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

3. COCHENOUR WILLANS GOLD MINES LIMITED, COCHENOUR, 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*

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SUMMARY

Representative mine samples from Cochenour Willans Gold Mines Limited have been analysed for gold using atomic absorption spectrophotometry. The analytical method used is given, and the results compared with fire assay results obtained at the Mines Branch and at Cochenour Willans. The precision of the values obtained by atomic absorption spectrophotometry has been calculated.

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* The previous reports in this series were

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

2. McIntyre Porcupine Mines Ltd., Schumacher, Ontario
   Mines Branch Investigation Report IR 67-1, January, 1967.

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INTRODUCTION

A request was received from D. A. Hutton, Chief Geologist, Cochenour Willans Gold Mines Limited, Cochenour, Ontario, to undertake experimental work to determine the applicability of atomic absorption spectrophotometry to the determination of gold on Cochenour Willans' ore. A series of ten representative samples was provided, and gold results as determined by fire assay at Cochenour Willans were supplied to permit comparisons with results obtained here by atomic absorption spectrophotometry. As coarse material was found in some of the samples, all the samples were reground here to -200 mesh, to minimize the effects of sample segregation on comparisons of values.

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 medium. 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 (1). A preliminary roast of the sample serves to convert sulfides to oxides, which are more amenable to acid attack.

Apparatus

Techtron Atomic Absorption Spectrophotometer, model AA-3

Separatory funnels, 125 ml

Reagents

Methyl isobutyl ketone, Fisher, analytical reagent grade

Hydrobromic acid
Hydrobromic acid, 15%

Potassium bromate

Standard gold solution:

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 and several drops of concentrated hydrochloric acid. Dilute to the required volume in strong bromide or chloride medium.

Procedure

a. Sample Dissolution

Weigh out a portion of the pulverised (-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 a dilute standard gold solution, bracketing the concentration range of the samples, into similar beakers. Add about 2 g 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 g 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.

b. Extraction

Transfer the entire contents of the beaker (solution and undissolved 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.

* 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.

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 and, if necessary, 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.

c. Atomic Absorption

Instrumental conditions were as follows(2): hollow cathode lamp current, 4 mA; wave length, 2427 A°; slit width, 300 microns; a 10 cm narrow-slit burner; and acetylene fuel with compressed air as the support gas.

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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.

TABLE 1

Suggested Sample Size for Various Types of Sample Material

Sample Type	Gold Concentration oz/ton Au	Sample Size grams	Gold present, Approx. Micrograms Au	Methyl Isobutyl Ketone Added ml MIBK	Acid Washes Required
Ores and Residues	0.01	10	3	two portions of 10 ml	2-3
Ores and Residues	0.1	5	17	two portions of 20 ml	2-3
Concentrates	0.5	2	34	two portions of 35 ml	2-3

d. The Samples

A mineralogical description of the samples abstracted from a letter dated May 19, 1966, from Mr. Hutton, Chief Geologist of Cochenour Willans, is given in Table 2.

RESULTS AND DISCUSSION

A comparison of early results obtained by atomic absorption spectrophotometry with fire assay results supplied by Cochenour Willans showed poor agreement on most samples. Accordingly, two steps were taken to reduce the differences: 1) regrinding of the samples to -200 mesh and subsequent repeating of analyses by the atomic absorption procedure; and 2) submission of the reground samples to the Mines Branch fire assay laboratory for analysis.

TABLE 2

Mineralogical Description of Cochenour Willans Ore Samples Supplied by Cochenour Willans

Cochenour Willans No.	EMM No.	Mineralogy
20500	249	Siliceous: Aspy - Py - V.G.
20595	250	Siliceous and Carb: Py - V.G.
20506	251	Carb: Aspy - Py - V.G.
20308	252	Talc: Py - Po - Aspy
20310	253	Carb: Aspy
20315	254	Talc: Aspy - Po - Py - V.G.
20382	255	Chert: Po - Py - Fe_3O_4 - Aspy
20651	256	Carb and Sil'd Lava: Po - Py - Aspy - V.G.
20652	257	Talc: Po - Py - Aspy - V.G.
20644	258	Talc: Po - Py - Aspy - V.G.

Carb: - Carbonate
Aspy: - Arsenopyrite
Py: - Pyrite
Po: - Pyrrhotite
V.G. - Virgin (free) gold

As shown in Table 3, results were in good agreement between atomic absorption spectrophotometry and both fire assay laboratories on only two samples (EMM 251 and 255). On seven other samples atomic absorption spectrophotometry showed greater agreement with the Mines Branch fire assay laboratory than with the Cochenour Willans laboratory. On one sample (EMM 258) the atomic absorption result was not in agreement with either fire assay laboratory. In all instances other than one (EMM 257) in which disagreement was found between Cochenour Willans and the other two laboratories, the Cochenour Willans result was the lowest reported.

TABLE 3

Comparison of Results by Atomic Absorption and Fire Assay

Sample Number EMM-	Sample Type	Atomic Absorption oz/ton Au	Fire Assay	
			Lab No. 1 * oz/ton Au	Lab No. 2 ** oz/ton Au
249	Siliceous	0.69 (10) ***	0.64 (2)	0.56
250	Siliceous and Carbonate	1.13 (15)	0.99 (2)	0.76
251	Carbonate	0.235 (6)	0.235 (2)	0.24
252	Talc.	0.37 (9)	0.32 (3) ****	0.24
253	Carbonate	0.34 (5)	0.35 (2)	0.24
254	Talc.	2.59 (6)	2.80 (2)****	2.00
255	Chert.	0.15 (4)	0.165(3)****	0.16
256	Carbonate and Sil'd lava	0.41 (6)	0.405(2)	0.32
257	Talc.	0.21 (6)	0.21 (2)	0.32
258	Talc.	0.95 (10)	0.80 ****	0.84

* Mineral Sciences Division
** Cochenour Willans Laboratory
*** Bracketed figures refer to number of determinations
**** Difficulty in obtaining suitable lead button (5).

The precision found for the atomic absorption procedure on the reground samples was calculated using procedures described by Dean and Dixon (3), and by Bauer (4). As shown in Table 4, the precision found varied considerably with the type of ore, indicating that replication of analyses is required to obtain good precision with this type of sample. The large spread found on certain samples (e.g. EMM 250) is not easily understood. It is believed, however, that two main sources of error are : a) varying efficiency of the acid leach on different types of ore, and on poorly ground and/or mixed samples, and b) non-homogeneity of the samples with regard to the form in which the gold occurs.

Handling of the samples was satisfactory with no blocking of the atomizer occurring, and no apparent difficulty arising from the presence of contaminants.

Any evaluation of the time requirement for analysis must consider the needs of the laboratory concerned with regard to precision and accuracy. It could be estimated that gold analysis of twenty solid samples, using a double extraction technique, would require 5 to 6 hours for the extraction and atomic absorption steps (exclusive of sample dissolution). This would be reduced to about 3 hours if a single extraction technique was used, instead of the described double extraction procedure. With the single extraction technique, however, the increased risk of loss of gold, due in part to the presence of undissolved residue during the extraction step could lead to poorer accuracy and precision.

It is advisable to run standards and redraw calibration curves with each set of samples analysed. If high accuracy is desired, it is also necessary to have the standards bracketing the samples. This is made necessary because of changing flame conditions, and also because of changes in the relationship between the volumes and nature of the organic and aqueous layers resulting from the solubility of the organic fraction in the aqueous fraction. A more accurate, but slightly longer, procedure 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 in sensitivity.

The typical calibration curves shown in Figure 1 illustrate the sensitivity found here in aqueous and organic media. Addition of a scale expander to the apparatus would be expected to increase the sensitivity of the procedure.

TABLE 4

Precision Found For Gold Determinations on Cochenour Willans Samples

Sample Number EMM-	Ore type	Following solvent extraction, Individual Determinations By Atomic Absorption oz/ton Au	Average Gold Found oz/ton Au	Precision	
				Standard Deviation	95% Confidence Limit for Average Result
249	Siliceous	0.61, 0.72, 0.91, 0.72, 0.65, 0.74, 0.59, 0.80, 0.51, 0.64	0.69	0.13	± 0.092
250	Siliceous and Carb	1.38, 1.52, 1.53, 1.24, 1.22, 1.08, 1.04, 1.23, 0.91, 0.87, 0.91, 0.96, 0.94, 0.97, 1.17	1.13	0.20	± 0.10
251	Carb.	0.23, 0.22, 0.25, 0.18, 0.28, 0.25	0.23	0.0395	± 0.041
252	Talc.	0.37, 0.38, 0.37, 0.35, 0.47, 0.32, 0.40, 0.34, 0.36	0.37	0.0505	± 0.038
253	Carb.	0.41, 0.34, 0.33, 0.28 0.35	0.34	0.056	± 0.068
254	Talc.	2.21, 2.70, 3.24, 2.33 2.67, 2.37	2.59	0.41	± 0.42
255	Chert.	0.15, 0.15, 0.15, 0.15	0.15	0.003	± 0.005
256	Carb. and Sil'd Lava	0.42, 0.45, 0.35, 0.46 0.36, 0.43	0.41	0.044	± 0.045
257	Talc.	0.26, 0.20, 0.19, 0.20, 0.20, 0.21	0.21	0.028	± 0.029
258	Talc.	1.06, 0.96, 0.93, 1.07, 0.94, 0.93, 1.01, 0.89, 0.77, 0.92	0.95	0.098	± 0.069

To summarize, the precision obtained for gold using atomic absorption on Cochenour Willans ore was not entirely satisfactory. That the problem of obtaining satisfactory precision has been encountered elsewhere by both atomic absorption and fire assay procedures is shown in reports by Tyndall (6) and Simmons (7). Our experience has been that the precision found is affected as much by the sample particle size and the dissemination of gold in the sample as by differences in the two analytical procedures used. It is felt, therefore, that the atomic absorption procedure is suitable for Cochenour Willans ore as an alternative to the fire assay procedure providing replicate determinations are carried out. Although the atomic absorption procedure for gold could require a longer time to carry out than the fire assay procedure, it presents certain advantages such as portability of the procedure and the small amount of sample required for an analysis.

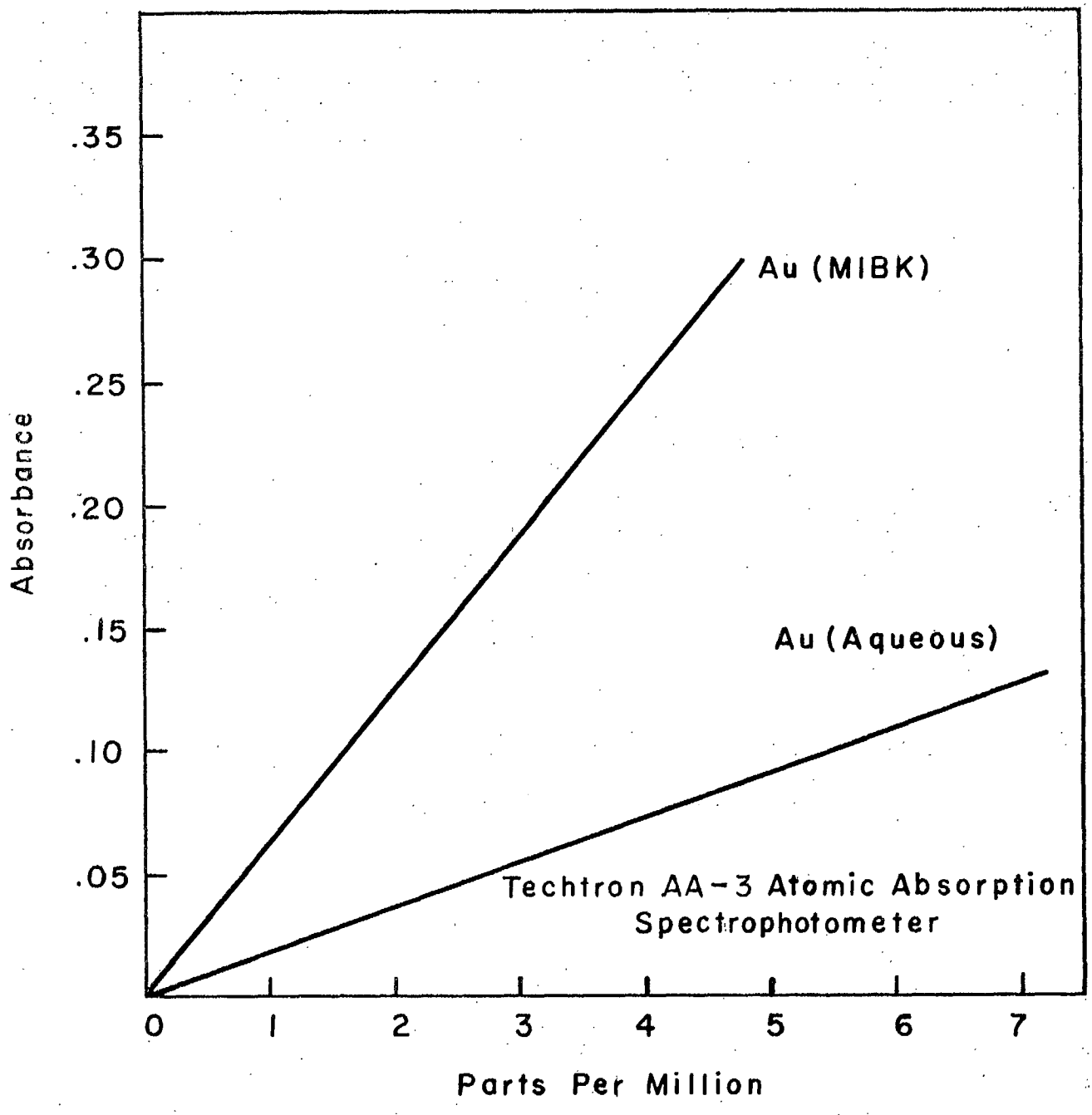

Figure 1. Comparative sensitivities of gold in aqueous and organic media, as determined by atomic absorption spectrophotometry.

REFERENCES

1. "Simplified Spectrophotometric Determination for Gold", by H.W. Lakin, and H.M. Nakagawa, Engineering and Mining Journal, 166, 108-10 (1965).

2. Techtron Instruction Manual for the Atomic Absorption Spectrophotometer, Model AA3, Techtron Pty. Ltd., Melbourne, Victoria (third reprint, 1965).

3. "Simplified Statistics for Small Numbers of Observations" by R.B. Dean and W.J. Dixon, Anal. Chem., 23, 636-8 (1951).

4. "A Statistical Manual for Chemists", by Edward L. Bauer, Academic Press, New York, pp 16-18 and 137-8 (1960).

5. C. Derry (verbal communication).

6. "Atomic absorption and X-ray fluoresence applications at Duval's Laboratories", by Frank W. Tyndall (Duval Co.), paper presented at the Conference of Metallurgists, Toronto, August 30, 1966.

7. "Gold Assay by Atomic Absorption Spectrophotometry", by E.C. Simmons, Atomic Absorption Newsletter (Perkin-Elmer Corp), 4, 281-7 (1965).

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