CONTENTS

METHODS FOR THE DETERMINATION IN AIR OF:

NOTE

The above Contents list relates to the eight Methods here following. For holders of earlier publications in this series, there follow next preliminary pages for the complete set, including the present Methods, to enable present holdings to be brought up to date.
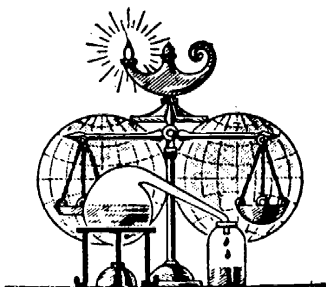
.

ANALYTICAL METHODS FOR USE IN OCCUPATIONAL HYGIENE

incorporating
THIRD REPLACEMENT-ADDITION ISSUE
up-to-date to 1973

CONTENTS

CONTENTS

METHODS FOR THE DETERMINATION IN URINE OF:

ANALYTICAL METHODS FOR USE IN OCCUPATIONAL HYGIENE

DETERMINATION OF AIRBORNE PARTICULATE VANADIUM BY SPECTROPHOTOMETRY
(Adopted 1973)

1. Field of application

The method is applicable to the measurement of the levels of suspended particulate vanadium found in either ambient or industrial atmospheres, including motor exhaust gases and stack effluents. Vanadium concentrations of 0.1 to 0.2 p.p.m. were found close to the exhaust pipe of an internal combustion engine. Similar investigations of diesel vehicles showed considerably higher levels of 10–15 p.p.m. Levels of 6–12 p.p.m. were found at the periphery of the chimney of a small oil-fired power station. These levels depended upon the quantity of oil burned per unit time (Ref. 11.1).

2. Principle

A prepared test sample containing the vanadium as vanadate, in aqueous acid solution, is reacted with salicylhydroxamic acid to form an inner complex compound. The vanadium compound is extracted with pentanol and the developed colour is measured by spectrophotometry.

3. Reactions

Vanadate ions react with salicylhydroxamic acid in weakly acid solution and under suitably defined conditions to form an inner complex salt of deep blue colour. This complex does not obey the Lambert–Beer law. In the present method, the procedure has been changed so that the dyestuff is extracted with pentanol. When this is done, there is a change from dark blue to brown, but the pentanol extract obeys both the Lambert and the Lambert–Beer laws.

4. Reagents

4.1. *Concentrated nitric acid*
Reagent grade, SG 1.4.

4.2. *Perchloric acid*
Reagent grade, SG 1.67.

4.3. *Hydrochloric acid*
Reagent grade, SG 1.19.

34-1

4.4 *Sodium hydroxide*
1 N solution.

4.5 *Glacial acetic acid*
Reagent grade, SG 1.050.

4.6 *Salicylhydroxamic acid (SHA)*
This must be synthesized according to instructions provided (Ref. 11.2).

4.7 *Working solution SHA*
A 10% solution of SHA, 4.6, is prepared by dissolving 10 grams SHA and making up to a final volume of 100 ml using 1 N sodium hydroxide solution, 4.4.

4.8 *N-pentanol-1*
Reagent grade.

4.9 *Vanadate standard solution*
A vanadate stock solution is prepared in distilled water, to contain 1000 micrograms V per millilitre.

4.10 *Vanadate working standard solutions*
Prepared from 4.9 by dilution to contain 1, 2, 3, 5, 10, etc. micrograms V per millilitre.

4.11 *Distilled water*
Distilled rather than deionized, free from vanadium and organic material.

5. Apparatus

5.1. *Spectrophotometer*
The instrument must be able to discriminate to ± 1 nanometre over the range 400 to 800 nm.

5.2 *Glass fibre filters*
Glass fibre filter discs, 9 cm in diameter. S&S No. 8 has been found satisfactory (F, see *Figure 1*).

5.3 *Sintered glass plate*
The supporting plate of the filter plate, coarse porosity (S).

5.4 *Filter funnel*
Glass filter funnel with integrated sintered glass filter support plate (N).

5.5 *Pump*
Air sampling pump able to draw at least 5 l.p.m. against the resistance of the air filter used (P).

5.6 Regulating valve
Valve for adjustment of air sampling flowrate (V).

5.7 Gas meter
Gas meter with appropriate indication of total air volume taken (G).

5.8 Manometer
Accurately calibrated manometer reading in degrees Torr (M).

5.9 Thermometer
Accurately calibrated thermometer reading in degrees C (T).

5.10 Centrifuge
Able to attain speed of 3 500 r.p.m.

5.11 Glassware
As described in method.

6. Sampling and samples

6.1 Air sampling
In the apparatus used, F is a glass filter disc, 9 cm in diameter. Using this arrangement, air can be drawn through the apparatus at a relatively high flowrate, which should not exceed 2 l.p.m., however, since small amounts of vanadium compounds may pass through the filter and render the analysis useless. It is strongly recommended that the water vapour partial pressure of the air should be measured and the volume of the air passed through the apparatus corrected by the appropriate factors.
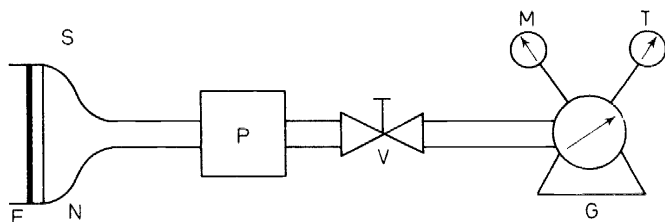
Figure 1.

6.2 Preparation of the laboratory sample
Carefully remove the glass filter disc from the sampling apparatus and transfer to a round-bottomed flask. Add 5 ml of hydrochloric acid (4.3). Then, depending upon the quantity of material to be digested, add 10–20 ml of nitric acid (4.1). Now add 5 ml of perchloric acid (4.2). Connect the reaction flask to an exhaust manifold as described in 11.1. Draw a vacuum of about 100 mmHg by means of a water jet vacuum pump. Maintain this vacuum, as closely as possible, throughout the duration of the digestion. When digestion is judged to be complete, apply heat until a white to light brown residue remains, which must be dry. If any black particles still re-

main in the residue, add 10 ml nitric and 5 ml perchloric acids, in that order. Repeat the digestion procedure and reduce the contents to ash. By carrying out the digestion and ashing procedure in a low vacuum, the risk of explosion is practically eliminated. WEAR SAFETY GOGGLES AND CARRY OUT ALL DIGESTIONS IN THE FUME HOOD.

6.3   *Preparation of the blank*
Prepare a blank consisting only of the three digestion acids, in the amounts used in the digestion of the laboratory sample. Carry this blank through the digestion procedure described in 6.2.

7. Procedure

7.1   *Analysis*
Take up residue from digestion with 5 ml of 6 N HCl, add several drops of alcoholic phenolphthalein solution and neutralize to a faint pink colouration with sodium hydroxide solution. Finally, allow the solution to stand overnight, or for at least ten hours, at room temperature. After standing for the designated time, transfer the digest solution to a 250 ml graduated flask, using water to rinse. Also transfer the remnants of the glass filter paper to the graduated flask as part of the same operation. Fill up to about 200–210 ml, add 10 ml 1 N sodium hydroxide, 5 ml acetic acid and 3 ml of 10% SHA solution, in that order. Mix thoroughly, add 20 ml pentanol and complete volume to 250 ml with water. Stopper the graduate and shake thoroughly by hand. After opening the graduate, allow the contents to settle for about ten minutes. Pipette the upper phase into centrifuge tubes and centrifuge for about ten minutes at 3000 r.p.m.

Carry the blank of 6.3 through the same procedure. Read the absorbance of the test solution at 460 nm against the blank as reference. Select a suitable light path depending upon the absorbance. If the absorbance is too high, the test solution may be diluted with pentanol to get the measurement on scale.

8. Expression of results

The calibration curve is linear over the range of 1 to 1000 micrograms of vanadium (V) under the conditions described. The results may be calculated directly from the absorbance obtained at 460 nm with a 10 mm cell, as follows:

$$\text{Absorbance } F = \text{Total vanadium, } \mu g$$

The calculation factor $F = 217$. If, in the photometric measurement, a light path other than 10 mm has been used, or if the test solution has had to be diluted, a correction must be made to an absorbance value corresponding to a 10 mm light path. For 1000 analyses, a maximum error of $\pm$ 0.5 per cent was obtained.

9. Notes on procedure

9.1

The collection efficiency of the apparatus was investigated for vanadium pentoxide fumes and dusts. Several filter funnels, with glass filter discs, were placed in series and air was drawn through. It was found that, up to a flowrate of 2 l.p.m., all the compounds containing vanadium, whether fumes, dust or organic material, were contained on the first filter disc while the filter discs of funnels 2 and 3 were free from vanadium.

9.2

Many investigators, in the past, have disregarded the effect of temperature and pressure during the sampling period. Since these factors affect the accuracy of the volume measurement, it is recommended that these corrections be introduced routinely. There is increasing agreement, that the standard conditions of temperature, used to correct the final volume, should be 25°C and 760 mmHg.

9.3

As stated, there is little danger in the use of perchloric acid as long as proper precautions are observed. Particulate samples taken from the ambient air are essentially inorganic in nature, the organic material being from 3–10 % of the total particulates. The particulate matter to be digested will amount to only a few milligrams and the possibility or intensity of an explosion will be minimal. Nevertheless, it is the part of discretion to wear goggles and to carefully inspect samples before digestion to ensure that they do not appear to contain too much organic matter.

10. Schematic representation of procedure

10.1

Draw laboratory air sample, 6.1.

10.2

Prepare test sample, 6.2.

10.3

Develop colour, 7.1.

10.4

Measure developed colour, 7.1.

10.5

Calculate vanadium, 8.

11. References

11.1 Pilz, W. and Komischke, S. 'Die Bestimmung von Vanadium in biologischem Material und Luft'. *Internat. J. Envir. Anal. Chem.* **1**, 275–282 (1972).

11.2 Pilz, W., Komischke, S. and Prior, G. 'Die Bestimmung von Vanadium in wässrigen Lösungen, Luft und biologischen Material'. *Internat. J. Envir. Anal. Chem.* **1**, 47–61 (1971).

ANALYTICAL METHODS FOR USE IN OCCUPATIONAL HYGIENE

DETERMINATION OF AIRBORNE PARTICULATE LEAD BY ATOMIC ABSORPTION SPECTROPHOTOMETRY
(*Adopted 1973*)

1. Field of application

The method is applicable to the measurement of the concentrations of airborne particulate lead found in either ambient or industrial atmospheres. The method is not applicable to the measurement of lead compounds in vapour form, such as tetraethyl or tetramethyl lead, but it may be readily adapted to the measurement of tetraethyl lead in gasoline. As airborne particulate lead may make up 1 to 5% of airborne particulate matter, analytical sensitivity is ordinarily not a problem. Based upon the flame mode, washed glass filters and a nominal air sample volume of 2000 cubic metres, lead is measurable to 0.010 micrograms per cubic metre. A slight improvement in sensitivity results from the use of cellulose filters, or down to 0.0075 micrograms per cubic metre. For the same test sample, the use of the flameless mode increases the sensitivity considerably.

2. Principle

A prepared test sample, containing the inorganic constituents in aqueous acidic solution is reduced in the flame or graphite furnace to the atomic state. The amount of the element of interest is measured by making use of its property of absorbing light of its characteristic frequency when in the atomic state.

3. Reactions

The most important reactions relate to the complete dissolution of the particulate sample in acidic media to form a homogeneous test sample. As microgram quantities of material may be involved, losses due to incomplete solution, volatility, or adsorption must be avoided.

4. Reagents

4.1   *Air, compressed*
   In pressure cylinders or online.

4.2   *Acetylene, compressed*
   In pressure cylinders.

4.3 *Glass filters*
Commercially available material, in size 203 by 254 mm, is exhaustively washed prior to use.

4.4. *Cellulose filters*
Ashless, acid washed, analytical grade, in size 203 by 254 mm.

4.5 *Water*
Distilled from glass or quartz, deionized, or prepared in any satisfactory way to produce a suitably low blank.

4.6 *Hydrofluoric acid*
49 %. Reagent grade, in polyethylene containers.

4.7 *Nitric acid*
71 %. Reagent grade.

4.8 *Standard solution of lead*
Dissolve 1.598 g of lead nitrate and make up to 1 litre with 1 % nitric acid. 1 ml of this stock solution contains 1000 μg of lead, Pb.

5. Apparatus

5.1 *Spectrophotometer, atomic absorption*
With meter, recorder or digital readout and monochromator with wavelength dial reading to 0.1 nanometre.

5.2 *Pipettes, glass*
Millilitre capacities, 'to deliver'.

5.3 *Volumetric flasks*
Borosilicate with ground glass stopper, 25 ml capacity.

5.4 *Bottles, polyethylene*
Screw cap 'leak free', for storage of test samples, 30 ml capacity.

5.5 *Beakers, teflon*
Griffin form, 100 ml capacity.

5.6 *Beakers, borosilicate*
Graduated, Griffin form, with teflon coated rim, 150 ml capacity.

5.7 *Hot plate*
Electric, with temperature control, thermostat and ceramic heating surface.

5.8 *Büchner funnel*
Polypropylene, custom made, with sintered false bottom and vacuum connection, 216 by 267 by 85 mm in free depth.

5.9 *Graphite furnace*
One suitable instrument is available commercially to the Massman design.

5.10 *Strip chart recorder*
To display and record the response from the furnace.

5.11 *Pipettes, automatic*
Eppendorf design, with capacities 10 to 100 microlitres.

6. Sampling and samples

6.1 *Preparation of the laboratory sample*
Cellulose filters (4.4) may be used without further treatment. Glass fibre filters (4.3) are purified by placing a group of 100 such filters in the special Büchner funnel and extracting repetitively with distilled water. Mount the filter in a conventional high volume or other sampler head. Draw air through the filter at a flowrate between 1.13 and 1.60 cubic metres per minute, for an appropriate period, such as 24 hours. The resistance to flow offered by the cellulose filters is much greater than for glass and an appreciably smaller total volume of air will be taken with cellulose. Calculate and record the total volume of air sampled, in cubic metres, as the product of mean flowrate and time.

6.2 *Preparation of test sample*
Cut areal aliquots from the exposed surface of a filter using a circular metal punch. The cutting edge of the punch is carefully wiped with lens tissue between each use to prevent carry over of contamination from one sample to another. Place one or more such discs in a teflon beaker. Initiate the dissolution of the filter matrix by the dropwise addition of 1 ml of hydrofluoric acid (4.6). Gently warm the contents of the beaker, at low heat, until the hydrofluoric acid is almost completely evaporated. At this point, add 1 to 2 ml of nitric acid (4.7) and continue to heat gently until a few drops of nitric acid are left. Add about 10 ml of water, bring nearly to the boil and filter through a Whatman 41 filter into a glass beaker (5.6). Transfer to a 25 ml volumetric flask (5.3). Rinse down the teflon beaker with another 10 ml quantity of water, warm and filter into the same beaker. Transfer to the 25 ml volumetric flask and make up test sample to mark at 25 °C. Mix the contents of the volumetric flask thoroughly after adjustment to volume. Transfer contents of volumetric flask to polyethylene storage bottle (5.4). The test sample is now ready for analysis. The above method applies to the digestion of glass fibre filters. Cellulose filters can be digested or extracted using nitric acid.

7. Procedure

7.1 *Safety precautions*
Follow normal precautions for the handling of compressed gases.

Observe manufacturer's instructions for lighting and extinguishing flame. TEST GAS SUPPLY SYSTEM FOR LEAKS BEFORE USE AND EACH TIME A CYLINDER OF GAS IS REPLACED.

7.2

7.2.1 *Test portions, flame.* Introduce the test portion into the flame by *continuous* aspiration, through polyethylene tubing, of an *unmeasured* portion of the test sample. Aspirate distilled water into flame, between the introduction of each test portion, to prevent cross contamination.

7.2.2 *Test portions, furnace.* Measure and insert in the furnace, test portions of 10 to 100 microlitres of the test sample using an automatic pipette (5.11).

7.3

7.3.1 *Calibration curves, flame.* Using 'to deliver' pipettes, prepare known concentrations of lead by dilution of standard solution (4.8) to cover the range of 1.0 to 40.0 micrograms of lead per millilitre. Install in the monochromator and align, if necessary, the hollow cathode source for lead. Set the wavelength of the monochromator at 283.3 nm. Using an air–acetylene flame, aspirate an unmeasured portion of each dilute standard lead solution (7.2.1).
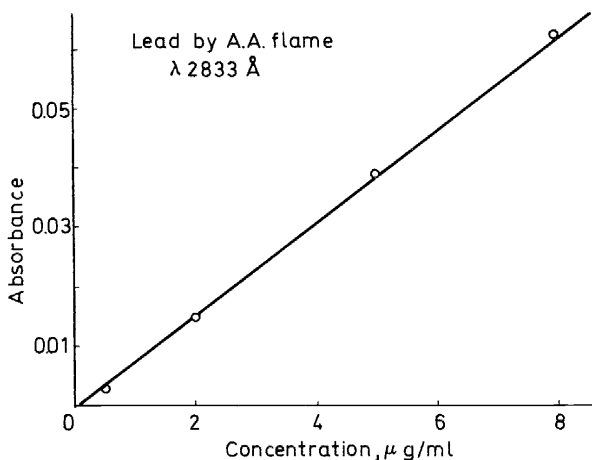
Figure 1.

After this, aspirate into the flame a blank of distilled water. From the instrumental responses obtained, prepare a calibration curve of absorbance against concentration of lead in micrograms per millilitre. Such a representative curve is given in *Figure 1.* Using the same dilute standard solutions of lead, and a distilled water blank, prepare a similar calibration curve with the wavelength of the
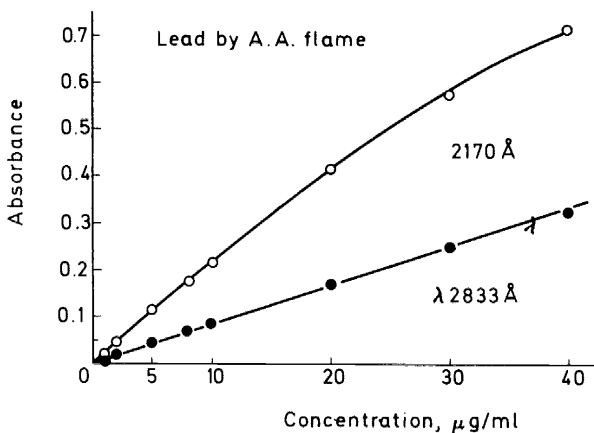
Figure 2.

monochromator set at 217.0 nm. Representative curves, covering wavelengths 217.0 and 283.3 nm, are given in *Figure 2*.

7.3.2 *Calibration curves, furnace.* By means of an automatic pipette with polyethylene tip, place identical microlitre portions of the dilute standard lead solutions and a distilled water blank in the furnace. Measure and record the response for each test portion following the predetermined measuring cycle. Cover the range 1 to 5 nanograms lead in steps of 1 nanogram; 0.1 to 0.5 micrograms per millilitre for a 10 microlitre volume. Prepare a calibration curve of response, in arbitrary units, against concentration of lead in micrograms per millilitre. Such a representative curve is given in *Figure 3*.
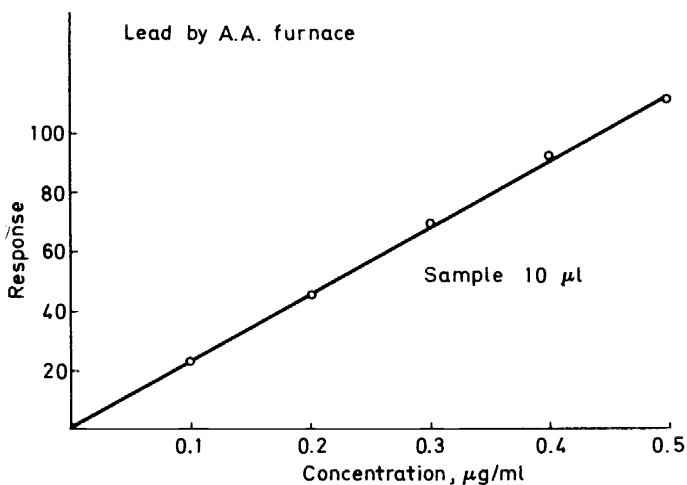
Figure 3.

7.4

7.4.1 *Determination, flame.* Set the wavelength of the mono-chromator at 283.3 nm. Observing conditions of 7.2.1 and 7.3.1, aspirate an unmeasured portion of each test sample into the flame. Record the response for each unknown. Measure the lead in all the unknown test samples which can be accommodated to the cali-bration curve for 283.3 nm. If greater sensitivity is required, this may be obtained by measuring at 217.0 nm, at the cost of more electronic noise. If the lead content of a given test portion should be too low for both calibration curves, it will be necessary to use the flameless mode. If the lead content should prove to be too high for the 217.0 nm curve it will then be necessary to dilute the test sample.

7.4.2 *Determination, furnace.* If insufficient sensitivity is available in the flame mode, measure into the furnace, by automatic pipette, a similar test portion of each unknown test sample. Follow the drying and heating programmes previously established. Record the response for each test portion in arbitrary units. If a test portion of 10 microlitres should provide insufficient response, repeat the measurement using larger test portions. Derive the amount of lead present, by referring to the appropriate calibration curve, *Figure 3*.

7.5 *Blank tests*

7.5.1 *Reagents.* In parallel with preparation of calibration curves, prepare a reagent blank of the acids and distilled water used in the preparation of calibration curves and test samples. Change or purify reagents, as necessary, if blanks are unsatisfactory.

7.5.2 *Reagents plus filters.* In parallel with the preparation of calibration curves and test samples, prepare areal test portions from unexposed filter media as described in 6.2. Measure lead and express blanks in micrograms of lead per millilitre.

8. Expression of results

8.1 *Blanks*

The glass filter blank value for any element may vary considerably with the batch. This has been very noticeable with the manganese and beryllium content of such filters. For this reason, filter blanks should be determined regularly. It should also be noted that part of the filter blank value is due to matrix interferences from elements present in large amounts in the filter such as Na, Ba, Si, Ca, Zn, K and Al.

8.2 *Instrumental precision*

This is defined as the standard deviation of a number of replicate determinations and is expressed in micrograms per millilitre. Typical precisions for ten repeat determinations on standard samples are: $15.00 \pm 0.04\,\mu g/ml$ for the flame mode, $0.4000 \pm 0.0093\,\mu g/ml$ for the flameless mode, on a 10 µl sample.

8.3 *Minimum measurable*

8.3.1 *Concentration in test sample.* This is taken as twice the blank deviation, or instrument precision, whichever is larger. This is 0.04 micrograms per millilitre in the case of lead, in the flame mode.

8.3.2 *Concentration in air.* This is based on a sample volume of 2000 cubic metres, two aliquot discs 36 mm in diameter and the use of the flame. This minimum measurable concentration is 0.010 micrograms of lead per cubic metre with glass and 0.0075 micrograms per cubic metre with cellulose.

8.4 *Calculations*

The lead content of the test portion is expressed in micrograms per millilitre, X_1. The blank, X_2, in the same units, is subtracted from X_1 to get the corrected concentration of lead in the test sample. Multiplication by the dilution factor, usually 25, gives the total quantity of lead in the test sample, in micrograms.
For high volume filters of nominal size 203 by 254 mm:

Total exposed filter surface	$= 4.159 \times 10^4 \text{ mm}^2$
Areal test portion, 2 × 36 mm discs	$= 2036 \text{ mm}^2$
Surface multiplication factor	$= 20.43$
Dilution factor	$= 25$
Volume of air sampled, cubic metres	$= V$
Response, unknown test portion	$= X_1$
Response, total blank	$= X_2$
Lead concentration, in μg/m³	$= T$

$$T = (X_1 - X_2) \times 20.43 \times 25/V$$

9. Notes on procedure

9.1 *Collection efficiencies*

Little is known about actual collection efficiencies and these efficiencies are usually ignored in methods for the analysis of particulate metals. The particle size of particulate lead is below 1 micron according to Lee (Ref. 11.1).

9.2

The effect of temperature and pressure during the sampling period has been largely disregarded in the past. Since these factors must have some effect on the measured air volume, it is recommended that these corrections be introduced routinely. There is increasing agreement, that if standard conditions of temperature and pressure are to be used to correct the final volume, these conditions should be 25 °C and 760 mmHg.

9.3

Although the method described is nominally based upon high volume samples taken for a 24-hour sampling period, there is no valid reason why samples may not be taken for shorter time periods, at slower flowrates, or both. If high volume samples are taken on

cellulose, it is particularly appropriate to take air sample volumes of 1000 cubic metres or less. The lower particulate loading, so obtained, minimizes particulate fall-off.

9.4

It is customary to assume that the decrease in air flowrate during sampling is linear and for usual purposes of calculation, the mean value of initial and final flowrates is taken. This is not correct, although the error introduced by this oversimplification is not ordinarily serious.

9.5

For the preparation of areal test portions, the use of a sharp circular metal die is to be preferred over the use of scissors or rectilinear templates of large perimeter. Areal test portions prepared by these latter are less likely to be identical in size. A circular die, of limited diameter, machined from solid metal, is very rigid and areal aliquots can be very easily reproduced with accuracy. In the method described, a punch of stainless steel is used. No lead contamination has been found to result from its use.

9.6

In the use of the repetitive and consecutive areal test portions cut from an exposed high volume filter, the assumption is implicit that the element of interest is uniformly distributed across the exposed surface of the filter. This assumption is established as fact, at least in the case of lead and cadmium measured on high volume filters (Refs. 11.2, 11.3, 11.4). This uniform distribution cannot be assumed in certain 'membrane' type filters due to inherently high pressure drop and faulty geometry of commercially available filter holders. In the case of such filters, areal aliquotting cannot be used (11.5).

9.7

It is helpful, when possible, to have several calibration curves, relating to different sensitivities. This minimizes the possibility that the concentration of the metal in the unknown test sample will not match one or another of the curves. Thus, a certain sensitivity is available at 283.3 nm, a higher sensitivity can be had at 217.0 nm, and a still higher sensitivity by using the furnace. See *Figures 1, 2 and 3*.

9.8   *Operating conditions, flame*

Wavelength   = 283.3 nm
Spectral band width = 0.7 nm
Source   = hollow cathode
Source current   = as recommended
Oxidant   = air
Fuel   = acetylene

Flame   = oxidizing, lean, blue
Sensitivity   = 0.54 µg/ml for 1 % absorption

Change acetylene container before cylinder pressure drops below 50 p.s.i.g.

9.9 Graphite furnace

The calibration curve for the flame mode obeys Beer's law up to and beyond 40 micrograms per millilitre for wavelength 283.3 nm and up to 10 micrograms per millilitre for wavelength 217.0 nm as shown in *Figures 1* and *2*. A representative curve for lead, measured by the graphite furnace, is given in *Figure 3*, which shows greatly increased sensitivity over the flame. Furnace operating conditions:

Wavelength   = 283.3 nm
Sample size   = 10 microlitres
Purging gas   = argon or nitrogen
Thermal decomposition = drying (15 s, 100 °C)
                                    charring (15 s, 490 °C)
                                    atomizing (10 s, 2400 °C)

The use of a deuterium lamp background compensator is recommended.

10. Schematic representation of procedure

10.1
Draw laboratory air sample.

10.2
Cut areal test portion from exposed filter surface.

10.3
Digest areal test portion.

10.4
Adjust digest to volume to give test sample.

10.5
Aspirate test portion into flame.

10.6
Or, add test portion to furnace.

11. References

11.1   Lee, R. E., Patterson, R. K., Crider, W. L. and Wagman, J. 'Concentration and particle size distribution of particulate emissions in automobile exhaust'. *Atmos. Environment*, **5**, 225 (1971).

11.2   Dubois, L., Teichman, T., Airth, J. M. and Monkman, J. L. 'The metal content of urban air'. *J. Air Pollut. Control Ass.* **16**, 2, 77 (1966).

11.3   Zdrojewski, A., Quickert, N., Dubois, L. and Monkman, J. L.

'The accurate measurement of lead in airborne particulates'. *Internat. J. Envir. Anal. Chem.*, **2**, 63 (1972).

11.4   Zdrojewski, A., Quickert, N. and Dubois, L. 'The accurate measurement of cadmium on airborne particulates.' *Internat. J. Envir. Anal. Chem.* **2**, 331 (1973).

11.5   Pierce, J. O. and Meyer, J. H. 'Sampling and analysis considerations in evaluating levels of atmospheric lead'. *Atmos. Environment*, **5**, 811 (1971).

ANALYTICAL METHODS FOR USE IN OCCUPATIONAL HYGIENE

DETERMINATION OF BENZO[a]PYRENE AND BENZO[k]FLUORANTHENE IN AIRBORNE PARTICULATES (CHROMATOGRAPHY AND OPTICAL FLUORESCENCE)

(Adopted 1973)

1. Introduction

Benzo[a]pyrene and benzo[k]fluoranthene are representatives of a class of polycyclic aromatic hydrocarbons some of which, including benzo[a]pyrene (BaP), are carcinogenic. Such hydrocarbons may be taken as indicators of the hazard which exposure may present. In addition to the fluorescence method to be outlined, other methods have been described, based on gas–liquid chromatography, thin-layer chromatography and ultra-violet absorption (Refs. 12.1, 12.2, 12.3). A Manual of Methods is being prepared by the International Agency for Research on Cancer, in conjunction with the International Union of Pure and Applied Chemistry (Ref. 12.4).

2. Scope

Airborne particulate matter is collected on suitable filters, the organic material is extracted with a suitable solvent and fluorescence measurements are made on chromatographed fractions.

3. Field of application

The method is applicable to airborne particulates collected from ambient air, industrial atmospheres or motor vehicle exhaust.

4. Principle

A portion of the organic extract of an air sample is chromatographed with an aromatic solvent, toluene, on a column of alumina which has been activated at 140°C. The concentration of BaP in the eluates is determined by fluorescence emission measurements. The aromatic solvent is used in preference to an aliphatic or a saturated cyclic, since this results in a more rapid chromatographic separation.

5. Reactions

It is to be noted, in optical fluorescence, that the wavelength positions for maximum excitation and emission spectra vary with the solvent.

6. Reagents

6.1   Cyclohexane, spectrograde

Material suitable for either fluorescence or ultra-violet assay is readily and cheaply prepared by percolating a good technical grade through a column of activated carbon. The purified material is stored in glass stoppered borosilicate bottles. Technical cyclohexane produced from benzene is unsuitable as starting material as the high benzene content makes it too expensive to purify.

6.2   Activated carbon

A suitable grade is available from Pittsburgh Chemical Co., Pittsburgh, Pennsylvania. A column of the 12 × 30 grade, 6.0 cm in diameter and at least 45 cm in depth, allows the preparation of spectrograde cyclohexane at the rate of several litres per hour.

6.3   Alumina

Activated alumina is prepared by heating 100–200 mesh material to 140 °C for 24 hours. A satisfactory grade is Peter Spence type H.

6.4   Toluene

Reagent grade, with a low fluorescence blank.

6.5   Benzo[a]pyrene

Is available from Fluka AG, Buchs, Switzerland or the WHO Reference Centre, Ottawa, Canada. CAUTION. THIS MATERIAL IS CARCINOGENIC!

6.6   Benzo[k]fluoranthene

This material is not available commercially. Limited quantities may be obtained for instrumental calibration from the WHO Reference Centre, Chemistry Division, Environmental Health Centre, Ottawa, K1A OH3. Canada.

6.7   Standard dilutions of BaP

Prepare solutions of BaP in fluorescence-free toluene to contain 0.005, 0.010, 0.015, 0.020 and 0.025 microgram per millilitre of final solution.

6.8   Standard dilutions of BkF

Prepare solutions of BkF in fluorescence-free toluene, to contain 0.005, 0.010, 0.015, 0.020 and 0.025 microgram per millilitre of final solution.

7. Apparatus

7.1   Soxhlet extractors

Extractors with a nominal solvent volume of 30 ml and a cycling time of two minutes are used (Ref. 12.5).

7.2   Chromatographic columns

Glass chromatographic columns with integral solvent reservoir

at top and teflon plug stopcock are convenient. Internal diameter should be 10.0 mm over a length of 30 cm.

7.3 Fluorimeter

A fluorimeter with motor driven excitation and emission mono-chromators is required. This should cover the wavelength range of 250 to 550 nm.

8. Sampling and samples

Air samples are taken by drawing air at known flowrate and time through filters of cellulose or glass fibre. It is important that the filters used be free of organic extractable material which might fluoresce at the excitation wavelengths used. It has been found that small quantities of such fluorescing material are actually present in the commercially available material and it may be necessary to extract these materials from the filters before use. High volume samples may be taken for 24 hours in glass or cellulose filters 8 × 10 inches in overall size. If the hydrocarbon-in-air concentrations are high enough, smaller volumes of air may be taken on 4 inch or 2 inch filter circles.

9. Procedure

Using a clean circular metal punch, cut 4 to 10 circles of 36 mm diameter from a high volume filter, or a suitably large aliquot from low volume filters. In the calculations given later, the factor 10.5 refers to an area aliquot equal to 1/10 of the total sample. Place the aliquot discs in a Soxhlet extractor on top of a wad of glass wool and cover with another wad of glass wool to lessen the possibility of the carry over of carbon particles into the extract. After six hours extraction with cyclohexane, evaporate the solvent extract carefully to 2 ml, at room temperature, using a clean air or nitrogen jet but no heat. The extract must on no account be allowed to become dry.

Set up the chromatographic columns in a fume hood. Carry out the preparation of column and the elution procedure in the fume hood. Prepare the column by slurrying the alumina with toluene and filling the tube to a depth of 12.0 cm. Place the concentrated extract, no more than 2 ml, carefully on top of the alumina which has been covered with a 1 cm depth of glass beads. Elute, using toluene. Discard the first 25 ml of eluate and collect 3 ml fractions, thereafter, up to a total of about 30 fractions, or about 90 ml. Scan each fraction separately on the fluorimeter and combine those fractions containing BaP and BkF for a further measurement. BaP and BkF are usually eluted between 30–45 ml but this can vary depending upon the activity of the particular batch of alumina in use. Combine all fractions showing BaP and BkF, evaporate carefully without heat, and make up to a final volume such that the concentrations of BaP and BkF fit the range of the standard curves. See *Figure 1*. Usually a 5 ml volume is satisfactory. Determine the fluorescence emission at 410 nm by using the height-above-baseline
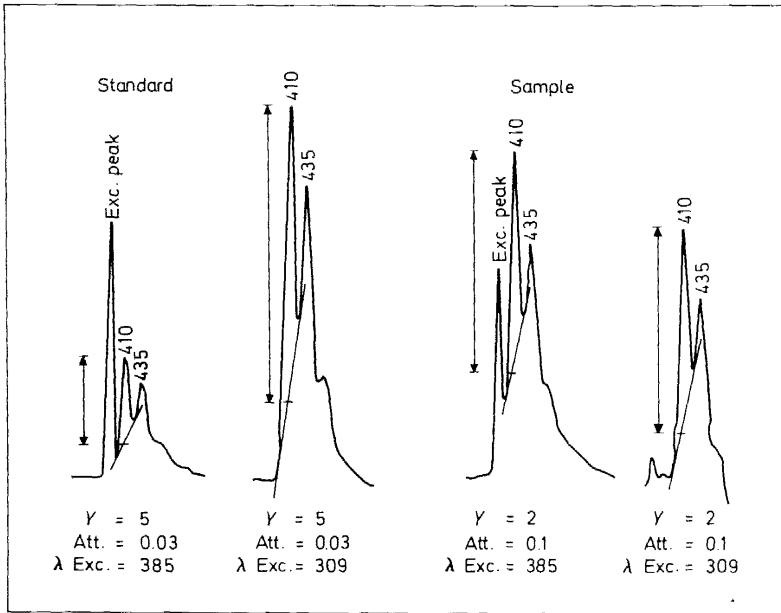
Figure 1. Fluorescence emission spectra for standard polycyclic hydrocarbons compared with the spectra obtained on air sample extracts. This illustrates the so-called baseline method of peak height measurement.

technique, while exciting at wavelengths 309 and 385 nm. These 'optimum' wavelengths were selected by running the excitation spectrum of the 0.015 µg/ml standards for both BaP and BkF. Four curves are obtained for solutions in toluene as shown in *Figure 2*.

10. Expression of results

10.1 *Calculations*

Since the fluorescence emission intensity of BkF is much greater than that of BaP when a solution containing both hydrocarbons in equal amount is excited at 309 nm, the reading at this wavelength is essentially due to BkF. Having determined the concentration of BkF, one can calculate the effect of this hydrocarbon when a mixture is excited at 385 nm, after which the BaP concentration may be calculated in micrograms per millilitre, as follows:

$$\text{conc. BkF} = \frac{\text{Emission at 309 exc.}}{\text{Slope of BkF curve at 309 exc.}},$$

$$\text{conc. BaP} = \frac{\text{Emission at 385} - \text{conc. BkF} \times \text{slope BkF curve 385}}{\text{Slope of BaP curve at 385 exc.}}$$

10.2 *Pro forma calculation*

Suppose an eluate of an unknown sample to give a peak height of 14.8 units at 385 exc. and 38.5 units at 309 exc. By reference to the
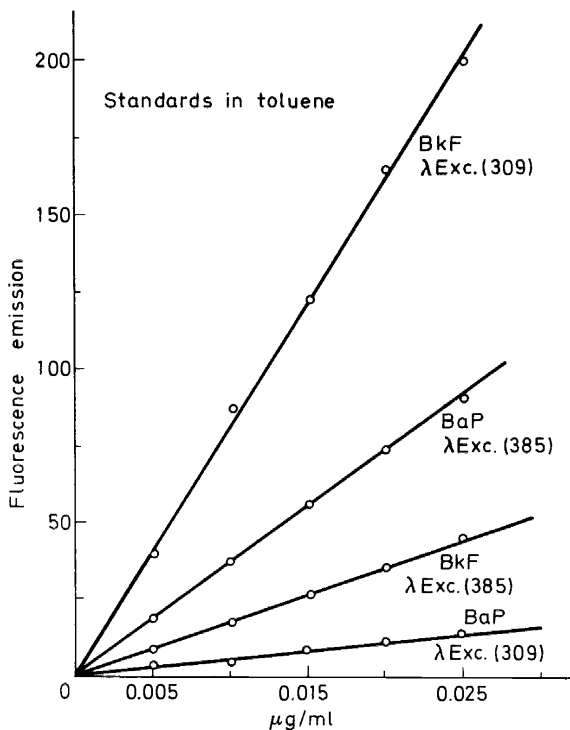
Figure 2. Four standard curves are given for benzo[a]pyrene and benzo[k]fluor-anthene solutions in toluene as each standard solution is extracted using the extraction wavelengths 309 and 385 nm.

calibration curves in *Figure 2*, the slopes, or the emissions per μg of compound are:

$$BkF\ (309) = 8\,800$$
$$BkF\ (385) = 1\,850$$
$$BaP\ (385) = 3\,850$$

From which the concentration of BkF = 38.5/8800 = 0.0044 μg/ml
And the concentration of BaP = {14.8 − (0.0044 × 1 850)}/3 850
= 0.0039 μg/ml
Concentration of hydrocarbon, μg/gram
= (μg/ml) × 5 × 10.5/particulate weight, grams
Concentration of hydrocarbon, μg/1 000 m³
= (μg/ml) × 5 × 10.5 × 1 000/air volume, m³

10.3   *Accuracy*

0.250 μg/ml of BaP can be measured with an accuracy of better than ± 0.002 microgram. 0.250 μg/ml of BkF can be measured with an accuracy of better than ± 0.001 μg. If the concentration of BaP found is more than twice the BkF concentration, the BkF results will be in error by a factor of ten per cent.

11. Notes on procedure

11.1 *Collection efficiencies*

Little is known about actual collection efficiencies and in reporting the analytical data these efficiencies are usually ignored. Preliminary studies suggest that BaP is associated with very small particles and that collection efficiency increases with colder ambient temperatures.

11.2 *Temperature and pressure*

The effect of these sampling variables has been largely disregarded in the past. Since these factors must have some effect on the accuracy of the measured air volume, it is recommended that these corrections be introduced routinely. There is increasing agreement, that if universal reference conditions of temperature and pressure are to be used to correct the final volume, these conditions should be 25 °C and 760 mmHg.

11.3

Although the method described is nominally based upon 'high volume' samples taken for a 24-hour sampling period, there is no valid reason why samples may not be taken for shorter time periods, at slower flowrates, or both. Lower particulate loadings obtained with smaller air volumes minimize particulate fall-off.

11.4

It is customary to assume that the decrease in air flowrate during sampling is linear and for usual purposes of calculation, the mean value of initial and final flowrates is taken. This is not correct, although the error introduced by this oversimplification is not ordinarily serious.

11.5

For the preparation of areal test portions, the use of a sharp circular metal die is to be preferred over the use of scissors or rectilinear templates of large area because of greater reproducibility and accuracy of the areal aliquot obtained.

11.6

In the use of replicate and consecutive areal test portions cut from an exposed high volume filter, the assumption is implicit that the material of interest is uniformly distributed across the exposed surface of the filter. This can be accepted as fact in the case of 'high volume' filters (Ref. 12.6). This uniform distribution cannot be assumed in certain 'membrane' type filters due to inherently high pressure drop and faulty geometry of commercially available filter holders. In such a case, it is necessary to use the complete filter (Ref. 12.7).

11.7 Sample preparation

Soxhlet extraction, using organic solvents, is most widely used to obtain the extract of the organic material in the airborne particulates. Sublimation procedures, which require no solvent, are worthy of consideration (Ref. 12.8). Recently, ultrasonic agitation of the sample in the presence of a solvent is said to be very rapid and effective. The procedure should be designed to avoid evaporation as much as possible, because of volatility losses. Heat should not be used and extracts should never be allowed to become dry. There is no blank problem with good quality glass or cellulose filters but, as mentioned, the absolute collection efficiency is unknown.

11.8 Optimum wavelengths

The optimum wavelengths may vary somewhat depending upon the instrument used. The values given are intended only as guides, since, because of instrumental variation, each laboratory must establish the optima which are obtained under their standard conditions. Calibration curves similar to *Figure 2* are obtained for standard solutions in cyclohexane. The sensitivity is somewhat less in toluene than in cyclohexane. However, the toluene-based BaP measurement is somewhat better than a BaP measurement made in cyclohexane because the emission of BaP at 385 exc. is higher than the emission of BkF at 385 exc.

12. References

12.1   Dubois, L. and Monkman, J. L. 'A technique for accurately measuring BaP or BkF by fluorescence in air samples either separately or in mixtures'. *Internat. J. Air Wat. Pollut.* **9**, 131 (1965).
12.2   Dubois, L., Zdrojewski, A., Baker, C. and Monkman, J. L. 'Some improvements in the determination of benzo[a]pyrene in air samples'. *J. Air Pollut. Control Ass.* **17**, No. 12 (1967).
12.3   Intersociety Committee. 'Tentative method of chromatographic analysis for BaP and BkF in atmospheric particulate matter'. *Health Laboratory Science*, **7**, 1, 60 (1970).
12.4   'Sampling and analysis of airborne polycyclic aromatic hydrocarbons'. Manual in preparation. International Agency for Research on Cancer (December 1974).
12.5   'Extraction of polycyclic hydrocarbons from air samples'. *IARC Report 71/002*, Appendix VI (1969).
12.6   Dubois, L., Teichman, T., Airth, J. M. and Monkman, J. L. 'The metal content of urban air'. *J. Air Pollut. Control Ass.* **16**, No. 2, 77 (1966).
12.7   Pierce, J. O. and Meyer, J. H. 'Sampling and analysis considerations in evaluating levels of atmospheric lead'. *Atmos. Environment*, **5**, 811 (1971).
12.8   Monkman, J. L., Dubois, L. and Baker, C. J. 'The rapid measurement of polycyclic hydrocarbons in air by microsublimation'. *Pure Appl. Chem.* **24**, 731–738 (1970).

ANALYTICAL METHODS FOR USE IN OCCUPATIONAL HYGIENE

DETERMINATION OF AIRBORNE PARTICULATE CADMIUM BY ATOMIC ABSORPTION SPECTROPHOTOMETRY
(Adopted 1973)

1. Field of application

The method is applicable to the measurement of the levels of suspended particulate cadmium found in either ambient or industrial atmospheres. Based upon the flame mode, washed glass filters and a nominal air sample volume of 2000 cubic metres, cadmium is measurable to 0.0025 micrograms per cubic metre. If the sample is taken on analytical grade cellulose the minimum quantity measurable is also 0.0025 micrograms per cubic metre. For the same test sample, the use of the flameless mode increases the sensitivity by up to two orders of magnitude. As levels of cadmium in urban air are low and since cadmium levels in the laboratory may be rather high by comparison every care must be taken to ensure that the cadmium being measured is actually due to the air sample.

2. Principle

A prepared test sample containing the inorganic constituents in aqueous acidic solution is atomized in a flame or heated graphite tube. The absorption of light of characteristic wavelength by the atoms of the element of interest is used to measure the concentration of that element.

3. Reactions

The most important reactions relate to the complete dissolution of the particulate sample in acidic media to form a homogeneous test sample. As microgram quantities of material may be involved, losses due to incomplete solution, volatility or adsorption must be avoided. Again care must be taken in preparation to avoid airborne cadmium in the laboratory air and equipment and apparatus which is cadmium plated.

4. Reagents

4.1 *Air, compressed*
In pressure cylinders or online.

4.2 *Acetylene, compressed*
In pressure cylinders.

4.3 Glass filters
Commercially available material in size 203 by 254 mm, is exhaustively washed prior to use.

4.4 Cellulose filters
Ashless, acid washed, analytical grade, in size 203 by 254 mm.

4.5 Water
Distilled from glass or quartz, deionized, or prepared in any way which produces a satisfactory blank.

4.6 Hydrofluoric acid
49 %. Reagent grade, in polyethylene containers.

4.7 Nitric acid
71 %. Reagent grade.

4.8 Standard solution of cadmium
Dissolve 1 gram of cadmium metal in the minimum volume of 50 % hydrochloric acid and dilute to 1 litre with water. 1 ml of this stock solution contains 1 000 micrograms of cadmium, Cd.

5. Apparatus

5.1 Spectrophotometer, atomic absorption
With meter, recorder or digital readout and monochromator with wavelength dial reading to 0.1 nanometre.

5.2 Pipettes, glass
Millilitre capacities, 'to deliver'.

5.3 Volumetric flasks
Borosilicate with ground glass stopper, 25 ml capacity.

5.4 Bottles, polyethylene
Screw cap, 'leak free', for storage of test samples, 30 ml capacity.

5.5 Beakers, teflon
Griffin form, 100 ml capacity.

5.6 Beakers, borosilicate
Graduated, Griffin form, with teflon coated rim, 150 ml capacity.

5.7 Hot plate
Electric, with temperature control, thermostat, and ceramic heating surface.

5.8 Büchner funnel
Polypropylene, custom made, with sintered false bottom and vacuum connection, 216 by 267 by 85 mm.

5.9 *Graphite furnace*

One suitable instrument is available commercially to the Mass-mann design.

5.10 *Strip chart recorder*

To display and record the response from the furnace.

5.11 *Pipettes, automatic*

Eppendorf design, with capacities 10 to 100 microlitres.

6. Sampling and samples

6.1 *Preparation of the laboratory sample*

Cellulose filters (4.4) may be used without further treatment. Glass fibre filters (4.3) are purified by placing a group of 100 such filters in the special Büchner funnel, and extracting repetitively with distilled water. Mount the filter in a conventional high volume or other sampler head. Draw air through the filter at a flowrate between 1.13 and 1.60 cubic metres per minute, for an appropriate period, such as 24 hours. The resistance to flow offered by the cellulose filter is much greater than for glass and an appreciably smaller total volume of air will be taken with cellulose. Calculate and record the total volume of air sampled, in cubic metres, as the product of mean flowrate and time.

7.2 *Preparation of test sample*

Cut areal aliquots from the exposed surface of a filter using a circular metal punch. The cutting edge of the punch is carefully wiped with lens tissue between each use to prevent carry over of contamination from one sample to another. Place one or more such discs in a teflon beaker. Initiate the dissolution of the filter matrix by the dropwise addition of 1 ml of hydrofluoric acid (4.6). Gently warm the contents of the beaker, at low heat, until the hydrofluoric acid is almost completely evaporated. At this point, add 1 to 2 ml of nitric acid (4.7) and continue to heat gently until a few drops of nitric acid are left. Add about 10 ml of water, bring nearly to the boil and filter through a Whatman 41 filter into a glass beaker (5.6). Transfer to a 25-ml volumetric flask (5.3). Rinse down the teflon beaker with another 10 ml quantity of water, warm and filter into the same beaker. Transfer to the 25 ml volumetric flask and make up test sample to mark at 25°C. Mix the contents of the volumetric flask thoroughly after adjustment to volume. Transfer contents of volumetric flask to polyethylene storage bottle (5.4). The test sample is now ready for analysis. The above method applies to the digestion of glass fibre filters. Cellulose filters can be digested or extracted using nitric acid.

7. Procedure

7.1 *Safety precautions*

Follow normal precautions for the handling of compressed gases. Observe manufacturer's instructions on lighting and extinguishing

flame. TEST GAS SUPPLY SYSTEM FOR LEAKS BEFORE USE AND EACH TIME A CYLINDER OF FUEL IS RE-PLACED.

7.2

7.2.1 *Test portions, flame.* Introduce the test portion into the flame by *continuous* aspiration, through polyethylene tubing, of an *unmeasured* portion of the test sample. Aspirate distilled water into flame, between the introduction of each test portion, to prevent cross contamination.

7.2.2. *Test portions, furnace.* Measure and insert in the furnace, test portions of 10 to 100 microlitres of the test sample using an automatic pipette (5.11).

7.3

7.3.1 *Calibration curves, flame.* Using 'to deliver' pipettes, prepare known concentrations of cadmium by dilution of standard solution (4.8) to cover the range of 0.1 to 1.0 micrograms of cadmium per millilitre. Install in the spectrophotometer and align, if necessary, the hollow cathode source for cadmium. Set the wavelength of the monochromator at 228.8 nm. Using an air–acetylene flame, aspirate an unmeasured portion of each dilute standard cadmium solution for 10 seconds (7.2.1). After this, aspirate into the flame a blank of distilled water. From the instrumental responses obtained, prepare a calibration curve of absorbance against concentration of cadmium, in micrograms per millilitre. Such a representative calibration curve is given in *Figure 1*.
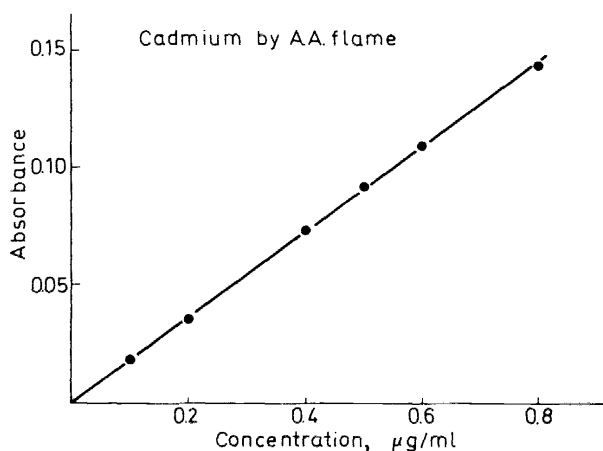

Figure 1.

7.3.2 *Calibration curves, furnace.* By means of an automatic pipette with polyethylene tip, place identical microlitre volumes of the dilute standard cadmium solutions and a distilled water blank
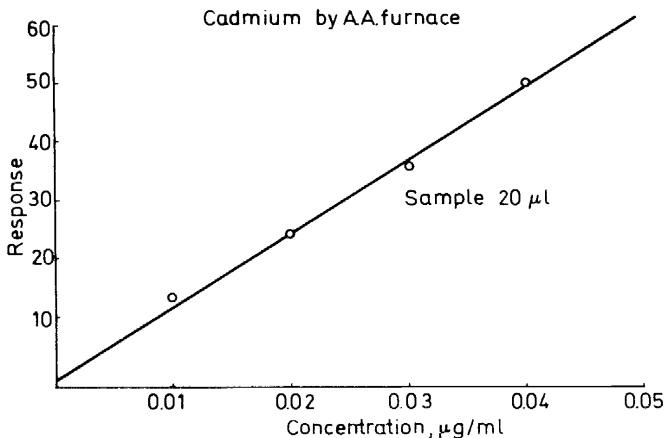
Figure 2.

in the furnace. Measure and record the response of each test portion following the predetermined measuring cycle. Cover the range 0.2 to 1.0 nanogram cadmium in steps of 0.2 nanogram; 0.01 to 0.05 microgram per millilitre for a 20 microlitre volume. Prepare a calibration curve of response, in arbitrary units, against concentration of cadmium in micrograms per millilitre. Such a representative calibration curve is given in *Figure 2.*

7.4

7.4.1 *Determination, flame.* Set the wavelength of the mono-chromator at 228.8 nm. Observing conditions of 7.2.1 and 7.3.1, aspirate an unmeasured test portion of each unknown test sample into the flame. Record the responses for each unknown. Aspirate distilled water into the flame between each unknown test portion to prevent cross contamination. Measure the cadmium in all the unknown test samples which can be accommodated to the wavelength 228.8 nm and the corresponding calibration curve.

7.4.2 *Determination, furnace.* Measure into the furnace, by automatic pipette, a similar test portion of each unknown test sample. Follow the drying and heating programmes previously established. Record the response for each test portion in arbitrary units. Derive the amount of cadmium present in the test sample by referring to the appropriate calibration curve, such as, for example, *Figure 2.*

7.5 *Blank tests*

7.5.1 *Reagents.* In parallel with preparation of calibration curves, prepare a reagent blank of the acids and distilled water used in the preparation of calibration curves and test samples. Change or purify reagents, as necessary, if blanks are unsatisfactory.

7.5.2 *Reagents plus filters.* In parallel with the preparation of calibration curves and test samples, prepare areal test portions from unexposed filter media as described in 6.2. Measure cadmium and express blanks in micrograms of cadmium per millilitre.

8. Expression of results

8.1 *Blanks*

The glass filter blank value for any element may vary considerably with the batch. This has been very noticeable with manganese and beryllium. For this reason, filter blanks should be determined regularly. Extreme care must be taken to isolate and eliminate cadmium interferences normally present in the laboratory. Part of the filter blank value is due to matrix interferences from elements present in larger amounts in the filter such as Na, Ba, Si, Ca, Zn, K and Al.

8.2 *Instrumental precision*

This is defined as the standard deviation of a number of replicate determinations and is expressed in micrograms per millilitre. Typical precisions for ten repeat determinations on standard samples are: $0.50 \pm 0.004\,\mu g/ml$ for the flame mode, $0.02 \pm 0.00035\,\mu g/ml$ for the flameless mode, on a 20 µl sample.

8.3 *Minimum measurable*

8.3.1 *Concentration in test sample.* This is taken as twice the blank deviation, or instrument precision, whichever is larger. This is 0.01 microgram per millilitre in the case of cadmium, using the flame mode. For the flameless mode the blank deviation is the determining factor and this may vary for different filter batches. A typical value is 0.001 micrograms per millilitre.

8.3.2 *Concentration in air.* This is based upon a sample volume of 2000 cubic metres and two aliquot discs 36 mm in diameter. The minimum measurable concentration is 0.0025 microgram per cubic metre for the flame mode and 0.00025 microgram per cubic metre for the flameless mode. These values are the same for washed glass or cellulose filters.

8.4 *Calculations*

The cadmium content of the test solution is expressed in micrograms of cadmium per millilitre, X_1. The blank, X_2, in the same units, is subtracted from X_1 to get the corrected concentration of cadmium in the test sample in µg/ml. Multiplication by the dilution factor, usually 25, gives the total quantity of cadmium in the test sample, in micrograms.

For high volume filters of nominal size 203 by 254 mm:

Total exposed filter surface $= 4.159 \times 10^4 \text{ mm}^2$
Areal test portion, 2×36 mm discs $= 2036 \text{ mm}^2$
Surface multiplication factor $= 20.43$
Dilution factor $= 25$

Volume of air sampled, cubic metres $= V$
Response, unknown test portion $\quad = X_1$
Response, total blank $\quad\quad\quad = X_2$
Cadmium concentration, in $\mu g/m^3 \quad = T$
$$T = (X_1 - X_2) \times 20.43 \times 25/V$$

9. Notes on procedure

9.1 *Collection efficiencies*

Little is known about actual collection efficiencies and in methods for the analysis of particulate metals, these efficiencies are usually ignored. The particle size of particulate cadmium is almost all between 1 and 3 micrometres according to Lee (Ref. 11.1).

9.2

The effect of temperature and pressure during the sampling period has been largely disregarded in the past. Since these factors must have some effect on the measured air volume, it is recommended that these corrections be introduced routinely. There is increasing agreement that if standard conditions of temperature and pressure are to be used to correct the final volume, these conditions should be 25 °C and 760 mmHg.

9.3

Although the method described is nominally based upon high volume samples taken for a 24-hour sampling period, there is no valid reason why samples may not be taken for shorter time periods, at slower flowrates, or both. If high volume samples are taken on cellulose, it is particularly appropriate to take air sample volumes of 1 000 cubic metres or less. The lower particulate loading, so obtained, minimizes particulate fall-off. This much more favourable blank resulting from the use of cellulose and the attendant increase in sensitivity should be borne in mind when the sampling procedure is being planned.

9.4

It is customary to assume that the decrease in air flowrate during sampling is linear and for usual purposes of calculation, the mean value of initial and final flowrates is taken. This is not correct, although the error introduced by this oversimplification is not ordinarily serious.

9.5

For the preparation of areal test portions, the use of a sharp circular metal die is to be preferred over the use of scissors or rectilinear templates of large perimeter. Areal test portions prepared by these latter are less likely to be identical in size. A circular die, of limited diameter, machined from solid metal, is very rigid and areal aliquots can be very easily reproduced with accuracy. In the method described, a punch of stainless steel is used. No cadmium contamination has been found to result from its use.

9.6

In the repetitive and consecutive areal test portions cut from an exposed high volume filter, the assumption is implicit that the element of interest is uniformly distributed across the exposed surface of the filter. This assumption is established as fact, at least in the case of lead (Refs. 11.2, 11.3, 11.4) and cadmium (one exception was noted in 11.4) measured on high volume filters. This uniform distribution cannot be assumed in certain 'membrane' type filters due to inherently high pressure drop and faulty geometry of commercially available filter holders. In the case of such filters, areal aliquotting cannot be used (11.5).

9.7

It is helpful, when it is possible, to have several calibration curves, relating to different sensitivities. This minimizes the possibility that the concentration of the metal, in the unknown test sample, will not match one or another of the curves. See method for lead where two calibration curves are given for the flame (11.3).

9.8   *Operating conditions, flame*
The optimum operating conditions are as given:

Wavelength	$= 228.8$
Spectral band width	$= 0.7\,\text{nm}$
Source	$= $ hollow cathode
Source current	$= $ as recommended
Oxidant	$= $ air
Fuel	$= $ acetylene
Flame	$= $ oxidizing, lean, blue
Sensitivity	$= 0.026\,\mu\text{g/ml}$ for 1% absorption

Change acetylene cylinder before pressure drops to 50 p.s.i.g.

9.9   *Graphite furnace*
The calibration curve for the flame mode obeys Beer's law up to 1.0 microgram of cadmium per millilitre of test sample as illustrated by *Figure 1*. A representative curve for cadmium, measured by the graphite furnace, is given in *Figure 2*, which shows greatly increased sensitivity over the flame. Furnace operating conditions:

Wavelength	$= 228.8\,\text{nm}$
Sample size	$= 20$ microlitres
Purging gas	$= $ argon or nitrogen
Thermal decomposition	$= $ drying $(15\,\text{s}, 100\,^\circ\text{C})$
	charring $(15\,\text{s}, 330\,^\circ\text{C})$
	atomizing $(10\,\text{s}, 1\,800\,^\circ\text{C})$

The use of a deuterium lamp background compensator is recommended.

10. Schematic representation of procedure

10.1

Draw laboratory air sample.

10.2

Cut areal test portion from exposed surface.

10.3

Digest areal test portion.

10.4

Adjust digest to volume to give test sample.

10.5

Aspirate test portion into flame.

10.6

Or, add test portion to furnace, measured by microlitre pipette.

11. References

11.1   Lee, R. E., Patterson, R. K. and Wagman, J. *J. Envir. Sci. and Tech.* **2**, 288 (1968).

11.2   Dubois, L., Teichman, T., Airth, J. M. and Monkman, J. L. 'The metal content of urban air', *J. Air Pollut. Control. Ass.* **16**, 2, 77 (1966).

11.3   Zdrojewski, A., Quickert, N., Dubois, L. and Monkman, J. L. 'The accurate measurement of lead in airborne particulates'. *Internat. J. Envir. Anal. Chem.* **2**, 63 (1972).

11.4   Zdrojewski, A., Quickert, N. and Dubois, L. 'The accurate measurement of cadmium on airborne particulates'. *Internat. J. Envir. Anal. Chem.* **2**, 331 (1973).

11.4   Pierce, J. O. and Meyer, J. H. 'Sampling and analysis considerations in evaluating levels of atmospheric lead'. *Atmos. Environment*, **5**, 811 (1971).

ANALYTICAL METHODS FOR USE IN OCCUPATIONAL HYGIENE

DETERMINATION OF AIRBORNE PARTICULATE VANADIUM BY ATOMIC ABSORPTION SPECTROPHOTOMETRY
(Adopted 1973)

1. Field of application

The method is applicable to the measurement of the levels of suspended particulate vanadium found in either ambient or industrial atmospheres. Based upon the flameless mode, washed glass filters and a nominal air sample volume of 2000 cubic metres, vanadium is measurable to 0.0004 microgram per cubic metre. For the same test sample, the use of the flame mode decreases the sensitivity to 0.025 microgram per cubic metre, as well as introducing possible errors due to matrix effects.

2. Principle

A prepared test sample, containing the inorganic constituents in aqueous acidic solution, is reduced in the flame or graphite tube to the atomic state. The amount of the element of interest is measured by making use of its property of absorbing light of its characteristic frequency when in the atomic state.

3. Reactions

The most important reactions relate to the complete dissolution of the particulate sample in acidic media to form a homogeneous test sample. As microgram quantities of material may be involved, losses due to incomplete solution, volatility or adsorption must be avoided.

4. Reagents

4.1   *Air compressed*
In pressure cylinders or online.

4.2   *Acetylene, compressed*
In pressure cylinders.

4.3   *Nitrous oxide, compressed*
In pressure cylinders.

4.4   *Glass filters*
Commercially available material, in size 203 × 254 mm, is exhaustively washed prior to use.

4.5 Cellulose filters
Ashless, acid washed, analytical grade, in size 203 by 254 mm.

4.6 Water
Distilled from glass or quartz, deionized or other means of preparation leading to satisfactorily low blank.

4.7 Hydrofluoric acid
49 %. Reagent grade, in polyethylene containers.

4.8 Nitric acid
71 %. Reagent grade.

4.9 Standard solution of vanadium
Dissolve 1.7856 g of vanadium pentoxide (V_2O_5) in 10 ml concentrated hydrochloric acid, and dilute to 1 litre with water. 1 ml of this stock solution contains 1000 micrograms of vanadium, V.

5. Apparatus

5.1 Spectrophotometer, atomic absorption
With meter, recorder or digital readout and monochromator with wavelength dial reading to 0.1 nanometre.

5.2 Pipettes, glass
Millilitre capacities, 'to deliver'.

5.3 Volumetric flasks
Borosilicate with ground glass stopper, 25 ml capacity.

5.4 Bottles, polyethylene
Screw cap, 'leak free', for storage of test samples, 30 ml capacity.

5.5 Beakers, teflon
Griffin form, 100 ml capacity.

5.6 Beakers, borosilicate
Graduated, Griffin form, with teflon coated rim, 150 ml capacity.

5.7 Hot plate
Electric, with temperature control, thermostat and ceramic heating surface.

5.8 Büchner funnel
Polypropylene, custom made, with sintered false bottom and vacuum connection, 216 by 267 by 85 mm in free depth.

5.9 Graphite furnace
One suitable instrument is available commercially to the Massmann design.

5.10 *Strip chart recorder*

To display and record the response from the furnace.

5.11 *Pipettes, automatic*

Eppendorf design, with capacities 10 to 100 microlitres.

6. Sampling and samples

6.1 *Preparation of the laboratory sample*

Cellulose filters (4.5) may be used without further treatment. Glass fibre filters (4.4) are purified by placing a group of 100 such filters in the special Büchner funnel and extracting repetitively with distilled water. Mount the filter in a conventional high volume or other sampler head. Draw air through the filter at a flowrate between 1.13 and 1.60 cubic metres per minute, for an appropriate period, such as 24 hours. The resistance to flow offered by the cellulose filters is much greater than for glass and an appreciably smaller total volume of air will be taken with cellulose. Calculate and record the total volume of air sampled, in cubic metres, as the product of mean flowrate and time.

6.2 *Preparation of test sample*

Cut areal aliquots from the exposed surface of a filter using a circular metal punch. The cutting edge of the punch is carefully wiped with lens tissue between each use to prevent carry over of contamination from one sample to another. Place one or more such discs in a teflon beaker. Initiate the dissolution of the filter matrix by the dropwise addition of 1 ml of hydrofluoric acid (4.7). Gently warm the contents of the beaker, at low heat, until the hydrofluoric acid is almost completely evaporated. Heating to dryness at this point may result in a loss of vanadium of about 15% (11.1). Then, add 1 to 2 ml of nitric acid (4.8) and continue to heat gently until a few drops of nitric acid are left. Add about 10 ml of water, bring nearly to the boil and filter through a Whatman 41 filter into a glass beaker (5.6). Transfer to a 25 ml volumetric flask (5.3). Rinse down the teflon beaker with another 10 ml quantity of water, warm and filter into the same beaker. Transfer to the 25 ml volumetric flask and make up test sample to mark at 25 °C. Mix the contents of the volumetric flask thoroughly after adjustment to volume. Transfer contents of volumetric flask to polyethylene storage bottle (5.4). The test sample is now ready for analysis. The above method applies to the digestion of glass fibre filters. Cellulose filters can be digested or extracted using nitric acid.

7. Procedure

7.1 *Safety precautions*

Follow normal precautions for the handling of compressed gases. Observe manufacturer's instructions on lighting and extinguishing flame. TEST GAS SUPPLY SYSTEM FOR LEAKS BEFORE USE AND EACH TIME A CYLINDER OF FUEL IS RE-PLACED.

7.2

7.2.1 *Test portions, flame.* Introduce the test portion into the flame by *continuous* aspiration, through polyethylene tubing, of an *unmeasured* portion of the test sample. Aspirate distilled water into flame, between the introduction of each test portion, to prevent cross contamination.

7.2.2 *Test portions, furnace.* Measure and insert in the furnace, test portions of 10 to 100 microlitres of the test sample using an automatic pipette (5.11).

7.3

7.3.1 *Calibration curves, flame.* Using 'to deliver' pipettes, prepare known concentrations of vanadium by dilution of standard solution (4.9) with filter blank solution (7.5.2) to cover the range of 20 to 200 micrograms of vanadium per millilitre. Install in the spectrophotometer and align, if necessary, the hollow cathode source for vanadium. Set the wavelength of the monochromator at 318.4 nm. Using a nitrous oxide–acetylene flame, aspirate an unmeasured portion of each dilute standard vanadium solution for 10 seconds (7.2.1). After this, aspirate into the flame a blank of distilled water. From the instrumental responses obtained, prepare a calibration curve of absorbance against concentration of vanadium in micrograms per millilitre. Representative calibration curves are given in *Figure 1*, graph 1 representing aqueous standards and graph 2, standards made up in a solution containing 180 μg of aluminium per millilitre. It can be seen that the matrix effect is considerable and is dependent on the concentrations of a number of interfering elements (Ref. 11.1).
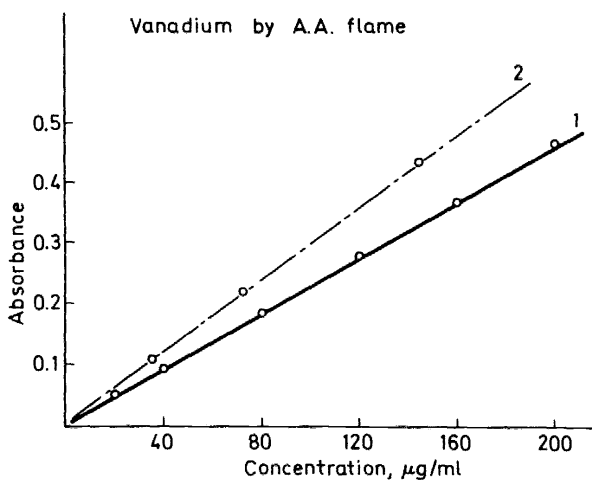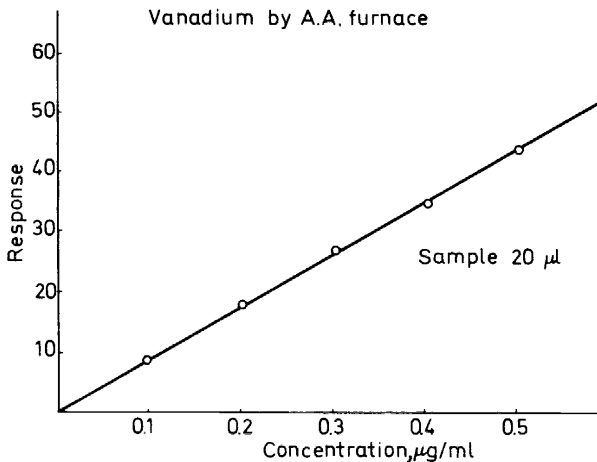

Figure 1.

Figure 2.

7.3.2 *Calibration curves, furnace.* By means of an automatic pipette with polyethylene tip, place identical microlitre volumes of the dilute standard vanadium solutions and a distilled water blank in the furnace. Measure and record the response of each test portion following the predetermined measuring cycle. Cover the range of 2 to 10 nanograms of vanadium in steps of 2 nanograms; 0.1 to 0.5 micrograms per millilitre for a 20 microlitre volume. Prepare a calibration curve of response, in arbitrary units, against concentration of vanadium in micrograms per millilitre. Such a representative calibration curve is given in *Figure 2.*

7.4

7.4.1 *Determination, flame.* Set the wavelength of the mono-chromator at 318.4 nm. Observing conditions of 7.2.1 and 7.3.1, aspirate an unmeasured test portion of each unknown test sample into the flame. Record the response for each unknown. Aspirate distilled water into the flame between each unknown test portion to prevent cross contamination. Measure the vanadium in all the unknown test samples which can be accommodated to the wavelength of 318.4 nm and the corresponding calibration curve.

7.4.2 *Determination, furnace.* Measure into the furnace, by automatic pipette, a similar test portion of each unknown test sample. Follow the drying and heating programmes previously established. Record the response for each test portion in arbitrary units. Derive the amount of vanadium present in the test sample, by referring to the appropriate calibration curve, such as, for example, *Figure 2.*

7.5 *Blank tests*

7.5.1 *Reagents.* In parallel with preparation of calibration

curves, prepare a reagent blank of the acids and distilled water used in the preparation of calibration curves and test samples. Change or purify reagents, as necessary, if blanks are unsatisfactory.

7.5.2 *Reagents plus filters.* In parallel with the preparation of calibration curves and test samples, prepare areal test portions from unexposed filter media as described in 6.2. Measure vanadium and express blanks in micrograms of vanadium per millilitre.

8. Expression of results

8.1 *Blanks*

The glass filter blank value for any element may vary considerably with the batch. This has been very noticeable with the manganese and beryllium content of such filters. For this reason, filter blanks should be determined regularly. It should also be noted that part of the filter blank value is due to matrix interferences from elements present in large amounts in the filter such as Na, Ba, Si, Ca, Zn, K and Al.

8.2 *Instrumental precision*

This is defined as the standard deviation of a number of replicate determinations and is expressed in micrograms per millilitre. Typical precisions for ten replicate determinations on standard samples are: $100.0 \pm 0.5 \,\mu g/ml$ for the flame mode, $0.500 \pm 0.012 \,\mu g/ml$ for the flameless mode, on a 20 µl sample.

8.3 *Minimum measurable*

8.3.1 *Concentration in test sample.* This is taken as twice the blank deviation, or instrument precision, whichever is larger. This is 0.1 µg per ml in the case of vanadium, in the flame mode, and 0.0014 µg per ml in the flameless mode.

8.3.2 *Concentration in air.* This is based on a sample volume of 2000 cubic metres and two aliquot discs 36 mm in diameter. This minimum measurable concentration is 0.0250 micrograms of vanadium per cubic metre for flame mode, regardless of whether glass or cellulose filters are used. The increased sensitivity of the graphite furnace reduces the minimum concentration measurable to 0.0004 micrograms vanadium per cubic metre.

8.4 *Calculations*

The vanadium content of the test portion is expressed in micrograms per millilitre, X_1. The blank, X_2, in the same units, is subtracted from X_1 to get the corrected concentration of vanadium in the test sample. Multiplication by the dilution factor, usually 25, gives the total quantity of vanadium in the test sample, in micrograms.

For high volume filters of nominal size 203 by 254 mm:

Total exposed filter surface	$= 4.159 \times 10^4 \, mm^2$
Areal test portion, 2×36 mm discs	$= 2036 \, mm^2$
Surface multiplication factor	$= 20.43$

Dilution factor $= 25$
Volume of air sampled, cubic metres $= V$
Response, unknown test portion $= X_1$
Response, total blank $= X_2$
Vanadium concentration, in $\mu g/m^3$ $= T$
$$T = (X_1 - X_2) \times 20.43 \times 25/V$$

For the flame mode, where standards are made up in a filter blank, $X_2 = 0$. It has been found experimentally that $X_2 = 0$ for the flameless mode.

9. Notes on procedure

9.1 *Collection efficiencies*

Little is known about actual collection efficiencies and in methods for the analysis of particulate metals, these efficiencies are usually ignored. The particle size of particulate vanadium is almost all between 1 and 3 micrometres, according to Lee (11.2).

9.2

The effect of temperature and pressure during the sampling period has been largely disregarded in the past. Since these factors must have some effect on the measured air volume, it is recommended that these corrections be introduced routinely. There is increasing agreement, that if standard conditions of temperature and pressure are to be used to correct the final volume, these conditions should be $25\,^\circ\text{C}$ and $760\,\text{mmHg}$.

9.3

Although the method described is nominally based upon high volume samples taken for a 24-hour sampling period, there is no valid reason why samples may not be taken for shorter time periods, at slower flowrates or both. If high volume samples are taken on cellulose, it is particularly appropriate to take air sample volumes of 1000 cubic metres or less. The lower particulate loading, so obtained, minimizes particulate fall-off.

9.4

It is customary to assume that the decrease in air flowrate during sampling is linear and for usual purposes of calculation, the mean value of initial and final flowrates is taken. This is not correct, although the error introduced by this oversimplification is not ordinarily serious.

9.5

For the preparation of areal test portions, the use of a sharp circular metal die is to be preferred over the use of scissors or rectilinear templates of large perimeter. Areal test portions prepared by these latter are less likely to be identical in size. A circular die, of limited diameter, machined from solid metal, is very rigid and areal aliquots can be very easily reproduced with accuracy. In the method

described, a punch of stainless steel is used. No vanadium contamination has been found to result from its use.

9.6

In the use of the repetitive and consecutive areal test portions cut from an exposed high volume filter, the assumption is implicit that the element of interest is uniformly distributed across the exposed surface of the filter. This assumption is established as fact, at least in the cases of lead and cadmium measured on high volume filters (11.3, 11.4, 11.5). This uniform distribution cannot be assumed in certain 'membrane' type filters due to inherently high pressure drop and faulty geometry of commercially available filter holders. In the case of such filters, areal aliquotting cannot be used (11.6).

9.7

It is helpful, when it is possible, to have several calibration curves, relating to different sensitivities. This minimizes the possibility that the concentration of the metal in the unknown test sample will not match one or another of the curves. See method for lead where two calibration curves are given for the flame (11.4). It may be asked why any details of the flame mode should be provided when the furnace gives so much higher sensitivity, without matrix effect. One reason might be that the flame mode instruments are very generally available, while the furnace is not. Also, if the quantities of vanadium involved should be high, the flame can be used.

9.8   *Operating conditions, flame*

The optimum operating conditions are as given:

Wavelength	= 318.4 nm
Spectral band width	= 0.7 nm
Source	= hollow cathode
Source current	= as recommended
Oxidant	= nitrous oxide
Fuel	= acetylene
Flame	= reducing, red
Sensitivity	= 2.2 µg/ml for 1 % absorption

Change acetylene container before cylinder pressure drops below 50 p.s.i.g.

9.9   *Graphite furnace*

A representative curve for vanadium measured by the graphite furnace, is given in *Figure 2*, which shows greatly increased sensitivity over the flame. Furnace operating conditions:

Wavelength	= 318.4 nm
Sample size	= 20 microlitres
Purging gas	= argon or nitrogen
Thermal decomposition	= drying (20 s, 100 °C)

charring (25 s, 1 100 °C)
atomizing (8 s, 2 500 °C)

The use of a deuterium lamp background compensator is recommended.

10. Schematic representation of procedure

10.1
Draw laboratory air sample.

10.2
Cut areal test portion from exposed surface.

10.3
Digest test portion.

10.4
Adjust digest to volume to give test sample.

10.5
Aspirate test portion into flame.

10.6
Alternatively, add test portion to furnace, as measured by micro-litre pipette.

11. References

11.1 Quickert, N., Zdrojewski, A. and Dubois, L. 'The accurate measurement of vanadium in airborne particulates'. *Internat. J. Envir. Anal. Chem.* **3**, 229 (1974).

11.2 Lee, R. E., Patterson, R. K. and Wagman, J. *Envir. Sci. and Tech.* **2**, 288 (1968).

11.3 Dubois, L., Teichman, T., Airth, J. M. and Monkman, J. L. 'The metal content of urban air', *J. Air Pollut. Control Ass.* **16**, 2, 77 (1966).

11.4 Zdrojewski, A., Quickert, N., Dubois, L. and Monkman, J. L. 'The accurate measurement of lead in airborne particulates'. *Internat. J. Envir. Anal. Chem.* **2**, 63–77 (1972).

11.5 Zdrojewski, A., Quickert, N. and Dubois, L. 'The accurate measurement of cadmium on airborne particulates'. In press, *Internat. J. Envir. Anal. Chem.* **2**, 331 (1973).

11.6 Pierce, J. O. and Meyer, J. H. 'Sampling and analysis considerations in evaluating levels of atmospheric lead'. *Atmos. Environment*, **5**, 811 (1971).

ANALYTICAL METHODS FOR USE IN OCCUPATIONAL HYGIENE

PERFORMANCE STANDARDS FOR DETECTOR TUBES
(Adopted 1973)

These Standards represent the minimal requirements for detector tubes to be used in occupational hygiene air analysis. The Standards are intended to provide guidance to manufacturers of detector tubes, in the quality control of their products.

It is essential that detector tubes should be designed to have an adequate accuracy at the permissible concentration in air, known in various countries as a TLV, MAC, MAK, etc. Such a concentration will be referred to as the 'design concentration'. Recommendations are made for two types of detector tubes; those which measure the concentration by the length of stain developed when a measured volume of air is drawn through the tube, and those where the air sample produces an overall change in the colour of the contents of the tube.

The performance of a tube should be assessed by sampling test atmospheres of known concentration; it is very desirable that the accuracy of these test atmospheres should be confirmed by an independent reliable analytical method.

The aspirating pump

The aspirating pump recommended for use with the detector tubes should have the same flow characteristics as those of the pump used by the manufacturer in calibrating the tube; these should be clearly stated. The recommended pump must have an accuracy within $\pm 10\%$ of the prescribed volume throughout its normal working life.

Interferences

The manufacturer should state clearly the general reactions involved in the system, and indicate possible interferences from other substances present in the atmosphere, particularly where these would result in a low reading.

Sensitivity

Stain length tubes. At the design concentration, the length of stain produced should be not less than 15 mm. The spread of the stain at the interface should be not greater than 20% of the stain length. If such a spread occurs, the manufacturer should indicate how the position of the stain front should be determined.

Colour change tubes. At least five pump strokes should be required to produce the colour change indicating the design concentration. There should be distinct colour differences at one stroke less and one stroke more than the number indicating the design concentration.

Accuracy

At the design concentration the error should not be in excess of $+30$ to -20%. At one-half and twice the design concentration the error should not be in excess of $+50$ to -20%.

To determine the accuracy, sufficient tubes should be tested to obtain 95% confidence limits.

Temperature range

The sensitivity and accuracy should be obtainable over a temperature range between 10 and 30 °C.

Humidity

The effect of humidity should be specified.

Storage

The conditions under which the detector tubes should be stored should be stated, and when stored under these conditions, the tubes should comply with these Standards for a period of at least one year. The expiry date for the effective life of the tubes should be stated.

ANALYTICAL METHODS FOR USE IN OCCUPATIONAL HYGIENE

PARTICULATE LEAD IN AIR
(Adopted 1973)

1. Field of application

The method, as described, is capable of measuring concentrations of airborne particulate lead in the range of 0.1 to 1.0 milligram per cubic metre of air.

2. Principle

The particulate lead is collected by drawing a sample of air through filter paper. After acid digestion of the filter paper, the lead is determined by a mixed colour dithizone procedure (9.1).

3. Reagents

3.1 *Dithizone solution*
Dissolve 12.5 milligrams dithizone in 100 ml chloroform and store the solution in the dark, preferably in a refrigerator. For use, dilute this stock solution, when required, 1 to 9 with chloroform. See note 8.2.

3.2 *Ammoniacal cyanide solution*
Dissolve 10 grams potassium cyanide in 15 ml water and shake the solution repeatedly with portions of the dithizone solution until the organic layer remains green. Wash the aqueous layer with chloroform until no more colour is extracted. Transfer the aqueous layer to a 250 ml volumetric flask with a little water, add 120 ml concentrated ammonia. and dilute to 250 ml with water. See notes 8.3 and 8.4.

3.3 *Hydroxylamine hydrochloride solution 20%*
Twenty grams of hydroxylamine hydrochloride are dissolved in water to a final volume of 100 ml.

3.4 *Standard lead solutions*
3.4.1 *Stock solution.* Dissolve 0.1600 gram of lead nitrate in 0.1 M nitric acid and dilute to 500 ml. See note 8.5.
3.4.2 *Working standard solution.* Dilute the stock solution, 1 volume to 100 using 0.1 M nitric acid. 1 ml of this solution contains 2 micrograms of lead, Pb.

3.5 *Dithizone*
Reagent quality as commercially available.

3.6 *Concentrated ammonia*
Reagent quality, SG 0.880, as commercially available.

3.7 *Concentrated nitric acid*
Reagent grade SG 1.41, 'lead free'.

3.8 *Concentrated sulphuric acid*
Reagent quality, SG 1.82, 'lead free'.

3.9 *Filter paper*
Analytical grade cellulose filters, suitable for air sampling, 'lead free'.

4. Apparatus

4.1 *Filter holder*
A filter paper holder, made of plastic or stainless steel. The exposed area may be a circle of diameters 25, 37 or 47 mm.

4.2 *Sampling pump*
A sampling pump, or other apparatus, which can draw air through the filter at a constant measured rate of 2 litres per minute.

5. Sampling procedure

5.1 *Air sampling*
Place a suitable filter paper in the holder. Draw a 50 litre sample of air through the filter at the rate of 2 litres per minute.

5.2 *Sample preparation*
Carefully remove the filter from its holder and introduce it into a 50 ml glass beaker. Add 2 ml nitric acid and 0.5 ml sulphuric acid. Heat gently to boiling and continue heating until white sulphuric acid fumes appear. If the solution darkens during this process, add a few drops of nitric acid to decolourize and continue heating. Allow the residue to cool and transfer it quantitatively to a 100 ml separatory funnel in a total of 25 ml of liquid. See note 8.6.

6. Colour

6.1 *Colour development*
Add to the separatory funnel containing this solution, 5 ml hydroxylamine hydrochloride solution and 5 ml ammoniacal cyanide solution, mixing after each addition. Add 15 ml dithizone solution, shake vigorously for one minute and allow the layers to separate. Plug the stem of the funnel with cotton wool and run off and discard about 2 ml of this chloroform layer. Retain sufficient of this layer for colour measurement.

6.2 *Colour measurement*
Prepare a set of colour standards by measuring 5, 10, 20 and 25 ml of standard lead solution into a series of separatory funnels,

adjusting the volume in each to 25 ml with 0.1 M nitric acid. Add the reagents and complete the procedure as described in 6.1. Compare visually the colour of the test solution with that of the colour standards, using tubes similar in size and colour. Select the colour standard which provides the best match for the test solution and note its lead content.

Alternatively, a more accurate result may be obtained using an instrumental method of colour measurement. Measure the absorbance of the colour standards, prepared as described above, in a 10 mm cell at 510 nm. using as the reference solution a reagent blank prepared in a similar manner but without the addition of lead. Construct a standard curve, relating the absorbance to the lead content of the solutions. Measure the absorbance of the test solution, as described and calculate the lead content from the standard curve. See notes 8.1 and 8.7.

7. Expression of results

If X is the lead content of the test solution in μg and V is the volume of the air sample in litres, the lead concentration in the atmosphere is X/V mg/m^3.

8. Notes on procedure

8.1

Great care should be taken to ensure that all reagents, including the distilled water, should be as free as possible from traces of lead. All glassware should be reserved solely for this analysis and washed with dilute nitric acid before use. The absorbance of the reagent flask, when measured against distilled water, should not be equivalent to more than 2 μg of lead.

8.2

The quality of the chloroform may be checked by adding a few drops of the concentrated dithizone solution to a 25 ml sample. The green tint should be maintained for several hours, if the test specimen is not in direct sunlight.

8.3

Cyanide solution is extremely poisonous and great care should be exercised when it is being prepared and used.

8.4

If an ammonia solution of another strength is used, the amount to be added should be such that the final ammonia concentration will be about 10 M.

8.5

The strength of the acid is not critical; it may be prepared by diluting nitric acid, SG 1.4, 1 to 100 with water.

8.6
A method of removing the lead from the filter by cold extraction using a mixture of dilute nitric acid and hydrogen peroxide has been described (Ref. 9.2). This can readily be used with the above procedure.

8.7
The sensitivity of the method may be increased by using a cell with a longer optical path.

9. References

9.1   *Recommended method.* 'Determination of lead in air and biological materials'. American Conference of Governmental Industrial Hygienists. Cincinnati 2, Ohio (March 1963).

9.2   Dixon, B. E. and Metson, P. *Analyst*, **85**, 122 (1960).

ANALYTICAL METHODS FOR USE IN OCCUPATIONAL HYGIENE

HYDROGEN CHLORIDE VAPOUR IN AIR
(Adopted 1973)

1. Field of application

The method, as described, is capable of measuring hydrogen chloride concentrations in air in the range of 2.5 to 15 p.p.m.

2. Principle

The hydrogen chloride vapour is absorbed in water. See note 8.1. The chloride ion is measured by the addition of mercuric thiocyanate, the thiocyanate ion, liberated by the chloride, being determined colorimetrically after the addition of a ferric salt.

3. Reagents

3.1 *Mercuric thiocyanate solution*
Prepare a solution of mercuric thiocyanate 0.3 % w/v in ethanol.

3.2 *Ferric iron solution*
Dissolve 12 g ferric ammonium sulphate $Fe(NH_4)(SO_4)_2$ in about 100 ml water, add 75 ml nitric acid, SG 1.42, and dilute to 200 ml with water.

3.3 *Standard chloride solution*
Dissolve 31.5 mg sodium chloride in 1 litre of water. One millilitre of this solution is equivalent to 20 µg hydrogen chloride.

4. Apparatus

4.1 *Absorber*
A bubbler type absorber, suitable for an air sampling rate of 1 to 2 litres per minute, is required.

4.2 *Sampling pump*
The recommended nominal flowrate may be obtained by means of an aspirator or by means of a suitable pump provided with a means of flow control and flow measurement.

5. Sampling procedure

Measure 10 ml of water into the absorber. Draw a 10 litre sample of the air to be analysed through the absorber at a rate not exceeding two litres per minute.

6. Procedure
7.1 *Colour development*

Remove the air entry tube from the absorber after allowing it to drain. Add 1 ml of mercuric thiocyanate reagent. Then add 2 ml ferric iron solution, mixing after each addition.

7.2 *Colour measurement*

Prepare a set of standard colour solutions by diluting 1, 2, 4, 8 and 10 ml standard chloride solution to 10 ml with water. Develop the colour as described above. Compare the colour of these standards with that of the test solution using tubes similar in size and colour. Select the standard which provides the closest match for the test solution. Note the amount of hydrogen chloride equivalent to this colour standard. For this visual comparison, the colour should be developed simultaneously in the test and standard solutions. Colour comparison of the tubes should be made at least ten minutes after colour development.

Alternatively, greater precision can be obtained by an instrumental colour measurement. Measure the absorbance of the standard colour solutions, using a cell with an optical path of 10 mm and a wavelength in the region 460 nm. A reagent blank, prepared by subjecting 10 ml of water to the same colour development procedure, should be used as the reference solution for these measurements which should be made ten minutes after colour development. See note 8.2. Construct a standard curve relating the absorbance to the hydrogen chloride equivalent of the standard solutions, expressed in micrograms.

Measure the absorbance of the test solution under the same conditions and derive its hydrogen chloride content by reference to the standard curve.

7. Expression of results

If the hydrogen chloride content of the test solution is X μg and the volume of the air sample is V litres, then the hydrogen chloride concentration in air is X/V mg/m^3. The corresponding concentration in parts per million is 0.66 X/V.

8. Notes on procedure
8.1

The sampling method described may not be suitable for fine aerosols.

8.2

Great care should be taken that all reagents and the water used should be free from chloride. The reagent blank should have very little colour, with an absorbance not exceeding 0.05. If the absorbance of the blank is higher than this, the water should be further purified by deionization or distillation and the reagents should be changed or recrystallized.