CANADA

DEPARTMENT OF ENERGY, MINES AND RESOURCES

OTTAWA

MINES BRANCH INVESTIGATION REPORT IR 68-6

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

4. GIANT YELLOWKNIFE MINES LIMITED, YELLOWKNIFE, NORTHWEST TERRITORIES

by

G.A. HUNT AND R.J. GUEST

EXTRACTION METALLURGY DIVISION

FEBRUARY 1968

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

4. Giant Yellowknife Mines Limited, Yellowknife, Northwest Territories.

by

G. A. Hunt* and R. J. Guest**

SUMMARY

As part of a continuing series illustrating the application of atomic absorption spectrophotometry in mill control, analytical methods are presented for the rapid, accurate determination of four key elements in a typical arsenical-antimonial gold ore. A novel approach to the sample-preparation procedure permits the determination of three of the four elements (arsenic, antimony and iron) in the solution from a single, weighed sample. The procedure for the gold determination, because of the low concentration involved, necessitates preparation of a separate sample solution, but as the studies presented here demonstrate, the method has been considerably shortened in comparison with the one used in the previous reports, without any loss in accuracy.

Each of the two procedures permits processing some 20 samples by one operator in an elapsed time of only four hours, and it is probable that by suitably intermeshing the operations, the actual throughput per man-day can be considerably increased over that indicated by this figure.

Although the methods were developed using products from a particular mill, they should be equally applicable to any operation processing similar materials. In particular, the speed inherent in the method should prove of great value in the case of the antimony determination for mine control, since high concentrations of this element must often be avoided because of its deleterious effect on roaster operation.

Repetitive analyses on typical products, and comparison with analyses carried out by other methods, provide ample evidence that the necessary levels of accuracy and precision can be met.

The methods are described in sufficient detail that an estimate of the overall analytical cost can be derived by mill personnel to permit comparison with methods currently being employed.

*Scientific Officer and ** Research Scientist, Chemical Analysis Section Extraction Metallurgy Division, Mines Branch, Department of Energy, Mines and Resources, Ottawa, Canada.

INTRODUCTION

A request was received from R.J. McLeod, Mill Superintendant, Giant Yellowknife Mines Limited, Yellowknife, Northwest Territories, for the evaluation of atomic absorption spectrophotometry as an analytical technique for gold, arsenic, antimony, iron and sulphur on samples of typical process material from mill operations at Giant Yellowknife Mines. Information was desired from the standpoint of a) the accuracy and precision to be expected, and b) the speed with which results could be obtained.

Hollow-cathode lamps were available for all elements requested except sulphur. Direct atomic absorption of this latter element is impractical so that its determination using this technique would require development of an indirect method. This would make an atomic absorption procedure for sulphur lengthy, and hence of doubtful usefulness for mill-control work. Accordingly, sulphur was not further considered in this work.

The determination of gold on the same sample as the other elements was not practical due to the low concentration of gold present compared to the other elements, therefore a separate sample would be required. The gold procedure which has been described in previous reports in this series would be more valuable for mill-control work if it could be shortened; therefore, the regular procedure was modified to provide a considerably shorter procedure which was evaluated for use on this sample material.

Although the determination of arsenic, antimony and iron in the same sample was desirable from the standpoint of speed, it presented unique problems as a procedure was required which would achieve sample dissolution, avoid the necessity of chemical separation, and minimize matrix effects. The development of a satisfactory analytical procedure to assist in mill control of antimony was considered to be of particular importance due to the deleterious effect of antimony during the roasting step, prior to cyanidation.

In an unpublished paper in 1963, Allan (1) discussed the determination of arsenic and selenium. Slavin et al in 1964 (2) reported a detection limit of 1 p.p.m. for arsenic. Later still in 1965, Slavin et al (3) discussed the selection of wavelength and flame mixture and chose the acetylene-air flame at 1937 Å for arsenic determination in glass, alloys and extracts. Their results, obtained by a combined perchloric acid and hydrofluoric acid leach, were about 10% high and the enhancement was not resolved. Preliminary work in this laboratory using an acid dissolution technique on Giant Yellowknife sample material indicated a similar enhancement. In consequence, alternative dissolution techniques were tried to see if this problem could be resolved.

Additional parameters involved in the determination of arsenic by atomic absorption were also investigated. These included monochromator drift, spectral-line peak, small-area technique and deviation from linearity of absorbance values.

Published reports on the determination of antimony by atomic absorption spectroscopy have been few and limited in scope. J.E. Allan in 1962 (4) and W. Slavin in 1966 (5) reported sensitivities for antimony of 0.5-1.0 ppm Sb at 2176 Å, and the latter included standard conditions for the analysis of antimony in gold. R.A. Mostyn and A.F. Cunningham in 1967 (6) described a detailed investigation into the practicability of determining antimony by atomic absorption in Pb-Sb and Pb-Sb-Sn alloys and bronze and duraluminum.

Preliminary work on establishing suitable instrumental conditions for antimony indicated that less stringent controls would be needed than with arsenic, as the 2176 Å resonance line is less affected by the flame composition and monochromator drift is absent.

Of the hollow-cathode lamps on hand, gold and iron were available as single-element lamps, while arsenic and antimony were available as a multi-element lamp. The latter lamp failed after a short period of use but a satisfactory replacement was subsequently provided by the manufacturer. In the interim, a single-element lamp for arsenic was used and was found to be reliable.

The instrument used in this investigation was the Techtron Atomic Absorption Spectrophotometer, Model AA3, with acetylene fuel and air as the support gas.

The procedures described have been developed with speed as one of the major considerations, so an estimate of the time required for each procedure is provided. Also, the procedures are described in detail so that their applicability in the Giant Yellowknife Laboratories can be evaluated.

A comparison was made of all results obtained by atomic absorption with those provided by Giant Yellowknife. In addition, several arsenic and iron results were checked chemically in this laboratory.

EXPERIMENTAL - ANALYTICAL PROCEDURES

A Determination of Gold

Outline

Gold is determined following its extraction with methyl isobutyl ketone from bromide or chloride medium (7) (8). The gold content of the ore is leached either by (i) aqua regia attack; or (ii) bromate-hydrobromic acid attack. Preliminary roasting of the sample is not required. Although complete dissolution of the sample is not obtained by these procedures, the gold content is effectively leached providing the sample is sufficiently well-ground.

Sample dissolution

(i) Aqua regia leach

Weight out an appropriate sample (0.3g - 15 g) of the well-pulverized ore (minus 200 mesh) into a 300-ml Erlenmeyer flask and add 40-ml of aqua regia. Place on a suitable mechanical shaker and allow the sample to leach in the cold for 45 minutes with moderate mixing. Transfer the solid and solution to a separatory funnel capable of holding approximately 150-ml, and dilute to 100-ml with water.

Alternatively, weigh out an appropriate sample into a 100-ml or 250-ml beaker and add 40-ml of aqua regia. Digest on a low-heat hot plate for 1-2 hours, cool, and transfer the solids and solution to the separatory funnel. Adjust the acidity to 25-30% in hydrochloric acid by making up with water to a suitable volume.

Carry aliquots of a standard gold solution through whichever of the above procedures is to be used, at the same time as the samples.

(ii) Bromate - hydrobromic acid leach

Weigh out 0.3 - 15 g of a well-pulverized sample (minus 200 mesh) into a 150-ml or 250-ml beaker, mix thoroughly with about 2g of potassium bromate, and wet with water. Rapidly pour 40-ml of concentrated hydrobromic acid (a) into the beaker containing the roasted sample and potassium bromate.

(a) Rapid addition of the hydrobromic acid is necessary to provide a sufficient solution volume to retain the bromine produced during the initial violent reaction.

Cover the beaker, and warm on the steam bath for one hour with occasional stirring, then transfer to a low temperature hot plate and evaporate to a final volume of 20-25 ml. Transfer solids and solution to an appropriate separatory funnel and dilute to 60 ml with water. Carry aliquots of a standard gold solution through the complete procedure at the same time as the samples.

Extraction

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 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(b).

(i) Single extraction procedure

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 or hydrobromic acid (depending on the acid treatment used) to remove contaminating ions. If the third 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 (c), or dilute to volume with MIBK in a volumetric flask.

(b) 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 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.

(c) On rare occasions the atomizer may block during atomic absorption measurement. In such a case, 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.

(ii.) <u>Double extraction procedure</u>

Add 10-ml or more of methyl isobutyl ketone depending on the amount of gold present (Table 1), shake vigorously for two 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 methyl isobutyl ketone. Discard the aqueous layer. Wash the organic layers three times by shaking with 30-ml portions of 15% hydrochloric acid or 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 pass them through a Whatman No. 40 filter paper into a suitable container for atomic absorption readings (see footnote (c) page 4), or dilute to volume with MIBK in a volumetric flask.

<u>Atomic Absorption Measurement</u>

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 (d). Use a recorder for the measurement if greater precision is required.

For details of the operating procedure refer to <u>APPENDIX I.</u>

RESULTS AND DISCUSSION

Results obtained for gold using atomic absorption were in good agreement with results provided by Giant Yellowknife Laboratories (Table 2) on all samples except the Baghouse Dust (EMM-2165). A fire assay on this sample at the Mines Branch agreed with the atomic absorption results. The two leaching and extraction procedures used before atomic absorption gave results which agreed very well. Both procedures are described in detail, although the procedure using a cold aqua regia leach and single extraction offers a considerable advantage in speed over the other procedure, while giving precision comparable to, or better than, the double extraction procedure (Table 3). Precision was calculated according to the procedures of Dean and Dixon (10) and Bauer (11) where three or more results were obtained.

(d) 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.

TABLE 1

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

Sample type	Gold concentration oz/ton Au	Sample Size grams	Methyl Isobutyl Ketone added ml MIBK	Dilution required before atomic absorption ml MIBK
Dust	0.3	5	40	-
Heads	0.7	2.5	40	-
Concentrate or Feed	3.5	0.5	40	-
		3	40	200
Roaster Calcine	5	0.4	40	-
		2.5	40	200

It was not found possible to eliminate the washing steps of the organic extract since without them, results were too high. (Table 2)

A set of 20 samples can be analysed readily within a few hours by the procedure described here. The time required will, of course, vary with the laboratory organization, and the requirements for precision and accuracy.

TABLE 2

Comparison of Gold Results by Atomic Absorption and Fire Assay

Sample number EMM-	Sample type	Fire Assay		Atomic Absorption (g)			
		Lab No.1 (a_1) oz/ton Au	Lab No.2 (b_1) oz/ton Au	Procedure 1 (c_1) oz/ton Au	Procedure 2 (d_1) oz/ton Au	Procedure 3(e_1) oz/ton/au	Procedure 4 (f_1) oz/ton Au
2159	Heads	0.72	-	0.71 (6)	0.74 (2)	0.72 (6)	0.94 (2)
2160	Roaster Feed	3.83	-	3.68 (4)	-	3.97 (5)	4.71 (2)
2161	Bulk conc.	3.72	-	3.76 (6)	-	3.92 (5)	4.47 (2)
2162	Roaster Calcine	4.83	-	4.77 (4)	5.24 (4)	5.10 (5)	5.91 (2)
2163	D-2 1st stage	4.17	-	4.39 (4)	-	4.31 (5)	5.59 (2)
2164	Hot Cottrell Dust	2.84	-	2.94 (4)	-	3.11 (2)	-
2165	Baghouse Dust	0.46	0.29	0.30 (6)	-	0.31 (2)	-

(a_1)   Giant Yellowknife Laboratory
(b_1)   Mineral Sciences Division Laboratory
(c_1)   Bromate-hydrobromic acid treatment – double extraction procedure
(d_1)   Hot aqua regia leach – single extraction procedure
(e_1)   Cold aqua regia leach – single extraction procedure
(f_1)   As (e) except no washing of MIBK fraction before its filtration and atomization.
(g)   Number of determinations are bracketed after the result.

TABLE 3

Precision of Analytical Results Obtained for Gold on Samples from Giant Yellowknife Mines Ltd.

Sample Number and Type EMM-	Individual Determinations by Atomic Absorption oz/ton (h)		Average Result oz/ton		Precision			
	Procedure No. 1	Procedure No. 2			Standard Deviation		95% Confidence for average result	
			Proc. No.1	Proc. No.2	Proc. No.1	Proc. No.2	Proc. No. 1	Proc No. 2
2159 Heads	0.72, 0.615, 0.70, 0.805, 0.67, 0.73	0.69, 0.73, 0.71, 0.72, 0.745, 0.71	0.71	0.72	0.075	0.0225	0.079	0.024
2160 Roaster Feed	3.83, 3.80, 3.24, 3.83	3.92, 4.31, 3.71, 3.98, 3.95	3.68	3.97	0.29	0.26	0.445	0.31
2161 Bulk Conc.	3.89, 3.47, 3.46, 4.03, 3.83, 3.88	3.72, 3.80, 4.16, 4.06, 3.88	3.76	3.92	0.225	0.19	0.24	0.23
2162 Roaster Calcine	4.69, 4.87, 4.81, 4.69	5.21, 4.98, 5.12, 5.12, 5.07	4.77	5.10	0.0875	0.099	0.14	0.12
2163 D-2 1st stage	4.73, 4.39, 4.27, 4.17	4.39, 4.69, 4.13, 4.30, 4.05	4.39	4.31	0.27	0.275	0.42	0.34
2164 Hot Cottrell Dust	3.10, 2.67, 3.04, 2.95	–	2.94	–	0.21	–	0.32	–
2165 Baghouse Dust	0.30, 0.28, 0.30, 0.30, 0.31, 0.33	–	0.30	–	0.0205	–	0.022	–

(h)   Procedure No. 1 - bromate-hydrobromic acid leach; double extraction.
Procedure No. 2 - cold aqua regia leach; single extraction.

B. Determination of Arsenic, Antimony and Iron

Outline

Arsenic, antimony and iron are determined on a single solution from the same sample portion. The sample is taken into solution by a sodium peroxide sinter, followed by a water leach of the melt, and acidification of the solution with perchloric acid, tartaric acid and acetic acid. Direct atomization of the acidic solution can be carried out, but dilution will usually be necessary for some of the elements to bring their concentration into a range where the instrumental absorbance-concentration range is usable. The necessity for one of these dilutions can be avoided if the weight of sample for each type of sample material is chosen to provide a solution where the concentration of one of the elements will be in the correct range, and the correct concentration of the others can be obtained by further dilutions.

PROCEDURE

Sample Dissolution

Weigh out 1.0-g samples of the ore or mill products into 50-ml zirconium crucibles and add 8-10 grams of sodium peroxide. Without delay, mix the sample and peroxide thoroughly with a narrow spatula and cover the mixture with an additional 1-2 grams of sodium peroxide. Cover the crucibles with zirconium lids and place them in a muffle furnace set at 650°C for 30 minutes.

Remove the crucibles from the furnace and allow them to cool to about 50-75°C. Place crucibles and lids in 250-ml Pyrex beakers, insert a glass stirring rod and cover with watchglasses. Add 75 mls of distilled water and allow to stand until the exothermic reaction subsides. Add 10 mls of concentrated (70%) perchloric acid and stir contents well; now add 5 grams of tartaric acid and 25 mls of glacial acetic acid. Place the beakers on a hotplate set at a medium heat and agitate the contents periodically to hasten the disintegration of the sintered mass. Sample dissolution is considered as complete when little or no residue can be seen on the bottom of the beaker.* Fifteen minutes is usually sufficient time for sample dissolution and digestion. During this time, remove the zirconium crucibles and lids from the beakers and wash them with a warm 0.1% V/V perchloric acid solution delivered as a fine jet from a wash bottle.

---

* Zirconium from the crucible and silica from the ore dissolve in the melt and result in a heavy white precipitate on acidification. This precipitate is ignored.

Transfer the leachates to 250-ml volumetric flasks, filtering on a fast paper such as Whatman No. 541 or No. 1 so as to remove the coarse material which otherwise might clog the delivery tube of the burner atomizer, but neglecting any fine colloidal suspension that may appear in the filtrates. Cool, dilute to the mark and mix. At this point, if speed is essential, atomize the solutions directly from the flasks, or after such further dilutions as may be required to adjust the metal concentrations to the level where a suitable concentration-absorbance relationship exists. Alternatively, if a delay of 30 minutes can be tolerated at this point, and if some other operation can be fitted into the time, transfer contents of the beakers directly, without filtering, into 250-ml flasks. Cool, dilute to the mark and mix. Allow the flasks to stand until the precipitates settle (usually 15-30 minutes), and then atomize the solutions (if they are not clear, filter the portion to be atomized), or suitably diluted aliquots, directly into the flame for the atomic absorption measurements.

If a standard addition technique is to be used, add an amount of a standard solution of the metal being determined to a suitable aliquot of the sample and dilute to volume. Compare the effect of the sample matrix on the added standard and calculate as described in APPENDIX 3.

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 (i). Use a recorder for the measurement if greater precision is required. It is recommended that didymium glasses be worn to protect the worker from the effect of sodium emission.

For details of the operating procedure refer to APPENDICES 2, 3, 4.

RESULTS AND DISCUSSION

A sodium peroxide sinter followed by acidification of the melt proved to be superior to multi-acid dissolution of the sample, especially if it was desired to carry out arsenic, antimony and iron determinations on the same sample. Results for arsenic and iron, obtained by direct aspiration of the sample solution following sinter and leaching, compared very well with results provided by Giant Yellowknife laboratories, and also with titrimetric and colorimetric results obtained here on several samples (Table 4).

(i) Some loss of accuracy would be caused by using standard curves because of the difficulty of obtaining identical operating parameters each time an analysis were carried out.

Antimony results obtained were also acceptable in the case of all samples except the Baghouse Dust and the Hot Cottrell Dust. On the latter samples the apparent effect of matrix enhancement was evident and led to results that were about 20% high. These discrepancies were resolved by using a simple standard-addition technique, with results obtained for antimony as shown in Table 4. Once a correction factor is established on a particular type of sample material by doing standard-addition tests, it may then be possible to apply this correction for routine work on a continuous basis if the nature of the sample remains reasonably constant.

The precision for the three elements was calculated according to the procedure of Dean and Dixon (10) and Bauer (11), where three or more results were obtained with the recommended procedure. These results as shown in Table 5 are believed to be quite satisfactory for most purposes and should be well suited for mill-control purposes.

As it was desirable to obtain not only as simple a procedure as possible, but also one which would use the simplest of apparatus, a considerable effort was made to apply a multi-acid dissolution technique to the various types of samples. Results higher by 20% than given values were obtained for all three metals using multi-acid attack, due to apparent matrix enhancement. This enhancement can be compensated for by standard-addition techniques in the case of antimony and iron as their absorbance-to-concentration relationship is linear. Arsenic absorbance, however, is not linear with respect to concentration, and standard-addition correction is applicable only when there is a correction device for deviation from the Beer-Lambert Law in the read-out facility of the spectrophotometer.

It is not clear why the enhancement effect was mostly eliminated following sodium peroxide sinter, although if ionization interference was responsible for the enhancement the presence of large quantities of sodium would be expected to aid in removal of this effect. However, in the case of multi-acid dissolution, addition of large amounts of lanthanum, strontium or potassium had no remedial effect.

In the recommended procedure, a combination of perchloric acid, tartaric acid and acetic acid is used to dissolve the melt after a sodium peroxide sinter. While this was the most suitable combination of acids of those tried, it was not necessarily the only satisfactory one. Perchloric acid medium is generally a suitable one for atomic absorption work, while acetic acid and tartaric acid aided in solution of the iron. Also, it was found that the presence of tartaric acid was very helpful in rendering the antimony soluble and maintaining its solubility. The combination of these acids appeared to minimize the apparent matrix-enhancement effect found with some acid combinations during direct multi-acid attack.

It is estimated that twenty samples (60 determinations) could be prepared, and all three elements read on the spectrophotometer (i.e. 60 determinations could be carried out) within a 4-hour interval. The next set of 20 samples might be processed while some of the preceding steps are being carried out, and so on, depending on the analysis stream that is set up, the personnel available, and the precision and accuracy required.

The following lower limits were found to be attainable using a 1-gram sample diluted to 250 ml in a volumetric flask: - arsenic, 0.2%; antimony, 0.1%, and iron, 0.01%. Much higher quantities can be handled following dilution. The range of the procedures was sufficiently wide to cover easily the concentrations of the elements in the Giant Yellowknife samples provided.

The recommended procedure of the manufacturer (9) for using the hollow-cathode lamps and atomic absorption spectrophotometer was used for the three elements with little modification. A certain amount of familiarity with the instrument would be required for best results, especially in the arsenic determination.

The cost of our atomic absorption equipment, including the spectrophotometer, chart recorder, digital readout, and hollow-cathode lamps, would be about eleven 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 4

Results of Comparative Analyses for Arsenic, Antimony and Iron
on Samples from Giant Yellowknife Mines Ltd.

Sample Number EMM-	Sample type	Element determined	Analysis by		
			Giant Yellowknife %	EMD Chemically %	EMD Atomic Absorption %
2159	Heads	As	1.67	1.70	1.70
		Sb	0.34	-	0.35
		Fe	7.7	7.55	7.62
2160	Roaster Feed	As	9.61	9.38	9.32
		Sb	1.42	-	1.43
		Fe	21.7	21.6	21.9
2161	Bulk Conc.	As	9.46	-	9.45
		Sb	1.37	-	1.37
		Fe	20.9	20.2	20.6
2162	Roaster Calcine	As	0.91	-	0.93
		Sb	0.45	-	0.44
		Fe	27.0	26.7	27.2
2163	D-2 1st stage	As	1.32	-	1.24
		Sb	0.39	-	0.35
2164	Hot Cottrell Dust	As	6.65	-	6.26
		Sb	5.66	-	5.69
2165	Baghouse Dust	As	67.0	-	67.2
		Sb	1.12	-	1.15

TABLE 5

Precision of Analytical Results Obtained for Arsenic, Antimony and
Iron on Samples from Giant Yellowknife Mines Ltd.

Sample Number and Type EMM-	Element Determined	Individual Determinations by Atomic Absorption %	Average Result %	Precision Standard Deviation	Precision 95% Confidence for average result
2159 Heads	As	1.70, 1.72, 1.69	1.70	0.018	0.042
	Sb	0.35, 0.35, 0.37, 0.34	0.35	0.015	0.023
	Fe	7.82, 7.67, 7.53, 7.62, 7.55, 7.53	7.62	0.115	0.12
2160 Roaster Feed	Sb	1.42, 1.39, 1.49, 1.43, 1.44	1.43	0.043	0.053
	Fe	22.7, 20.5, 22.6	21.9	1.30	3.0
2161 Bulk Conc.	As	9.46, 9.33, 9.57	9.45	0.14	0.33
2162 Roaster Calcine	As	0.93, 0.92, 0.95	0.93	0.018	0.042
	Fe	27.2, 26.9, 27.4	27.2	0.30	0.70
2164 Hot Cottrell Dust	As	6.22, 6.23, 6.32	6.26	0.059	0.14
	Sb	5.70, 5.78, 5.52, 5.75	5.69	0.11	0.17
2165 Baghouse Dust	As	67.8, 66.8, 67.0	67.2	0.59	1.39
	Sb	5.70, 5.78, 5.52, 5.75	5.69	0.11	0.17

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 (9.9$\overset{o}{A}$ bandpass)
Wave length	— 2428 A°
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 p. s. i.
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 II

Atomic Absorption Operating Procedure - Arsenic

The monochromator must be adjusted to select the peak of the 1937-Å resonance line, since absorption and emission from the shoulder of the peak are both unstable. The adjustment must be checked after an initial warm-up period, as both lamp signal and flame noise cause drift in the monochromator and compensation and correction must be made (12).

Absorption is dependent on flame type(13), so that whatever amount of acetylene is required to obtain the best absorbing flame, conditions should be maintained throughout the running of the unknowns and suitable standards (14)(15).

The arsenic absorbances are enhanced when the " small-area technique" is used, in which a small-aperture mask is placed over the lens between the burner and the entrance slit of the monochromator. The mask isolates light from a portion of the cathode where the cross-sectional density of spectral

lines is maximum and this results in higher absorbance values for arsenic.
This requires an increase in the voltage supplied to the photomultiplier
circuit, as the total amount of light passing through the slit is reduced.
The higher voltage increases the magnitude of the fluctuations in the readings
which in turn require somewhat more damping. Regardless, the increase
in sensitivity and linearity resulting from the use of the " small-area
technique" more than compensates for any loss in stability.

The mask (which has a 5 to 6-mm aperture) is moved about the
centre of the lens until a maximum signal is displayed on the photomultiplier
readout. Peak signal is obtained when the most concentrated spectral line
source is selected from the cathode of the lamp. The burner is not lit
during this adjustment.

As arsenic absorption is non-linear with respect to concentration,
showing concavity towards the concentration axis, a readout device having
an analog digital display, with curvature correction for deviation from
Beer-Lambert's law such as the Techtron Digital Indicator Unit DI-20, may be
employed to advantage.

Instrumental conditions were as follows:

Hollow-cathode lamp	– Westinghouse No. 23147, multi-element for As, Sb, Bi
Photomultiplier tube	– Hamamatsu R 106
Lamp current	– 9 – 12 mA
Phototube circuit	– 600 volts
Monochromator split (9)	– 300 microns (9.9$\overset{\circ}{A}$ bandpass)
Wave length	– 1937 $\overset{\circ}{A}$
Burner height	– burner top 8 mm below centre of light path
Flame type	– acetylene-air, somewhat fuel-rich (reducing) for maximum absorption
Small-area mask	– 5 to 6-mm aperture, placed on lens between burner and slit
Air supply	– 15 p.s.i. to variable atomizer
Sample uptake	– 3.5 ml per minute
Flame emission	– 8 per cent signal (with lamp off, the difference between flame off and flame on)
Flame absorption	– 75 per cent signal (with lamp on, the difference between flame off and flame on)
Sensitivity	– 2ppm As for 1-per-cent absorption
50 per cent absorption	– 75 – 100 ppm As (depending on operating parameters).

Standard Solutions and Calibration Curve – Arsenic

Dissolve 1.3204 g of arsenious oxide (As_2O_3), dried at 110°C, in
20 ml of concentrated perchloric acid and 10 ml of concentrated nitric acid.
Heat to dense fumes of perchloric acid, cool and dilute to one litre and mix.

This solution should contain 1000 ppm As. Titrate a suitable aliquot with
0.1N iodine solution to establish that none of the arsenic has been lost in
the dissolution of As_2O_3.

Make appropriate dilutions to cover the range of 10 - 150 ppm As,
measure the corresponding absorbancies and plot absorbance versus ppm
As on cross-section graph paper.

As mentioned before, linearity extends only to about 50 ppm As
so that sample readings must be obtained by close bracketing with arsenic
standards, or by the use of a digital readout facility with curvature correction.

APPENDIX III

Atomic Absorption Operating Procedure - Antimony

As the resonance line for the determination of antimony at 2176 Å
is closer to the visible portion of the spectrum, there is much less flame
emission detected, and only one third the flame absorption that is found
with arsenic determinations at 1937 Å (a less sensitive resonance line suitable
for antimony determinations is located at 2312 Å This spectral line may be
selected if flame emission causes excessive fluctuation in absorption readings,
as less overall instrumental noise occurs at 2312 Å (6).

There is much less monochromator drift involved in the antimony
determinations, and absorption is relatively independent of flame composition.
No observable advantage is gained using the " small-area technique", and it
is therefore not recommended since it requires the application of a higher
voltage to the photomultiplier tube. The absorption of antimony in the flame
is linear with respect to concentration (6).

Instrumental conditions are as follows:

Hollow-cathode lamp	- Westinghouse No. 23147, multi-element for As, Sb, Bi
Photomultiplier tube	- Hamamatsu R 106
Lamp current	- 9 - 12 mA
Phototube circuit	- 560 volts
Monochromator slit(9)	- 100 microns (3.3 Å bandpass)
Wave length	- 2176 Å
Burner height	- burner top 8mm below centre of light path
Flame type	- acetylene-air, stoichiometric
Air supply	- 15 psi to variable atomizer
Sample uptake	- 3.5 ml per minute

Flame emission   - 1-per-cent signal (with lamp off, difference between flame off and flame on)

Flame absorption   - 20-per-cent signal (with lamp on, difference between flame off and flame on)

Sensitivity   - 0.5 ppm Sb for 1-per-cent absorption

50-per-cent absorption   - 30 ppm Sb.

When matrix composition results in an increase or decrease in the expected absorption readings for antimony in the flame (as indicated by standard additions), the standard-addition technique must be used for all such samples. In this case, the results must be calculated by the " spiking" formula, ie,

$$\frac{X}{X+a} = \frac{A_1}{A_2} \quad \text{or} \quad X = \frac{aA_1}{A_2-A_1} \, , \quad \text{where}$$

X is the unknown concentration of the metal in the leachate, a_1 is the known concentration of metal added, and A_1 and A_2 are the absorbances before and after the standard addition of a_1

Standard Solutions and Calibration Curve - Antimony

Dissolve at low heat 1.000 g of antimony metal powder (Fisher Catalogue No. 482896 or its equivalent), or 1.2628 g of antimony tetroxide (Sb_2O_4), dried at 110°C, in 20 ml of concentrated hydrochloric acid. Cool and dilute to 100ml with distilled water. Add 10 g of tartaric acid and stir. Dilute to one litre and mix. This solution contains 1000 ppm Sb.

Make appropriate dilutions to cover the range of 5 - 50 ppm Sb, measure the corresponding absorbancies and plot absorbance versus ppm Sb on cross-section graph paper. The resulting plot should be linear.

APPENDIX IV

Atomic Absorption Operating Procedure - Iron

The emission spectrum from the iron hollow-cathode lamp is somewhat complex and the monochromator is limited in its ability to resolve the resonance and the non-resonance lines of iron, although use of a narrow bandpass slit of 25 microns (0.8 Å) is advantageous (16, 17). The presence of the non-resonance lines causes curvature of the calibration graph.

The 2483-Å resonance line is selected for most atomic absorption determinations of iron as it is the most intense and is highly absorbed by iron atoms in the flame. Thus, a narrow bandpass may be used without excessive amplification in the readout facility. The result is a steady signal with a minimum of background noise.

The acetylene-air flame neither absorbs nor emits light of consequence to atomic absorption measurements at the 2483-Å spectral line. There is no increase in sensitivity derived from the "small-area technique" in this determination.

Instrumental conditions were as follows:

Hollow-cathode lamp	– Atomic Spectral Lamps, Australia, single-element Fe
Photomultiplier tube	– Hamamatsu R 106
Lamp current	– 10 mA
Phototube circuit	– 580 volts
Monochromator slit(9)	– 25 microns (0.8Å bandpass)
Wave length	– 2483 Å
Burner height	– burner top 6 mm below centre of light path
Flame type	– acetylene-air, stoichiometric
Air supply	– 15 psi, to variable atomizer
Sample uptake	– 3.5 ml per minute
Flame emission	– < 1-per-cent signal (with lamp off, the difference between flame off and flame on)
Flame absorption	– 8-per-cent signal (with lamp on, the difference between flame off and flame on)
Sensitivity	– 0.2 ppm Fe for 1-per-cent absorption
50 per cent absorption	– 8 ppm Fe

Standard Solutions and Calibration Curve - Iron

Dissolve 0.5000 g of clean and dry iron wire or pure iron granules (such as British Chemical Standards No. 149/1) in 20 ml of 1:1 hydrochloric acid, warming if necessary. Dilute to one litre and mix. This solution contains 500 ppm Fe.

Make appropriate dilutions to cover the range of 1 - 10 ppm Fe, measure the corresponding absorbancies and plot absorbance versus ppm Fe on cross-section graph paper. The resulting plot should be linear.

REFERENCES

1. J.E. Allan, 4th Annual Spectroscopy Conference, Canberra, Aug.,1963.

2. W. Slavin, S. Sprague, D.C. Manning, Atomic Absorption Newsletter, No. 18, (1964).

3. W. Slavin, Carl Sebens, S. Sprague, Atomic Absorption Newsletter, 4, No. 9, (1965).

4. J.E. Allan, Spectrochim. Acta, 18, 259 (1962).

5. W. Slavin, Atomic Absorption Newsletter, No. 24, 15 (1964).

6. R.A. Mostyn and A.F. Cunningham, Anal. Chem., 39, 433-5 (1967).

7. H.W. Lakin and H.M. Nakagawa, Engineering and Mining Journal, 166, 108-10 (1965).

8. F.W.E. Strelow et al., Anal. Chem., 38, 115-7 (1966).

9. Techtron Instruction Manual for the Atomic Absorption Spectrophotometer, Model AA3, Techtron PTY. Ltd., Melbourne, Victoria (Second reprint, ca 1965).

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

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

12. W.W. Harrison and K. Caufield, Anal. Chim Acta, 39, 161-6(1967).

13. W. Slavin, Applied Spectroscopy, 20, 281-8 (1966).

14. M.D. Amos, The Element, Aztec Instrument Corp. Conn., No. 16 (1967).

15. E. Pungor, "Flame Photometry Theory", D. Van Nostrand Co., London, p. 162, 1967.

16. J.W. Robinson, Anal. Chim. Acta, 27, 465-9 (1962).

17. W.T. Elwell and J.A.F. Gidley, "Atomic-Absorption Spectrophotometry", MacMillan Co., New York, p. 81, 1962.
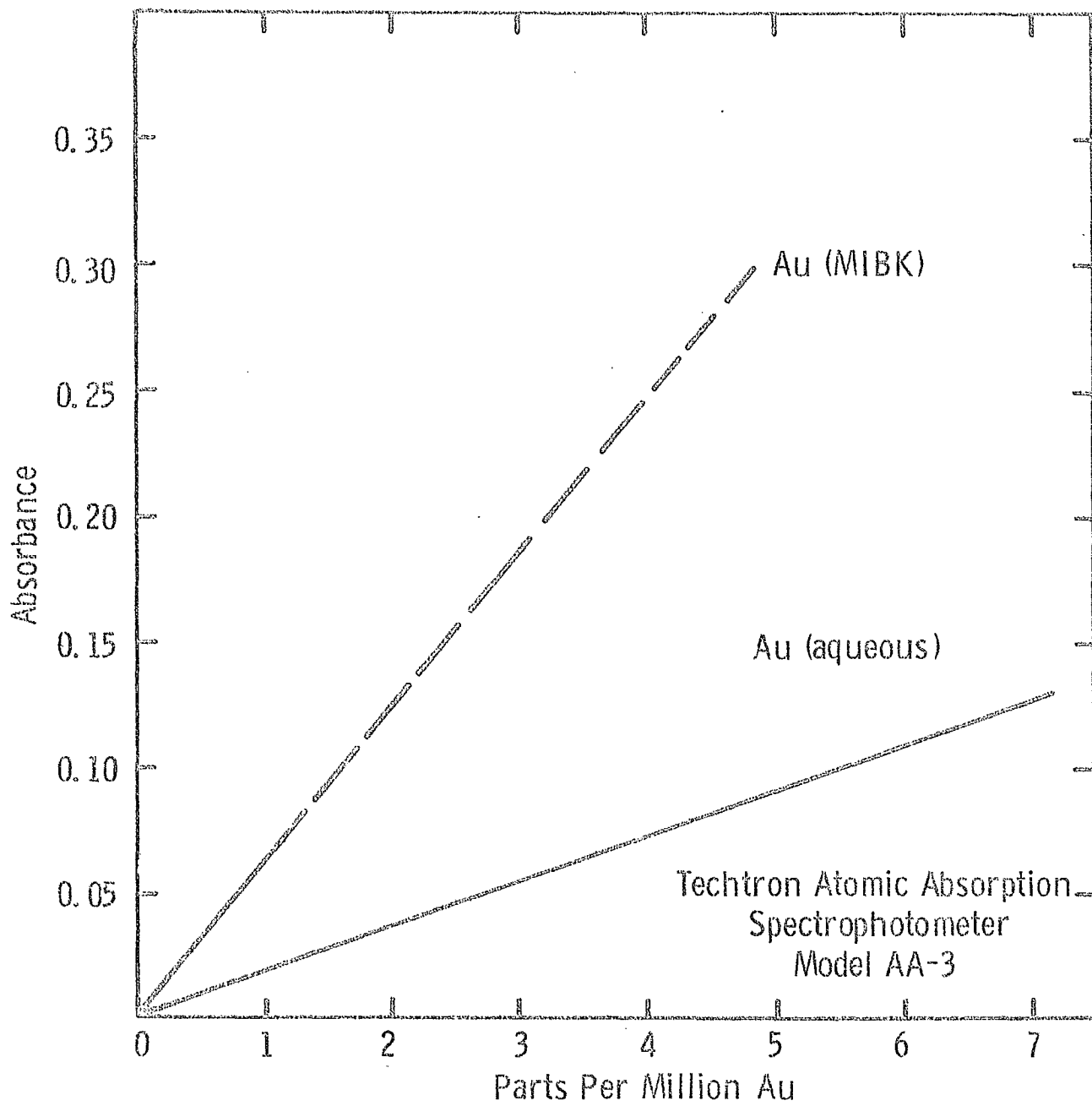
ACKNOWLEDGEMENTS

=====

GAH:RJG:mn

Figure 1: Comparative Sensitivities of Gold in Aqueous and Organic Medium, using Atomic Absorption Spectrophotometry
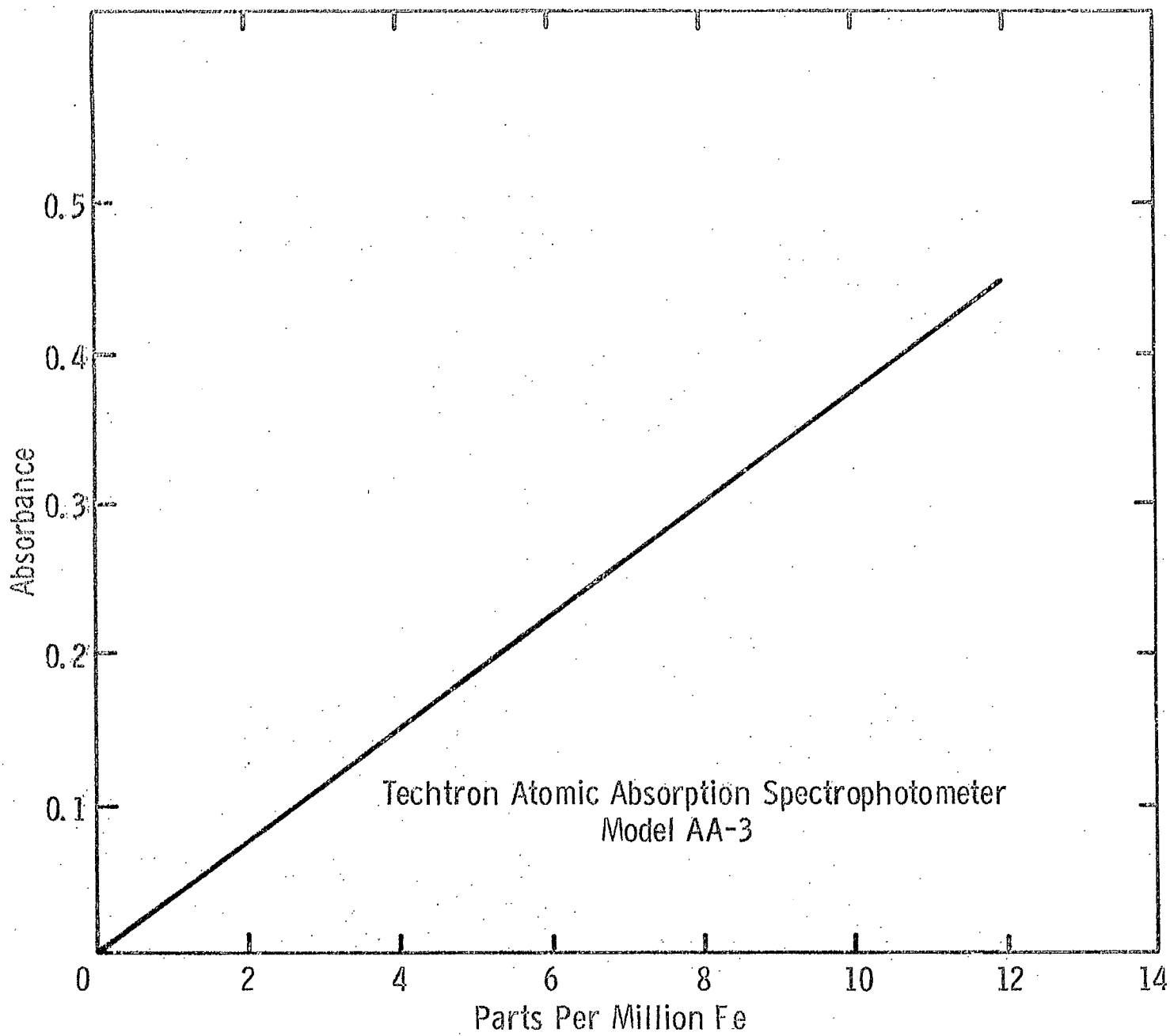
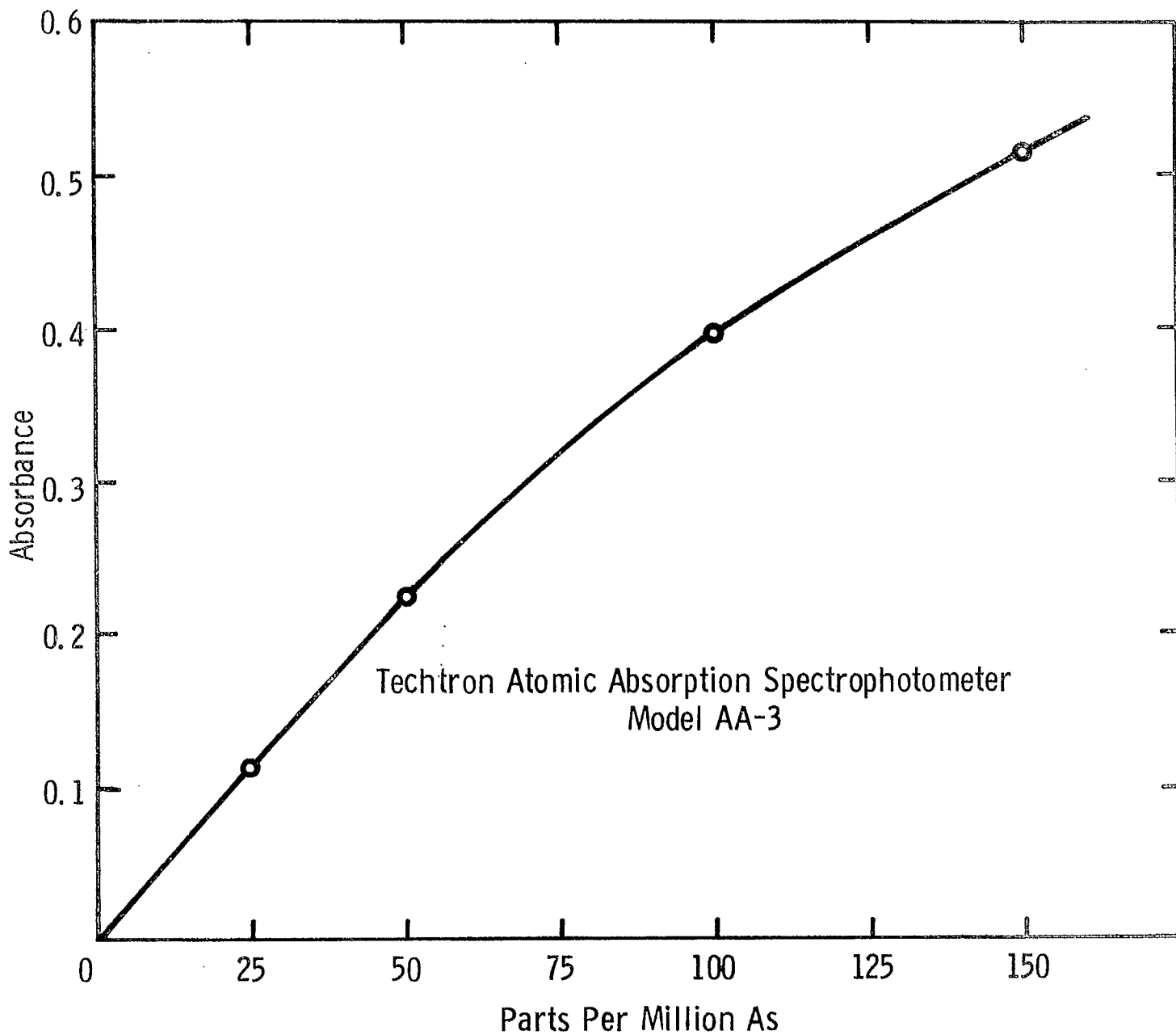Figure 2: Calibration Graph of Iron using Atomic Absorption Spectrophotometry

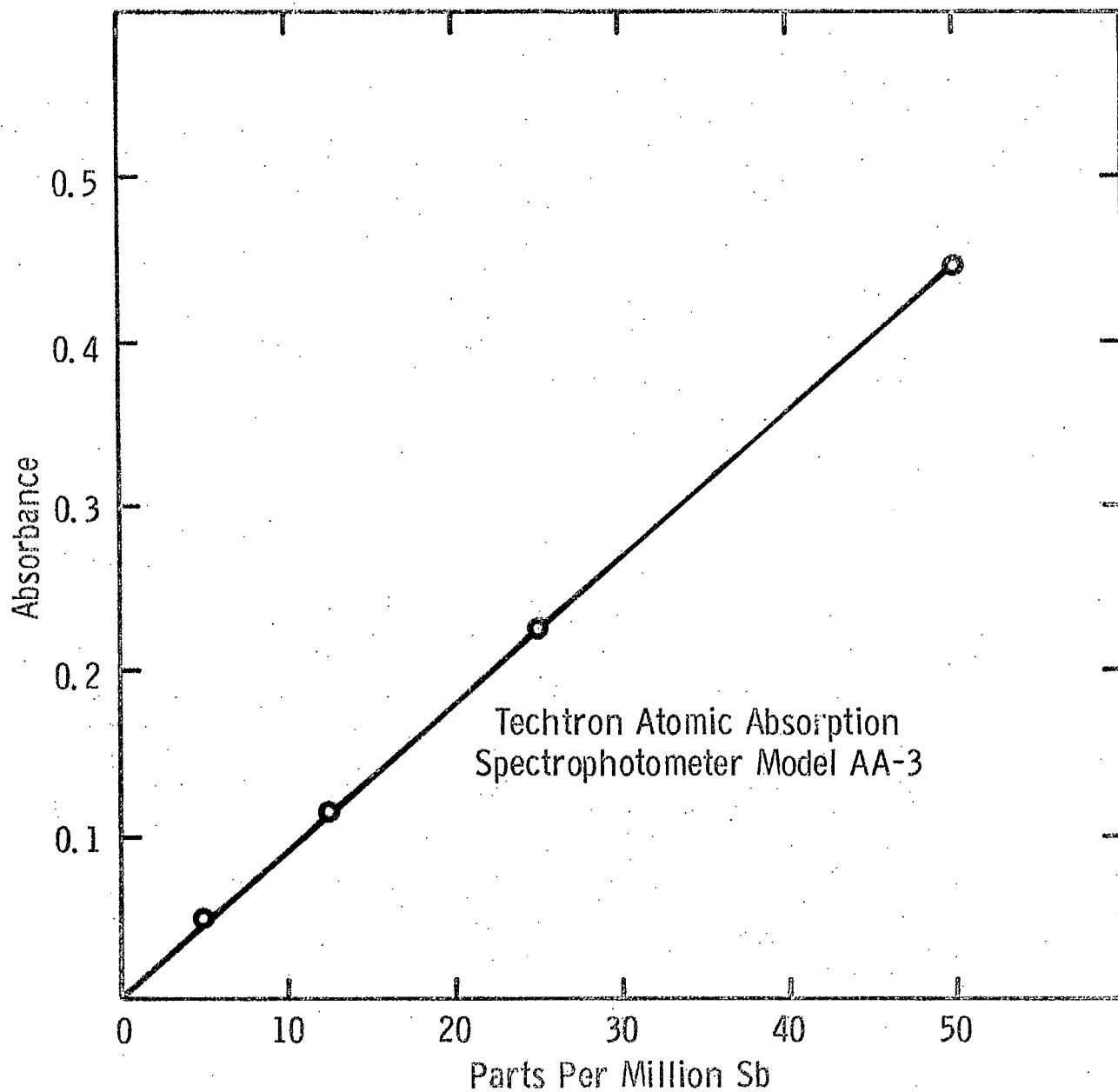Figure 3: Calibration Graph of Arsenic using Atomic Absorption Spectrophotometry

Figure 4: Calibration Graph of Antimony using Atomic Absorption
Spectrophotometry