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

7.   CAMPBELL-CHIBOUGAMAU MINES LTD.,
      CHIBOUGAMAU, QUEBEC - GOLD IN CU
      CONCENTRATES

by

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Extraction Metallurgy Division

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7. Campbell-Chibougamau Mines Ltd., Chibougamau, Quebec -
    Gold in Cu Concentrates

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SUMMARY

This report describes an investigation into the
causes of the erratic results which are often obtained in the
determination of gold in copper concentrates; the con-
centrate from Campbell-Chibougamau Mines Ltd. is used as a typical
material. It was found that an important source of such errors
is the contamination of the gold-bearing organic extract, which
is used for the analysis, by iron, copper, and zinc. Conditions
for minimizing this contamination of the extract (by controlling
the concentration of hydrochloric acid in the aqueous phase,
and by scrubbing the extract with dilute hydrochloric acid)
are given. Other factors investigated include the effect of
a preliminary roasting of the sample and the effect of varying
the flame type by using oxidizing and reducing conditions.

It is shown that the use of a modified atomic
absorption method provides results which agree with the fire
assay results within acceptable limits.

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INTRODUCTION

General

Atomic absorption spectrometry has achieved a high degree of acceptance for the assaying of gold ores, and has replaced the fire assay in many applications. The assay of gold in certain concentrates (notably those of copper ores) has presented problems, however. Since the concentrates are usually sold to a smelter and the smelter settlement includes the value of the contained gold, agreement between buyer and seller as to the gold content is necessary. The accuracy requirements for these assays are therefore greater than for those used in mill control. At the same time, when the routine atomic absorption gold procedure is applied to these materials, the assay results are often inferior to the values obtained on mill feeds and flotation tails.

Campbell-Chibougamau Mines Ltd. Sample Material

A request from Campbell-Chibougamau Mines Ltd.** to carry out gold analyses on their copper concentrates provided the occasion for an investigation to establish the causes of the generally poor response of these concentrates to the routine procedure and to ascertain whether or not agreement to within 0.02 oz/ton with the fire assay results could be obtained.

The causes of the erratic results and the comparatively poor agreement with the fire assays were not known. Experiments were therefore carried out in an attempt to establish whether or not the problems were associated with the dissolution step, the extraction step (which serves to transfer the gold to the organic medium for greater sensitivity and freedom from contaminants), or the atomization and excitation steps.

On the basis of previous experience, it was concluded that an aqua regia attack could be assumed to solubilize all the gold even though the copper concentrates were not completely dissolved. Investigations on dissolution procedures were therefore confined to a study of the effect of prior roasting on gold liberation and to a comparison of the effectiveness of hot and cold leaching. The tests on the extraction step were directed to finding means for reducing the co-extraction of contaminants which was found in preliminary work to cause atomizer blocking during the course of the atomic-absorption measurements. Finally, an investigation of the atomic absorption measurement step was carried out to compare the effect of two different flame types and to introduce a more closely controlled readout technique.

** letter from J. Malette, Chief Chemist, Campbell-Chibougamau Mines Ltd.

ANALYTICAL PROCEDURE

Determination of Gold

The sample is leached with aqua regia at room temperature, and following filtration and washing of the insoluble residue, the gold is extracted from the filtrate with methyl isobutyl ketone (MIBK) and atomized directly in the organic medium. Although the sample is not completely soluble in aqua regia, the gold is effectively leached if the sample is adequately ground.

Roasting

If roasting of the sample is necessary, weigh the sample into a porcelain crucible and roast at 640°C for 2 hours with occasional mixing. Transfer to an appropriate flask for leaching.

Sample Dissolution

Weigh out an appropriate sample (5-10 g) of the well-pulverized concentrate (minus 200-mesh) into a 300-ml Erlenmeyer flask and add 30 ml of aqua regia. Shake the flask for 1 to 2 hours at room temperature using a 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 solution into a separatory funnel capable of holding approximately 150 ml and adjust the sample volume to 100 ml. Carry aliquots of a standard gold solution through the same procedure as the sample, making the gold content of the standards approximately the same as the sample. The volume of the standard solutions and the sample should be similar at this point, and the number and volume of extractant portions and scrubbing portions used should be the same for any particular group of samples which is to be compared (a).

(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, thus making the procedure of more general application.

Extraction

Add an appropriate amount (40 ml) of methyl isobutyl ketone (Fisher), shake vigorously for 2 minutes and allow the layers to separate. Drain off and discard the aqueous layer. Scrub the organic layer four times by shaking with 25 ml of 10% hydrochloric acid to remove contaminating ions. If the fourth wash is coloured, continue washing with acid until no further change is noted. 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 four or more atomic absorption readings, interspacing reading of samples and prepared standards in a manner similar to that described in the operating procedure (APPENDIX 1).

EXPERIMENTAL

Preliminary Observations

First attempts to analyse these samples of copper concentrate met with mixed success as results tended to be erratic and problems were encountered with atomizer blocking. Subsequent investigation indicated that much of this difficulty was caused by organic pickup of contaminants during the MIBK extraction. Analysis of the organic extract indicated that large amounts of iron, together with some copper and zinc, were extracted by the MIBK at the acidity levels used in the procedure. Although a scrubbing operation was an integral part of the procedure, it apparently was not sufficiently thorough to efficiently clean-up the organic fraction. Also, following acid leaching of the sample, careful filtration and washing of the undissolved solids was found to be highly desirable in order to keep contamination of the organic fraction to a minimum.

Effect of Scrubbing the Extracts with Dilute Hydrochloric Solution on Removal of Iron, Copper and Zinc

Portions of one of the copper concentrates was leached with varying amounts of aqua regia, extracted with MIBK and the organic fraction given a number of scrubbings with dilute hydrochloric acid. Results, as shown in Table 1 and Figures 1 and 2, indicated the advantages of using a scrubbing procedure. It was found advantageous to use as small an amount of acid as possible during the leaching step in order to minimize dissolution of contaminants as well as reduce the extraction of contaminants in the subsequent extraction step.

TABLE 1

Effect of Scrubbing on Removal of Copper,
Zinc and Iron from MIBK

Element	Treatment*	ppm found in scrubbing						Remarks
		1	2	3	4	5	6	
Copper	4 g sample-40 ml aqua regia at room temp. for 1 hour - 25 ml MIBK to 100 ml aqueous for extraction	10.2	2.0	<0.3	–	–	–	scrubbed with 25 ml portions of 15% HCl
Zinc	4 g sample-40 ml aqua regia at room temp. for 1 hour - 25 ml MIBK to 100 ml aqueous for extraction	9.1	0.06	<0.02	–	–	–	scrubbed with 25 ml portions of 15% HCl
Iron	4 g sample-40 ml aqua regia at room temp. for 1 hour - 25 ml MIBK to 100 ml aqueous for extraction	4025	1583	458	186	48	–	scrubbed with 25 ml portions of 15% HCl
Iron	4 g sample-40 ml aqua regia at room temp. for 1½ hours - 30 ml MIBK to 100 ml aqueous for extraction	5667	849	53	10	3	1.2	scrubbed with 30 ml portions of 10% HCl
Iron	4 g sample-30 ml aqua regia at room temp. for 2 hours - 30 ml MIBK to 100 ml aqueous for extraction	2320	273	33	7	–	–	scrubbed with 25 ml portions of 10% HCl
Iron	4 g sample-20 ml aqua regia at room temp. for 1 hour - 30 ml MIBK to 100 ml aqueous for extraction**	391	37	6.5	2	–	–	scrubbed with 25 ml portions of 10% HCl

*sample of copper concentrate (Lot 3457) from Campbell-Chibougamau
**greater than 99.9% of the acid soluble iron found in the aqueous
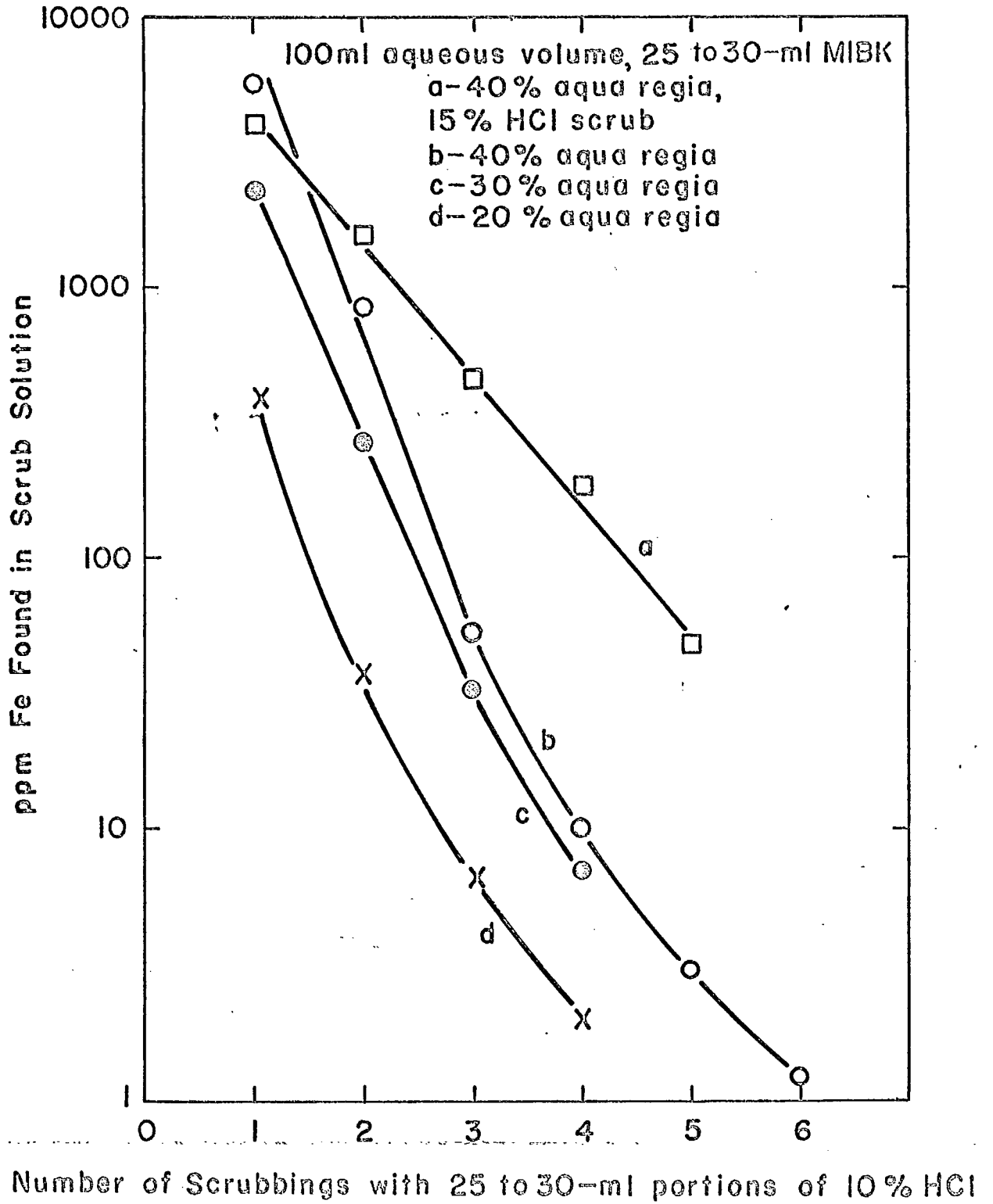 fraction following extraction

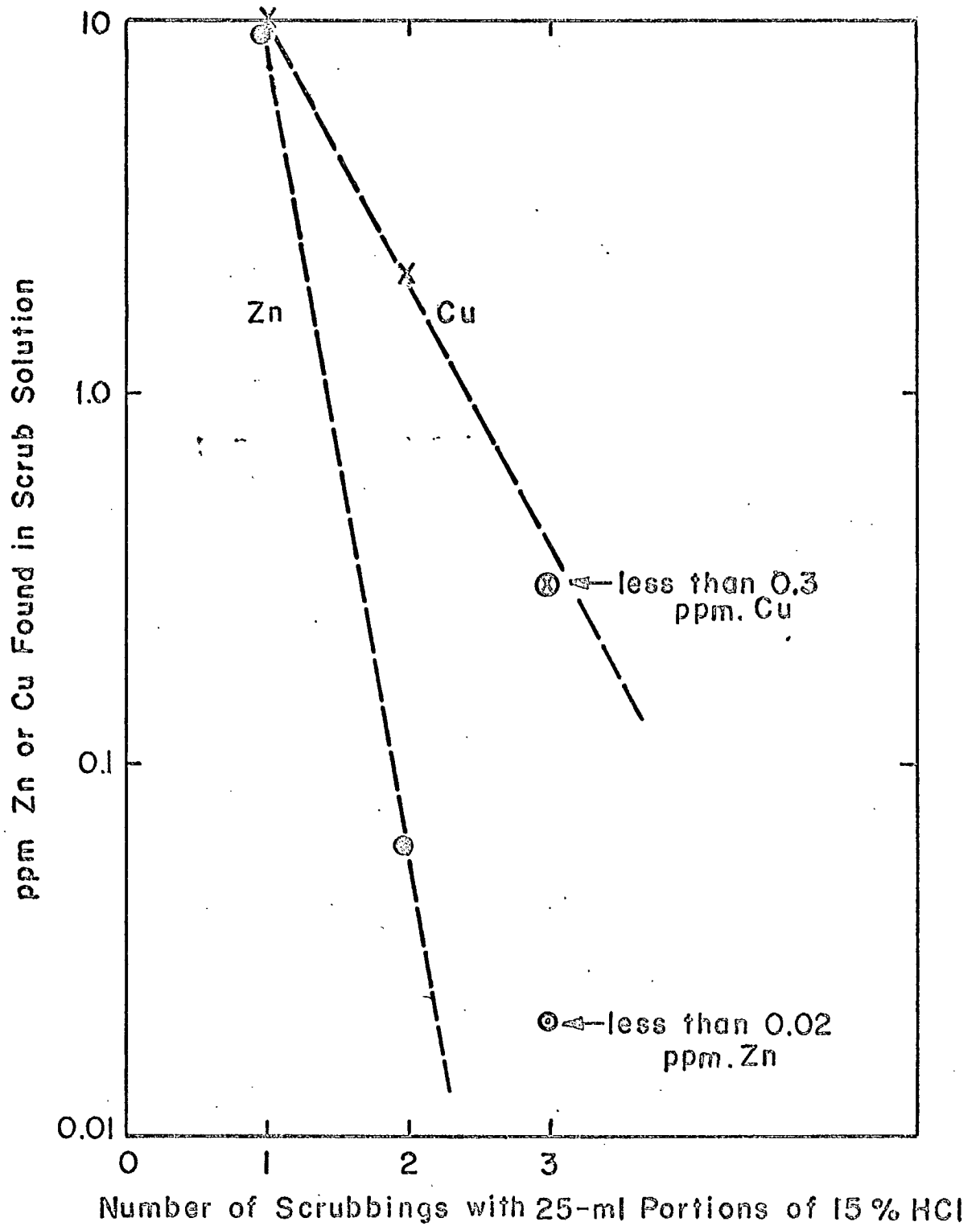Figure 1. Effect of scrubbing of the MIBK fraction –
removal of iron.

Figure 2. Effect of scrubbing of the MIBK fraction –
removal of copper and zinc.

Extraction of Gold from Diluted Aqua Regia Medium

Because of the desirability of working at reasonably
low acid levels during the extraction, a series of tests was
carried out to establish the efficiency of gold extraction in
diluted aqua regia medium containing the equivalent of 5-25% (v/v)
of hydrochloric acid. The results, as shown in Table 2 and
Figure 3, confirm the literature data that gold extraction is
virtually complete over a wide range of hydrochloric acid
content (1,2). The presence of nitrates appeared to have
little effect on the gold extraction.

Results Obtained by Atomic Absorption Procedures
on Copper Concentrates.

Analysis of Campbell-Chibougamau copper concentrates
using various acidity conditions and sample sizes was carried
out in order to indicate the most effective conditions for
satisfactory leaching of the samples. As no consistent difference
was found between cold and hot aqua regia leaching, the cold
leach was chosen for the sake of simplicity. A comparison of
fire assay results was then made with atomic absorption results
found on samples, as received and following a preliminary sample
roast (Table 3). A similar comparison of results was made,
using roasted samples, to evaluate the effect of different flame
types on results (Table 4).

Calculation of the Precision of the Atomic
Absorption Procedures

The precision obtained using the most efficient atomic
absorption procedure found was calculated with results as shown
in Table 5. The effects, on the precision found, of using oxidizing
and reducing flames are shown in Table 6.

RESULTS AND DISCUSSION

Results obtained using the atomic absorption procedures
compared very well with fire assay results (Table 3). If a
preliminary roast of the sample was carried out, a difference of less
than 0.01 oz/ton of gold was found between procedures. On samples
analyzed without preliminary roasting treatment, one sample
exceeded the desired agreement limit of 0.02 oz/ton primarily as
a result of the inclusion of one high result out of four. In all
cases, however, agreement with fire assay results was superior
after preliminary sample roasting had been done.

TABLE 2

Extraction of Gold from Diluted Aqua Regia Medium with MIBK

Gold Present Micrograms Au	Acidity in HCl %	Gold Present in First Organic Extract (40 ml)		Gold Present in Second Organic Extract (10 ml)		*Distribution Coefficient E_A^O
		Micrograms Au	%	Micrograms Au	%	
215.4	5	214.6	99.9	0.31	0.14	1731
215.4	10	214.2	99.8	0.51	0.24	1050
215.4	15	213.9	99.7	0.61	0.28	877
215.4	25	213.4	99.6	0.84	0.39	635

*calculated from the 1st organic fraction (40 ml) and the aqueous fraction (100 ml), assuming all gold remaining in the aqueous fraction following the 1st extraction is removed by the 2nd extraction
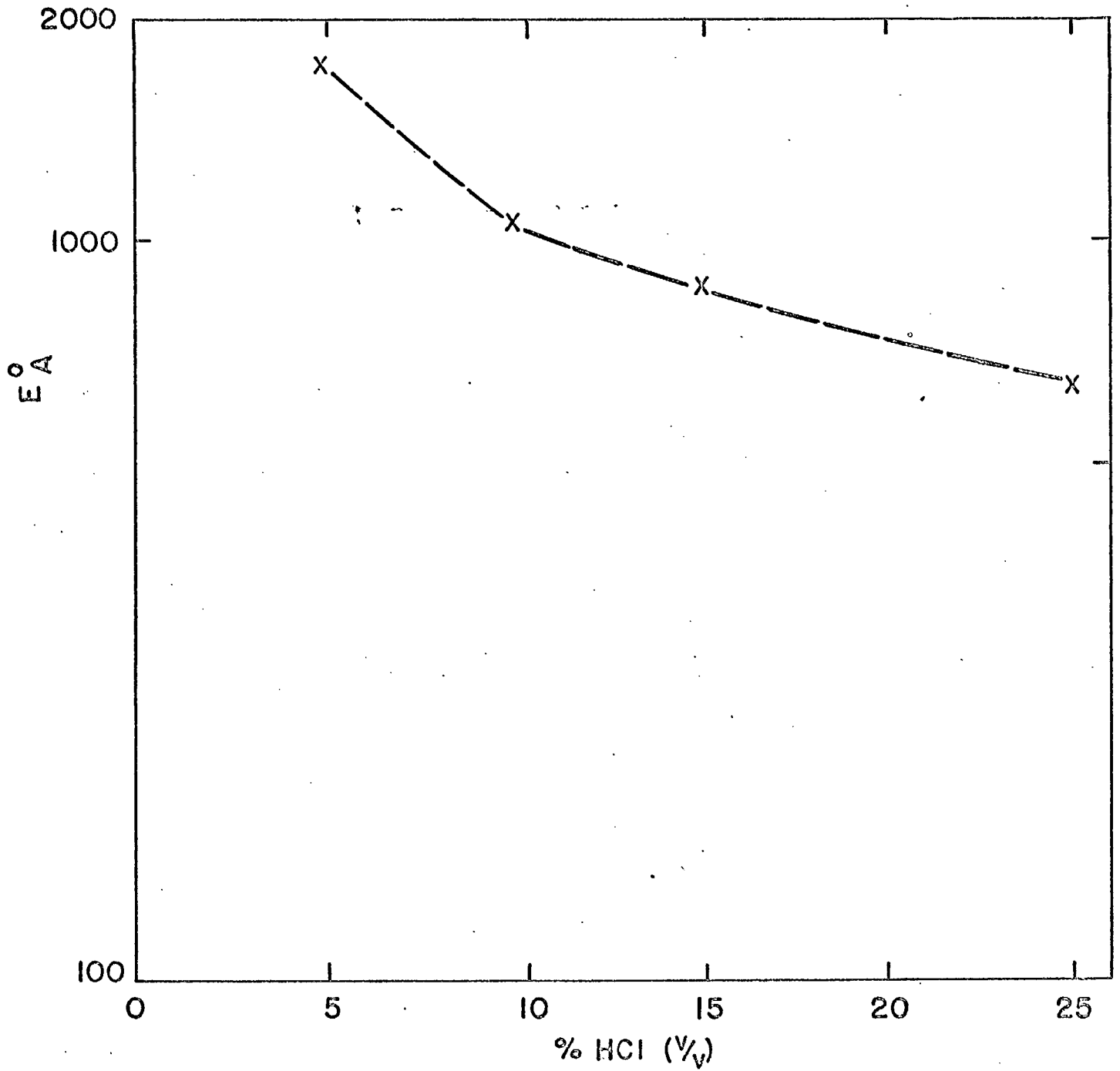
Figure 3.   Extraction coefficient of gold in diluted aqua
            regia medium.

TABLE 3

Comparison of Atomic Absorption and Fire Assay
Results for Gold on Copper Concentrates
from Campbell-Chibougamau Mines

Lab-oratory Number EMP-	Sample Type	Gold[a] Present oz/ton Au	Gold Found oz/ton Au[b]		Random Deviation of Average Result from Fire Assay Result			
			Samples[c] Roasted	Samples[c] Not Roasted	Roasted Samples		Samples Not Roasted	
					oz/ton Au	%	oz/ton Au	%
2410	Copper Concentrate Lot 3445	0.613	0.623(6)	0.625(5)	+0.010	+1.63	+0.012	+1.96
2411	Copper Concentrate Lot 3447	0.537	0.536(6)	0.563(4)	-0.001	-0.19	+0.026	+4.84
2412	Copper Concentrate Lot 3448	0.482	0.485(6)	0.470(4)	+0.003	+0.62	-0.012	-2.59
2413	Copper Concentrate Lot 3457	0.367	0.360(6)	0.353(4)	-0.007	-1.91	-0.014	-3.81

(a) average of fire assay results provided by Campbell-Chibougamau and the Mines Branch
(b) number of determinations in brackets following results
(c) results for roasted samples were obtained using both oxidizing and
reducing flames. Results for non-roasted samples were obtained
using an oxidizing flame.

TABLE 4

Comparison of Results Obtained by Atomic Absorption
Using Two Flame Types with Fire Assay Results

Laboratory Number and Sample Type	Gold[a] Present oz/ton Au	Gold Found oz/ton Au[b] (Roasted Samples)		Random Deviation of Average Result from Fire Assay Result			
		Oxidizing Flame	Reducing[c] Flame	Oxidizing Flame		Reducing Flame	
				oz/ton Au	%	oz/ton Au	%
EMP 2410 Copper Conc. Lot 3445	0.613	0.639(4)	0.610(4)	+0.026	+4.24	-0.003	-0.49
EMP 2411 Copper Conc. Lot 3447	0.537	0.545(4)	0.526(4)	+0.008	+1.49	-0.011	-2.05
EMP 2412 Copper Conc. Lot 3448	0.482	0.480(4)	0.489(4)	-0.002	-0.41	+0.007	+1.45
EMP 2413 Copper Conc. Lot 3457	0.367	0.367(4)	0.345(4)	0.0	0.0	-0.022	-5.99

(a) average of fire assay results provided by Campbell-Chibougamau and the Mines Branch
(b) number of determinations in brackets following results
(c) yellow fringe

TABLE 5

Precision of Analytical Results Obtained for Gold on Samples
of Copper Concentrate from Campbell-Chibougamau Mines

Laboratory Number EMP-	Sample Type	Sample Treatment	Individual Determinations using Atomic Absorption oz/ton Au(a)	Average Result oz/ton Au	Precision	
					Standard Deviation	95% Confidence Limits for Average Result
2410	Copper Concentrate Lot 3445	Roast	0.625, 0.635, 0.591, 0.605, 0.619, 0.661	0.623	0.028	0.028
		No Roast	0.643, 0.598, 0.650, 0.618, 0.615	0.625	0.022	0.027
2411	Copper Concentrate Lot 3447	Roast	0.566, 0.514, 0.506, 0.525, 0.540, 0.565	0.536	0.024	0.024
		No Roast	0.598, 0.549, 0.544, 0.560	0.563	0.026	0.041
2412	Copper Concentrate Lot 3448	Roast	0.475, 0.475, 0.488, 0.489, 0.471, 0.511	0.485	0.012	0.012
		No Roast	0.475, 0.457, 0.472, 0.474	0.470	0.009	0.014
2413	Copper Concentrate Lot 3457	Roast	0.339, 0.369, 0.358, 0.360, 0.379, 0.354	0.360	0.016	0.016
		No Roast	0.343, 0.358, 0.355, 0.354	0.353	0.007	0.012

(a) results for roasted samples were obtained using both oxidizing and
reducing flames. Results for non-roasted samples were obtained
using an oxidizing flame.

TABLE 6

Effect of Flame Type on the Precision of
Analytical Results Obtained for Gold

Laboratory Number and Sample Type	Individual Determinations using Atomic Absorption(a)		Precision Found			
	Oxidizing Flame	Reducing(b) Flame	Oxidizing Flame		Reducing Flame(b)	
			Standard Deviation	95% Confidence Limits for Average Result	Standard Deviation	95% Confidence Limits for Average Result
EMP 2410 Copper Conc. Lot 3445	0.665, 0.631, 0.635, 0.623	0.584, 0.578, 0.609, 0.669	0.020	0.032	0.044	0.069
EMP 2411 Copper Conc. Lot 3447	0.594, 0.546, 0.504, 0.537	0.537, 0.504, 0.489, 0.574	0.046	0.071	0.041	0.064
EMP 2412 Copper Conc. Lot 3448	0.492, 0.507, 0.461, 0.461	0.457, 0.470, 0.501, 0.528	0.022	0.035	0.035	0.053
EMP 2413 Copper Conc. Lot 3457	0.357, 0.373, 0.359, 0.379	0.321, 0.347, 0.358, 0.352	0.011	0.017	0.015	0.023

(a) roasted samples
(b) small yellow fringe

Standard deviations, and 95% confidence limits (as calculated by the methods of Dean and Dixon (3) and Bauer (4)), are shown in Table 5. No marked divergence was shown between the values obtained on the roasted and those obtained on the unroasted samples (Table 5).

A comparison was made of the effect of flame type on results to evaluate whether or not an improvement in accuracy and precision could be obtained by varying this parameter. Results obtained using oxidizing and reducing flames showed that, in most cases, the random deviation from fire assay results found with an oxidizing flame was less than that found with a reducing flame. The calculated precision also indicated a modest superiority for an oxidizing over a reducing flame on three out of four samples (Table 6).

It was found that one of the more significant points, in obtaining atomic absorption results that agreed closely with fire assay results and also showed good precision, was adequate scrubbing of the organic fraction following sample extraction. If this step was not employed when using our acid dissolution procedure, atomizer blocking took place and results were very erratic. Table 1 and Figures 1 and 2 show the extent of the pickup of contaminants and the efficiency of the washing step. It is evident that iron is picked up more readily and is not as easily removed as copper and zinc. It was concluded, therefore, that it is desirable to use as low a hydrochloric acid concentration as possible for the leaching, extraction, and scrubbing steps. Although we used 10% hydrochloric acid scrub solution, it was indicated that use of weaker hydrochloric acid scrub solutions could lessen the number of scrubbings required without harmful effect on the gold extraction. Figure 3 and Table 2 show that gold extraction is efficient over a wide acidity range.

It was necessary, therefore, to exercise close control over the amount of aqua regia added in relation to the sample size taken. If the amount of acid present was too small leaching of the gold was inadequate but, if overly large amounts of acid were used, contaminant leaching and pickup in the organic fraction was excessive. A cold aqua regia leach was found to be preferable to a hot leach because gold extraction was similar for both and contaminant extraction was greater after a hot leach.

The size of sample taken must be large enough to be representative but not too large because sample handling problems became troublesome. In order to obtain a more representative sample, weights of 15 g and 30 g of sample were leached with large amounts of aqua regia, made up to volume, and aliquots taken for extraction. These techniques were not successful because results were low, partly due to difficulties found in obtaining thorough leaching and/or adequate washing following filtration. Although it has been found satisfactory here on some types of ore samples to extract gold from the leach slurry and thus avoid a filtration step before extraction, this was not found to be feasible for these copper concentrates. It was found, in such cases, that because of high organic pickup of contaminants and mechanical pickup of fine solids, it was difficult to obtain a contaminant-free organic fraction without performing a prohibitive number of scrubbings.

The procedure chosen, then, was considered to be the best compromise found after giving due consideration to the above factors; further improvements might be expected from trying other procedural variations.

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3. R.B. Dean and W.J. Dixon, Anal. Chem., 23, 636-8 (1951).

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ACKNOWLEDGEMENTS

APPENDIX 1

Atomic Absorption Operating Procedure - Gold

Carry out four readings for each determination, reading against MIBK as the blank. Use of a recorder is recommended as an aid in obtaining a high level of 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 (9.9$\overset{\circ}{A}$ bandpass)
Wave length	- 2428$\overset{\circ}{A}$
Burner height	- organic medium, 12 mm below centre of light path for best sensitivity; 6 mm below centre of light path for best stability.
	- aqueous medium, 6 mm 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 - 0.07 ppm gold

General Observations

It has been found more satisfactory when working in
the organic medium to use the lower end of the gold concentration
range (i.e., less than 0.15 absorbance). Thus, for higher
concentrations of gold, it is advantageous to increase the amount
of MIBK used rather than work at very high absorbance readings.
This is partly because of the tendency for the relationship between
the gold present in the original aqueous solution and the absorbance
in the organic medium to depart from linearity as the gold con-
centration of the MIBK increases.

The standards were prepared from a stock gold solution
which was made up from gold metal or a suitable gold salt,
dissolved in aqua regia, diluted, and made up to volume.

The following procedure was used in reading the
samples, with the objective of improving the precision:- four
readings were taken for each sample using a spanning technique
such as 1. baseline, 2. sample A, 3. standard A, 4. sample B,
5. standard A, 6. baseline.

Four standards were carried along with each group of
samples so that each sample was compared with each standard
at least once. An absorbance level of 0.10 to 0.15 was used
as the working range, without scale expansion.

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