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**THE SPECTROPHOTOMETRIC DETERMINATION
OF MERCURY IN A ZINC CONCENTRATE
FROM MANITOU-BARVUE MINES LIMITED,
VAL D'OR, QUEBEC**

by

LEONARD G. RIPLEY

MINERAL SCIENCES DIVISION

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Mines Branch Investigation Report IR 64-83

THE SPECTROPHOTOMETRIC DETERMINATION OF MERCURY
IN A ZINC CONCENTRATE FROM MANITOU-BARVUE MINES
LIMITED, VAL D'OR, QUEBEC

by

Leonard G. Ripley*

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SUMMARY OF RESULTS

A suitable procedure has been developed for the determination of microgram quantities of mercury in zinc concentrates. Mercury sulphide in this type of material can be dissolved by a two-step acid treatment. The mercury is then extracted with dithizone chloroform reagent at pH2. The main interferences, copper and silver, are eliminated by extracting their dithizonates with 9N ammonium hydroxide. If copper is present in more than trace amounts, E.D.T.A. is used to complex the bulk of this element, thereby avoiding unnecessary consumption of dithizone. The purified mercury dithizonate is then determined spectrophotometrically at $\lambda=495$ m μ . The standard curve is applicable in the range 0 to 300 micrograms of mercury per 50 ml of dithizone-chloroform reagent.

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INTRODUCTION

Manitou-Barvue Mines Limited, Val d' Or, Quebec, requested that mercury be determined in a sample of their zinc concentrate. This product has been reported to contain mercury in the range of 60 to 80 ppm*.

A semi-quantitative spectrographic analysis was performed at the Mines Branch Laboratories, Ottawa with the following results:

TABLE 1

Semi-quantitative Spectrographic Analysis**

%												
Si	Al	Mn	Fe	Mg	Pb	Ca	Cu	Zr	Zn	Ti	Cd	Hg
3	2	0.02	2	2	0.04	0.2	2	0.01	Pc	0.06	0.5	N.D.

** From Internal Report MS-AC-63-7

Although mercury was reported in Table 1 as "not detected", the threshold sensitivity of this method for mercury is 0.1%; therefore, it could have been present in an amount less than 0.1%.

Microgram quantities of mercury are usually determined spectrophotometrically with diphenylthiocarbazone (dithizone) dissolved in either carbon tetrachloride or in chloroform. This is a very sensitive reagent but it reacts with many elements; however, by controlling the pH, by complexation, and by selective extraction, it can be made specific for mercury (1), (2), (3).

Although this spectrophotometric procedure has been used for the determination of mercury in a variety of organic and inorganic materials, it had never been applied to zinc concentrates.

* This letter is in Appendix I on page 11 of this report.

Mercury is probably present in this zinc concentrate as a sulphide. This compound is difficult to dissolve since it is one of the few sulphides that is very slowly attacked by either hydrochloric or by nitric acid alone. Noyes (4) states that a mixture of hydrochloric and nitric acids, which produces free chlorine, will oxidize mercury sulphide into complete solution. Kozelka (5), on the other hand, observed that the loss of mercury from a digest was greater when the chloride ion concentration in the solution was increased. However, it was reasoned that if careful temperature control were exercised, it should be possible to achieve complete destruction of mercury sulphide with a mixture of hydrochloric and nitric acids without a loss of mercury.

The investigation of the variables and the development of a procedure for the determination of mercury in zinc concentrate was handicapped by the absence of certified mercury standards.

A preliminary report, in the form of a letter*, was sent to Mr. D.A. Livingstone of Manitou-Barvue Mines on June 11, 1963. At that time, a mercury content of approximately 100 ppm was reported.

APPARATUS

1. Leeds and Northrup pH meter equipped with calomel and glass electrodes.
2. Beckman B Spectrophotometer equipped with one-centimeter cells.

REAGENTS

1. Dithizone solution: Dissolve 0.012g of reagent-grade dithizone in 500 ml of chloroform. Prepare fresh daily.
2. Mercury stock solution: Dissolve 0.250g of pure mercury in 30 ml of nitric acid, then dilute with water to 500 ml.
3. Sulphuric Acid (1.8N): Dilute 100 ml of concentrated acid with water to 2 liters.
4. Potassium permanganate (0.5N): Dissolve 15.5g of KMnO_4 in 1 liter of water.

* This letter is in Appendix II on page 12 of this report.

5. Sulphurous Acid solution: Bubble reagent-grade SO_2 into 200 ml of water for 10 minutes. Prepare fresh daily.
6. Ammonium hydroxide (9N): Dilute 600 ml of concentrated NH_4OH with water and make up to 1 liter.

EXPERIMENTAL

Dissolution of zinc concentrate

Early experiments showed that elemental sulphur was formed when the zinc concentrate was heated with aqua regia. Since this sulphur could have occluded some mercury sulphide, this solution procedure was discarded.

Experiments have shown that mercury sulphide present in zinc sulphide concentrates can be completely dissolved by a two-step procedure. The matrix, zinc sulphide, was dissolved with concentrated hydrochloric acid in a covered vessel at room temperature over a twenty-four hour period. Concentrated nitric acid was then added to produce free chlorine which at room temperature during the next twenty-four hour period, completely dissolved the remaining portion of the sample. Although this method was time-consuming, it gave a complete solution. Also, since the solution was not heated, there was no loss of mercury through volatilization.

Preparation of the solution for spectrophotometry

The method of Miller (6) was adopted as a suitable way of preparing the above solution for the spectrophotometric determination of mercury. This method involved oxidation with permanganate to insure that all the mercury was in the bivalent state, and the destruction of the excess permanganate with a slight excess of sulphurous acid*.

One observation of Miller (6) was confirmed in the present investigation. When mercury is present in a sulphuric acid medium, a large excess of sulphurous acid causes errors due to reduction of some mercury to the metal. However, this reduction does not occur in a hydrochloric acid medium.

Variables in the spectrophotometric procedure

The variables in the spectrophotometric procedure, viz. organic solvent, light, pH, shaking time, interferences, spectral transmission

* It has been found desirable to prepare the sulphurous acid daily.

curve, and standard curve were all investigated. The conclusions were as follows:

1. Organic solvent

Mercury can be isolated from a suitable solution by extraction with dithizone dissolved either in carbon tetrachloride or in chloroform as described by Wichmann (1). Since the solubility of dithizone is much higher in chloroform, the author considered this solvent to be more desirable.

2. Light

The adverse effect of light on dithizone and mercury dithizonate has been reported (2), (6), (7). However, Irving et al. (8), who worked in a room with indifferent west lighting in England, did not experience any light effects until March 1946, during the year's first bright sunlight.

In order to assess this variable, part of the present research was carried out in a darkened room that was free of daylight and was lighted only by small indirect electric lamps. The conclusion was that the dithizone solution definitely deteriorates with time even under this limited intensity lighting and that this effect was probably enhanced by sunlight. However, when the dithizone-chloroform reagent was prepared daily, the effects of time and light were insignificant.

3. pH

The pH of the solution controls the selectivity of dithizone for various metal ions. Good recoveries of mercury were obtained at pH 2 and 3, but slightly lower values were obtained at pH 1. A working pH of 2 was selected because, at this value, the other element interferences were minimized with only silver and copper reacting.

4. Shaking time

The shaking time required for the extraction of mercury with dithizone is dependent upon the rate of reaction of dithizone with mercury. The procedure adopted was to add 50 ml of the dithizone reagent and shake with the mercury solution in a separatory funnel.

A 30 sec shake gave at least 95% recovery of the mercury, whereas a 60 sec shake gave complete extraction. A longer shaking time (120 sec) did not affect the results.

5. Interferences

Dithizone reacts in the pH range 1 to 3 with Hg, Cu, Ag, Pd, Au and Pt to form complexes (2), (3). Since X-ray fluorescence did not detect any Au or Pt-Group metals in the extracted dithizonates from the sample in question, the following procedure is based on the assumption that these interfering metals are absent and the main interferents are silver and copper. The interference due to silver and copper can be eliminated in the following manner. The bulk of the copper can be complexed with ethylenediamine tetra-acetic acid (E.D.T.A.) (9). The uncomplexed copper forms a dithizonate that, along with the unreacted dithizone, is soluble in 9N ammonium hydroxide, whereas the mercury dithizonate is not affected (5). Experiments have shown that silver dithizonate is also completely extracted into a 9N ammonium hydroxide solution.

6. Spectral transmission curve

The spectral transmission curve for 50 μg of mercury as the dithizonate is shown in Figure 1. The maximum optical density was obtained at a wavelength of 495 $\text{m}\mu$.

7. Standard curve

The standard calibration curve was prepared from synthetic solutions to which known amounts of mercury had been added. This calibration curve is shown in Figure 2. The resulting curve is linear; therefore, Beers' law is obeyed over the entire scale.

The reagent blank gave an optical density reading of 0.02 which is probably due to a little oxidized product in the dithizone reagent.

PROCEDURE

The following general procedure was consequently adopted:

Weigh a 1 g sample and place in a 500 ml Erlenmeyer flask. Add 10 ml of HCl, cover with lid, and let stand at room temperature for 24 hours. Add 10 ml HNO_3 and let the solution stand at room temperature for a further 24 hours. Wash down the walls of the flask and dilute the solution to 100 ml. Add 25 ml of dilute H_2SO_4 (1.8N) and 10 ml KMnO_4 (0.5N). Transfer the solution to a 600 ml beaker. Add 10 ml of H_2SO_3 to reduce the excess KMnO_4 . Add 1 g of E.D.T.A., which had been dissolved in 20 ml of 1:4 NH_4OH . Adjust the acidity to pH 2 with 1:4 NH_4OH . Cool in a cold water bath to just below room temperature, then transfer to a 500 ml separatory funnel. Add 10 ml of CHCl_3 and shake the resulting solution for 30 sec to saturate the solution with CHCl_3 . Allow the two

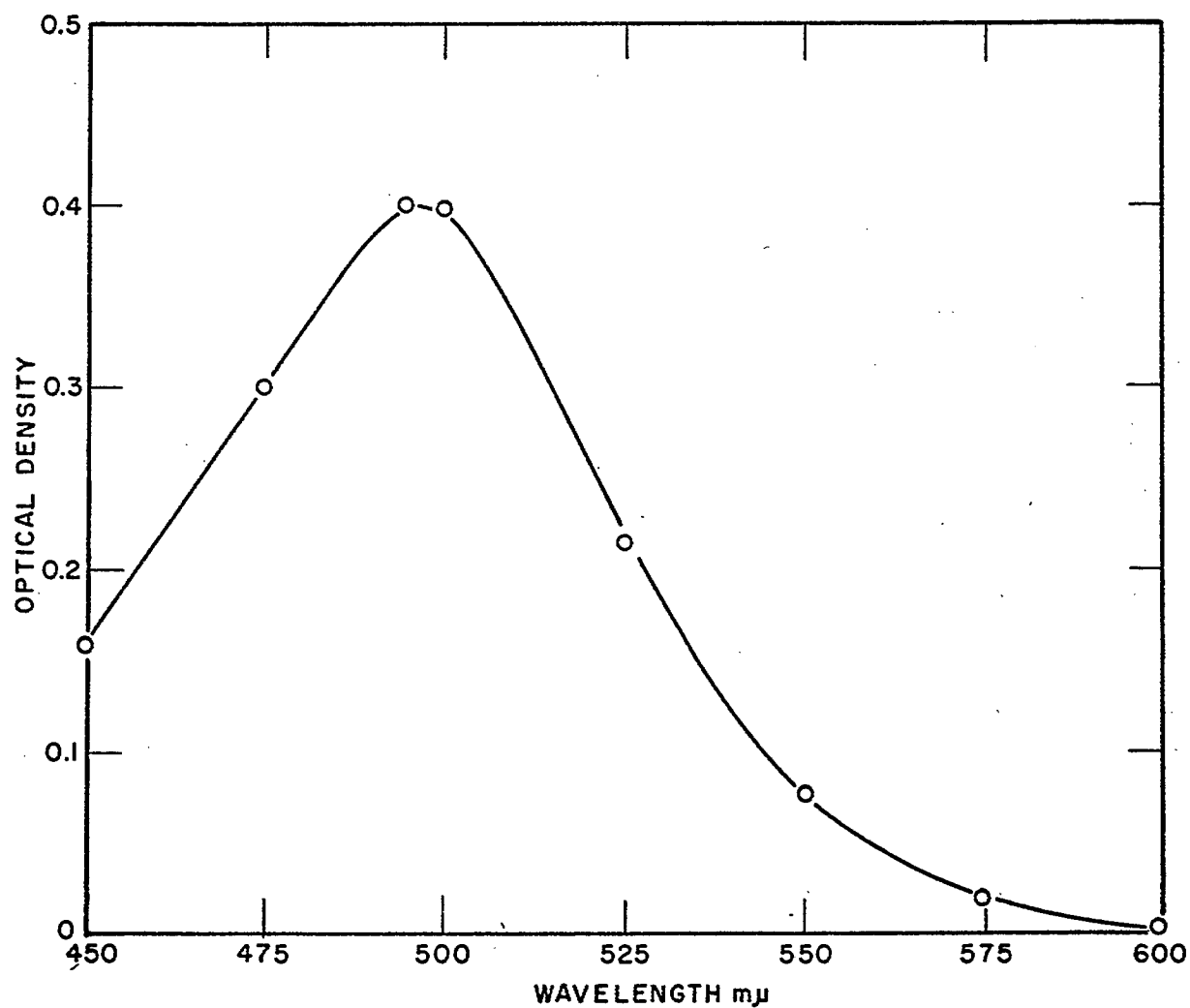


FIGURE I - SPECTRAL TRANSMISSION CURVE FOR MERCURY DITHIZONATE.

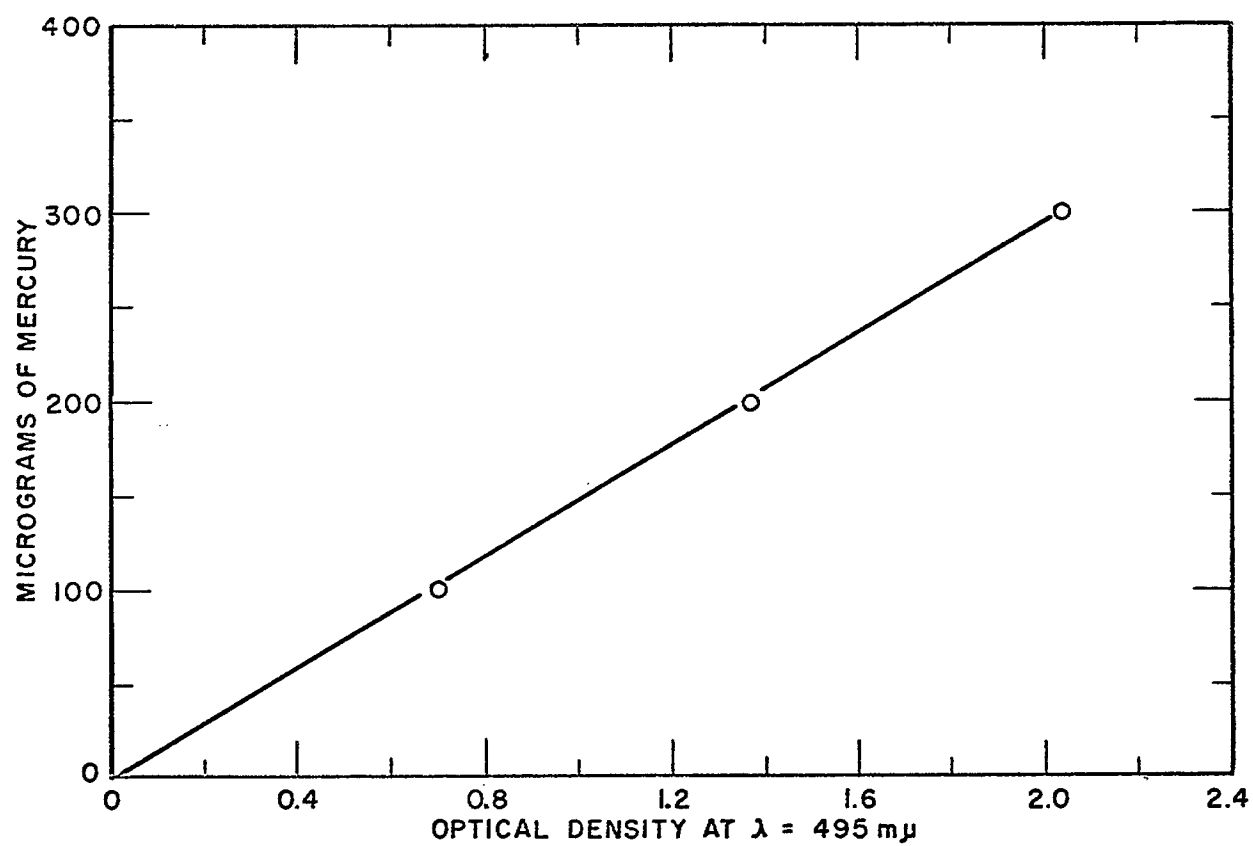


FIGURE 2- CALIBRATION CURVE FOR MERCURY DITHIZONATE.

liquid layers to separate, then remove the excess CHCl_3 and discard it. Add exactly 50 ml of the dithizone-chloroform reagent and shake the solution for 1 minute*. Allow the two liquid layers to separate. Transfer the chloroform layer to a second separatory funnel and add 50 ml of 9N NH_4OH and shake for 30 sec.

Allow the layers to separate. Transfer the chloroform layer to a third separatory funnel and add a second 50 ml of 9N NH_4OH . Shake for 30 sec. Allow the layers to separate. Transfer the chloroform layer to a fourth separatory funnel. Add 25 ml of distilled water and shake for 30 sec. Allow the layers to separate. Wipe out the stem of this fourth separatory funnel with tissue. Draw off some of the chloroform extract into a 1 cm cuvette. Compare this extract against chloroform in the blank cell in the spectrophotometer at $\lambda = 495 \text{ m}\mu$. Calculate the mercury content from the standard curve, that is shown in Figure 2.

RESULTS

Synthetic mixtures of mercury, silver and copper were tested at various pH values; the results are given in Table II.

TABLE II

Recovery of Mercury from Synthetic samples

$\mu\text{g Hg added}$	$\mu\text{g Ag added}$	$\mu\text{g Cu added}$	pH	$\mu\text{g Hg found}$
100	170	5000	1	98
100	170	5000	2	99
100	170	5000	3	98

Undoubtedly, the above-described procedure has yielded an essentially pure solution of mercury dithizonate. X-ray fluorescence examination of this isolated mercury dithizonate indicated that only trace amounts of copper and silver were present.

* Although subdued lighting in the room would be desirable, it was not found to be essential. Also, the burette for the dithizone-chloroform reagent was kept stoppered to minimize evaporation.

The zinc concentrate sample from Manitou-Barvue Mines was assigned the Mineral Sciences Analytical number of 5758 (1962). This sample was analysed as received. Five portions of the sample were analysed as follows:

- (a) on three portions, mercury was determined directly;
- (b) on two portions, known amounts of mercury were added, which were later subtracted to obtain the true mercury value of the sample. The results are shown in Table III.

TABLE III

Mercury Found in the Manitou-Barvue Zinc Concentrate

wt of sample (g)	µg Hg added	ppm Hg found
1.1220	0	118.5
1.0075	0	117
1.0550	0	119
1.0405	50	115 (by diff)
1.0832	100	113 (by diff)

These five portions of the zinc concentrate indicate that the average mercury content is 116.5 ± 2.5 ppm. When the extract of the first sample was examined by X-ray fluorescence, only mercury was detected; but when the extracts from the first three samples were combined, the X-ray fluorescence indicated:

Major = Mercury

Very slight trace = Silver and Copper.

It is assumed that the slight traces of copper and silver would not affect the result appreciably, and it is considered that the mercury content of the Manitou-Barvue zinc concentrate is 116.5 ± 2.5 ppm.

ACKNOWLEDGEMENTS

The author thanks the following personnel: Miss E. Kranck, formerly of the Mineral Sciences Division, Mines Branch, for semi-quantitative spectrographic analysis; and Mrs. D. Reed, Mineral Sciences Division, Mines Branch, for X-ray fluorescence analyses.

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APPENDIX I

October 31st, 1962.

Mr. L. E. Djingheuzian,
Chief, Mineral Processing Division,
Department of Mines and Technical
Surveys,
40 Lydia Street,
Ottawa, Ontario.

Dear Djing:

We have just received word from our zinc concentrate buyer that our product contains 60-80 ppm of mercury, which is reportedly affecting their process adversely.

The presence of this metal in our zinc concentrates comes as a surprise to us, and we have never heard of zinc concentrates containing this contaminant before.

We do not have facilities for determining such small amounts of Hg, nor do we know off hand of a suitable custom laboratory that can do so. Under separate cover we are mailing to your attention approximately 100 grams of our September composite zinc concentrates which we would greatly appreciate having assayed for mercury content, and shall be obliged if you can arrange to have this done for us.

I regret that I was not able to join you at the Conference of Metallurgists at Hamilton in September. In a way I am sorry to see this division in the ranks of the C.I.M., but I suppose this is a natural outcome of growth. If this breach between practical and theoretical metallurgists widens, it will indeed be unfortunate.

I have not heard further from Bob Bruce since his visit here and to Willroy during the summer. I do hope the current austerity program will not entirely cancel your plans for research.

With kind regards,

Yours sincerely,

D.A. Livingstone

APPENDIX II

Mineral Sciences Division

A.T. Prince, Chief.

555 Booth Street,
Ottawa 4, Ontario.
June 11, 1963.

Mr. D.A. Livingstone,
Manitou-Barvue Mines Limited,
Val d'Or, Quebec.

Dear Mr. Livingstone:

Please refer to your letter of Oct. 31, 1962 to
Mr. Djingheuzian.

I must apologize for being so tardy in advising you of the progress of our investigation into the determination of mercury in your zinc concentrate. Actually we tried a number of methods before we found a procedure which might be considered really reliable. While some of the techniques appeared promising we encountered many difficulties in the application to high sulphide material. Now we are confident that we have the problem practically solved. It appears that your concentrate does contain mercury. The amount present is approximately 100 parts per million. We say approximately because the replicate determinations do not check closely enough for us to give a definite figure. The technique is being refined and apparatus modified in an attempt to improve the precision of our method. We hope to send you our method, along with our best results in the near future.

Yours sincerely,

W.R. Inman,
Chief Chemist.

LGR:ST