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

6. UPPER CANADA MINES LTD., DOBIE, ONT.

by

R. J. Guest

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

Analytical procedures are described for the determination of gold and copper on several types of sample material from Upper Canada Mines and Upper Beaver Mines. It is shown that both elements can be determined on the same portion of the sample solution if a hot aqua regia attack is used. If the gold determination only is required, cold aqua regia attack is adequate. Gold is extracted with methyl isobutyl ketone and atomized in the organic medium, while copper is determined directly on the diluted sample solution either before or after extraction of gold. The formation of emulsions during gold extraction on some samples presented special problems which were overcome by including a filtration step in the procedure, and by taking suitable precautions during the scrubbing of the organic fraction.

Results obtained were compared with those provided by Upper Canada Mines and the two procedures showed satisfactory agreement for both elements. The precision found was calculated where four or more results were available. As an aid to the Mine's evaluation of the adaptability of atomic absorption procedures to its process control, an estimation of the time requirement for analyses is provided.

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INTRODUCTION

A request was received from Mr. E. Marcotte, Mill Superintendent, Upper Canada Mines Ltd., Dobie, Ont., for an evaluation of the suitability of atomic absorption spectrophotometry for the analysis of gold and copper. It was understood that Upper Canada Mines was interested in 1) analysing for both gold and copper on the same sample, and 2) obtaining information on the accuracy and precision obtainable, especially for copper on copper concentrates, using atomic absorption procedures.

Nine samples were submitted, three from Upper Canada Mines, and six from Upper Beaver Mines. The samples from Upper Beaver Mines included samples from three shipping lots of copper concentrates. For comparison purposes, Upper Canada Mines provided analysis results for gold on all samples, and for copper on three copper concentrates and one head sample.

Gold and copper were determined following aqua regia attack, and copper determined following multi-acid attack. In the latter procedure, complete dissolution of the sample was obtained and copper determinations were carried out on these samples for comparison with results obtained following aqua regia attack in which complete dissolution of the sample was not obtained. It was considered desirable to use an aqua regia attack, either hot or cold, because of the speed obtainable, and the suitability of the medium for rendering gold soluble and maintaining its solubility.

The procedure for gold was based on one described in earlier reports in this series. Modifications were necessary because of the formation of emulsions during the extraction of gold with methyl isobutyl ketone, and because of the requirement to determine copper on the aqueous portion either before or after gold extraction.

EXPERIMENTAL - ANALYTICAL PROCEDURE

An acid attack with aqua regia is used on the sample, and, although complete dissolution is not obtained by this treatment, the gold and copper content is effectively leached providing the sample is adequately ground. Filtration and washing of the insoluble residue is carried out and, following dilution to volume, separate aliquots are analysed for gold and copper. Gold is extracted with methyl isobutyl ketone (1) following adjustment of the chloride content to approximately 25% hydrochloric acid, and atomized from the organic medium, while copper is atomized directly from aqueous medium either before or after gold extraction.

Sample dissolution

Weigh out an appropriate sample (0.3 - 15 g) of the well-pulverized ore (minus 200-mesh) into a 300-ml Erlenmeyer flask and add 40 ml of aqua regia. Place the flask on a low-temperature hot plate and heat below boiling for 1 to 2 hours with periodic shaking to assure adequate sample contact with the acid. Alternatively, shake the flask in the cold for 1 to 2 hours using a suitable mechanical shaker to assure adequate mixing. Filter the sample using a Buchner funnel and Whatman No. 3 paper, washing the residue well with water or weak hydrochloric acid solution. Transfer the filtrate and washings into a volumetric flask and make up to volume with water. Using aliquots of this solution, determine gold and copper as described.

Determination of Gold

Extraction

Transfer an appropriate portion (Table 1) of the sample solution into a separatory funnel capable of holding approximately 150 ml and dilute to 100 ml with water. Carry an aliquot of a standard gold solution through the procedure from this point, having made the acidity conditions similar to that of the sample. The volume of the sample and standard solutions should be approximately similar at this point, and the number and volumes of extractant portions used should be the same for any particular group of samples 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 (a).

Add 10 ml or more of methyl isobutyl ketone (Fisher), depending on the amount of gold present (Table 1), shake vigorously for 2 minutes and allow the layers to separate. Drain off and discard the aqueous layer. Wash the organic layer three times by shaking with 30 ml of 15% hydrochloric acid to remove contaminating ions. If the third wash is coloured, continue washing with acid until no further change is noted. The organic fraction is now ready for atomization unless it is cloudy. In this case, filter a portion of the organic fraction through a Whatman No. 40 filter paper and collect the filtrate in a small test tube or other suitable container before atomizing the sample.

Atomic Absorption Measurement

Carry out two or more atomic absorption readings and compare the readings with those obtained on prepared standards read at the same time as the samples (b). Use a recorder for the measurement if greater precision is required.

For details of the operating procedure refer to APPENDIX 1.

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- (a) 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 more accurate procedure would be to transfer the organic layer to a suitable volumetric flask and dilute to the mark with MIBK, for most work, we prefer to use the organic extracts directly for the atomic absorption measurement. This shortens the time and provides the higher sensitivity required for the determination of traces of gold.
- (b) Some loss of accuracy would be caused by using standard curves because of the difficulty of obtaining identical operating parameters each time an analysis is carried out.

After the sample has been filtered and diluted to volume, transfer an appropriate aliquot of the sample solution into a second volumetric flask of a suitable size (Table 1), add enough perchloric acid to make its strength 1% in the final solution, and dilute to volume with water.

Atomic Absorption Measurement

Carry out two or more atomic absorption readings and compare the readings with those obtained on prepared standards read at the same time as the samples (see footnote (b), page 3).

For details of the operating procedure refer to APPENDIX 2.

TABLE 1

Suggested Sample Size for Gold and Copper Determination on Various Types of Sample Material

Sample Type	Sample Size g	Gold Present oz/ton Au	MIBK used for Gold Analysis ml	Copper Present % Cu	Dilution for	
					Gold	Copper
					ml	ml
Upper Canada Heads	5.0	0.30	25	0.04	100/90	100/10 x 50
Upper Canada Tails	15.0	0.02	15	0.03	100/95	100/5 x 50
Upper Beaver Heads	5.0 5.0	0.24	25	1.80	100/98	100/2 x 500
Upper Beaver Tails	10.0	0.03	15	0.06	100/95	100/5 x 100
Upper Beaver Conc	0.5	3.00	25	25 - 30	100/98	100/2 x 500

RESULTS AND DISCUSSION

Early tests carried out on this material to evaluate an extraction procedure for gold from strong hydrochloric acid solution, using methyl isobutyl ketone, and following aqua regia attack, met with only partial success due to emulsion formation. Extractions were made on a) the sample solution containing undissolved residue, b) a centrifuged portion of the sample, and c) the sample solution following filtration.

Of these procedures, c) proved to be superior as emulsion formation during the extraction step was less than with the other two procedures. It was found that both Upper Canada and Upper Beaver ore were considerably more prone to emulsion formation than most other Canadian ores analysed in our laboratory and that our usual extraction procedure a) was not very suitable. Following filtration, however, emulsion formation during extraction was considerably reduced and layer separation was possible, although slower than when analysing many other types of sample material. A preliminary sample roasting step was tried but did not lessen this emulsion effect. It was found that careful scrubbing of the organic fraction with weaker acid was helpful in achieving a clean separation, although here again, layer separation was slower than usual.

Atomic absorption gold results agreed very well with fire assay results on head samples and copper concentrates but tended to be lower for tailing samples (Table 2). Little difference was found in results by using either a hot or a cold aqua regia leach. Analytical agreement between atomic absorption and fire assay tended to become better on the mill-control samples, however, when the samples were reground to 200- mesh before atomic absorption treatment.

As insufficient sample was available to carry out fire assays here, we were unable to resolve the small remaining differences between the two procedures. It was felt, however, from the evidence obtained, that agreement was sufficiently good that the atomic absorption procedure would serve satisfactorily for the determination of gold on mill-control work.

Test work on atomic absorption determination of copper centred on the leaching efficiency for copper with an aqua regia attack as compared to a multi-acid, complete, sample-dissolution procedure. Comparison of hot and cold aqua regia attack showed that copper results were consistently higher following the hot acid treatment of tailing and concentrate samples (Table 3).

Results compared well with those found by multi-acid treatment, in which complete dissolution of the samples was obtained, and with results provided by Upper Canada Mines.

It was concluded, therefore, that a hot aqua regia attack was the preferred sample treatment. A cold aqua regia attack could probably be quite satisfactory, however, for most mill-control work especially if a correction factor were applied for sample material which remained constant as to copper content.

The precision found for the determination of the two elements was calculated according to the procedure of Dean and Dixon (2) and Bauer (3), where four or more results were available. These results as shown in Table 4 indicate that atomic absorption procedures for gold and copper are well suited for mill-control and many other purposes. It will be noted that the precision reported for gold on the head sample from Upper Canada Mines was not very satisfactory, primarily because of one result which was suspected to have been caused by a variable amount of free gold present. Spurious results such as these are often encountered in fire assay work, although the effect of sample variation is moderated because of the large sample size taken for fire assay (4,5,6). Other atomic absorption results much closer to the average value were obtained on the Upper Canada head sample, but, as minor changes in the procedure were made they were not included in calculating the precision.

Because of variations in laboratory organization and requirements for precision and accuracy, it is difficult to predict the potential analytical throughput. It is estimated, however, that twenty samples could be analysed for both gold and copper within a 3-hour interval. At the same time as these samples are being processed, further sets of samples could be started on the analysis stream, with the final throughput dependent on such factors as available personnel and space, as well as the precision and accuracy required.

The recommended procedure (7) for using the atomic absorption spectrophotometer and hollow-cathode lamps was suitable for this work. The cost of our atomic absorption equipment, including the spectrophotometer, hollow-cathode lamps, chart recorder and digital readout, would be about eleven thousand dollars. The price range on this type of equipment is quite wide depending on the analytical requirements; however, some instruments with accessories may be purchased at prices beginning at less than four thousand dollars. A large cylinder of acetylene (about 300 cu. ft) would last from one to two weeks, assuming that the spectrophotometer was in almost constant use for one eight-hour shift each day.

TABLE 2

Comparison of Results for Gold by Atomic Absorption and
Fire Assay Procedures

Sample Type	% Of Plus 200-Mesh Ore Present Before Regrinding	Gold Present (c) oz/ton Au	Gold Found oz/ton Au		
			Cold Aqua Regia Leach (Sample as received)	Hot Aqua Regia Leach (Sample as received)	Cold Aqua Regia Leach Following Regrinding to Minus 200-mesh
Upper Canada Heads	-	0.33	0.32(4)	-	-
Upper Canada Tails	23.0	0.022	0.016(4)	0.017(2)	0.0185(2)
Upper Canada #8 Agitator	19.0	0.034	0.028(4)	0.029(2)	0.032(2)
Upper Beaver Heads	-	0.24	0.25(6)(d)	-	-
Upper Beaver Flotation Tails	29.0	0.030	0.026(4)	0.023(2)	0.028(2)
Upper Beaver De-watering Tails	0.1	0.010	0.009(4)	0.009(2)	0.009(2)
Shipping Lot 41	-	3.30	3.20(4)	-	-
Shipping Lot 42	-	3.29	3.38(4)	-	-
Shipping Lot 43	-	3.02	3.14(4)	-	-

(c) Results provided by Upper Canada Mines Ltd.

(d) Average results of analyses on Roasted and Unroasted samples.

TABLE 3

Comparison of Results for Copper Using Atomic Absorption and Other Analytical Procedures

Sample Type	Copper (e) Present % Cu	Copper Found % Cu			
		Complete Sample Dissolution Using Multi-Acid Attack (f)		Atomic Absorption Following Aqua Regia Attack	
		A.A.	Titrimetric	Cold	Hot
Upper Canada Heads	0.042	-	-	0.047(4)	-
Upper Canada Heads	-	0.033(2)	-	0.030(4)	0.032(2)
Upper Canada #8 Agitator	-	0.036(2)	-	0.034(4)	0.038(2)
Upper Beaver Heads	-	-	1.77(2)	1.74(8)	-
Upper Beaver Float Tails	-	0.066(2)	-	0.062(4)	0.066(2)
Upper Beaver De-watering Tails	-	0.077(2)	-	0.075(4)	0.077(2)
Upper Beaver Shipping Lot 41	27.5	27.5(2)	27.5(2)	24.7(4)	27.2(2)
Upper Beaver Shipping Lot 42	27.8	27.3(2)	27.8(2)	23.6(4)	27.5(2)
Upper Beaver Shipping Lot 43	26.7	27.0(2)	26.8(2)	24.5(4)	26.8(2)

(e) Results provided by Upper Canada Mines Ltd.

(f) Nitric, hydrochloric, hydrofluoric and perchloric acids.

TABLE 4

Precision of Analytical Results Obtained for Gold and Copper
on Samples from Upper Canada Mines and Upper Beaver Mines

Sample Type	Element Determined	Individual Determinations by Atomic Absorption (g) oz/ton Au or % Cu	Average Result oz/ton or %	Precision	
				Standard Deviation	95% Confidence Limit for Average Result
Upper Canada Heads	Au	0.29, 0.32, 0.29, 0.38	0.32	0.044	0.068(h)
	Cu	0.049, 0.045, 0.048, 0.047 0.049, 0.046, 0.049, 0.046	0.047	0.0014	0.001
Upper Canada Tails	Au	0.018, 0.015, 0.014, 0.016	0.016	0.002	0.003
	Cu	0.029, 0.029, 0.031, 0.031	0.030	0.001	0.0015
Upper Canada #8 Agitator	Au	0.027, 0.027, 0.030, 0.028	0.028	0.001	0.002
	Cu	0.033, 0.034, 0.035, 0.035	0.034	0.001	0.0015
Upper Beaver Heads	Au	0.24, 0.245	0.24	-	-
	Cu	1.77, 1.78, 1.75, 1.71 1.75, 1.74, 1.81, 1.58	1.74	0.081	0.068
Upper Beaver Float Tails	Au	0.029, 0.025, 0.024, 0.024	0.0255	0.002	0.004
	Cu	0.061, 0.062, 0.064, 0.060	0.062	0.002	0.003
Upper Beaver Dewatering Tails	Au	0.009, 0.008, 0.009, 0.009	0.009	0.0005	0.0008
	Cu	0.074, 0.076, 0.074, 0.075	0.075	0.001	0.0015
Upper Beaver Shipping Lot 41	Au	3.28, 3.20, 3.21, 3.10	3.20	0.088	0.14
Upper Beaver Shipping Lot 42	Au	3.33, 3.31, 3.66, 3.22	3.38	0.214	0.33
	Cu	(i) 27.18, 27.68, 28.16, 27.30, 27.48, 27.05	27.48	0.44	0.45
Upper Beaver Shipping Lot 43	Au	3.13, 2.88, 3.36, 3.20	3.14	0.233	0.36

(g) Cold aqua regia attack except as noted

(h) See RESULTS AND DISCUSSION

(i) Hot aqua regia attack with varying washing procedures following filtration

REFERENCES

1. F.W.E. Strelow et al., Anal. Chem., 38, 115-7 (1966).
2. R.B. Dean and W.J. Dixon, Anal. Chem., 23, 636-8 (1951).
3. Edward L. Bauer, "A Statistical Manual for Chemists", Academic Press, New York, pp 16-18 and 137-8, 1960.
4. A. Clow and F.E. Beamish, Can. Mining Journal, 88, 66-9 (1967).
5. J.R. Beevers, Econ. Geol., 62, 426-8 (1967).
6. A.C. Fitzgerald, R.J. Graham, W.H. Gross and J.C. Rucklidge, Econ. Geol., 62, 502-16 (1967).
7. Techtron Instruction Manual for the Atomic Absorption Spectrophotometer, Model AA3, Techtron PTY. Ltd., Melbourne, Victoria (Second reprint, ca 1965).

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APPENDIX I

Atomic Absorption Operating Procedure - Gold

Carry out two or three readings for each determination, reading against MIBK as the blank. Use of a recorder will provide a considerable improvement in precision.

Instrumental conditions were as follows:

Hollow-cathode lamp	- Atomic Spectral Lamps, Australia, single element
Photomultiplier tube	- Hamamatsu R 106
Lamp current	- 4 mA, regulated
Phototube circuit	- 500 volts
Monochromator slit	- 300 microns (9.9Å bandpass)
Wave length	- 2428 Å
Burner height	- organic medium, 12mm below centre of light path for best sensitivity; 6mm below centre of light path for best stability. - aqueous medium, 6mm below centre of light path for best sensitivity; stability similar for 6- and 12-mm settings.
Flame type	- organic medium, an oxidizing flame gave about 20 per cent greater sensitivity than a reducing flame, but the flame setting is harder to maintain than when using the fringe shown by a slightly reducing flame. - aqueous medium, an oxidizing flame gave slightly better sensitivity than a reducing flame especially at smaller distances below the centre of the light path. The oxidizing flame setting is harder to maintain than when using the fringe shown by a slightly reducing flame.
Air supply	- 15 psi
Atomizer	- variable type
Sample uptake	- 3.5 ml per minute
Flame emission	- 2 per cent signal (with lamp off, the difference between flame off and flame on)
Flame absorption	- 10 per cent signal (with lamp on, the difference between flame off and flame on)

Sensitivity	- 1 per cent absorption - organic, 0.07ppm (approx)
	- 1 per cent absorption - aqueous, 0.25 " "
	- 20 per cent absorption - organic, 1.5 " "
	- 20 per cent absorption - aqueous, 5.4 " "

Calibration - Gold

A plot of absorbance versus concentration for gold in organic and aqueous medium, is shown in Figure 1.

With the described procedure, 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 concentration of the MIBK increases. It has been found more satisfactory when working in organic medium to use the lower end of the gold concentration range (ie, less than 0.125 absorbance). Thus, for higher concentrations it is advantageous to increase the amount of MIBK used, choose standards to cover this range by reference to Figure 1, and carry them through the procedure with the samples. The standards are prepared for extraction in aqueous chloride medium and, after extraction, the organic medium is atomized directly for both samples and standards. A stock gold solution is made up from gold metal or a suitable salt of gold, dissolved in aqua regia, diluted and made up to volume.

APPENDIX 2

Atomic Absorption Operating Procedure - Copper

Instrumental conditions were as follows:

Hollow-cathode lamp - Atomic Spectral Lamps, Australia, single-element cu

Photomultiplier tube - Hamamatsu R 106

Lamp current - 4 mA

Monochromator slit - 50 microns

Wave length - 3247 Å

Burner height - burner top 7 cm below centre of light path

Flame type - acetylene - air

Air supply - 15 psi

Sample uptake - 3.5 ml per min.

Sensitivity - 0.07 ppm for 1 per cent absorption
- 5 ppm for 50 per cent absorption

Standard Solutions - Copper

Dissolve 0.1 gm of pure copper wire in hydrochloric acid and dilute to 1 litre (1 ml = 100 ppm cu).

Make up diluted standards in 1% perchloric acid to cover the range 0.2 - 10.0 ppm copper.

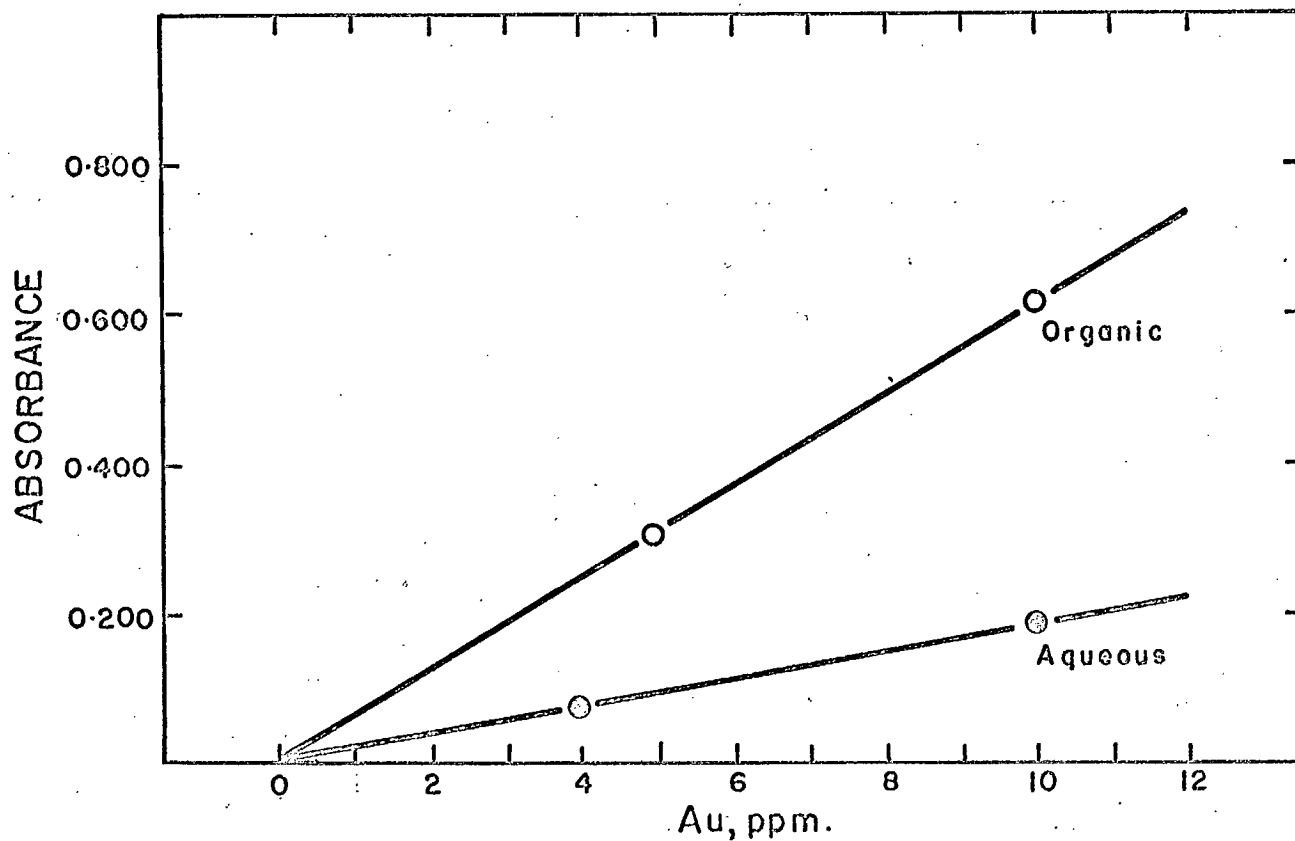


Figure 1. Comparative Sensitivities of Gold Determination in Aqueous and in Organic Medium, by Atomic Absorption Spectrophotometry (Techtron AA3 Spectrophotometer without Scale Expansion).