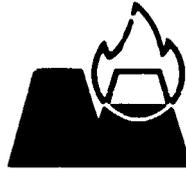


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MINTEK

REPORT

No. M39

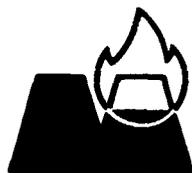
THE USE OF MASKING AGENTS IN THE DETERMINATION, BY
HYDRIDE GENERATION AND ATOMIC-ABSORPTION SPECTROPHOTOMETRY,
OF ARSENIC, ANTIMONY, SELENIUM, TELLURIUM, AND
BISMUTH IN THE PRESENCE OF NOBLE METALS

by

S.P. Kellerman

16th July, 1982

COUNCIL FOR MINERAL TECHNOLOGY
200 Hans Strijdom Road
RANDBURG
South Africa



MINTEK

(ANALYTICAL CHEMISTRY DIVISION)

REPORT

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SYNOPSIS

The effectiveness of thiosemicarbazide, tellurium, and potassium iodide as masking agents to eliminate interferences was assessed. Thiosemicarbazide was found to be effective in eliminating or reducing the interferences on arsenic, antimony, and bismuth, and tellurium reduced the interferences on selenium. The interferences on tellurium could not be eliminated.

Arsenic, antimony, selenium, and bismuth were determined in metal sulphide concentrates that were spiked with the noble metals (defined here as gold plus all the platinum-group metals except osmium). The relative standard deviations for arsenic, antimony, bismuth, and selenium were 0,061, 0,017, 0,029, and 0,145 respectively. The values obtained for all the analytes agreed favourably with the preferred values for two in-house reference samples.

The laboratory method is detailed in an appendix.

SAMEVATTING

Die doeltreffendheid van tiosemikarbasied, telluur en kaliumjodied as maskeermiddels om steurings uit te skakel is geëvalueer. Daar is gevind dat tiosemikarbasied doeltreffend is om steurings ten opsigte van arseen, antimoon en bismut uit te skakel of te verminder, terwyl telluur die steurings ten opsigte van seleen verminder het. Die steurings ten opsigte van telluur kon nie uitgeskakel word nie.

Arseen, antimoon, seleen en bismut is bepaal in metaalsulfiedkonsentrate wat met die edelmetale (hier omskryf as goud plus al die platinumgroepmetale behalwe osmium) gesoek is. Die betrokke standaardafwykings vir arseen, antimoon, bismut en seleen was onderskeidelik 0,061, 0,017, 0,029 en 0,145. Die waardes wat vir al die analiete verkry is, het gunstig vergelyk met die voorkeurwaardes vir twee interne verwysingsmonsters.

Die laboratoriummetode word in 'n aanhangsel uiteengesit.

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1. INTRODUCTION

Because of its high sensitivity, the technique involving atomic-absorption spectrophotometry (AAS) with hydride generation is commonly used for the determination of low concentrations of arsenic, antimony, selenium, bismuth, and tellurium. However, in the application of this technique, a variety of metal ions cause serious interference. Several authors have studied the interference effects caused by different metal ions^{1,2} and have suggested the use of masking or complexing agents for their elimination³⁻⁶. In a comprehensive study Robert² showed that there were severe interferences from some of the noble metals (defined in this report as gold plus all the platinum-group metals except osmium), especially platinum, palladium, rhodium, and gold, and that the most serious base-metal interferences appeared to be copper and nickel. In the determination of arsenic, Kirkbright and Taddia⁶ overcame the interferences caused by copper, nickel, palladium, and platinum by using thiosemicarbazide and 1,10 phenanthroline. They also managed to successfully determine selenium by using tellurium as a complexing agent⁵. Yamamoto *et al.*³ suggested the use of potassium iodide in the determination of antimony.

It was decided that an attempt should be made to assess whether, and to what extent, some of the complexing and masking agents that are recommended in the literature are effective in overcoming interference from the noble metals during the determination of arsenic, antimony, selenium, bismuth, and tellurium by hydride generation and AAS.

2. EXPERIMENTAL METHODS

2.1. Apparatus and Reagents

The reduction apparatus used in all the work described in this report is a simplified version of the Perkin-Elmer balloon-reservoir apparatus (Figure 1). It consists of a 500 ml Buchner filtration flask (reaction vessel) fitted with a rubber stopper having three outlets, one of which has a rubber septum to allow sodium borohydride solution to be injected. The other two outlets are connected by Tygon tubing (with an internal diameter of 1 cm) to the atomic-absorption spectrophotometer's nitrogen inlet and spray chamber.

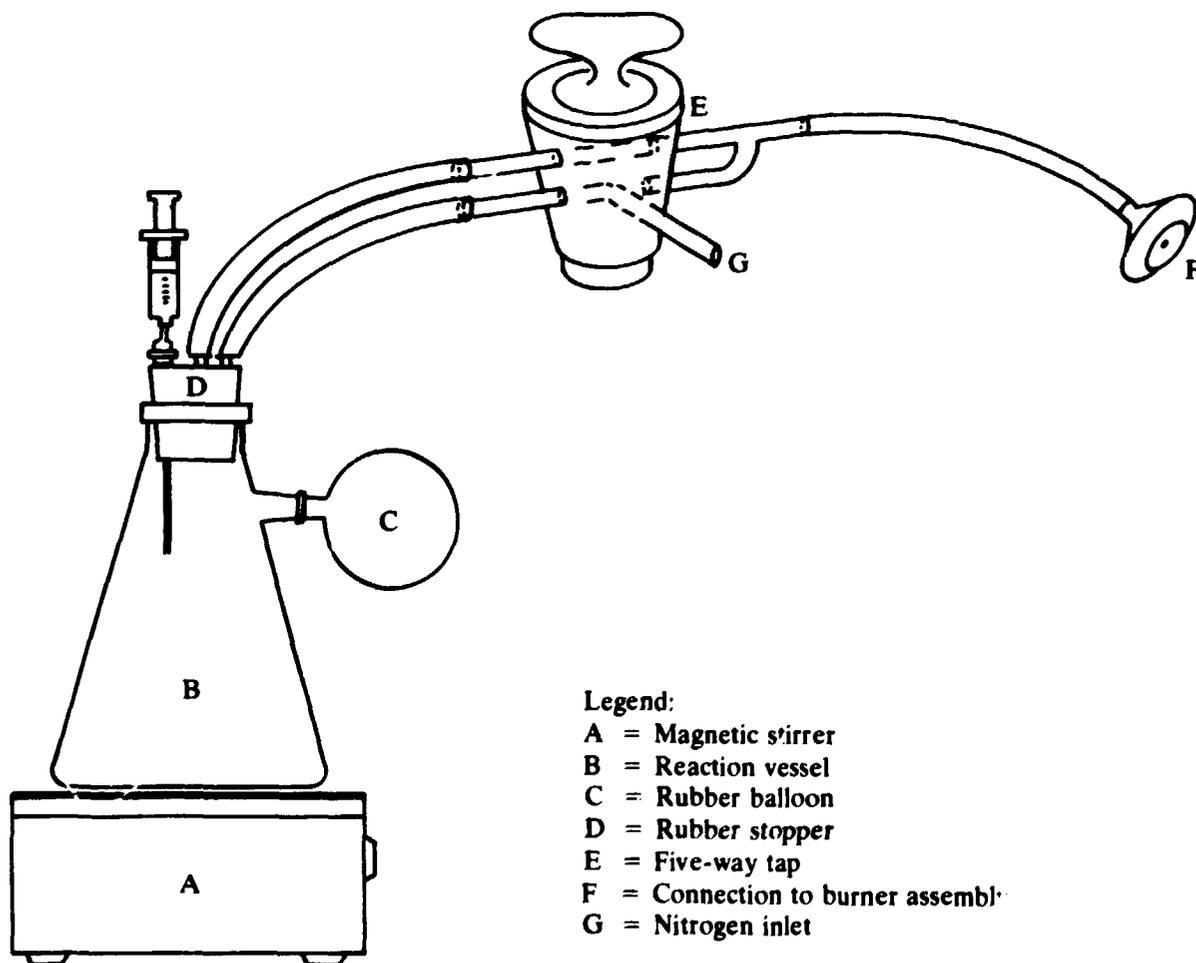


FIGURE 1. The apparatus used for hydride generation (after Robert²)

MASKING AGENTS

A five-way glass tap allows the nitrogen to by-pass the reaction vessel or to enter it and sweep the evolved hydrides into the flame. A rubber balloon, which is connected to the glass outlet of the Buchner filtration flask, provides a reservoir for the evolved hydrides and hydrogen.

A Varian Techtron Model AA6 spectrophotometer fitted with a Varian Techtron BC-6 simultaneous background corrector (hydrogen hollow-cathode lamp), an automatic gas-control unit, and a Corning recorder Model 840, were used throughout the experimental work. Varian Techtron hollow-cathode lamps were used in the measurement of all the hydride-forming elements except arsenic, for which a lamp manufactured by Pye Unicam was used.

Standard stock solutions of antimony, arsenic, bismuth, selenium, and tellurium were prepared from the pure metals or their oxides (details are given in the Appendix), and were diluted for use with 40 per cent (v/v) hydrochloric acid. For the interference studies, standard solutions of the noble metals were prepared from the high-purity metals; the rest of the standard solutions were prepared from chloride salts.

A solution (40 g/l) of sodium borohydride was prepared by dissolution of the reagent (Merck Analar) in water in which two pellets of sodium hydroxide had been dissolved. This solution was freshly prepared immediately before use. Merck's A.R.-grade hydrochloric acid (37 per cent) was used throughout.

A solution that was used to spike the sample solutions was prepared as follows. Solutions of the individual noble metals were mixed in the following ratio: platinum 60 per cent, palladium 24 per cent, gold 5 per cent, rhodium 5 per cent, ruthenium 5 per cent, and iridium 1 per cent. The total noble-metal concentration of the solution was 10 g/l.

2.2. Interference Studies

According to Rob rt², there is severe interference from some of the noble metals at the 1 mg level during measurement of the hydride-forming elements. Interference tests were therefore carried out, synthetic solutions of the five hydride-forming elements being used in the presence of 1 mg amounts of the noble metals. This is the highest concentration that is expected to be present in the sample materials usually analysed by hydride generation in the laboratory of the Council for Mineral Technology (Mintek). Individual noble metals were added as well as combinations of all of them.

Of the suggested masking agents, only thiosemicarbazide, tellurium, and potassium iodide were chosen for testing, since preliminary tests with 1,10 phenanthroline had been unsuccessful, and some of the other masking agents suggested in the literature⁷ required a pH value that was too high for use with hydride generation.

Standard solutions of the analytes were prepared, reduced as described in the Appendix, and diluted to the concentrations given in Table 1. The degree of interference was determined from measurements of the recovery* of each of the analytes in the presence of each of the interferents and in the presence of a combination of the interferents mixed as described in Section 2.1. The measurements were repeated after the addition of 1 ml of the masking agent, and the recovery was again calculated. The preparation of the masking agents is described in the Appendix.

A mixture containing the interferent and the masking agent was used as a blank solution. The results shown in Table 1 confirm Rob rt's findings² on the interference from the noble metals, and show that there is severe interference in the determination of all the elements in the presence of platinum, palladium, rhodium, and gold. Although less interference occurs in the presence of ruthenium and iridium, it is still severe enough to be significant in some instances, e.g., with arsenic and tellurium. As was expected, the recovery of the analytes in the presence of a solution of mixed noble metals was in all cases less than 10 per cent.

Thiosemicarbazide appears to be the most effective of the masking agents, but tellurium was used with more success in the determination of selenium. Potassium iodide eliminated the interference from gold in the determination of antimony but generally had little masking effect on the remaining analytes. However, it reduced arsenic and antimony to their lower oxidation states, a necessary step in the complete reduction of these elements to their hydrides.

It can therefore be concluded that, when arsenic, antimony, selenium, and bismuth are measured by hydride generation and AAS, the interference caused by the noble metals (at the levels investigated) can be eliminated or reduced by the addition of an appropriate masking agent whether the noble metals are present individually or in combination.

No masking agent could be found to effectively eliminate the interference in the determination of tellurium.

* In this report, *recovery* means amount determined as a percentage of the amount present.

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TABLE 1

The effect of masking agents on interference

Analyte concentration, µg/g

Arsenic 0.2 Tellurium 0.5

Antimony 0.2 Bismuth 0.5

Selenium 0.5

Interferent (1 mg) and masking agent	Recovery, %				
	As	Sb	Se	Te	Bi
Pt	4	5	6	4	11
Pt + TSC	100	100	6	4	100
Pt + Te	-	-	100	-	-
Pt + KI	-	-	-	4	-
Pd	1	0	3	2	0
Pd + TSC	100	42	3	7	29
Pd + Te	-	0	95	-	0
Pd + KI	-	0	-	2	0
Rh	4	3	10	8	4
Rh + TSC	100	100	10	64	100
Rh + Te	-	-	31	-	-
Rh + KI	-	-	10	8	-
Au	2	3	50	0	3
Au + TSC	95	44	50	0	12
Au + Te	-	-	78	-	3
Au + KI	-	100	50	0	3
Ru	93	88	68	49	90
Ru + TSC	100	100	68	80	100
Ru + Te	-	-	70	-	-
Ru + KI	-	-	68	49	-
Ir	17	100	100	74	100
Ir + TSC	100	-	-	75	-
Ir + Te	-	-	-	-	-
Ir + KI	-	-	-	74	-
Noble metals	6	3	2	2	0
Noble metals + TSC	100	91	2	2	70
Noble metals + Te	-	-	86	-	0
Noble metals + KI	-	3	2	2	0

TSC = Thiosemicarbazide, 0.5 M (1 ml)

Te = Tellurium, 0.2 per cent (1 ml)

KI = Potassium iodide, 10 per cent (1 ml)

2.3. Accuracy and Precision

In the assessment of the effectiveness of masking agents in the analysis of sample material, the main difficulty was the unavailability of suitable reference materials that contain the noble metals and have recommended values for the analytes. It was therefore decided that use should be made of two metal sulphide concentrates that had previously been analysed at Mintek. The major constituents of these concentrates are given in Table 2.

MASKING AGENTS

TABLE 2

Major constituents of sulphide concentrates

Sample no.	Major constituent, %				
	Cu	Fe	Pb	S	Zn
1	1,1	3,4	71,0	14,0	3,0
2	27,0	21,0	17,0	28,4	5,9

These concentrates were spiked with a solution of mixed noble metals prepared as described in Section 2.1 so that the noble-metal concentration of the final sample solution was 0.5 mg/l.

The noble metals were added as follows. A portion (5 ml) of the spiking solution, which contained 10 g of the mixed noble metals per litre (Section 2.1), was evaporated to dryness in a carbon crucible, after which the sulphide concentrates were added and the mixture fused with sodium peroxide.

Arsenic and selenium were determined after being separated from copper and nickel, and bismuth and antimony were determined in separate portions of the samples after the precipitation of their hydroxides with lanthanum (as described in the Appendix). All the analytes were reduced to their lower oxidation states by use of the methods suggested by Sinemus *et al.*⁸, which are also described in the Appendix. The appropriate masking agent was added to the solutions immediately prior to the reduction with sodium borohydride. The results obtained are given in Table 3, which compares the values obtained in the presence of the noble metals with the preferred values. The relative standard deviation (s_r) for each analyte, obtained from the average analysis of ten portions of sample material, are also given. The relative standard deviations for arsenic, antimony, and bismuth varied between 0.017 and 0.061, which is acceptable. The poor precision for selenium ($s_r = 0,145$) can be ascribed to its low concentration in the sample (close to the limit of determination of $1 \mu\text{g/g}$). At the 95 per cent confidence level, the values obtained for all four of the analytes agree favourably with the recommended values.

TABLE 3

Accuracy and precision of the results

Sample no.	Element	Relative standard deviation s_r	Value obtained p.p.m.	Recommended value p.p.m.
2	As	0,061	2,2	2,4
2	Sb	0,017	60	60
1	Bi	0,029	1175	1238
2	Se	0,145	1,7	1,4

3. DISCUSSION

Although in many instances the addition of a masking agent completely eliminated interferences in the determination of some noble metals (Table 1), complete elimination of interference from all of the noble metals examined could be achieved only for arsenic. The arsenic concentration could therefore be determined direct by reference to a set of calibration standards. Antimony, selenium, and bismuth all exhibited some degree of interference in the presence of 1 mg of the combined noble metals, even when an excess of masking agent was used. These elements would therefore normally need to be measured by the method of standard additions. However, in the samples analysed, the concentrations of bismuth and antimony were sufficiently high to allow for considerable dilution of the solutions. As a result, there was less interference and therefore no need for the method of standard additions to be used.

It was very difficult for selenium (VI) to be reduced to selenium (IV) by the usual procedure of heating it for 30 minutes in a solution of 5 M hydrochloric acid just under boiling point. According to Sinemus *et al.*⁸, selenium can be reduced more efficiently if it is boiled. If boiled in polypropylene or

polytetrafluoroethylene (PTFE), the selenium is not volatilized and lost as it would be in glass. The solutions containing selenium were therefore boiled in covered Teflon beakers for approximately 15 minutes, after which more precise and much higher peak heights were recorded, indicating that the reduction of selenium had been more efficient.

Vijan and Leung⁴ have suggested that, in the determination of selenium, 9 M hydrochloric acid should be used to overcome the interferences from heavy-metal ions. Tests were done with 9 M hydrochloric acid, but it was found to be ineffective in overcoming interferences from the noble metals.

In the present work, none of the masking agents tested was found to be effective when tellurium was measured in the presence of the combined noble metals. This is probably because tellurium forms very stable tellurides with many of the interfering ions. (Tellurium can be used as a masking agent in the determination of selenium.) Tests in which two other possible masking agents, 1,10 phenanthroline and thiourea, were used were also unsuccessful.

4. CONCLUSIONS

Severe interference from the noble metals is encountered during the determination of arsenic, antimony, selenium, bismuth, and tellurium by hydride generation and AAS. In the determination of arsenic, bismuth, and antimony, thiosemicarbazide either eliminates these interferences completely or reduces them to such an extent that the measurement can be made successfully by use of the method of standard additions. In the determination of selenium, tellurium is, to some extent, effective as a masking agent, but, in the determination of tellurium, none of the masking agents tested eliminates the interferences.

The precisions for arsenic, antimony, and bismuth are acceptable, the relative standard deviations being 0.061, 0.017, and 0.029 respectively. The poor relative standard deviation recorded for selenium (0.145) is a result of its low concentration (1.5 $\mu\text{g/g}$) in the sample and its poorer sensitivity. The values obtained for all the analytes in the in-house reference materials used were found to agree favourably with the preferred values.

5. REFERENCES

1. PIERCE, F.D., and BROWN, H.R. Comparison of inorganic interferences in atomic absorption spectrometric determination of arsenic and selenium. *Analyt. Chem.*, vol. 49, no. 9, 1977, pp. 1417-1421.
2. ROBERT, R.V.D. Atomic-absorption determination, in metal sulphide concentrates, of the elements that form gaseous hydrides. Johannesburg, National Institute for Metallurgy, *Report 1838*, 1976, 38 pp.
3. YAMAMOTO, M., SHOHJI, T., KUMARARU, T., and YAMAMOTO, Y. Masking effect of potassium iodide on the interferences in the atomic absorption spectrophotometric determination of antimony utilizing stibine generation by sodium borohydride tablet reduction. *Fresenius Z. analyt. Chem.*, vol. 305, 1981, pp. 11-14.
4. VIJAN, P.M., and LEUNG, D. Reduction of chemical interference and speciation studies in the hydride generation-atomic absorption method for selenium. *Analyt. chim. Acta*, vol. 120, 1980, pp. 141-146.
5. KIRKBRIGHT, G.F., and TADDIA, M. Use of tellurium (IV) to reduce interferences from some metal ions in the determination of selenium by hydride generation and atomic absorption spectrometry. *Atom. Abs. Newsl.*, vol. 18, no. 3, 1979, pp. 68-70.
6. KIRKBRIGHT, G.F., and TADDIA, M. Application of masking agents in minimizing interferences from some metal ions in the determination of arsenic by atomic absorption spectrometry with the hydride generation technique. *Analyt. chim. Acta*, vol. 100, 1978, pp. 145-150.
7. AGGETT, J., and ASPELL, A.C. The determination of arsenic (III) and total arsenic by atomic absorption. *Analyst, Lond.*, vol. 10, 1976, p. 341.
8. SINEMUS, H.W., MELCHER, M., and WELZ, B. Influence of valence state on the determination of antimony, arsenic, bismuth, selenium and tellurium in lake water using the hydride A.A. technique. *Atom. Spectrosc.*, vol. 2, no. 3, 1981, pp. 81-86.

MASKING AGENTS

E.1 Arsenic Antimony, Bismuth, Selenium

APPENDIX

THE DETERMINATION, BY HYDRIDE GENERATION AND ATOMIC-ABSORPTION SPECTROPHOTOMETRY, OF MICROGRAM AMOUNTS OF ARSENIC, ANTIMONY, BISMUTH, AND SELENIUM IN THE PRESENCE OF NOBLE METALS (Laboratory Method No. 0/23)

1. OUTLINE

The sample is fused with sodium peroxide in a zirconium crucible. For the determination of arsenic and selenium, the melt is leached in water and the copper and nickel are separated by filtration. Arsenic and selenium are determined in the filtrate by evolution of their hydrides and measurement by atomic-absorption spectrophotometry (AAS).

For the determination of antimony and bismuth, another portion of the sample is fused, and the melt is leached in hydrochloric acid. The elements to be determined are precipitated as hydroxides, leaving copper and nickel in solution. After dissolution of the precipitate, antimony and bismuth are determined in the same manner as are arsenic and selenium.

2. APPLICATION

The method is applicable to the determination of arsenic, antimony, bismuth, and selenium in sample materials containing base metals as well as the noble metals (which are defined here as gold plus all the platinum-group metals except osmium), and should be effective in the analysis of most types of samples. The lower limit of determination of the analytes (for an error of 10 per cent) is $1\ \mu\text{g/g}$.

3. APPARATUS

(1) *Atomic-absorption Spectrophotometer*

This could be a Varian Techtron AA6, and should be fitted with a simultaneous background corrector and a chart recorder.

(2) *Reduction Vessel*

This should be fitted with a five-way tap¹ (Figure 1-1).

(3) *Magnetic Stirrer*

(4) *Rubber Balloon*

Any small balloon of good quality can be used.

4. REAGENTS

(1) *Hydrochloric Acid, 40 per cent (v/v)*

Dilute 40 ml of hydrochloric acid (A.R. grade) to 100 ml with water.

(2) *Sodium Peroxide*

A.R. grade.

(3) *Lanthanum Nitrate*

Merck $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$.

(4) *Sodium Borohydride Solution, 50 g/l*

Dissolve 2 pellets of sodium hydroxide in 50 ml of water. Add 4 g of sodium borohydride (Merck A.R. grade), stir to dissolve, and dilute to 100 ml. Prepare this solution immediately before use.

(5) *Potassium Iodide, 100 g/l*

Dissolve 10 g of potassium iodide (A.R. grade) in water, and dilute to 100 ml with water.

(6) *Thiosemicarbazide, 0.5 M*

Dissolve 4.55 g of thiosemicarbazide (Merck A.R. grade) in water, and dilute to 100 ml with water.

(7) *Tellurium, 2 g/l*

Dissolve 2 g of tellurium metal in 90 ml of a 1:1:1 solution of nitric acid, hydrochloric acid, and water, and dilute to 100 ml with water.

(8) Standard Solutions of Arsenic, Antimony, Bismuth, and Selenium

1 ml \equiv 1 mg.

Prepare all standard solutions as described by Varian Techtron².

Prepare working standard solutions for arsenic, antimony, and bismuth by diluting the standard solution with 40 per cent (v/v) hydrochloric acid so that 1 ml of solution is the equivalent of 0.1 μ g of the analyte element.

Prepare a working solution of selenium as follows. Add sufficient hydrochloric acid to the required aliquot portion of the selenium standard solution to give a concentration of 6 M. Boil the solution in a covered Teflon beaker for 15 minutes to reduce the selenium to its lower oxidation state. Cool, and dilute to the required volume so that the final solution has a hydrochloric acid concentration of about 40 per cent (v/v).

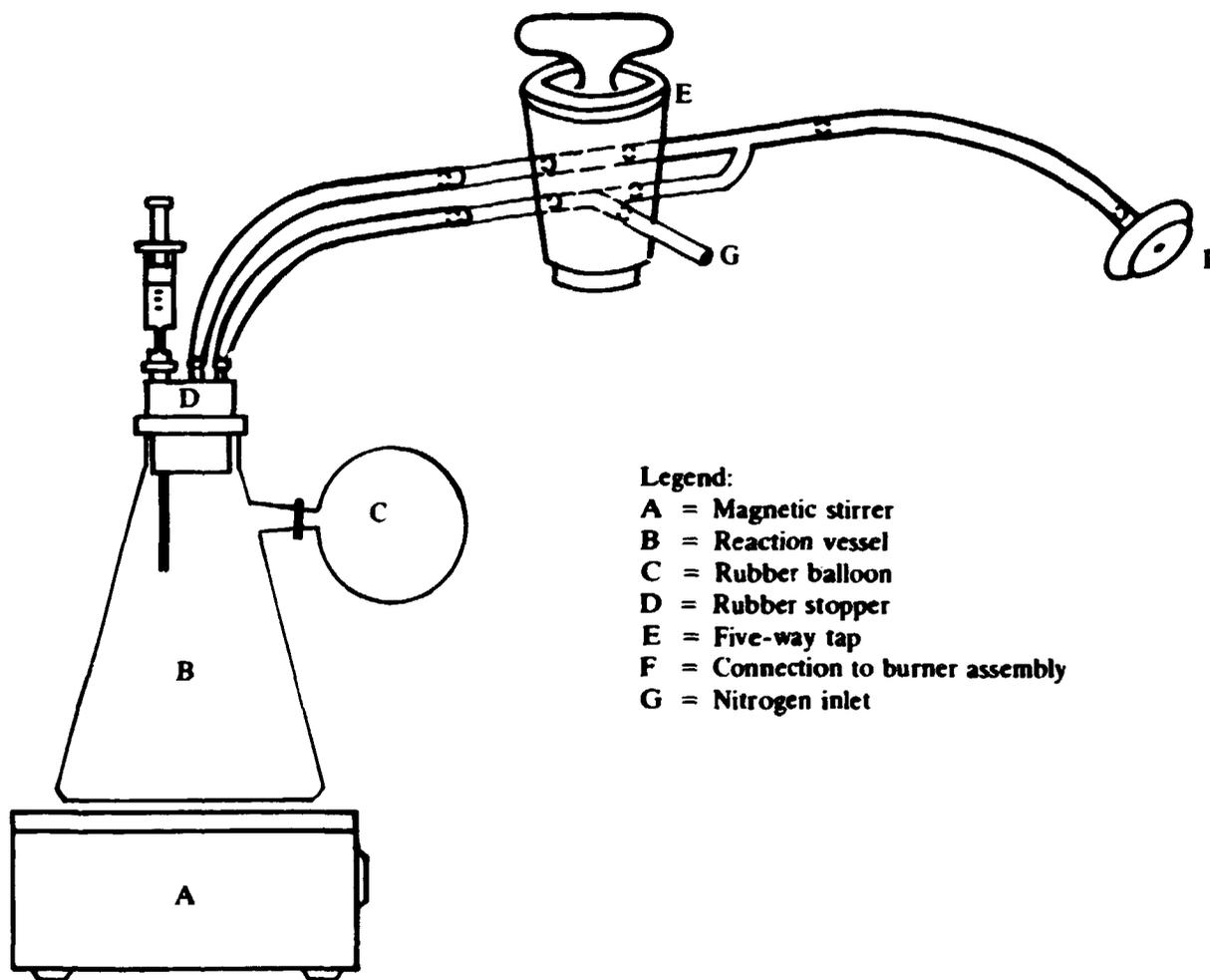


FIGURE 1-1. The apparatus used for hydride generation (after Robert¹)

5. PROCEDURE

5.1. Dissolution of the Sample

- a. Accurately transfer 1.0g of the sample to a zirconium crucible. Add 3.5 g of sodium peroxide and mix intimately with the aid of a small spatula. For the blank solution (of the reagent) transfer 3.5 g of sodium peroxide to a zirconium crucible and follow the same steps as for the sample.
- b. To fuse the sample, heat it gently until the initial vigorous reaction has ceased, and then use a dull-red heat until the contents of the crucible have completely dissolved. Cool partly.

5.2. Separation of Arsenic and Selenium from Copper and Nickel

- a. Transfer the crucible to a 400 ml squat beaker containing 150 ml of water. Cover the beaker and heat it slowly. Insert a boiling rod, and boil the solution for 20 minutes to expel peroxides. Remove the crucible, and wash it with water.
- b. Cool the solution to room temperature, filter it through a no. 540 Whatman 15 cm filter paper, and collect the filtrate in a 400 ml beaker. Wash the precipitate thoroughly with water. Evaporate the filtrate down to a volume of approximately 40 ml. Cool the filtrate, transfer it to a 100 ml volumetric flask, add 40 ml of hydrochloric acid, and dilute to the mark with water. Discard the precipitate. Continue as described in Section 5.5.

5.3. Separation of Bismuth and Antimony from Copper and Nickel

- a. Transfer the crucible to a 400 ml squat beaker containing 25 ml of hydrochloric acid and 75 ml of water. Cover the beaker and, if necessary, heat the solution until the fusion bead has completely dissolved (Note 1).
- b. Remove the crucible and wash it with water. Add 150 mg of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ to the beaker, and stir to dissolve. Cool the solution to room temperature, and adjust the volume to 200 ml with water.
- c. While stirring the solution, slowly add concentrated ammonium hydroxide solution until a pH value of between 9 and 10 (indicated by test papers) is obtained (about 30 ml).
- d. Allow the precipitated hydroxides to settle for 15 minutes, filter the solution through a no. 541 Whatman 15 cm filter paper, and collect the filtrate in a beaker (Note 2).
- e. Wash the beaker and precipitate six times with water adjusted to a pH value of 9 with ammonium hydroxide. Discard the filtrate. Remove the filter paper containing the precipitate from the funnel and, with a jet of water, wash as much of the precipitate as possible into the original beaker.
- f. Treat the filter paper with 25 ml of hydrochloric acid to dissolve any remaining precipitate. Wash the paper with water and collect the washings in the original beaker (Note 3).
- g. Add 25 ml of hydrochloric acid. Transfer the solution to a 100 ml volumetric flask, cool, and dilute to the mark with water. Proceed as described in Section 5.4.

5.4. Reduction of the Sample Solutions

(a) *Antimony*

Transfer the solution to be analysed to the reaction vessel. Add 1 ml of a potassium iodide solution (100 g/l) to the analyte before adding sodium borohydride.

(b) *Arsenic*

Transfer 20 ml of the analyte solution to a 25 ml volumetric flask, and add 2 ml of potassium iodide solution (100 g/l). Make up to the mark with 40 per cent (v/v) hydrochloric acid, and let the solution stand for 1 hour before measurement.

(c) *Selenium*

Transfer 20 ml of the sample solution to a Teflon beaker and cover with a watch-glass. Boil the solution for 15 minutes, cool, transfer to a 20 ml volumetric flask, and make up to the mark with 40 per cent (v/v) hydrochloric acid.

(d) *Bismuth*

No prereduction is necessary for the determination of bismuth.

5.5. Setting-up of Apparatus

- a. With a length of tubing, connect a cylinder of hydrogen to the propane inlet at the rear of the gas-control unit of the AA6 spectrophotometer. With a connecting tube from a cylinder of nitrogen, replace the connecting tube that carries compressed air to the gas-control unit.
- b. Depress the air-propane button on the gas-control unit, and ignite the burner (which has an air-acetylene head). With the appropriate instrumental parameters (Table I-1) and a solution of the analyte, optimize the wavelength setting, the alignment of the hollow-cathode lamp, and the height of the burner for minimum absorbance. Extinguish the flame. Incorporate the background corrector as described in the instruction manual².
- c. Disconnect the tube from the nebulizer and reconnect it to inlet G of the hydride-generation apparatus (Figure I-1). Replace the nebulizer assembly with connection F.

TABLE I-1

Instrumental parameters for the Varian Techtron AA6 spectrophotometer

Setting for gas flow:

Hydrogen 4

Nitrogen 6

	As	Sb	Bi	Se
Wavelength, Å	193,7	217,6	223,0	196,0
Width of slit, μm	300	100	100	300
Lamp current, mA	7	10	8	10

5.6 Evolution and Measurement of the Hydrides

5.6.1. Preparation of the Samples

(a) Antimony

Transfer 2 ml of the sample solution to the reaction vessel. Add 1 ml of a 10 per cent potassium iodide solution and 1 ml of 0,5 M thiosemicarbazide. Add enough 40 per cent (v/v) hydrochloric acid to give a total volume of 10 ml. Proceed as described in steps a to e of Section 5.6.2.

(b) Arsenic

Transfer 2 ml of the sample solution containing potassium iodide to the reaction vessel. Add 1 ml of 0,5 M thiosemicarbazide and then add enough 40 per cent (v/v) hydrochloric acid to give a total volume of 10 ml. Proceed as described in steps a to e of Section 5.6.2.

(c) Selenium

Transfer 2 ml of the reduced sample solution to the reaction vessel. Add 1 ml of the 0,2 per cent tellurium solution, and then add enough 40 per cent (v/v) hydrochloric acid to give a total volume of 10 ml. Proceed as described in steps a to e of Section 5.6.2.

(d) Bismuth

Transfer 2 ml of the sample solution to the reaction vessel. Add 1 ml of 0,5 M thiosemicarbazide, and then add enough 40 per cent (v/v) hydrochloric acid to give a total volume of 10 ml. Proceed as described in steps a to e of Section 5.6.2.

5.6.2. Preliminary Estimate of Concentration

- Insert the stirrer magnet and the rubber stopper, and place the flask on the magnetic stirrer.
- Ignite the burner with the tap in the by-pass position, and allow nitrogen to flow to the flame. Allow about 10 minutes for the instrument to stabilize. Place the pen of the chart recorder on zero.
- Turn the tap through 45° to allow nitrogen to enter the vessel, and flush the system clear of air. Return the tap to the by-pass position. With the aid of a syringe, withdraw about 5 ml of sodium borohydride solution. Invert the syringe and expel any air bubbles from the solution. Adjust the volume in the syringe to 4 ml, and inject the sodium borohydride into the reaction vessel through the rubber septum in D (Figure I-1). With the evolution of volatile hydride, the balloon C expands. After the required amount of time has elapsed (Table I-2), turn the tap to flush the evolved hydrides into the flame, and record the absorbance on the chart recorder.
- Return the tap to the by-pass position and remove the rubber stopper. Discard the contents and rinse the flask with water. Repeat the procedure for the other standards and samples.
- Compare the peak heights obtained and calculate the approximate value of the sample solution (Note 4).

5.6.3. Determination of True Concentration

- Apply the method of standard additions as follows (Note 5).
- Transfer an aliquot portion of the sample solution (which is equivalent to approximately 0,2 μg of the element to be determined and must not exceed 5 ml) to the reaction vessel (Note 6).
- For the first determination, proceed as described in Section 5.6.2.

MASKING AGENTS

- d. For the next determination, proceed as described in Section 5.6.2 but also add 1 ml of dilute standard solution to the reaction vessel. Adjust the volume of the 40 per cent (v/v) hydrochloric acid added so that the total volume of solution does not exceed 10 ml. Proceed as described in steps a to c of Section 5.6.2.
- e. Repeat the procedure, adding 2 ml and 3 ml of dilute standard solution to the sample solution (and adjusting the volume of hydrochloric acid accordingly).
- f. Measure the blank solution in the same way as the sample solution was measured.

TABLE I-2

Conditions for the evolution of the hydrides

	As	Sb	Bi	Se
Total vol. after HCl added, ml	10	10	10	10
Sodium borohydride added, ml	4	4	4	4
Time between evolution and measurement, s	30	15	30	30

5.7. Calculation

- a. Measure the peak heights in millimetres.
- b. Plot the four measurements obtained for the sample and the blank solutions on linear graph paper and draw a graph of peak height versus concentration. Extrapolate the graph to the base line, and determine the number of micrograms present in the sample and blank solutions as negative intercepts on the axis showing concentration (Note 7).

$$\text{Element in sample p.p.m.} = \frac{\text{Element in aliquot portion of sample, } \mu\text{g} - \text{blank solution, } \mu\text{g}}{\text{aliquot portion of sample} \times \text{mass of sample, g}} \times 2.$$

6. NOTES

- (1) The hydroxide precipitate includes iron, lead, chromium, aluminium, and manganese, none of which interferes to the extent that the technique of standard additions cannot be used.
- (2) During the analysis of samples in which the copper or nickel concentrations exceed 0.5 per cent, carry out a second hydroxide precipitation to reduce the amount of copper and nickel that is coprecipitated in the first precipitation, i.e., repeat steps c, d, e, and f of Section 5.3.
- (3) Since, in any batch of measurements, the first peak height recorded is often incorrect, ignore it. If necessary, repeat the preliminary measurement with a different aliquot portion of sample solution; if the first estimate was incorrect.
- (4) If necessary, use a scale expansion of 2 to obtain a reasonable peak height (between 2 and 3 cm) for 0.2 μg of element.
- (5) If the addition of a masking agent has completely eliminated an existing interference (this is usually the case with arsenic), measure the analyte direct, without using the method of standard additions. If desired, carry out a preliminary recovery to determine the extent of the interferences.
- (6) For the reason given in Note 3, and also in order to determine whether reasonably consistent peaks are being obtained, measure a few standards before measuring each batch of samples.
- (7) Draw the best possible straight line through the four points. Should the graph tend to curve at the highest point, ignore this point.

7. REFERENCES

1. ROBERT, R.V.D. Atomic-absorption determination, in metal sulphide concentrates, of the elements that form gaseous hydrides. Johannesburg, National Institute for Metallurgy, *Report 1838*. 1976. 38 pp.
2. VARIAN TECHTRON. Analytical methods for flame spectroscopy. Australia, Varian Techtron, 1972.