CSIR TECHNICAL GUIDE

A laboratory manual for the determination of metals in water and wastewater by atomic absorption spectrophotometry

by

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SYNOPSIS

This guide presents, in addition to a brief discussion of the basic principles and practical aspects of atomic absorption spectrophotometry, a scheme of analysis for the determination of 19 metals in water and wastewater, 16 by flame atomic absorption and 3 by vapour generation techniques. Simplicity, speed and accuracy were the main criteria considered in the selection of the various methods.

SAMEVATTING

Hierdie gids bespreek kortliks, benewens die grondbeginsels en praktiese aspekte van atoomabsorpsiespektrofotometrie, 'n ontledingskema vir die bepaling van 19 metale in water en afvalwater, 16 deur vlamatoomabsorpsie en 3 deur dampgenerator-tegnieke. Eenvoud, spoed en akkuraatheid was die vernaamste kriteria wat tydens seleksie van die verskillende metodes gegeld het.

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1. INTRODUCTION

1.1 Basic principles

Metals in water and wastewater may be present in any or all of the following forms, each of which may require determination:

(a) <u>Dissolved (filterable) metals</u>: Those metals which pass through a 0,45 µm membrane filter.

(b) <u>Suspended (non-filterable) metals</u>: Those metals which are retained by a 0,45 µm membrane filter.

(c) <u>Total metals</u>: The concentration of metals in solution after vigorous digestion of an unfiltered sample, or the sum of the concentrations of metals in both the dissolved and suspended fractions.

(d) <u>Acid-extractable metals</u>: The concentration of metals in solution after treatment of an unfiltered sample with hot dilute mineral acid.

Most metals present in water in the dissolved state, as well as those in the other three forms, after suitable treatment to bring them into the dissolved state, can conveniently be determined by means of atomic absorption spectrophotometry. This technique involves the study of the absorption of radiant energy (usually in the UV and visible regions) by neutral atoms in the gaseous state. In an atomic absorption analysis, the element being determined must be reduced to the elemental state, vaporized, and imposed in the beam of radiation from the light source. This process is most frequently accomplished by drawing a solution of the sample, as a fine mist, into a suitable flame. The flame thus serves a function analagous to that of the cell and solution in conventional absorption spectrophotometry. The absorption is measured at a selected wavelength which is characteristic for each individual element. The absorbance measured is proportional to the concentration, and analysis is carried out by comparing this absorbance with that given under the same conditions by reference samples of known composition. Flame atomic absorption spectrophotometry (FAAS) is a simple, rapid, accurate, and highly specific technique, with a high degree of freedom from interferences. A flame atomic absorption spectrophotometer consists essentially of the following components:

(i)   A stable light source, emitting the sharp resonance line of the element to be determined.

(ii) A flame system, into which the sample solution may be aspirated at a steady rate, and which is of sufficient temperature to produce an atomic vapour of the required species from the compounds present in the solution.

(iii) A monochromator to isolate the resonance line and focus it upon a photomultiplier.

(iv) A photomultiplier to detect the intensity of light energy failing upon it, which is followed by facilities for simplification and readout.

1.2 Atomic absorption techniques

(a) Direct flame absorption: This technique is employed for the determination of most metals in routine water samples (arsenic, selenium and mercury are exceptions). An air-acetylene flame is generally used, except in the case of elements such as barium which form heat-resistant compounds with oxygen in this flame. For the determination of these metals, the higher temperature nitrous oxide-acetylene flame is preferred. This flame is also useful in some situations for the elimination of certain inter-ferences, e.g. in calcium, chromium and magnesium determinations.

In some cases, elements may be present at concentrations below the normal detection limit of the technique. Various procedures can be used to increase the concentration of these elements. The two most commonly used in water analysis are evaporation and chelation/solvent extraction, other less used techniques being ion-exchange and co-precipitation.

In evaporation, the sample is simply evaporated to a known smaller volume before analysis. This procedure, however, is

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rather time-consuming, and may also introduce problems due to matrix or background interferences.

Chelation/solvent extraction techniques have several benefits for atomic absorption. Not only is the element being determined concentrated, but, if the correct organic solvent is chosen, the inherent analytical sensitivity may be increased several-fold merely by the presence of the sample in the organic solvent instead of in water. Chelation/solvent extraction procedures are generally designed to extract several metals simultaneously so they may all be determined in the same organic solvent solution. The most commonly used chelating agent is ammonium pyrrolidine dithiocarbamate (APDC) which chelates most of the heavy metals at the same time. For metals such as aluminium, 8-hydroxyquinoline may be used. Methyl isobutyl ketone (MIBK) is the most commonly used solvent.

(b) Hydride generation: For the determination of the very low levels found in most waters of arsenic, selenium and other metallic elements which form volatile covalent hydrides under suitable chemical conditions, an accessory device - the hydride generation system - can be utilized. An acid solution of the sample to be analysed is treated with sodium borohydride, and the volatile hydride released is passed into a quartz tube heated in an air-acetylene flame. Detection limits of below 5 µg/ℓ can be attained using this technique.

(c) Cold vapour generation: With conventional flame absorption methods the detection limit for mercury is about 200 µg/ℓ . In water analysis, the need exists for routine mercury determinations down to levels of below 1 µg/ℓ . Mercury is unique in that the elemental form cf this metal has appreciable vapour pressure at room temperature, and it is therefore possible to determine its concentration in water without the use of the conventional burner system. Several highly sensitive flameless systems for mercury determinations have been developed, the most widely used being those designed according to the system first described by Hatch and Ott. In this 'cold vapour' technique, the mercury in

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the sample is reduced chemically to its elemental state and aerated from solution in a closed system. The mercury vapour passes through a cell positioned in the light path of the atomic absorption spectrophotometer. Absorbance is measured as a function of mercury concentration.

(d) <u>Flameless atomization</u>: Improved sensitivity and considerably lower detection limits may be obtained by use of flameless atomization or 'furnace' techniques. These systems are built around a small electrically heated graphite tube situated in the light path of an atomic absorption spectrophotometer in place of the burner system. A small volume of sample (generally 0,005 to 0,1 mℓ) is pipetted into the graphite furnace. The furnace power supply is then programmed to pass increasing amounts of current through the graphite tube to successively dry the sample, char off any organic material, and finally atomize the sample into the light path. During the drying and charring stages, water vapour and vapourized organic material are swept out of the tube by a high flow of an inert gas such as argon or nitrogen. During atomization, the gas flows are automatically reduced to allow the sample atoms to stay in the light path for a longer time and thus give a larger absorption signal. The graphite tube is water-cooled, thus allowing it to return from its maximum temperature to room temperature in less than 30 seconds. A typical analysis takes about 90 seconds, including furnace cooling time. By use of this technique, typical detection limits can be improved by a factor of one hundred or more. The use of all the sample and the longer residence time in the light path greatly enhances the sensitivity in comparison to that of the flame technique.

1.3 <u>Interferences</u>

One of the advantages of flame atomic absorption spectrophotometry lies in its comparative lack of interferences. Those interferences which do occur are well documented and fairly easily controlled. In the field of water analysis, the most commonly encountered interferences are <u>chemical</u> and <u>ionization</u> interferences. Other types, less commonly encountered, include <u>non-atomic absorption</u> and <u>matrix</u> interferences.

(a) Chemical interferences occur wh·· the element being determined combines chemically with another reactive component in the sample. The resulting compound influences the atomization process in the flame, thus altering the number of free atoms available to absorb light. Chemical interferences can be controlled by either:

 (i) Addition of a releasing agent: A releasing agent is a chemical which reacts preferentially with either the element being determined or with the interfering component. A common example is the addition of a solution of a lanthanum salt to calcium solutions to overcome the depressing effect of phosphate on the calcium signal.

 (ii) Use of a higher temperature flame: This can overcome many interferences because more energy is available to break down compounds which would be stable in cooler flames. Fo. example, the interference of phosphate on calcium observed in the air-acetylene flame is eliminated in the nitrous oxide-acetylene flame.

(b) Ionization interferences occur when the flame temperature is high enough to ionize a significant fraction of the element being determined. This lowers the number of atoms which can absorb radiation and reduces the analytical signal. Analytical errors can occur when the sample and standards exhibit different degrees of ionization. The simplest way to control ionization interference is to add a large excess of an easily ionizable cation, such as potassium or caesium, to both samples and standards. The electrons provided by the more easily ionized element combine with the ions of the element being determined, and increase the number of atoms which can absorb radiation. A common example is the addition of a solution of a potassium or caesium salt to barium solutions to overcome the ionization of this metal in the nitrous oxide-acetylene flame. The use of a lower temperature flame can also control ionization effects. For example, sodium is partially ionized in the air-acetylene flame, but ionization is negligible in the air-propane flame.

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(c) <u>Non-atomic absorption</u> results from the absorption of radiation from the hollow cathode lamp by materials in the flame other than the element of interest. It may be due to either:

(i) <u>Molecular absorption</u>, which is caused by the presence of molecular species which absorb light at the same wavelength as that of the element being determined.

(ii) <u>Light scattering</u> by particles in the flame, which occurs when solutions containing high amounts of dissolved solids are aspirated into the burner.

Non-atomic absorption may be controlled by the use of a 'continuum source corrector', which may be either a hydrogen-filled hollow cathode lamp or a deuterium arc lamp.

(d) <u>Matrix interferences</u> occur when the sample matrix is so complex that viscosity, surface tension and components cannot be accurately matched with standards, resulting in the uptake rate, nebulization efficiency and atomization processes in the fl me being affected, causing erroneous results. Matrix interferences may be controlled by use of standard addition techniques or by means of MIBK extractions with APDC, which are particularly useful with seawater samples, for example.

1.4 <u>Sample handling and preservation</u>

For the determination of trace metals, contamination and loss are of prime concern. Dust in the laboratory environment, impurities in reagents, and impurities in laboratory apparatus with which the sample makes contact are all sources of potential contamination. Sample containers can introduce either positive or negative errors in the measurement of trace metals by either contributing contaminants through leaching or surface desorption or by depleting concentrations through adsorption. Thus the collection and treatment of the sample prior to analysis for metals requires particular attention. The sample container, whether borosilicate glass, polyethylene, polypropylene or Teflon, should be thoroughly washed with detergent and tap water, then rinsed with 1:1

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nitric acid, tap water, 1:1 hydrochloric acid, tap water, and finally deionized distilled water, in that order. Samples should be preserved immediately after sampling by acidifying with concentrated nitric acid to pH <2. (Addition of 10 mℓ of concentrated nitric acid per litre of sample will normally be sufficient).

After acidification, the sample should be stored in a refrigerator at approximately 4 °C . Under these conditions, samples with metal concentrations of several milligrams per litre are stable for up to 6 months (except mercury, for which the limit is 38 days in glass and 14 days in plastic). For microgram per litre metal levels, the sample should be analysed as soon as possible after collection. Alternatively, samples for mercury determination may be preserved by the addition of 2 mℓ of 200 mg/ℓ potassium dichromate solution (prepared in 1:1 nitric acid) per litre of sample.

1.5 Preparation of standard solutions

Standard solutions of known metal concentrations in water should be prepared in water with a matrix similar to that of the sample. Standards which bracket the expected sample concentration and are within the working range of the method should be employed. It is preferable to prepare stock solutions of standards in concentrations above 500 mg/ℓ and store them in a refrigerator, diluting as required. For samples containing high and variable concentrations of matrix materials, the diluted standard solutions should contain similar concentrations of the major ions in the sample. If the sample matrix is complex and components cannot be matched accurately with standards, the method of standard additions should be used to correct for matrix interference effects.

1.6 Sensitivity, detection limits and optimum concentration ranges

The sensitivity of flame atomic absorption spectrophotometry is defined as the metal concentration that produces an absorption of
% (approximately 0,0044 absorbance).

The detection limit is defined as the metal concentration that produces absorption equivalent to twice the magnitude of the background fluctuation.

Sensitivity and detection limits vary with instrument, element analysed, and technique.

The optimum concentration range usually starts from a concentration of several times the sensitivity and extends to a concentration at which the calibration curve begins to flatten. For best results, concentrations of samples and standards should be within the optimum concentration range. In many cases the concentration range may be extended downward by use of scale expansion and upward by rotation of the burner or use of a less sensitive wavelength.

1.7 Instrument operation

Because of the difference between makes and models of atomic absorption spectrophotometers, it is not possible to formulate instructions applicable to every instrument. The manufacturer's instructions for each particular instrument should be followed. In general, however, the following procedure is employed (air-acetylene flame):

(a) Install the hollow cathode lamp for the metal being measured and roughly set the desired wavelength (see Table 1).

(b) Set the slit width and lamp current at the values suggested in the manufacturer's instructions, and allow the instrument to warm up until the energy source becomes stable (10-20 minutes). Readjust the current as necessary after warm up.

(c) Optimize wavelength by adjusting wavelength dial until optimum energy gain is obtained. Align lamp in accordance with manufacturer's instructions.

(d) Install air-acetylene burner and adjust burner head position. Turn on air and adjust flow rate to that specified by manufacturer

to give maximum sensitivity for the metal being measured. Turn on acetylene, adjust flow rate to value specified, and ignite flame.

(e) Aspirate a standard solution of the desired metal and adjust aspiration rate of the nebulizer (if variable) to obtain maximum sensitivity. Aspirate a standard solution near the middle of the linear working range and adjust the burner vertically and horizontally to obtain maximum response.

(f) The instrument is now ready for operation.

(g) On completion of the analysis, extinguish flame by turning off first acetylene and then air.

For determinations involving the use of a nitrous oxide - acetylene flame, proceed as in (a) to (c) above and then continue as follows : -

(d) Install nitrous oxide-acetylene burner and adjust burner head position. Turn on acetylene (without igniting flame) and adjust flow rate to specified value, then turn off acetylene. With both air and nitrous oxide supplies turned on, set the T-junction valve to nitrous oxide and adjust flow rate to specified value. Turn the switching valve to the air position and check that flow rate is the same. Turn on acetylene and ignite to a bright yellow flame. With a rapid motion, turn switching valve to nitrous oxide. The flame should now have a red cone above the burner. If not, adjust the fuel flow to obtain a red cone. After ignition, allow the burner to come to thermal equilibrium before commencing analysis.

(e) Aspirate a standard solution of the desired metal and adjust aspiration rate of the nebulizer (if variable) to obtain maximum sensitivity. Aspirate a standard solution near the middle of the linear working range and adjust the burner vertically and horizontally to obtain maximum response.

(f) The instrument is now ready for operation.

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(g) On completion of the analysis, extinguish flame by first turning the switching valve from nitrous oxide to air and then turning off the acetylene. This procedure eliminates the danger of flashback occurring on direct ignition or shutdown of nitrous oxide and acetylene.

Actual determination and standardization procedures for the various metals are described in Sections 2 to 5.

1.8 Scheme of analysis

Presented in this technical guide is a scheme of analysis, currently employed by the Water Quality Division of the National Institute for Water Research, for the determination by atomic absorption of the metals most commonly analysed for in water and wastewater. Flame and vapour generation techniques have been preferred to flameless atomization methods, mainly for reasons of simplicity, speed and accuracy. Throughout the scheme, it has been assumed that all samples have been preserved by the addition of 10 mℓ of concentrated nitric acid per litre of sample. In the case of calcium, magnesium, potassium and sodium, an automated as well as a manual method has been described. This technique can, of course, be adapted for use with the other metals determined by flame absorption, should the need arise. A list of recommended wavelengths and flame gases for each metal determined is shown in Table 1.

TABLE 1: Recommended wavelengths and flame gases

Element	Wavelength (nm)	Flame gases
Aluminium	309,3	Nitrous oxide-acetylene
Barium	553,6	Nitrous oxide-acetylene
Cadmium	228,8	Air-acetylene
Calcium	422,7/239,9	Air-acetylene or nitrous oxide-acetylene
Chromium	357,9	Air-acetylene or nitrous oxide-acetylene
Cobalt	240,7	Air-acetylene
Copper	324,7	Air-acetylene
Iron	248,3	Air-acetylene
Lead	217,0/283,3	Air-acetylene
Magnesium	285,2/202,5	Air-acetylene or nitrous oxide-acetylene
Manganese	279,5	Air-acetylene
Nickel	232,0	Air-acetylene
Potassium	766,5/769,9	Air-acetylene
Silver	328,1	Air-acetylene
Sodium	589,5/589,0/330,2	Air-acetylene
Zinc	213,9	Air-acetylene
Arsenic	193,7	Hydride generation
Selenium	196,0	Hydride generation
Mercury	253,7	Cold vapour generation

2. DETERMINATION OF CALCIUM, MAGNESIUM, POTASSIUM AND SODIUM (direct flame absorption)

2.1 Manual method

2.1.1 Preparation of reagents

(a) Nitric acid: Use concentrated AR grade.

(b) Caesium-lanthanum interference suppressant solution: Add 400 mℓ of hydrochloric acid (concentrated, AR grade) slowly and carefully (fume cupboard) to 117,0 g lanthanum oxide (AR grade) in a 2 ℓ pyrex beaker. Stir the mixture until the lanthanum oxide is completely dissolved, then add 25,3 g caesium chloride (AR grade) and again stir until dissolved. Cool the solution and add it to 800 mℓ of deionized distilled water. Dilute to 2 ℓ with deionized distilled water. This solution contains 10 g/ℓ Cs and 50 g/ℓ La.

(c) Standard stock solutions: Use standard solutions of metals (1 000 mg/ℓ) for atomic absorption spectrophotometry (BDH 'Spectrosol'* or equivalent).

2.1.2 Preparation of standard solutions

Add from a burette, the following quantities of standard stock solutions to 500 mℓ standard volumetric flasks, each containing 5 mℓ nitric acid and 50 mℓ caesium-lanthanum solution:

Standard No.	Calcium (mℓ)	Magnesium (mℓ)	Potassium (mℓ)	Sodium (mℓ)
MS1	0	0	0	0
MS2	1,0	1,0	0,5	2,0
MS3	5,0	5,0	2,0	10,0
MS4	10,0	10,0	4,0	20,0
MS5	15,0	15,0	6,0	30,0
MS6	25,0	25,0	10,0	50,0
MS7	35,0	35,0	14,0	70,0
MS8	50,0	50,0	20,0	100,0

*Mention of trade names is for information purposes only and does not imply endorsement by the National Institute for Water Research.

Dilute these solutions to 500 mℓ with deionized distilled water and transfer to 500 mℓ polythene bottles. The concentrations of the solutions are as follows:

Standard No.	Calcium (mg/ℓ)	Magnesium (mg/ℓ)	Potassium (mg/ℓ)	Sodium (mg/ℓ)
MS1	0	0	0	0
MS2	2	2	1	4
MS3	10	10	4	20
MS4	20	20	8	40
MS5	30	30	12	60
MS6	50	50	20	100
MS7	70	70	28	140
MS8	100	100	40	200

2.1.3 Pretreatment of samples

Add 5 mℓ of caesium-lanthanum solution to a clean dry 50 mℓ standard volumetric flask and dilute to 50 mℓ with the sample or sample aliquot solution.

2.1.4 Procedure

Aspirate the standard and sample solutions under the conditions stipulated for the particular instrument being operated (refer also Table 1) and note the absorbance values obtained. Choice of either the air-acetylene or the nitrous oxide-acetylene flame for calcium and magnesium determinations will be dependent on the sample constitution. Calculate the concentration of each metal ion by reference to the calibration curves obtained by plotting concentrations of the standard solutions versus the corresponding absorbance readings. (For instruments equipped with direct concentration readout, this step will be unnecessary). A correction factor of $^{10}/9$ should be applied to each result in order to allow for the addition of the caesium-lanthanum solution.

2.2 Automated method

2.2.1 Preparation of reagents

(a) Nitric acid: Refer 2.1.1 (a).

(b) Caesium interference suppressant solution (potassium and sodium determinations): Dissolve 15,0 g caesium chloride (AR grade) in a solution of 50 mℓ hydrochloric acid (concentrated, AR grade) and 450 mℓ deionized distilled water, and dilute to 1 ℓ with deionized distilled water. This solution contains 11,7 g/ℓ Cs, equivalent to 1 g/ℓ in the aspirate.

(c) Lanthanum interference suppressant solution (calcium and magnesium determinations): Add 400 mℓ of hydrochloric acid (concentrated, AR grade) slowly and carefully (fume cupboard) to 68,8 g lanthanum oxide (AR grade) in a 2 ℓ pyrex beaker. Stir the mixture until the lanthanum oxide is completely dissolved, cool, and add it to 400 mℓ deionized distilled water. Dilute to 1 ℓ with deionized distilled water. This solution contains 58,6 g/ℓ La, equivalent to 5 g/ℓ in the aspirate.

(d) Standard stock solutions: Refer 2.1.1. (c).

2.2.2 Preparation of standard solutions

Refer 2.1.2. Omit addition of caesium-lanthanum solution.

2.2.3 Procedure

Set up the manifold as shown in Figure 1 (sodium and magnesium) and Figure 2 (calcium and potassium). Set sampling and washing times and fill the sample plate. Aspirate the standard solutions and samples under the conditions stipulated for the particular instrument being operated (refer also Table 1) and record the absorbance values obtained as peaks on a chart recorder. Calculate the concentration of each metal ion by reference to the calibration curves obtained by plotting concentrations of the standard solutions versus the corresponding peak heights.

Figure 1. Sodium/magnesium manifold

AUTOMATIC
SAMPLER
RATE:40-1:2

mℓ/min.

TO SAMPLER ◄─────────────────────────── 3,9   DISTILLED WATER

0,42   SUPPRESSANT SOLUTION

0,6   DISTILLED WATER

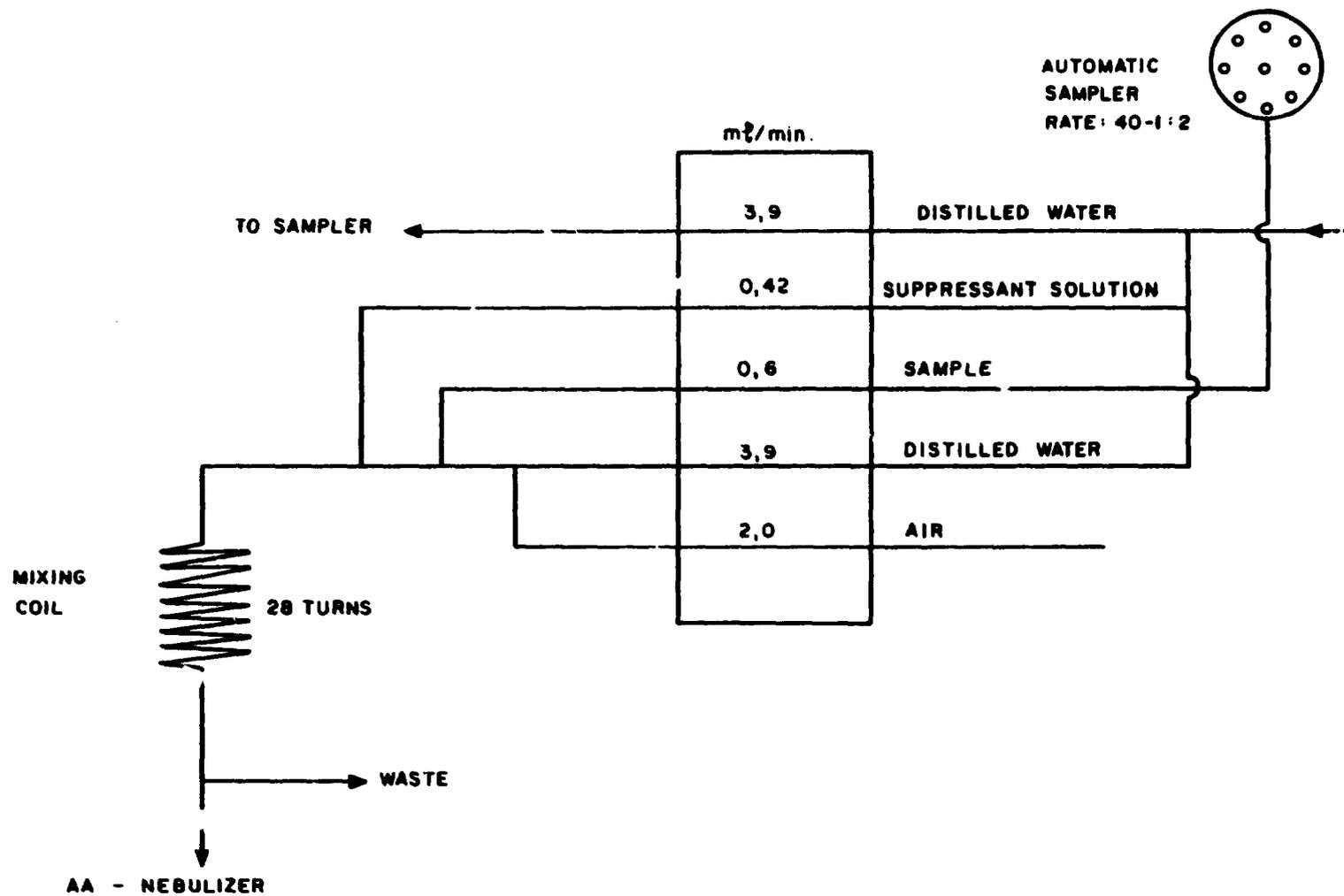3,9   SAMPLE

2,0   AIR

MIXING
COIL   28 TURNS

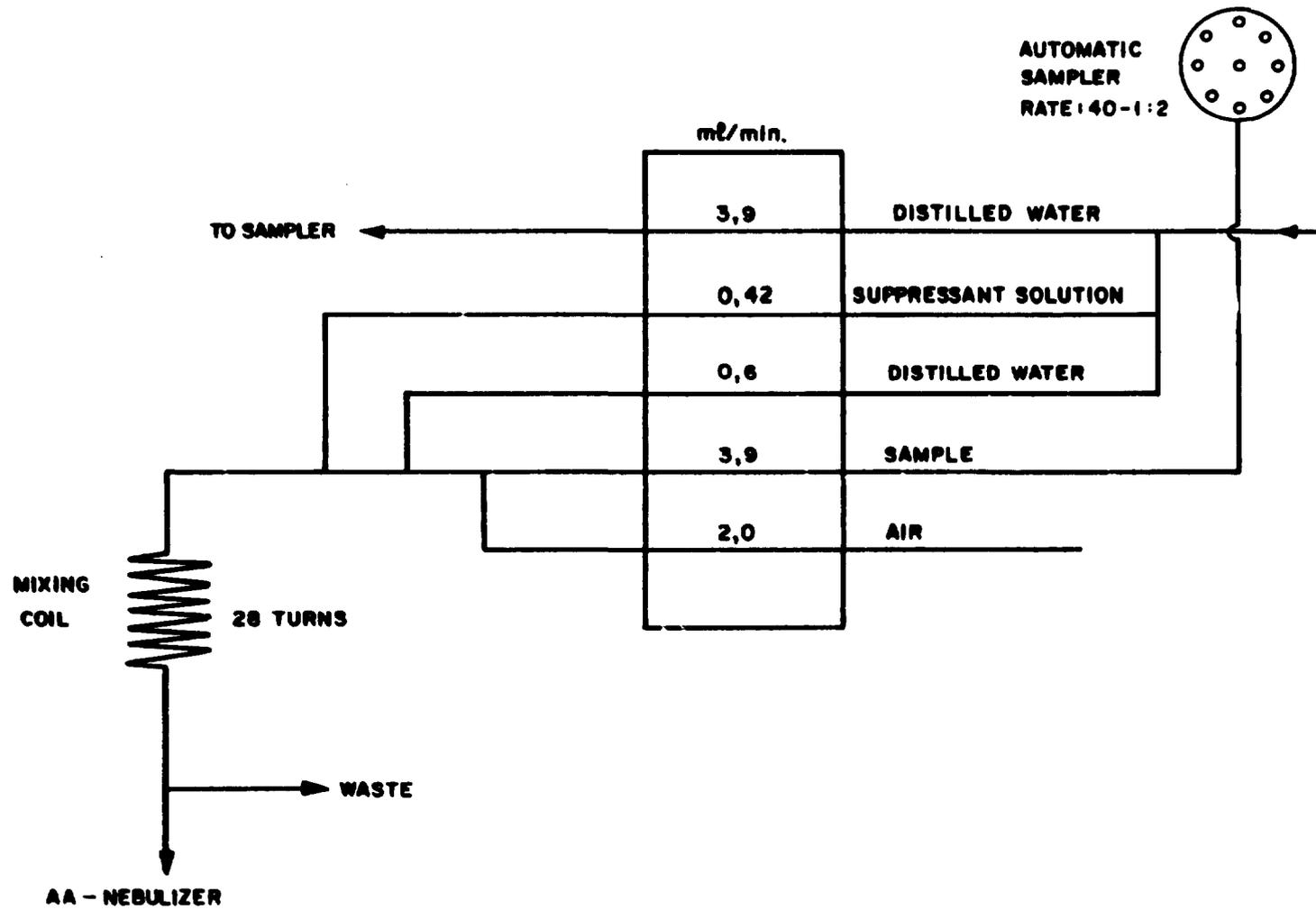─────► WASTE

AA – NEBULIZER

Figure 2.   Potassium/calcium manifold

3. DETERMINATION OF ALUMINIUM, BARIUM, CADMIUM, CHROMIUM, COBALT, COPPER, IRON, LEAD, MANGANESE, NICKEL, SILVER and ZINC (direct flame absorption)

3.1 Preparation of reagents

(a) Nitric acid: Refer 2.1.1 (a).

(b) Caesium-lanthanum interference suppressant solution: Add 400 mℓ of hydrochloric acid (concentrated, AR grade) slowly and carefully (fume cupboard) to 47,0 g lanthanum oxide (AR grade) in a 2 ℓ pyrex beaker. Stir the mixture until the lanthanum oxide is completely dissolved, then add 12,7 g caesium chloride (AR grade) and again stir until dissolved. Cool the solution and add it to 800 mℓ of deionized distilled water. Dilute to 2 ℓ with deionized distilled water. This solution contains 5 g/ℓ Cs and 20 g/ℓ La.

(c) Standard stock solutions: Refer 2.1.1 (c).

3.2 Preparation of standard solutions

3.2.1 Cadmium, chromium, cobalt, copper, iron, lead, manganese, nickel and zinc standard solutions

Secondary stock solution 1: Transfer, by pipette, 100 mℓ of the standard stock solutions (1 000 mg/ℓ) of chromium, cobalt, copper, iron, lead, manganese, nickel and zinc and 20 mℓ of the standard stock solution (1 000 mg/ℓ) of cadmium to a 1 ℓ standard volumetric flask, and dilute to 1 ℓ with deionized distilled water. This solution contains 20 mg/ℓ Cd and 100 mg/ℓ Cr, Co, Cu, Fe, Pb, Mn, Ni, Zn.

Secondary stock solution 2: Transfer, by pipette, 100 mℓ of secondary stock solution 1 to a 1 ℓ standard volumetric flask, and dilute to 1 ℓ with deionized distilled water. This solution contains 2 mg/ℓ Cd and 10 mg/ℓ Cr, Co, Cu, Fe, Pb, Mn, Ni, Zn.

Add the following quantities of secondary stock solutions 1 and 2 to 250 mℓ standard volumetric flasks, each containing 2,5 mℓ nitric acid and 25 mℓ caesium-lanthanum solution, and dilute to 250 ml with deionized distilled water:

Standard No.	Secondary stock solution No.	Volume of secondary stock solution added (mℓ)	Concentration (µg/ℓ) Cadmium	Concentration (µg/ℓ) Others
TS1	–	0	0	0
TS2	2	0,63	5	25
TS3	2	2,5	20	100
TS4	2	12,5	100	500
TS5	1	2,5	200	1000
TS6	1	5,0	400	2000
fS7	1	7,5	600	3000
TS8	1	10,0	800	4000
TS9	1	12,5	1000	5000

3.2.2 Barium standard solutions

Secondary stock solution: Transfer, by pipette, 100 mℓ of the standard stock solution (1000 mg/ℓ) of barium to a 1 ℓ standard volumetric flask, and dilute to 1 ℓ with deionized distilled water. This solution contains 100 mg/ℓ Ba.

Add the following quantities of secondary stock solution to 100 mℓ standard volumetric flasks, each containing 1 mℓ nitric acid and 10 mℓ caesium-lanthanum solution, and dilute to 100 mℓ with deionized distilled water:

Standard No.	Volume of secondary stock solution added (mℓ)	Concentration (µg/ℓ)
Ba1	0	0
Ba2	0,25	250
Ba3	1,0	1000
Ba4	5,0	5000
Ba5	15,0	15000
Ba6	25,0	25000

3.2.3 Silver standard solutions

Secondary stock solution: Transfer, by pipette, 10 mℓ of the

standard stock solution (1000 mg/ℓ) of silver to a 1 ℓ standard
volumetric flask, and dilute tc 1 ℓ with deionized distilled
water. This solution contains 10 mg/ℓ Ag.

Add the following quantities of secondary stock solution to 100
mℓ standard volumetric flasks, each containing 1 mℓ nitric acid
only, and dilute to 100 mℓ with deionized distilled water:

Standard No.	Volume of secondary stock solution added (mℓ)	Concentration (µg/ℓ)
Ag1	0	0
Ag2	0,25	25
Ag3	1,0	100
Ag4	5,0	500
Ag5	10,0	1000
Ag6	20,0	2000

3.2.4 Aluminium standard solutions

Secondary stock solution: Transfer, by pipette, 100 mℓ of the
standard stock solution (1000 mg/ℓ) of aluminium to a 1 ℓ
standard volumetric flask, and dilute to 1 ℓ with deionized
distilled water. This solution contains 100 mg/ℓ Al.

Add the following quantities of secondary stock solution to
100 mℓ standard volumetric flasks, each containing 1 mℓ nitric
acid and 10 mℓ caesium-lanthanum solution, and dilute to 100 mℓ
with deionized distilled water:

Standard No.	Volume of secondary stock solution added (mℓ)	Concentration (µg/ℓ)
A11	0	0
A12	1,0	1000
A13	5,0	5000
A14	10,0	10000
A15	25,0	25000
A16	50,0	50000

3.3 Pretreatment of samples

Add 5 mℓ of caesium-lanthanum solution to a clean dry 50 mℓ standard volumetric flask and dilute to 50 mℓ with the sample or sample aliquot solution. (This step is omitted for silver determinations, the samples being aspirated directly).

3.4 Procedure

Aspirate the standard and sample solutions under the conditions stipulated for the particular instrument being operated (refer also to Table 1) and note the absorbance values obtained. Choice of either the air-acetylene or the nitrous oxide-acetylene flame for chromium determinations will be dependent on the sample constitution. Calculate the concentration of each metal ion by reference to the calibration curves obtained by plotting concentrations of the standard solutions versus the corresponding absorbance readings. (For instruments equipped with direct concentration readout, this step will be unnecessary). Except in the case of silver determinations, a correction factor of $^{10}/_9$ should be applied to each result in order to allow for the addition of the caesium-lanthanum solution.

4. DETERMINATION OF ARSENIC AND SELENIUM (hydride generation)

4.1 Preparation of reagents

(a) Nitric acid: Refer 2.1.1 (a).

(b) Hydrochloric acid, 500 mℓ/ℓ : Add 500 mℓ hydrochloric a. ⌣ (concentrated, AR grade) slowly and carefully to 500 mℓ deionized distilled water.

(c) Potassium iodide solution, 200 g/ℓ : Dissolve 200 g potassium iodide (AR grade) in deionized distilled water and dilute to 1 ℓ with deionized distilled water.

(d) Sodium borohydride (98 %): Use ^{10}/32" pellets made by Alfa Division. Ventron Corporation, Danvers, Massachusetts, USA* (available from various S.A. suppliers).

(e) Standard stock solutions: Refer 2.1.1 (c).

4.2 Preparation of standard solutions

Secondary stock solution: Transfer, by graduated pipette, 1,0 mℓ of the standard stock solutions (1000 mg/ℓ) of arsenic and selenium to a 1 ℓ standard volumetric flask and dilute to 1 ℓ with deionized distilled water. This solution contains 1,0 mg/ℓ As and Se.

Add the following quantities of secondary stock solution to 100 mℓ standard volumetric flasks, each containing 1 mℓ nitric acid, and dilute to 100 mℓ with deionized distilled water:

Standard No.	Volume of secondary stock solution added (mℓ)	Concentration (μg/ℓ)
As/Se1	0	0
As/Se2	0,5	5
As/Se3	1,0	10
As/Se4	2,0	20
As/Se5	3,0	30

*Mention of trade names is for information purposes only and does not imply endorsement by the National Institute for Water Research.

Prepare a fresh set of standard solutions from a freshly prepared secondary stock solution for each set of determinations.

4.3 Pretreatment of samples and standard solutions

Transfer, by pipette, 10 mℓ (or portion diluted to 10 mℓ) of the sample or standard solutions to a 50 mℓ beaker and add 10 mℓ of 500 mℓ/ℓ hydrochloric acid. Separate portions of the sample and standard solutions should be taken for arsenic and selenium determinations.

Arsenic-reduction of As^V to As^{III}: Add 1 mℓ of 200 g/ℓ potassium iodide solution to each 20 mℓ sample or standard aliquot. Reduction will be complete in about 50 minutes at room temperature. Alternatively, heat the solutions to 50 °C for about 4 minutes and cool to room temperature.

Selenium-reduction of Se^{VI} to Se^{IV}: Heat the sample and standard aliquots to 70 °C for 10 minutes and cool to room temperature.

4.4 Procedure

Set the operating parameters of the instrument and a connected chart recorder according to the manufacturers' instructions (refer also Table 1), and connect the hydride vapour generation accessory (Figure 3 - Varian-Techtron Ltd Vapor Generation Accessory* or equivalent) to the instrument. Set the nitrogen supply regulator to 140 kPa . Turn the inert gas control of the accessory to NORMAL. Remove the stopper assembly from the reaction vessel of the accessory. Remove the cap from the pellet dispenser and, using tweezers, load the dispenser with sodium borohydride pellets. Replace the dispenser cap and stopper assembly. Set the acetylene and air flows to give a fuel-rich air-acetylene mixture. Raise the quartz tube clear of the burner, ignite the flame, and lower the tube back to its normal position. Adjust the fuel flow so that the flame has a primary zone (blue cone) between 2 and 3 mm high.

*Mention of trade names is for information purposes only and does not imply endorsement by the National Institute for Water Research.

Ensure that the stirrer is OFF and remove the stopper assembly from the reaction vessel. Using the funnel supplied, transfer the contents of a beaker containing a sample or standard solution to the reaction vessel. Replace the stopper assembly and switch the stirrer ON. Wait about 25 seconds to ensure that all the air has been flushed from the system, then turn the dispenser knob through 180 ° and pause briefly to allow a pellet to drop into the solution. Check that a flame is burning quietly at both ends of the quartz tube, indicating the start of the hydride reaction, then turn the dispenser knob back to the closed position. Wait until the reaction is complete, then, with the stirrer still ON, press the drain button on the reaction vessel and keep it pressed until all the solution has been drained from the vessel. Turn the stirrer OFF. The absorbances obtained are recorded as peak heights on the chart recorder.

Calculate the concentration of arsenic or selenium in each sample by reference to the calibration curve obtained by plotting concentrations of the standard solutions versus the corresponding peak heights.

For most determinations, satisfactory results can be obtained by measurement of peak heights. In some cases, however, the sample matrix may be such that the peaks obtained may 'tail off' considerably, or multiple peaks may be produced due to delayed reactions. Under these circumstances, linearity of the calibration curve as well as reproducibility and accuracy of the results may be significantly improved by using peak area measurements. It is also strongly recommended that simultaneous background correction be employed for all hydride determinations.

Only inorganic arsenic and selenium are determined by this technique. If total (organic + inorganic) arsenic or selenium is required, the organo-arsenic and organo-selenium species should first be converted to the inorganic forms by means of a digestion procedure, for example acid/persulphate or mixed acid digestion.
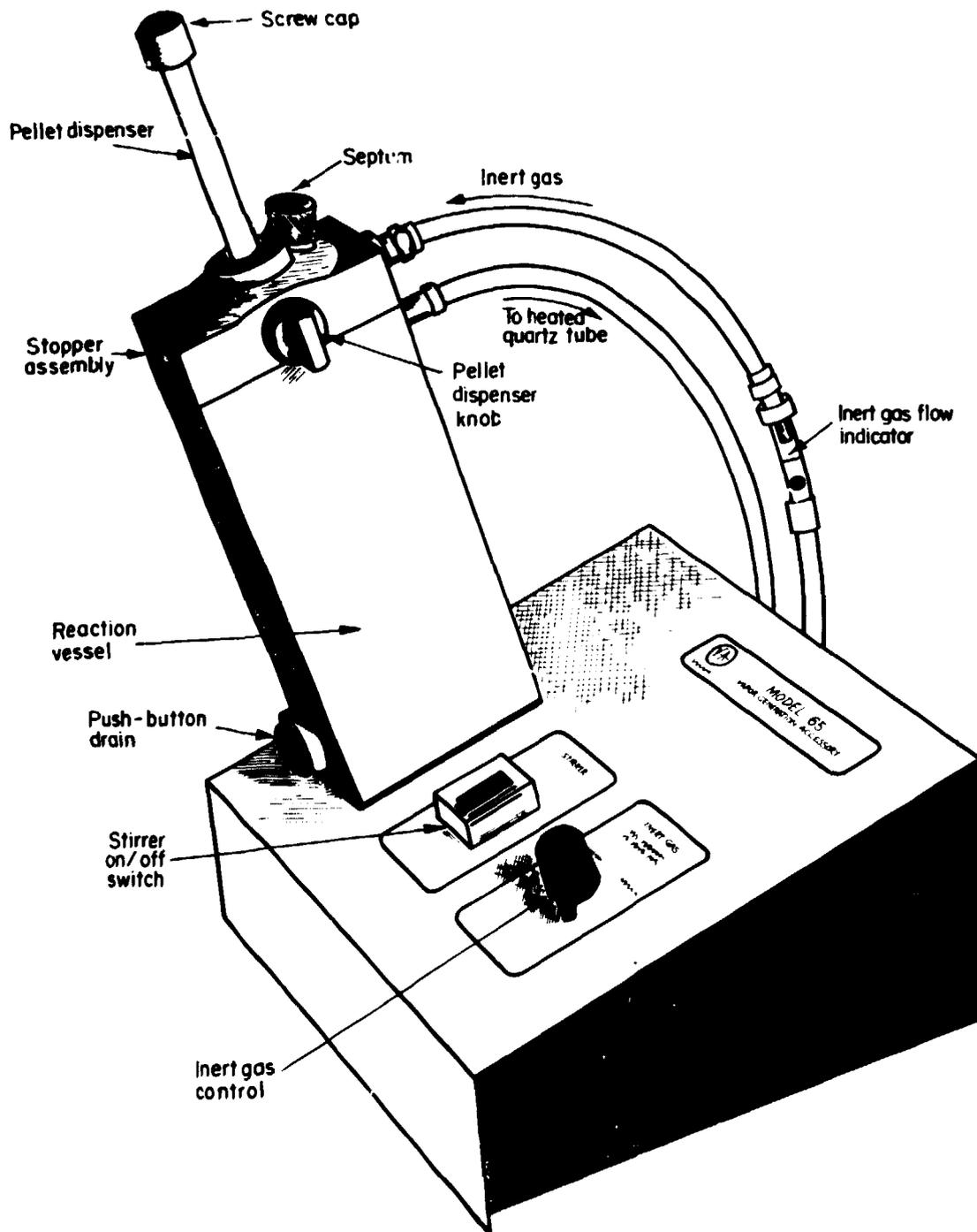
Figure 3. Vapour generation accessory - arsenic and selenium

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through their agents, SMM Instruments (Pty) Ltd., Johannesburg

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5. **DETERMINATION OF MERCURY (cold vapour generation)**

    5.1 Pre. .ration of reagents

    (a) Nitric acid: Refer 2.1.1 (a).

    (b) Sulphuric acid, 500 mℓ/ℓ : Add 500 mℓ sulphuric acid (concentrated, AR grade) slowly and carefully to 500 mℓ deionized distilled water.

    (c) Potassium permanganate solution, 50 g/ℓ : Dissolve 50 g potassium permanganate (AR grade) in deionized distilled water and dilute to 1 ℓ with deionized distilled water.

    (d) Potassium persulphate solution, 50 g/ℓ : Dissolve 50 g of potassium persulphate (AR grade) in deionized distilled water and dilute to 1 ℓ with deionized distilled water.

    (e) Sodium chloride-hydroxylamine sulphate solution, 120 g/ℓ : Dissolve 120 g sodium chloride (AR grade) and 120 g hydroxylamine sulphate (AR grade) in deionized distilled water and dilute to 1 ℓ with deionized distilled water.

    (f) Stannous chloride solution, 100 g/ℓ : Dissolve 100 g stannous chloride (AR grade) in 500 mℓ deionized distilled water containing 50 mℓ hydrochloric acid (concentrated, AR grade) and dilute to 1 ℓ with deionized distilled water. Add one piece of granulated tin (AR grade). The solution will remain at the required strength as long as a piece of tin is present.

    (g) Standard stock solution: Refer 2.1.1 (c).

    5.2 Preparation of standard solutions

    Secondary stock solution: Transfer, by graduated pipette, 1,0 mℓ of the standard stock solution (1000 mg/ℓ) of mercury to a 1 ℓ standard volumetric flask and dilute to 1 ℓ with deionized distilled water. This solution contains 1,0 mg/ℓ Hg .

    Add the following quantities of secondary stock solution to 250 mℓ standard volumetric flasks, each containing 2,5 mℓ nitric acid, and dilute to 250 mℓ with deionized distilled water:

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Standard No.	Volume of secondary stock solution added (mℓ)	Concentration (µg/ℓ)
Hg1	0	0
Hg2	0,50	2
Hg3	1,50	6
Hg4	2,50	10
Hg5	5,00	20

Prepare a fresh set of standard solutions from a freshly prepared secondary stock solution for each set of determinations.

5.3 Pretreatment of samples and standard solutions

Transfer, by graduated cylinder, 100 mℓ of each of the sample and standard solutions to clean dry 250 mℓ Erlenmeyer flasks. Add 10 mℓ 500 mℓ/ℓ sulphuric acid, 2,5 mℓ nitric acid and 15 mℓ of 50 g/ℓ potassium permanganate solution to each flask, swirling to mix after each addition. Allow to stand for at least 15 minutes. (If the colour of the potassium permanganate disappears, add an additional known volume of the potassium permanganate solution, repeating if necessary, until the colour remains). Add 8 mℓ of 50 g/ℓ potassium persulphate solution to each flask and heat for 2 hours on a waterbath at 95 °C . Cool to room temperature. Add 6 mℓ of 120 g/ℓ sodium chloride-hydroxylamine sulphate solution, or more if necessary (note volume), to reduce the excess potassium permanganate, swirling the solution until colourless.

5.4 Procedure

Set the operating parameters of the instrument and a connected chart recorder according to the manufacturers' instructions (refer also Table 1) and connect the mercury vapour generation accessory (Figure 4) to the instrument. Transfer, by graduated cylinder, 50 mℓ (or portion diluted to 50 mℓ) of the treated sample or standard solution to the reaction vessel of the accessory, and add 3 mℓ of 100 g/ℓ stannous chloride solution.

Immediately insert the bung assembly in the reaction vessel and stir the solution vigorously with the magnetic stirrer for 90 seconds. Simultaneously turn off the stirrer and turn on the air supply to the vessel. Record the absorbance obtained as peak height on the chart recorder.

Calculate the concentration of mercury in each sample by reference to the calibration curve obtained by plotting concentrations of the standard solutions versus the corresponding peak heights.

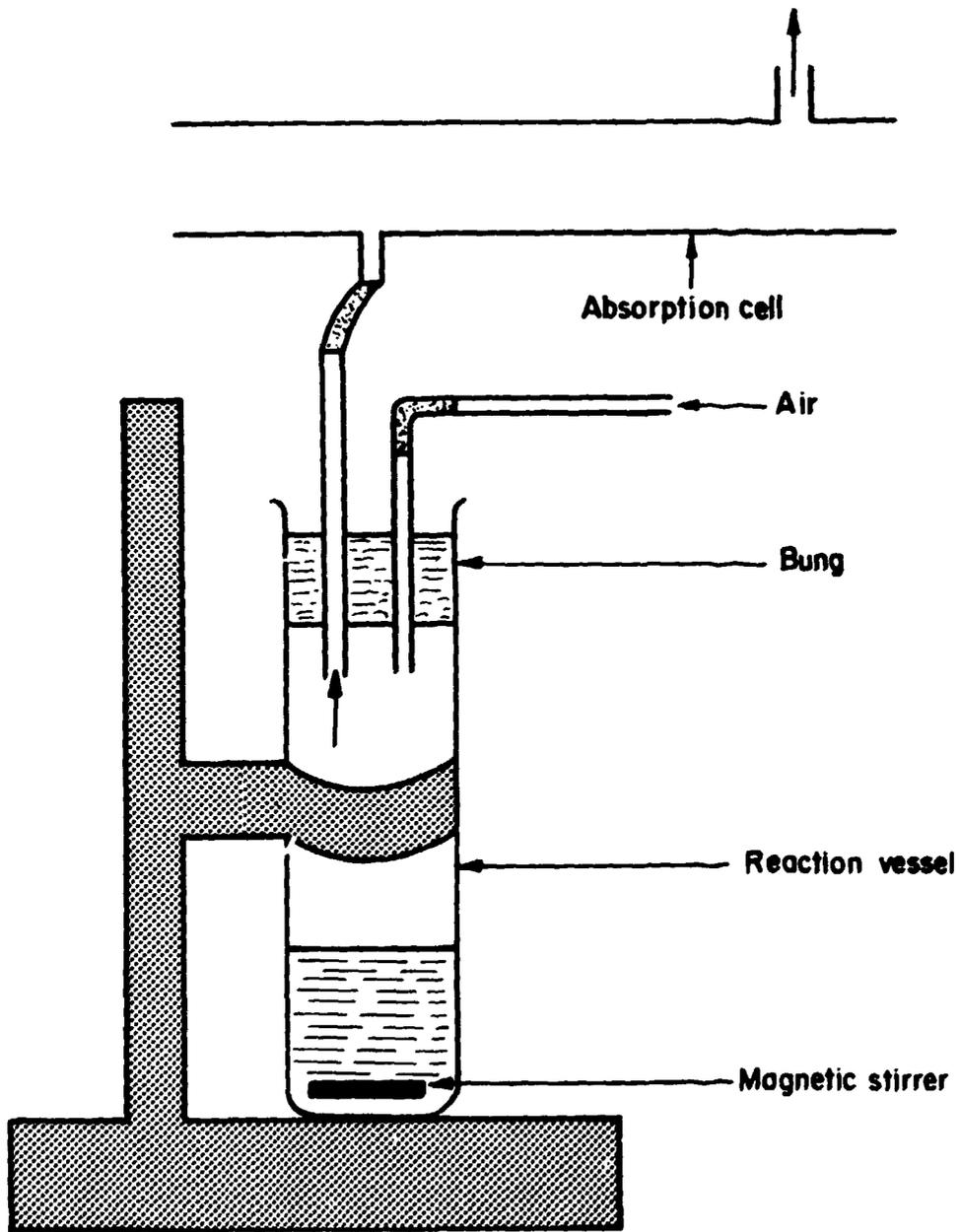Total (organic + inorganic) mercury is determined by this technique.

Figure 4. Vapour generation accessory - mercury

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