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**MINES BRANCH INVESTIGATION REPORT IR 67-1**

**APPLICATION OF ATOMIC ABSORPTION  
SPECTROPHOTOMETRY TO ANALYSIS OF MILL  
PRODUCTS FROM METAL MINING OPERATIONS  
2. McINTYRE PORCUPINE MINES LTD.,  
SCHUMACHER, ONTARIO**

by

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**EXTRACTION METALLURGY DIVISION**

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APPLICATION OF ATOMIC ABSORPTION  
SPECTROPHOTOMETRY TO ANALYSIS OF MILL PRODUCTS  
FROM METAL MINING OPERATIONS \*

2. McINTYRE PORCUPINE MINES LTD., SCHUMACHER, ONT.

by

R. J. Guest \*\*

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SUMMARY

Typical mill products from the cyanide leach circuit at McIntyre Porcupine Mines, Ltd., Schumacher, Ontario, have been analysed for gold using atomic absorption spectrophotometry. The results obtained and the analytical method employed are given, and the results are compared to fire assay results obtained at the Mines Branch and at McIntyre. The precision of the values obtained by atomic absorption spectrophotometry has been calculated.

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\* The previous report in this series was

1. Solbec Copper Mines Ltd., Stratford, Quebec  
Mines Branch Investigation Report IR 66-72, September, 1966.

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## INTRODUCTION

In May, 1966, Mr. E. W. Johnson, Mill Superintendent, McIntyre Porcupine Mines Ltd., Schumacher, Ontario, requested to have a number of typical McIntyre samples analysed for gold using atomic absorption spectrophotometry. The purpose of these tests was to establish whether or not this analytical technique would offer any advantages over the fire assay as a mill control method. Samples provided included gold feed, concentrate and tailings, and copper feed, concentrate and tailings, as well as pregnant and barren solutions from the cyanide circuit.

The solid samples as received contained a high proportion of coarse material. To ensure meaningful comparisons between successive tests, they were all reground here to -200 mesh. One bottle of the barren solution was lost enroute through spillage and was replaced by two bottles of barren solution sent from McIntyre.

The instrument used in this investigation was the Techtron Atomic Absorption Spectrophotometer, Model AA-3, with acetylene fuel and air as the support gas.

## EXPERIMENTAL - ANALYTICAL PROCEDURE

### Determination of Gold

#### Outline of the Method

Gold is determined by means of atomic absorption spectrophotometry following its extraction with methyl isobutyl ketone (MIBK) from bromide or chloride medium (1). On many types of solid sample material, an acid leach with bromate and hydrobromic acid provides an effective leach of the gold content even though complete dissolution of the sample may not be obtained(2). A preliminary roast of the sample serves to convert sulfides to oxides, which are more amenable to acid attack.

Solution samples are analysed by extraction with methyl isobutyl ketone from chloride medium after preliminary destruction of cyanide with hydrogen peroxide and hydrochloric acid. If the gold content is sufficiently high, direct atomisation of the cyanide solution may be carried out on some types of solution samples (3).

Apparatus

Techtron Atomic Absorption Spectrophotometer, model AA-3

Separatory funnels, 125 ml and 500 ml

Reagents

Methyl isobutyl ketone, Fisher, analytical reagent grade

Hydrobromic acid, Conc

Hydrobromic acid, 15%

Hydrochloric acid, Conc

Hydrochloric acid, 15 %

Hydrogen peroxide, 30%

Potassium bromate

Standard gold solution: Acid medium

Weigh out an appropriate amount of gold metal or gold cyanide of accurately known gold content and dissolve it in aqua regia. Dilute the solution to the desired volume by diluting the aqua regia to 25% with water and store as a stock solution. Make up dilute solutions as required by evaporating aliquots to dryness on a steam plate in the presence of 2 ml of 1% sodium chloride, then diluting to the required volume in chloride or bromide medium.

Standard gold solution: Alkaline cyanide medium

Evaporate appropriate aliquots of the acid solution to dryness on the steam plate in the presence of 1 ml of 1% sodium chloride solution. Take up the gold salts in a measured synthetic solution containing concentrations of sodium cyanide and calcium oxide similar to those used in the gold mill. Alternatively, take up the gold salts in a portion of the barren solution (of known gold content) from the gold mill concerned.

A. Sample Preparation

I. Ores and Residues

a. Acid Attack: MIBK Extraction Procedure

(i) Acid Attack

Weigh out a portion of the pulverized (-200 mesh) and well-mixed sample, of appropriate size in relation to its gold content

(see Table 1), transfer it to a porcelain dish, and roast it for two periods of 15 minutes each at 750°C (red heat), mixing the sample by stirring between the two heating periods. If less than 10 g of sample is needed, transfer the samples to 150 ml beakers, and at the same time, pipette aliquots of the standard solution, bracketing the concentration range of the samples, into similar beakers. Add about 2g of potassium bromate to each of the beakers. Mix thoroughly and wet with water. Rapidly pour 40 ml of concentrated hydrobromic acid\* into each of the beakers (if it is necessary to take a 10 gram sample, leach it in a 250 ml beaker using 3 g of potassium bromate and 60 ml of concentrated hydrobromic acid). Cover the beaker and warm on the steam bath for one hour with occasional stirring, then transfer it to a low-temperature hot plate and evaporate the solution to a final volume of 20-25 ml.

TABLE 1

Suggested Sample Size for Various Types of Sample Material  
(Acid Attack - MIBK Extraction Procedures)

Sample Type	Gold Concentration oz/ton Au	Sample Size	Gold Present, Approximate Micrograms, Au	Methyl Isobutyl Ketone Added ml MIBK	Acid Washes Required
Barren Solution	.0001	300 ml	1	10	1-2
Pregnant Solution	0.1	5 ml	17	25	0-1
Ores and Residues	0.01	10 g	3	two portions of 10 ml each	2-3
Concentrates	0.5	2 g	35	two portions of 35 ml each	2-3

\* Rapid addition of the hydrobromic acid is necessary in order to provide sufficient solution volume for retention of the bromine produced during the initial violent reaction.

(ii) Extraction

Transfer the entire contents of the beaker (solution and dissolved residue) to a 125 ml separatory funnel, using 30-40 ml of water to effect the transfer and to dilute the acid to approximately 30% in hydrobromic acid.

It is important that the volume of the sample and standard solutions be approximately similar at this point, and that the number and volumes of extractant portions used be the same for any particular group of samples and standards which are to be compared. For this reason, group low-grade samples separately from high-grade samples and analyze each group, with its appropriate standards, using a fixed routine of extractions and washings \*.

Add 10 ml or more of methyl isobutyl ketone depending on the amount of gold present (Table 1), shake vigorously for 3 minutes and allow the layers to separate. Drain off the aqueous layer into a second separatory funnel and extract with the second portion of 10 ml or more of MIBK. Discard the aqueous layer. Wash the organic layers three times by shaking with 40 ml, 25 ml and 25 ml of 15% hydrobromic acid to remove contaminating ions. If the third wash is coloured, continue washing with acid until no further change is noted. Wash the organic fractions consecutively in the order first fraction, then second fraction, using the same wash for each. Combine the organic fractions and transfer them to a suitable container for atomic absorption readings. If blocking of the atomizer occurs, dilute the combined organic fractions with an equal volume of methyl alcohol. If this does not correct the condition, increase the proportion of methyl alcohol in known increments until blocking no longer occurs. If it is found necessary to use methyl alcohol for the samples, dilute the standards with methyl alcohol in exactly the same way. Carry out two or three readings for each determination, reading against MIBK as the blank. Use a recorder for the measurements if greater precision is required.

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\* The relationship between the gold present in the original aqueous solution and the absorbance in the organic medium tends to depart from linearity as the gold content of the MIBK extract increases. In addition, the final volume of the organic extract obtained will depend both on the volume and nature of the aqueous layer, due to the solubility of the organic solvent in the aqueous portion. Although the most accurate procedure would be to transfer the organic layer to a suitable volumetric flask and dilute to the mark with MIBK, we prefer to use the combined organic extracts directly for the atomic absorption spectrophotometry measurement, to shorten the time required for the determination and to aid in providing the higher sensitivity required for the determination of traces of gold.

b. Cyanide Attack

A published procedure (6) using a cyanide leach of the solid sample was tried briefly on two of these samples, the copper feed (EML-192) and the gold tailings (EML-197).

II. Cyanide Solutions

a. Extraction Procedure

(i) Removal of Cyanide

Place an appropriate aliquot of the solution sample in a 250 ml or 400 ml beaker and add 1 ml of 30% hydrogen peroxide. Stir and let stand for five minutes. Add enough hydrochloric acid to make the final aqueous volume about 30% in hydrochloric acid, and let stand for 5-10 minutes with occasional stirring, or, preferably, boil the sample for 1-2 minutes to speed up decomposition of the cyanide. Carry standards through the whole procedure in the same manner as the samples, keeping solution volumes the same.

(ii) Extraction

Transfer the sample to an appropriate size of separatory funnel, add 10 ml or more of MIBK (see Table 1, page 3, and footnote\*\* page 4) and shake the mixture for three minutes. Allow the layers to separate and drain the organic layer into an appropriate container preparatory to atomic absorption spectrophotometry. If necessary, wash the organic fraction with 15% hydrochloric acid solution to remove any solid or highly colored material which may be present.

b. Direct Procedure

Atomize the cyanide solution directly and compare readings with standards prepared as described under EXPERIMENTAL (page 2). Sensitivity is much less than with the organic extraction procedure, and the lower limit with this procedure using our equipment was approximately 0.005-0.01 oz/ton, as compared to a limit of 0.0001 oz/ton using the extraction procedure.

B. Atomic Absorption

Instrumental conditions were as follows(4): hollow cathode lamp current, 4 mA; wavelength, 2427A°; slit width, 300 microns; a 10 cm narrow-slit burner; and acetylene fuel with compressed air as the support gas.

## RESULTS AND DISCUSSION

Results obtained by atomic absorption spectrophotometry were compared with fire assay results found here using different cuts from the same sample, and with analyses provided by McIntyre. This comparison, as shown in Table 2, indicated that results between methods were generally in good agreement although some discrepancies were noted. For example, on the copper tails (EML-194), results by atomic absorption agreed with fire assay results here, but not with those provided by McIntyre. Also, on the gold concentrate (EML-196), atomic absorption results were consistently higher than those obtained by fire assay.

The most surprising results are those shown for the copper feed (EML-192). The result by fire assay here was considerably higher than that provided by McIntyre, while atomic absorption results agreed with both laboratories when different cuts of the sample were analysed and different size samples were taken. It was concluded that non-homogeneity of the sample was probably responsible for this disparity. Preliminary results on all the solid samples showed poor agreement and since the grind of these materials appeared somewhat coarse, it was decided to regrind each sample to -200 mesh. Following this additional sample preparation, agreement markedly improved and the earlier results were discarded. Apparently, however, the problem of non-homogeneity on the copper feed was not completely solved by regrinding.

The precision obtained on these samples using atomic absorption spectrophotometry was calculated according to the method of Dean and Dixon (5) and is shown in Table 3. It was found that McIntyre solid samples were amenable to treatment by the described procedure but that the precision obtained was not quite as good as that found here on some other types of ores. There could be at least an average risk, then, in carrying out a determination in singlicate, rather than in duplicate or triplicate. Two possible sources of error are believed to be a) non-homogeneity of the samples with regard to the state in which the gold is found, and b) irregularity in the effectiveness of the acid leach, especially on poorly ground and/or mixed samples.

There was no apparent difficulty arising from the presence of contaminants in the samples. Also, the mechanical handling of these samples during the extraction and atomization steps was satisfactory, with no difficulty being noted due to blocking of the atomizer, as had occurred with some other types of samples.

Any appraisal of the time requirements for analysis must, of course, take into consideration the precision and accuracy desired by the individual laboratory. With this in mind, therefore, it might be estimated that



TABLE 2

Comparison of Gold Results by Atomic Absorption and Fire Assay

Sample Number EML-	Sample Type	Gold Found - oz/ton Au *					Remarks
		Fire Assay		Directly by Atomic Absorption	Solvent Extraction Atomic Absorption		
		McIntyre	Mines Branch		Series No. 1 **	Series No. 2 ***	
192	Copper feed	0.015	0.0225 (6)	-	0.014 (6)	0.020 (7)	-
193	Copper conc	0.525	0.44 (4)	-	0.49 (6)	-	-
194	Copper tails	0.009	0.004 (5)	-	0.003 (1)	0.003 (2)	-
195	Gold feed	0.27	0.24 (4)	-	0.26 (8)	-	-
196	Gold conc	1.41	1.36 (4)	-	1.55 (13)	-	Sample size of 1 gram or less for atomic absorption
197	Gold tails	0.015	0.015 (6)	-	0.015 (5)	0.017 (2)	-
198	Pregnant solution	0.11	-	0.12	0.13 (8)	-	3, 4 and 5 ml samples
224	Barren solution	-	-	-	<0.0001 (2)	-	100 to 300 ml samples
225	Barren solution	-	-	-	<0.0001 (3)	-	100 to 300 ml samples

\* bracketed figures refer to number of determinations carried out.

\*\* series No. 1 - 5 g or less samples.

\*\*\* series No. 2 - 10 g samples.

TABLE 3

Precision Found for Gold Determinations on McIntyre Samples

Sample Number EML-	Sample Type	Individual Determinations by Atomic Absorption Following Solvent Extraction oz/ton	Average Result Oz/ton	Precision	
				Standard Deviation	95% Confidence Limit For Average Result
192	Copper feed	A 0.014, 0.015, 0.017, 0.013, 0.013, 0.013	0.014	$\pm 0.002$	$\pm 0.002$
		* 0.020, 0.021, 0.018,	0.020	$\pm 0.001$	$\pm 0.001$
		B 0.019, 0.018, 0.022, 0.022			
193	Copper conc	0.59, 0.48, 0.53, .44, 0.47, 0.46	0.49	$\pm 0.057$	$\pm 0.057$
194	Copper tails	0.003, 0.003*, 0.003*	0.003	$\pm 0.0002$	$\pm 0.0006$
195	Gold feed	0.34, 0.23, 0.22, 0.26, 0.29, 0.25, 0.22, 0.29	0.26	$\pm 0.041$	$\pm 0.037$
196	Gold conc	1.59, 1.75, 1.70, 1.69, 1.70, 1.53, 1.59, 1.29, 1.29, 1.50, 1.42, 1.51, 1.64	1.55	$\pm 0.14$	$\pm 0.10$
197	Gold tails	0.014, 0.014, 0.014, 0.016, 0.011, 0.019*, 0.015*	0.015	$\pm 0.003$	$\pm 0.003$
198	Pregnant solution	0.13, 0.14, 0.13, 0.13, 0.13, 0.15, 0.13	0.13	$\pm 0.009$	$\pm 0.008$

\* 10 gram samples whereas all other solid samples were 5 grams.

On sample 192, two cuts of the main sample were analysed using atomic absorption spectrophotometry.

gold analysis of twenty solid samples, after dissolution of sample and using a double extraction technique, could require 5 to 6 hours for the extraction and atomic absorption steps. It has been found, however, that solution samples can be analysed for gold using a single extraction technique, thereby virtually cutting in half the estimated time requirement for the above number of samples with little or no apparent loss in precision and accuracy. A considerable saving in time could be obtained by using a single extraction technique on solid samples but less precision and accuracy could be expected due to the presence of undissolved residue during the extraction step.

Changing flame conditions make it necessary to redraw calibration curves with each set of samples carried out, and it is always advisable to have the standards bracketing the samples if high accuracy is to be expected. This is, at least in part, because the volume of the organic layer will change in relation to the volume and nature of the aqueous layer during the extraction step, due to the solubility of the organic fraction in the aqueous fraction. A more accurate procedure, where time permits, is to transfer the organic layer to a suitable volumetric flask and dilute to the mark with MIBK, thus nullifying variations due to volume changes, although causing some loss of sensitivity.

To illustrate the sensitivity which may be expected, typical calibration curves in aqueous and organic media are shown in Figure 1. It is anticipated that the addition of a scale expander to the apparatus would extend the sensitivity of the procedure.

These results suggest that the described procedure could be a suitable alternative to the fire assay procedure for gold analysis on McIntyre solid sample material. Analysis of the McIntyre solution samples indicated that atomic absorption spectrophotometry would also be suitable for this type of sample.

The direct cyanide attack of solid samples, however, did not appear promising from the brief tests carried out. Gold results following the cyanide leaching were low and erratic, with no result being as high as 75% of the known gold content.

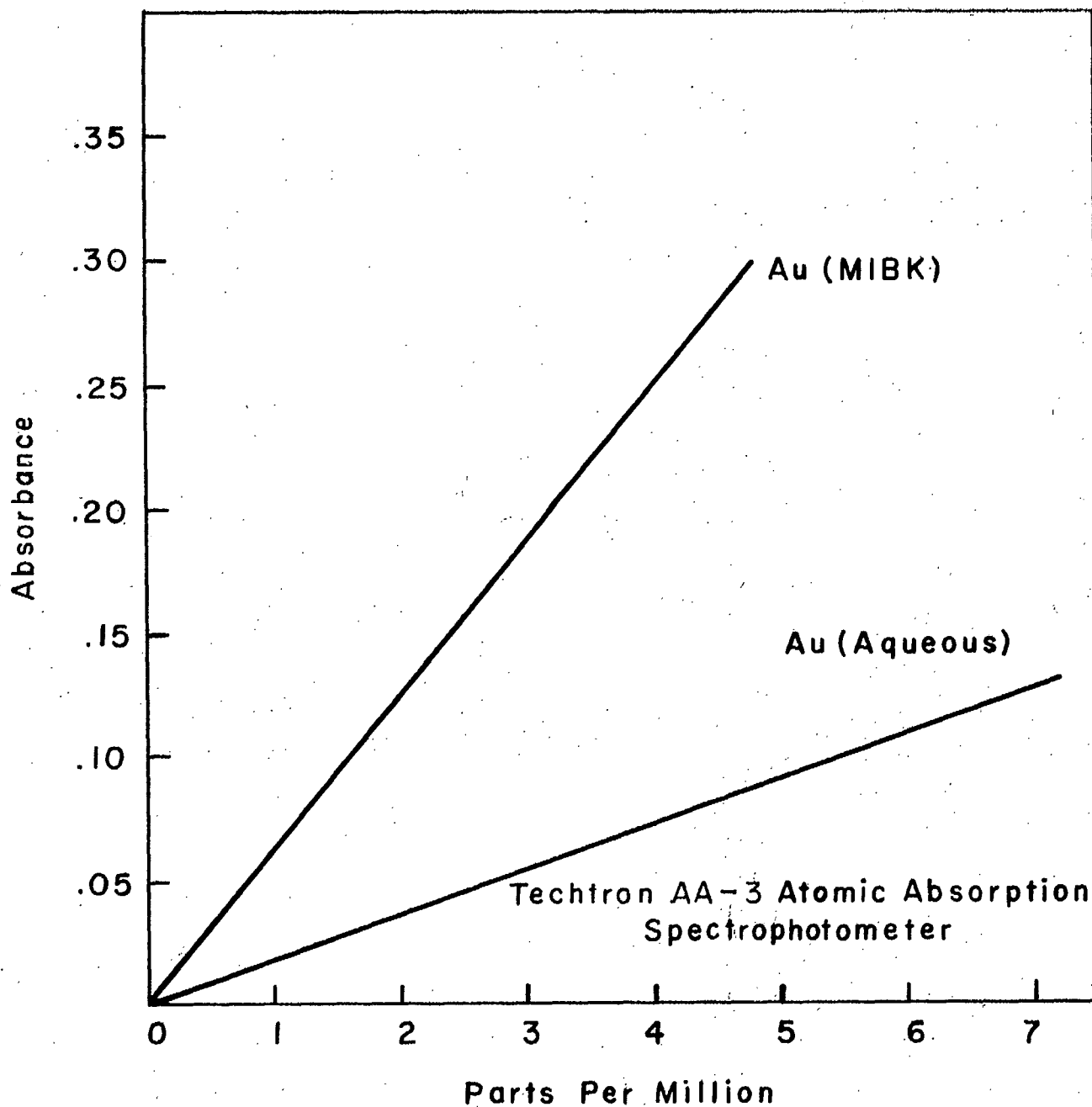


Figure 1. Comparative sensitivities of gold in aqueous and organic media, as determined by atomic absorption spectrophotometry.



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