before analysis. Both procedures are described in detail below.

RECOMMENDED PROCEDURE

Apparatus:

pH meter
Spectrophotometer

Reagents:

Standard Mercury Solution: Weigh 1.0798 g. of dried analytical grade yellow mercuric oxide into a beaker, dissolve with 30 ml of nitric acid, and dilute to 1 litre.

Diphenylthiocarbazono Solution: Dissolve 0.012 g. of the reagent (dithizone) in chloroform and dilute to 500 ml. Prepare fresh daily.

Sulphuric Acid (1.8 N): Dilute 100 ml of concentrated acid with water to 2 litres.

Potassium Permanganate (0.5 N): Dissolve 15.5 g. of KMnO_4 in 1 litre of water.

Sulphurous Acid Solution: Bubble reagent grade SO_2 into 200 ml of water for 10 minutes. Prepare fresh daily.

Ammonium Hydroxide (9 N): Dilute 600 ml of concentrated NH_4OH with water to 1 litre.

Decomposition of Sample:

Weigh exactly 0.5000 g of sample, ground to -65 mesh, into a 500 ml Erlenmeyer flask. Moisten, add 20 ml HCl, cover, and allow to stand at room temperature for 24 hours without shaking. Add 20 ml HNO₃ and allow to stand another 24 hours.

Add 50 ml water and some dry filter paper pulp to the flask, and filter through a Whatman #40 paper into a 250 ml volumetric flask. Discard the residue after washing it with water and 10% HNO₃. Dilute the solution to volume with water.

Standardization:

The standard mercury solution is diluted one hundredfold and aliquots of 5, 10, 15, 20, 25 and 30 ml are added to separate 600-ml beakers, resulting in mercury concentrations of 50, 100, 150, 200, 250 and 300 micrograms respectively.

To each beaker, add 25 ml of 1.8 N H₂SO₄ and 10 ml of 0.5 N KMnO₄ and mix well. Add 10 ml of sulphurous acid solution and 1 g of E. D. T. A. dissolved in 20 ml of 1:4 NH₄OH. Adjust to pH 2.0 with 1:4 NH₄OH and cool to room temperature.

Transfer the solution to a 500-ml separatory funnel, add 10 ml of chloroform, shake for 30 seconds, and allow the layers to separate. Draw off and discard the excess CHCl₃. Add exactly 50 ml of the dithizone solution, shake for 1 minute, and allow the layers to separate.

Transfer the chloroform layer to a second funnel, add 50 ml of 9N NH₄OH, shake for 30 seconds and allow to separate. Transfer the chloroform layer to a third funnel, add a further 50 ml of 9N NH₄OH, shake and allow to separate.

Finally transfer the chloroform layer to a fourth funnel, add 25 ml of water, shake for 30 seconds and allow to separate. Insert a filter plug of absorbent paper tissue into the stem of the fourth funnel, and fill a 1-cm cuvette with the chloroform extract.

Read the absorbance of this extract from the spectrophotometer at 495 mμ, using chloroform as a blank. Draw a calibration curve of absorbance vs. mercury concentration; Beer's Law will apply.

Determination of Mercury:

Withdraw an aliquot containing up to 300 micrograms of mercury from the 250-ml flask containing the sample solution, and add to a 600-ml beaker.

Carry this sample through the complete procedure described above.

Use the absorbance of the sample solution, and the calibration curve, to find the amount of mercury in the aliquot, and from this calculate the percentage of mercury in the original sample.

RAPID PROCEDURE

Weigh exactly 0.5000 g of sample into a zirconium crucible, and add about 5 g of sodium peroxide. Heat the crucible and contents over a burner to a dull cherry red colour and maintain at this temperature with occasional swirling for about five minutes.

Cool the crucible almost to room temperature, and place it in a 600-ml beaker containing 50 ml of water. When the violent reaction has subsided and the melt has been dissolved, remove the crucible and wash with water. Slowly add 35 ml of nitric acid to the beaker. Rinse the crucible with 15 ml of nitric acid and add this to the beaker.

Warm the beaker on the hot-plate until all the residue has dissolved, leaving a clear colourless solution. Cool the solution, wash into a 250-ml volumetric flask, and dilute to volume with water.

Remove a suitable aliquot to a 600-ml beaker, and carry through the complete separation and spectrophotometric procedures described above.

APPLICATION TO SAMPLES

Ore Sample:

An ore sample of special interest from this deposit was analysed by the recommended procedure. The four results, and their mean, are shown in Table 4.

TABLE 4

Analysis of Ore Sample

<u>% Hg</u>
0.127, 0.130
<u>0.132, 0.123</u>
Mean 0.128

Tetrahedrite:

A hand-picked specimen of tetrahedrite mineral, from the orebody in question, was obtained. This shiny, black, opaque specimen was very brittle, and for analysis was crushed in a mortar to particles of 1 mm or less in cross-section.

Mercury was determined in a portion of the sample by the recommended procedure; the tetrahedrite dissolved completely during leaching. Iron, copper, silver, zinc and lead were determined in the leach solution by atomic absorption. Sulphur was determined after wet oxidation of separate duplicate samples. Antimony and arsenic were determined in another sample by titration after appropriate fusion and distillation. The results appear in Table 5.

TABLE 5

Analysis of Tetrahedrite

<u>Element</u>	<u>%</u>
Cu	37.1
Sb	21.29
S	25.58
Hg	3.87
Fe	4.63
Ag	0.37
Zn	1.39
As	3.40
Pb	<0.1

The elements determined in the tetrahedrite and shown in Table 5 total 97.7%. It is expected that the remainder of the specimen would consist of water, oxygen, silica, aluminum, calcium and magnesium.

The mercury analysis shown in Table 5 is of interest because it indicates the degree of mercury substitution occurring in the tetrahedrite from the particular orebody under investigation.

Mill Products:

A large amount of tetrahedrite-bearing ore from the orebody was received by the Mineral Processing Division of the Mines Branch. A head sample was taken from this ore and three processing tests were carried out, resulting in various products.

These products were analyzed by the recommended procedure. In addition, copper and other elements were determined in some samples by suitable methods. The results are shown in Tables 6 and 7. In Table 7, the mercury determinations for each test, together with the weights of the products, were used to find a calculated head value for mercury.

TABLE 6

<u>Analysis of Head Sample</u>				
<u>% Hg</u>	<u>% Cu</u>	<u>% Zn</u>	<u>% Pb</u>	<u>Oz/ton Ag</u>
0.0255	0.37	0.03	0.04	0.67

TABLE 7

<u>Analysis of Ore Products</u>				Calculated Head
<u>Test</u>	<u>Product</u>	<u>% Hg</u>	<u>% Cu</u>	<u>% Hg</u>
1	Cleaner concentrate	0.467	8.42	0.025
	Recleaner tails	0.100	1.33	
	Rougher tails	0.006	---	
- - - - -				
2	Concentrate	0.604	10.25	0.026
	Tails	0.008	---	
- - - - -				
3	Concentrate	0.760	13.24	0.024
	Rougher tails	0.008	---	
- - - - -				

It will be seen from Table 7 that the calculated head for each Test is in excellent agreement with the actual head sample analysis shown in Table 6.

CONCLUSION

The leaching procedure investigated and recommended in this report for the determination of mercury in this tetrahedrite-bearing ore deposit and its products is accurate and precise.

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