

ENVIRONMENTAL
POLLUTANTS-
SELECTED
ANALYTICAL
METHODS

SCOPE 6

BUTTERWORTHS

ENVIRONMENTAL POLLUTANTS—
SELECTED ANALYTICAL
METHODS

INTERNATIONAL COUNCIL OF SCIENTIFIC UNIONS

Scientific Committee on Problems of the Environment (SCOPE)
Working Group on Methodology of Determination
of Toxic Substances in the Environment

ENVIRONMENTAL POLLUTANTS— SELECTED ANALYTICAL METHODS (SCOPE 6)

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INTRODUCTION

This compilation of analytical methods was prepared by the Working Group set up by SCOPE on "The Methodology of Determination of Toxic Substances in the Environment".

SCOPE was formed as a committee of ICSU, following a recommendation of an ad hoc committee set up by the latter. In its report, the ad hoc committee listed substances of importance in environmental problems. Another listing was given by the SCOPE Commission on Monitoring in their report entitled "Global Environmental Monitoring". In selecting which pollutants to consider, the Working Group has given special consideration to these listings, and during its discussions decided on the addition of other substances. It is recognized by the Working Group that the list of substances to be considered is by no means complete, but it was felt advisable to publish these at this juncture; and to follow these with supplements as necessary.

The range of substances covered by the methods chosen should not itself be taken as indicative of a need for a monitoring program, nor should it be assumed that a substance for which a method has been included is necessarily a pollutant. The sensitivity or limit of detection of the analytical methods described are not necessarily indicative of the toxicity of the substance being measured.

It is well known that some elements play a beneficial role in living organisms, and this in some instances is a matter of essentiality. At higher levels, the same elements may exert toxic effects, and there is need in all cases to establish precise dose-effect relationships to evaluate these regions. In addition, the ratio of concentration of one element to another may be of importance. The work of the Ecotoxicology Commission of SCOPE will have a direct bearing on these matters.

It is apparent that many methods have been published and used in the past for these substances. The Group was aware of other compilations of methods which are of interest in the same field and of the work, in some cases still in progress, of other national and international bodies in this connection. A considerable amount of information is available on experience of the extent of validity and shortcomings of the various methods. There is in fact a growing need for a wider discussion of these activities on a common basis, especially against a background of an increasing understanding of the extent of occurrence of the various compounds in the environment and of their significance with respect to environmental quality. This is of particular importance in view of the increased sensitivity and specificity of analytical methods now available and of the prospect that even greater sensitivities may yet be achieved. The number of individual organic substances which theoretically could be present, for example, increases enormously as these aspects of analysis are improved.

The Working Group has devoted a great deal of consideration to the mass of information available. The choices of the methods presented in this compilation, based on the considered opinion of the Working Group, have necessarily been somewhat arbitrary. Unless designated as reference methods, the procedures described should be regarded as offering guidance in the choice of methods rather than as mandatory procedures. Other methods, or variations of the same method, may be available. Although specific advice relating to the choice has in some cases been given indicating why certain methods should not be used, this should not be regarded as excluding all other variations where they can be shown to give equivalent results or better results in individual circumstances. For example where a good neutron activation facility is available, this may be suitable for the estimation of trace metals.

The methods described assume the availability of laboratory facilities and qualified analytical chemists. Where possible, attempts have been made to avoid the use of very expensive equipment normally found only in the largest laboratories. Wherever feasible, general purpose (utility) methods have been described as alternatives. These methods have good reliability and precision, but accuracy and degree of sensitivity may be somewhat less than with a reference method. Where feasible, methods have been described for some substances in different substrates. When using the methods indicated, it is assumed that the analyst will establish the normal criteria of satisfaction with respect to control and recovery experiments.

Sampling is a most important consideration and this is thoroughly recognized by all analysts. The details and the precautionary measures to be taken have been widely discussed and described elsewhere. For air analysis, the methods may be based on high or low volume sampling techniques or on high or low flow rates, according to program requirements. This is discussed in more detail in the methods concerned. The methods based on the ring oven technique are relatively new in practice but have proved themselves over years of research. The technique has the advantage of being simple, cheap and rapid. It is well suited for field studies and for use in laboratories where sophisticated equipment and highly specialized personnel are unavailable. It appears likely that this technique will be adapted to a wider range of application in the future, including the analysis of various substances in water. The methods described for traces of lead and cadmium in water can also be simply adapted for use in the estimation of traces of other elements such as zinc, copper, nickel, manganese, cobalt and beryllium.

The format recommended by the International Organization for Standardization has been used for the presentation of methods.

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FOREWORD

The Scientific Committee on Problems of the Environment (SCOPE) was established by ICSU in 1969 to (a) advance knowledge of the influence of man and his activities upon his environment, as well as the effects of these alterations upon man, his health and his welfare with particular attention to those influences and effects which are either global or shared in common by several nations; and (b) serve as a non-governmental, interdisciplinary and international council of scientists and as a non-governmental source of advice for the benefit of governments and intergovernmental agencies with respect to environmental problems.

Much of the work of SCOPE is concerned with the effects of small or trace quantities of a variety of chemical elements and compounds in various segments of the environment, in air, water, soil and biota. The determination of trace amounts of certain substances entail difficulties. It is obviously of paramount importance that results obtained in various parts of the world be strictly comparable, and the present volume presents a number of carefully chosen analytical methods for use by those seeking advice on the choice of method.

SCOPE expressed its gratitude to the Chairman and members of the working group on methods of analysis for selected pollutants for the extensive work which they have carried out. It is hoped that this task will be further extended in a succeeding volume dealing with other chemical substances including the revision of methods as required.

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President, SCOPE

SCOPE - 1974

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Determination of Airborne Particulate Lead by Atomic Absorption Spectrophotometry

1. INTRODUCTION

Lead in air and biological materials may be measured by dithizone methods. These methods suffer from pH dependency and instability of developed colours. Polarography may be used, but unless the test sample is very carefully prepared to eliminate all traces of organic materials, the lead wave may be masked and lead thought to be absent. Methods using anodic stripping voltammetry show promise but more practical experience must be obtained. The sensitivity of methods using emission or X-ray spectrography is low and the accuracy is affected by matrix error. A limit of identification of $0.1\mu\text{g}$ of lead is reached by using the Weisz ring oven (12.1).

In the method to be described, airborne particulates are collected by drawing the air through a filter. The filter, or an areal aliquot, with collected particulates, is digested to prepare a test sample. Preparation of this sample is simple and rapid. The aqueous acidic sample is scrutinized by an atomic absorption spectrophotometer at a suitable wavelength and the lead is calculated by referring the absorbance found to the appropriate calibration curve. By the use of a graphite furnace, additional sensitivity may be achieved beyond that of the usual flame mode. The lead levels found are expressed in micrograms per cubic metre of air sampled. Some practical details of accuracy and precision obtainable will be found under the section "Expression of Results" (9).

2. 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 vapor form, such as tetraethyl or tetramethyl lead. The method 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 2,000 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.

3. 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.

4. 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.

5. REAGENTS

5.1 *Air, compressed*

In pressure cylinders or online.

5.2 *Acetylene, compressed*

In pressure cylinders.

5.3 *Glass filters*

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

5.4 *Cellulose filters*

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

5.5 *Water*

Distilled at least twice from glass or quartz.

5.6 *Hydrofluoric acid*

49%. Reagent grade, in polyethylene containers.

5.7 *Nitric acid*

71%. Reagent grade.

5.8 *Standard solution of lead*

Dissolve 1.598g of lead nitrate and make up to 1 litre with 1% nitric acid. 1ml of this stock solution contains 1,000 μ g of lead, Pb.

6. APPARATUS

6.1 *Spectrophotometer, atomic absorption*

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

6.2 *Pipettes, glass*

Millilitre capacities, "to deliver".

6.3 *Volumetric flasks*

Borosilicate with ground glass stopper, 25ml capacity.

6.4 *Bottles, polyethylene*

Screw cap, for storage of test samples, 30ml capacity.

6.5 *Beakers, teflon*

Griffin form, 100ml capacity.

6.6 *Beakers, borosilicate*

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

6.7 *Hot plate*

Electric, with temperature control, thermostat and ceramic heating surface.

6.8 *Büchner funnel*

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

6.9 *Graphite furnace*

One suitable instrument is available commercially to the Massmann design.

6.10 *Strip chart recorder*

To display and record the response from the furnace.

6.11 *Pipettes, automatic*

Eppendorf design, with capacities 10 to 100 microlitres.

7. SAMPLE AND SAMPLES

7.1 *Air Sampling*

7.2 *Preparation of the laboratory sample*

Cellulose filters (5.4) may be used without further treatment. Glass fibre filters (5.3) 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 flow rate 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 flow rate and time.

7.3 *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 1ml of hydrofluoric acid (5.6). Gently warm the contents of the beaker, at low heat, until the hydrofluoric acid is almost completely evaporated. At this point, add 1 to 2ml of nitric acid (5.7) and continue to heat gently until a few drops of nitric acid are left. Add about 10ml of water, bring nearly to the boil and filter through a Whatman 41 filter into a glass beaker (6.6). Transfer to a 25ml volumetric flask (6.3). Rinse down the teflon beaker with another 10ml quantity of water, warm and filter into the same beaker. Transfer to the 25ml 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 (6.4). 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.

8. PROCEDURE

8.1 *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 GAS IS REPLACED.

8.2 *Test Portions*

8.2.1 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.

8.2.2 Test portions, furnace

Measure and insert in the furnace, test portions of 10 to 100 microlitres of the test sample using an automatic pipette (6.11).

8.3 *Calibration Curves*

8.3.1 Calibration curves, flame

Using "to deliver" pipettes, prepare known concentrations of lead by dilution of standard solution 5.8 to cover the range of 1.0 to 40.0 micrograms of lead per ml. Install in the monochromator and align, if necessary, the hollow cathode source for lead. Set the wavelength of the monochromator at 283.3nm. Using an air-acetylene flame, aspirate an unmeasured portion of each dilute standard lead solution (8.2.1). At the same time, 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 ml. 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 monochromator set at 217.0nm. Representative curves, covering wavelengths 217.0 and 283.3nm, are given in Figure 2 (Page 11).

8.3.2 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 nano-

grams lead in steps of 1 nanogram (0.1 to 0.5 micrograms per ml for a 10 microlitre volume). Prepare a calibration curve of response, in arbitrary units, against concentration of lead in micrograms per ml. Such a representative curve is given in Figure 3 (Page 12).

8.4 *Determination*

8.4.1 *Determination, flame*

Set the wavelength of the monochromator at 283.3nm. Observing conditions of 8.2.1 and 8.3.1, 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 calibration curve for 283.3nm. If greater sensitivity is required, this may be obtained by measuring at 217.0nm, 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 217.0nm curve it will then be necessary to dilute the test sample.

8.4.2 *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 (Page 12).

8.5 *Blank Tests*

8.5.1 *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.

8.5.2 *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 7.3. Measure lead and express blanks in micrograms of lead per ml.

9. EXPRESSION OF RESULTS

9.1 *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. 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.

9.2 *Instrumental precision*

This is defined as the standard deviation of a number of replicate determinations and is expressed in micrograms per ml. Typical precisions for ten repeat determinations on standard samples are: $15.00 \pm 0.04 \mu\text{g/ml}$ for the flame mode; $0.40 \pm 0.0093 \mu\text{g/ml}$ for the flameless mode, on a $10 \mu\text{l}$ sample.

9.3 *Minimum measurable*

9.3.1 Concentration in test sample

This is taken as twice the blank deviation, or instrument precision, whichever is larger. This is 0.04 micrograms per ml in the case of lead, in the flame mode.

9.3.2 Concentration in air

This is based on a sample volume of 2,000 cubic metres, two aliquot discs 36mm 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.

9.4 *Calculations*

The lead content of the test portion is expressed in micrograms per ml, 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 254mm:

Total exposed filter surface	=	$4.159 \times 10^4 \text{ mm}^2$
Areal test portion, 2 x 36mm discs	=	$2,036 \text{ mm}^2$
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/m ³	=	T

$$T = \frac{(X_1 - X_2) \times 20.43 \times 25}{V}$$

10. NOTES ON PROCEDURE

10.1 *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 (12.2).

10.2 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 760mm Hg.

10.3 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 flow rates, 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.

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

10.5 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.

10.6 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 and cadmium measured on high volume filters (12.3, 12.4, 12.5). 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 (12.6).

10.7 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. Thus, a certain sensitivity is available at 283.3nm, a higher sensitivity can be had at 217.0nm, and a still higher sensitivity by using the furnace. See Figures 1, 2 and 3 (Pages 11,12).

10.8 *Operating conditions, flame*

Wavelength	=	282.3nm
Spectral band width	=	0.7nm
Source	=	Hollow cathode
Source current	=	As recommended
Oxidant	=	Air
Fuel	=	Acetylene
Flame	=	Oxidizing, lean, blue
Sensitivity	=	0.54 μ g/ml for 1% absorption

Change acetylene container before cylinder pressure drops below 50psig.

10.9 *Graphite furnace*

The calibration curve for the flame mode obeys Beer's Law up to and beyond 40 micrograms per ml for wavelength 283.3nm and up to 10 micrograms per ml for wavelength 217.0nm 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	=	283.3nm
Sample size	=	10 microlitres
Purging gas	=	Argon or nitrogen
Thermal decomposition	=	drying (15sec, 100°C) charring (15sec, 490°C) atomizing (10sec, 2,400°C)

The use of a deuterium lamp background compensator is recommended.

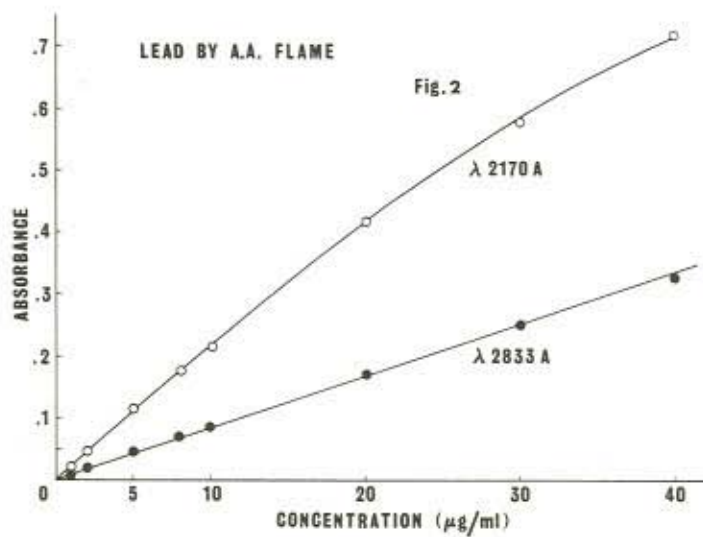
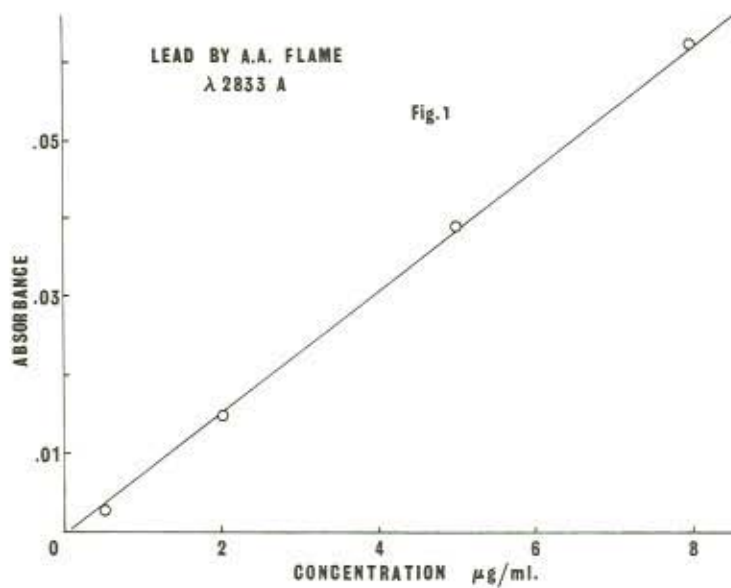
11. SCHEMATIC REPRESENTATION OF PROCEDURE

11.1 Draw laboratory air sample.

- 11.2 Cut areal test portion from exposed filter surface.
- 11.3 Digest areal test portion.
- 11.4 Adjust digest to volume to give test sample.
- 11.5 Aspirate test portion into flame.
- 11.6 Or, add test portion to furnace.

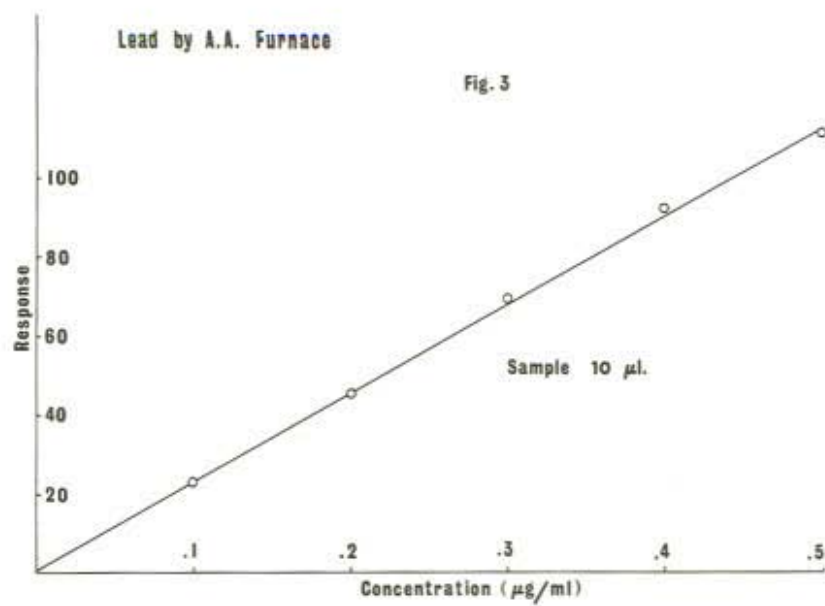
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- 12.5 Zdrojewski, A., Quickert, N. and Dubois, L. The Accurate Measurement of Cadmium in Airborne Particulates. *Int. J. Envir. Anal. Chem.*, **2**, 331, 1973.
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Lead by A.A. Furnace

Fig. 3



Determination of Airborne Particulate Cadmium by Atomic Absorption Spectrophotometry

1. INTRODUCTION

Cadmium is a relatively rare metal that occurs mainly as minerals in zinc, lead-zinc, copper-zinc and lead-copper-zinc ores. Cadmium is found in nearly all ores containing zinc and it has been suggested that there is a direct concentration relationship between these two elements. Cadmium is produced as a byproduct in the refining of other metals, particularly zinc. There are no economic cadmium ores as such. Refining processes involving zinc, copper and lead are the production sources which emit cadmium into the atmosphere.

Cadmium in air and biological materials may be measured by dithizone methods. These methods suffer from pH dependency and instability of developed colors. Polarography may be used, but unless the test sample is very carefully prepared to eliminate all traces of organic materials, the cadmium wave may be masked and cadmium thought to be absent. Methods using anodic stripping voltammetry show promise but more practical experience must be obtained. The sensitivity of methods using emission or X-ray spectrography is low and the accuracy is affected by matrix error. The measurement of cadmium by the Weisz ring oven on paper tape samples, is simple and sensitive. The limit of identification, per individual assay, is given as 0.05 micrograms of cadmium as the element (12.1).

In the method to be described, airborne particulates are collected by drawing the air through a filter. The filter, or an areal aliquot, with collected particulates, is digested to prepare a test sample. Preparation of this sample is simple and rapid. The aqueous acidic sample is scrutinized by an atomic absorption spectrophotometer at the wavelength 228.8nm and the cadmium is calculated by referring the absorbance found to the appropriate calibration curve. By the use of a graphite furnace, additional sensitivity may be achieved beyond that of the usual flame mode. The cadmium values found are expressed in micrograms per cubic metre of air sampled. Some practical details of accuracy and precision obtainable will be found under the section "Expression of Results" (9).

2. 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 2,000 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.

3. 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.

4. REACTIONS

The most important reactions relate to the complete dissolution of the particulate sample in acid 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.

5. REAGENTS

5.1 *Air, compressed*

In pressure cylinders or online.

5.2 *Acetylene, compressed*

In pressure cylinders.

5.3 *Glass filters*

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

5.4 *Cellulose filters*

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

5.5 *Water*

Distilled at least twice from glass or quartz.

5.6 *Hydrofluoric acid*

49%. Reagent grade, in polyethylene containers.

5.7 *Nitric acid*

71%. Reagent grade.

5.8 *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. 1ml of this stock solution contains 1,000 micrograms of cadmium, Cd.

6. APPARATUS

6.1 *Spectrophotometer, atomic absorption*

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

6.2 *Pipettes, glass*

Millilitre capacities, "to deliver".

6.3 *Volumetric flasks*

Borosilicate with ground glass stopper, 25ml capacity.

6.4 *Bottles, polyethylene*

Screw cap, for storage of test samples, 30ml capacity.

6.5 *Beakers, teflon*

Griffin form, 100ml capacity.

6.6 *Beakers, borosilicate*

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

6.7 *Hot plate*

Electric, with temperature control, thermostat, and ceramic heating surface.

6.8 *Büchner funnel*

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

6.9 *Graphite furnace*

One suitable instrument is available commercially to the Massmann design.

6.10 *Strip chart recorder*

To display and record the response from the furnace.

6.11 *Pipettes, automatic*

Eppendorf design, with capacities 10 to 100 microlitres.

7. SAMPLING AND SAMPLES

7.1 *Air Sampling*

7.2 *Preparation of the laboratory sample*

Cellulose filters (5.4) may be used without further treatment. Glass fibre filters (5.3) 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 flow rate 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 flow rate and time.

7.3 *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 1ml of hydrofluoric acid (5.6). Gently warm the contents of the beaker, at low

heat, until the hydrofluoric acid is almost completely evaporated. At this point, add 1 to 2ml of nitric acid (5.7) and continue to heat gently until a few drops of nitric acid are left. Add about 10ml of water, bring gently to the boil and filter through a Whatman 41 filter into a glass beaker (6.6). Transfer to a 25ml volumetric flask (6.3). Rinse down the teflon beaker with another 10ml quantity of water, warm and filter into the same beaker. Transfer to the 25ml 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 (6.4). 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.

8. PROCEDURE

8.1 *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 REPLACED.

8.2 *Test Portions*

8.2.1 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.

8.2.2 Test portions, furnace

Measure and insert in the furnace, test portions of 10 to 100 microlitres of the test sample using an automatic pipette (6.11).

8.3 *Calibration Curves*

8.3.1 Calibration curves, flame

Using "to deliver" pipettes, prepare known concentrations of cadmium by dilution of standard solution (5.8) to cover the range of 0.1 to 1.0 micrograms of cadmium per ml. Install in the spectrophotometer and align, if necessary, the hollow cathode source for cadmium. Set the wavelength of the monochromator at 228.8nm. Using an air-acetylene flame, aspirate an *unmeasured* portion of each dilute standard cadmium solution for 10

seconds (8.2.1). At the same time, 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 ml. Such a representative calibration curve is given in Figure 1 (Page 23).

8.3.2 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 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 nanograms cadmium in steps of 0.2 nanograms (0.01 to 0.05 micrograms per ml for a 20 microlitre volume). Prepare a calibration curve of response, in arbitrary units, against concentration of cadmium in micrograms per ml. Such a representative calibration curve is given in Figure 2 (Page 23).

8.4 Determination

8.4.1 Determination, flame

Set the wavelength of the monochromator at 228.8nm. Observing conditions of 8.2.1 and 8.3.1, 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 228.8nm and the corresponding calibration curve.

8.4.2 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 (Page 23).

8.5 Blank Tests

8.5.1 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.

8.5.2 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 7.3. Measure cadmium and express blanks in micrograms of cadmium per ml.

9. EXPRESSION OF RESULTS

9.1 *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.

9.2 *Instrumental precision*

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

9.3 *Minimum measurable*

9.3.1 Concentration in test sample

This is taken as twice the blank deviation, or instrument precision, whichever is larger. This is 0.01 micrograms per ml 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 ml.

9.3.2 Concentration in air

This is based upon a sample volume of 2,000 cubic metres and two aliquot discs 36mm in diameter. The minimum measurable concentration is 0.0025 micrograms per cubic metre for the flame mode and 0.00025 micrograms per cubic metre for the flameless mode. These values are the same for washed glass or cellulose filters.

9.4 *Calculations*

The cadmium content of the test solution is expressed in micrograms of cadmium per ml, 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

per 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 254mm:

Total exposed filter surface	=	$4.159 \times 10^4 \text{ mm}^2$
Areal test portion, 2 x 36mm discs	=	$2,036 \text{ mm}^2$
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
Cadmium concentration, in $\mu\text{g}/\text{m}^3$	=	T

$$T = \frac{(X_1 - X_2) \times 20.43 \times 25}{V}$$

10. NOTES ON PROCEDURE

10.1 *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 microns according to Lee (12.2).

10.2 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 760mm Hg.

10.3 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 flow rates, 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.

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

10.5 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.

10.6 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 (12.3, 12.4, 12.5) and cadmium (one exception was noted in 12.5) 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 (12.6).

10.7 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 in this series where two calibration curves are given for the flame and one for the furnace (12.7).

10.8 *Operating conditions, flame*

The optimum operating conditions are as given:

Wavelength	=	228.8nm
Spectral band width	=	0.7nm
Source	=	Hollow cathode
Source current	=	As recommended
Oxidant	=	Air
Fuel	=	Acetylene
Flame	=	Oxidizing, lean, blue
Sensitivity	=	0.026 μ g/ml for 1% absorption

Change acetylene cylinder before pressure drops to 50psig.

10.9 *Graphite furnace*

The calibration curve for the flame mode obeys Beer's Law up to 1.0 micrograms of cadmium per ml 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	=	228.8nm
Sample size	=	20 microlitres
Purging gas	=	Argon or nitrogen

Thermal decomposition = drying (15sec, 100°C)
charring (15sec, 330°C)
atomizing (10sec, 1,800°C)

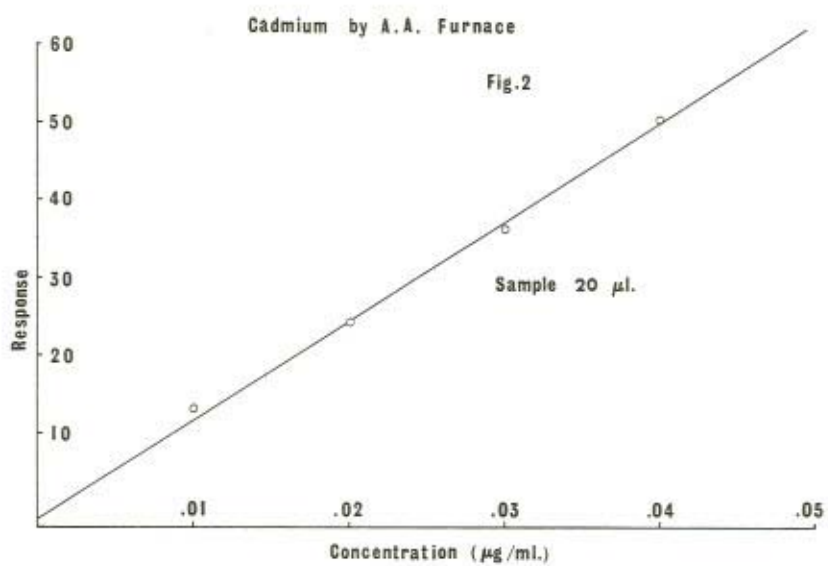
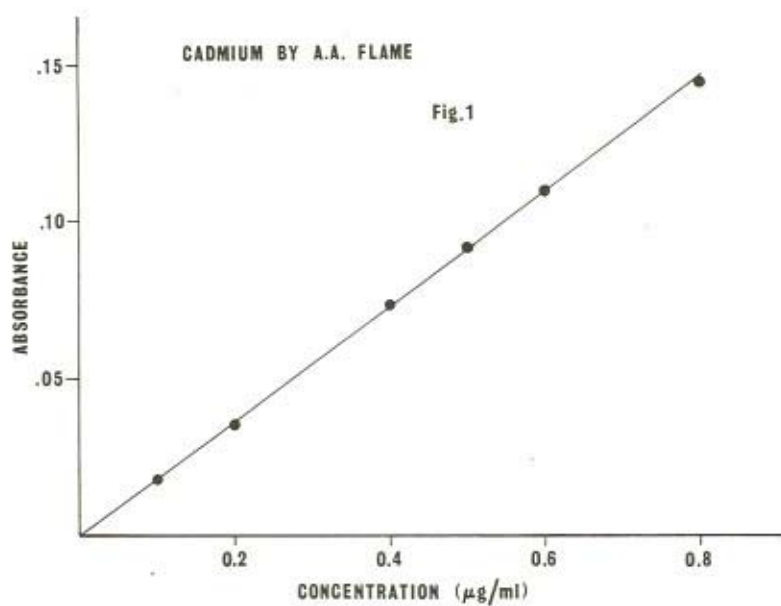
The use of a deuterium lamp background compensator is recommended.

11. SCHEMATIC REPRESENTATION OF PROCEDURE

- 11.1 Draw laboratory air sample.
- 11.2 Cut areal test portion from exposed surface.
- 11.3 Digest areal test portion.
- 11.4 Adjust digest to volume to give test sample.
- 11.5 Aspirate test portion into flame.
- 11.6 Or, add test portion to furnace, measured by microlitre pipette.

12. REFERENCES

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Determination of Airborne Particulate Zinc by Atomic Absorption Spectrophotometry

1. INTRODUCTION

Zinc is widely distributed in the earth's surface and occurs in small quantities in almost all igneous rocks. Underground mining accounts for most of the production. The reduction of zinc ores and concentrates is accomplished by electrolytic deposition of zinc from solution or by distillation in retorts. The primary sources of emissions of zinc compounds into the atmosphere are these zinc operations as well as lead and copper smelting. Zinc compounds are emitted in the production of steel. The quantities emitted are not thought to be economically recoverable, although probably significant with respect to air quality.

Zinc in air and biological materials may be measured by dithizone methods. These methods suffer from pH dependency and the calibration curve may differ from day to day. Polarography may be used, but unless the test sample is very carefully prepared to eliminate all traces of organic materials, the zinc wave may be masked and zinc thought to be absent. The sensitivity of methods using emission or X-ray spectrography is low and the accuracy is affected by matrix error. Losses of zinc may occur if sample preparation includes dry ashing at elevated temperatures. Zinc may be measured on cellulose filter samples to a limit of identification of 0.05 micrograms, using the Weisz ring oven (12.1).

In the method to be described, airborne particulates are collected by drawing the air through a filter. The filter, or an areal aliquot, with collected particulates, is digested to prepare a test sample. Preparation of this sample is simple and rapid. The aqueous acidic sample is scrutinized by an atomic absorption spectrophotometer at the wavelength of 213.8nm and the zinc is calculated by referring the absorbance found to the appropriate calibration curve. The zinc values found are expressed in micrograms per cubic metre of air sampled. Some practical details of accuracy and precision obtainable will be found under the section "Expression of Results" (9).

2. FIELD OF APPLICATION

The method is applicable to the measurement of the levels of suspended particulate zinc found in either ambient or industrial atmospheres. Based upon the flame mode, cellulose filters and a nominal air volume of 1,000 cubic metres, one may determine down to 0.0050 microgram of zinc per cubic metre of air.

3. PRINCIPLE

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

4. 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.

5. REAGENTS

5.1 *Air, compressed*

In pressure cylinders or online.

5.2 *Acetylene, compressed*

In pressure cylinders.

5.3 *Cellulose filters*

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

5.4 *Water*

Distilled at least twice from glass or quartz.

5.5 *Nitric acid*

71%. Reagent grade.

5.6 *Standard solution of zinc*

Dissolve 1 gram of metallic zinc in 5ml of nitric acid and make up to 1 litre with water. 1ml of this stock solution contains 1,000 μ g of zinc, Zn.

6. APPARATUS

6.1 *Spectrophotometer, atomic absorption*

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

6.2 *Pipettes, glass*

Millilitre capacities, "to deliver".

6.3 *Volumetric flasks*

Borosilicate with ground glass stopper, 25ml capacity.

6.4 *Bottles, polyethylene*

Screw cap, for storage of test samples, 30ml capacity.

6.5 *Beakers, borosilicate*

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

6.6 *Hot plate*

Electric, with temperature control, thermostat and ceramic heating surface.

7. SAMPLING AND SAMPLES

7.1 *Air Sampling*

7.2 *Preparation of the laboratory sample*

Cellulose filters (5.3) may be used without further treatment. Glass filters, whether washed or unwashed, have a very high zinc blank and are unsuitable for the measurement of zinc in air. Mount a cellulose, or other suitable zinc-free filter in a sampling head. Draw air through the filter at an appropriate flow rate. If a cellulose filter is used with a high volume sampler, it may be better to draw a total of only 1,000 cubic metres to minimize subsequent fall-off of particulates from the filter. Calculate and record the total volume of air sampled, in cubic metres, as the product of mean flow rate and time. The resistance to air 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.

7.3 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 beaker (6.5) and add 2ml nitric acid (5.5). Gently warm the contents of the beaker, at low heat, to initiate digestion. When the amount of liquid reaches about one-half ml, add an additional 3ml acid and continue digestion until the volume is again about one-half ml. Add about 10ml water and bring nearly to a boil. The solution will not be clear at this point due to an incomplete digestion of the cellulose with this procedure. The solution should then be filtered with suction through Whatman 41 or other suitable membrane filter. Rinse the beaker and funnel with an additional 10ml of water, transfer to the 25ml 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 (6.4). The test sample is now ready for analysis.

The above digestion procedure has been checked for complete recovery of zinc. Extraction methods may also be used but experiments must be carried out in each case to ensure that added known amounts of zinc can be completely recovered from the filter.

8. PROCEDURE

8.1 Safety precautions

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

8.2 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.

8.3 Calibration curves, flame

Using "to deliver" pipettes, prepare known concentrations of zinc by dilution of standard solution (5.7) to cover the range of 0.1 to 1.0 micrograms of zinc per ml. Install in the spectrophotometer and align, if necessary, the hollow cathode source for zinc. Set the wavelength of the monochromator at 213.8nm. Using an air-acetylene flame, aspirate an unmeasured portion of each dilute standard zinc solution for 10 seconds (8.2). At the same time, aspirate into the flame a blank of distilled water.

From the instrumental responses obtained, prepare a calibration curve of absorbance against concentration of zinc in micrograms per ml. Such a representative calibration curve is given in Figure 1 (Page 32).

8.4 *Determination, flame*

Set the wavelength of the monochromator at 213.8nm. Observing conditions of 8.2 and 8.3, 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 zinc in all the unknown test samples which can be accommodated to the wavelength of 213.8nm and the corresponding calibration curve.

8.5 *Blank tests*

8.5.1 *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.

8.5.2 *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 7.3. Measure zinc and express blanks in micrograms of zinc per ml.

9. EXPRESSION OF RESULTS

9.1 *Blanks*

Although others have used glass fibre filters to sample and measure airborne zinc, it is difficult to see how such measurements can have any validity (12.2). The zinc blank in 8 x 10 inch glass fibre filters, whether washed or unwashed, is 0.1g. Glass can not, therefore, be recommended for sampling airborne particulate zinc. Cellulose filters contain about 50 micrograms zinc by comparison.

9.2 *Instrumental precision*

This is defined as the standard deviation of replicate determinations, expressed in micrograms per ml. For ten repeat measurements on a standard sample, the precision was found to be $0.50 \pm 0.003\mu\text{g/ml}$ (flame mode).

9.3 Minimum measurable

9.3.1 Concentration in test sample

This is taken as twice the blank deviation, or instrument precision, whichever is larger. This is $0.01\mu\text{g}$ per ml in the case of zinc.

9.3.2 Concentration in air

This is based on a sample volume of 1,000 cubic metres and two aliquot discs 36mm in diameter. This minimum measurable concentration is 0.0050 micrograms of zinc per cubic metre, when cellulose filters are used.

9.4 Calculations

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

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

Total exposed filter surface	=	$4.159 \times 10^4 \text{ mm}^2$
Areal test portion, 2 x 36mm discs	=	$2,036 \text{ mm}^2$
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
Zinc concentration, in $\mu\text{g}/\text{m}^3$	=	T

$$T = \frac{(X_1 - X_2) \times 20.43 \times 25}{V}$$

10. NOTES ON PROCEDURE

10.1 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 zinc is almost all between 1 and 3 microns according to Lee (12.3).

10.2 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 760mm Hg.

10.3 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 flow rates, 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.

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

10.5 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 area aliquots can be very easily reproduced with accuracy. In the method described, a punch of stainless steel is used. No zinc contamination has been found to result from its use. As cellulose is more difficult to cut than glass fibre the die should be exceedingly sharp.

10.6 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 and cadmium measured on high volume filters (12.4, 12.5, 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 the case of such filters, areal aliquotting cannot be used (12.7).

10.7 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 in this series where two calibration curves are given for the flame and one for the furnace (12.8).

10.8 *Operating conditions, flame*

The optimum operating conditions are as given:

Wavelength	=	213.8nm
Spectral band width	=	0.7nm
Source	=	Hollow cathode
Source current	=	As recommended
Oxidant	=	Air
Fuel	=	Acetylene
Flame	=	Oxidizing, lean, blue
Sensitivity	=	0.019 μ g/ml for 1% absorption

Change acetylene container before pressure drops below 50 psig.

10.9 Graphite furnace

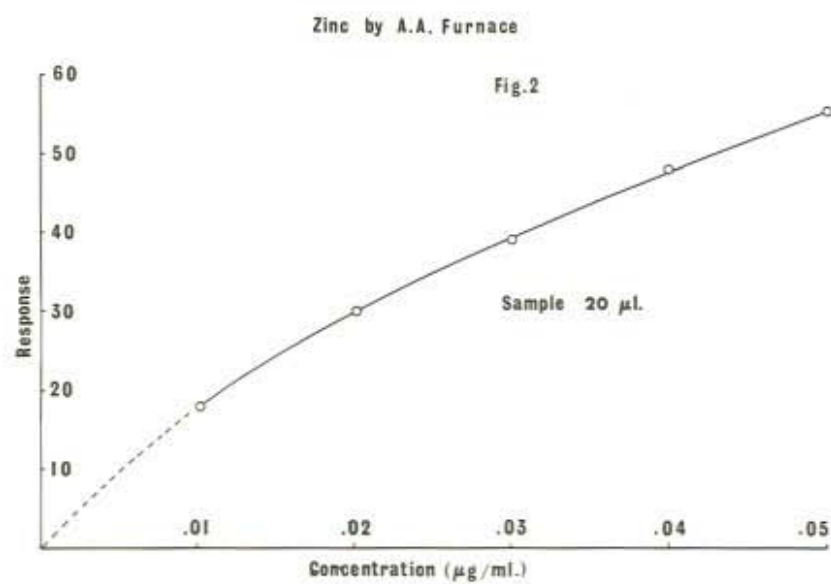
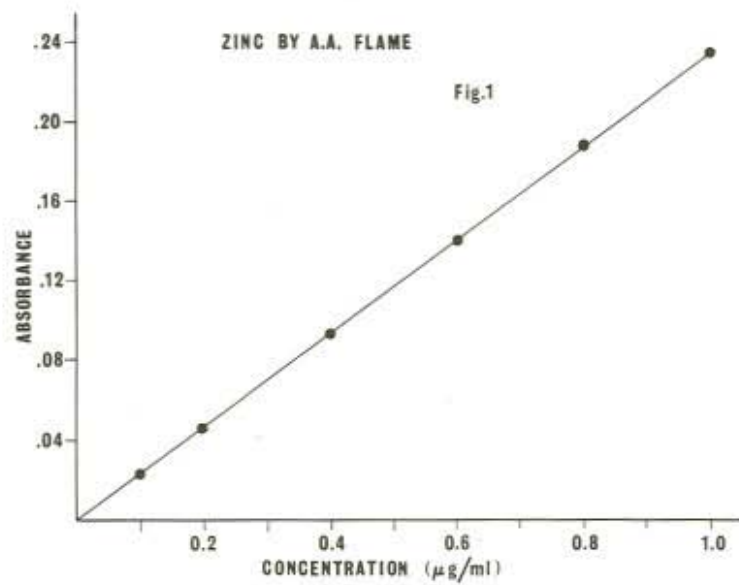
Since the analytical sensitivity of the flame mode is so high and since the analytical response of zinc in the furnace seems anomalous, there is no point in recommending the furnace mode at this time. A representative curve for the measurement of zinc in the furnace is given in Figure 2 (Page 32).

11. SCHEMATIC REPRESENTATION OF PROCEDURE

- 11.1 Draw laboratory air sample
- 11.2 Cut areal test portion from exposed surface.
- 11.3 Digest areal test portion.
- 11.4 Adjust digest to volume to give test sample.
- 11.5 Aspirate test portion into flame.

12. REFERENCES

- 12.1 West, P. W. Symposium on Air Quality, American Chemical Society, Los Angeles, April 1, 1971.
- 12.2 Air Pollution Measurements of the National Air Sampling Network, U.S. Department Health, Education and Welfare, Cincinnati, Ohio, 1953-57 et seq.
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- 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., et al. Determination of Airborne Particulate Lead by Atomic Absorption Spectroscopy, see p.1.



Determination of Airborne Particulate Copper by Atomic Absorption Spectrophotometry

1. INTRODUCTION

Copper in suspended particulates may be measured by conventional polarography, but sample preparation to remove organic residues must be meticulous. Methods using anodic stripping voltammetry show promise but more practical experience must be obtained. The measurement of copper by the Weisz ring oven on paper tape samples, is simple and sensitive. The limit of identification, per individual assay, is given as 0.08 micrograms of copper as the element (12.1).

In the method to be described, airborne particulates are collected by drawing the air through a filter. The filter, or an areal aliquot, with collected particulates, is digested to prepare a test sample. Preparation of this sample is simple and rapid. The aqueous acidic sample is scrutinized by an atomic absorption spectrophotometer at the wavelength 324.7nm and the copper is calculated by referring the absorbance found to the appropriate calibration curve. By the use of a graphite furnace, additional sensitivity may be achieved beyond that of the usual flame mode. The copper values found are expressed in micrograms per cubic metre of air sampled. Some practical details of accuracy and precision obtainable will be found under the Section "Expression of Results" (9).

2. FIELD OF APPLICATION

The method is applicable to the measurement of the levels of suspended particulate copper found in either ambient or industrial atmospheres. Based upon the flame mode, washed glass filters and a nominal air sample volume of 2,000 cubic metres, copper is measurable to 0.0050 micrograms per cubic metre. If the sample is taken on analytical grade cellulose the minimum quantity measurable is 0.0025 micrograms per cubic metre. For the same test sample, the use of the flameless mode decreases the measurable amount to 0.001 micrograms per cubic metre.

3. PRINCIPLE

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

4. REACTIONS

The most important reactions relate to the complete dissolution of the particulate sample in acid 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.

5. REAGENTS

5.1 *Air, compressed*

In pressure cylinders or online.

5.2 *Acetylene, compressed*

In pressure cylinders.

5.3 *Glass filters*

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

5.4 *Cellulose filters*

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

5.5 *Water*

Distilled at least twice from glass or quartz.

5.6 *Hydrofluoric acid*

49%. Reagent grade, in polyethylene containers.

5.7 *Nitric acid*

71%. Reagent grade.

5.8 *Standard solution of copper*

Dissolve 3.929 grams copper sulfate pentahydrate in water and make up to 1 litre. This stock solution contains 1,000 micrograms per ml of copper, Cu.

6. APPARATUS

6.1 *Spectrophotometer, atomic absorption*

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

6.2 *Pipettes, glass*

Millilitre capacities, "to deliver".

6.3 *Volumetric flasks*

Borosilicate with ground glass stopper, 25ml capacity.

6.4 *Bottles, polyethylene*

Screw cap, for storage of test samples, 30ml capacity.

6.5 *Beakers, teflon*

Griffin form, 100ml capacity.

6.6 *Beakers, borosilicate*

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

6.7 *Hot plate*

Electric, with temperature control, thermostat and ceramic heating surface.

6.8 *Büchner funnel*

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

6.9 *Graphite furnace*

One suitable instrument is available commercially to the Massmann design.

6.10 *Strip chart recorder*

To display and record the response from the furnace.

6.11 *Pipettes, automatic*

Eppendorf design, with capacities 10 to 100 microlitres.

7. SAMPLING AND SAMPLES

7.1 *Air Sampling*

7.2 *Preparation of the laboratory sample*

Cellulose filters (5.4) may be used without further treatment. Glass fibre filters (5.3) 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 flow rate 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 flow rate and time.

7.3 *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 1ml of hydrofluoric acid (5.6). Gently warm the contents of the beaker, at low heat, until the hydrofluoric acid is almost completely evaporated. At this point, add 1 to 2ml of nitric acid (5.7) and continue to heat gently until a few drops of nitric acid are left. Add about 10ml of water, bring nearly to the boil and filter through a Whatman 41 filter into a glass beaker (6.6). Transfer to a 25ml volumetric flask (6.3). Rinse down the teflon beaker with another 10ml quantity of water, warm and filter into the same beaker. Transfer to the 25ml 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 (6.4). The test sample is now ready for analysis. The above procedure is applicable to the digestion of glass fibre filters. Cellulose filters may be digested or extracted with nitric acid.

8. PROCEDURE

8.1 *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 REPLACED.

8.2 Test Portions

8.2.1 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.

8.2.2 Test portions, furnace

Measure and insert in the furnace, test portions of 10 to 100 microlitres of the test sample using an automatic pipette (6.11).

8.3 Calibration Curves

8.3.1 Calibration curves, flame

Using "to deliver" pipettes, prepare known concentrations of copper by dilution of standard solution (5.8) to cover the range of 1.0 to 5.0 micrograms of copper per ml. Install in the spectrophotometer and align, if necessary, the hollow cathode source for copper. Set the wavelength of the monochromator at 324.7nm. Using an air-acetylene flame, aspirate an unmeasured portion of each dilute standard copper solution for 10 seconds (8.2.1). At the same time, aspirate into the flame a blank of distilled water. From the instrumental responses obtained, prepare a calibration curve of absorbance against concentration of copper, in micrograms per ml. Such a representative calibration curve is given in Figure 1 (Page 42).

8.3.2 Calibration curves, furnace

By means of an automatic pipette with polyethylene tip, place identical microlitre volumes of the dilute standard copper solutions and a distilled water blank in the furnace. Measure and record the response of each test portion following predetermined measuring cycle. Cover the range of 0.2 to 1.0 nanograms of copper in steps of 0.2 nanograms (0.01 to 0.05 micrograms per ml for a 20 microlitre sample). Prepare a calibration curve of response, in arbitrary units, against concentration of copper in micrograms per ml. Such a representative calibration curve is given in Figure 2 (Page 43).

8.4 *Determination*

8.4.1 Determination, flame

Set the wavelength of the monochromator at 324.7nm. Observing conditions of 8.2.1 and 8.3.1, 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 copper in all the unknown test samples which can be accommodated to the wavelength of 324.7nm and the corresponding calibration curve.

8.4.2 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 copper, present in the test sample, by referring to the appropriate calibration curve, such as, for example, Figure 2 (Page 43).

8.5 *Blank Tests*

8.5.1 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.

8.5.2 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 7.3. Measure copper and express blanks in micrograms of copper per ml.

9. EXPRESSION OF RESULTS

9.1 *Blanks*

The glass filter blank value for any element may vary considerably with the batch. This has been very noticeable with manganese and beryllium, and to some extent copper. 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 larger amounts in the filter such as Na, Ba, Si, Ca, Zn, K and Al.

9.2 Instrumental precision

This is defined as the standard deviation of a number of replicate determinations, expressed in micrograms per ml. For ten repeat measurements on standard samples, the following was obtained: $3.00 \pm 0.01 \mu\text{g/ml}$ for the flame mode and $0.040 \pm 0.0013 \mu\text{g/ml}$ for the flameless mode.

9.3 Minimum measurable

9.3.1 Concentration in test sample

This is taken as twice the blank deviation or instrument precision, whichever is larger. Using the flame mode, this is 0.02 micrograms per ml for glass and 0.01 micrograms per ml for cellulose. The use of the flameless mode reduces the minimum measurable to 0.004 micrograms per ml for glass and cellulose.

9.3.2 Concentration in air

This is based upon a sample volume of 2,000 cubic metres and two aliquot discs 36mm in diameter. This minimum measurable concentration is 0.0050 micrograms per cubic metre for glass and 0.0025 micrograms per cubic metre for cellulose filters, for the flame mode. The increased sensitivity of the graphite furnace reduces this to 0.001 micrograms per cubic metre.

9.4 Calculations

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

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

Total exposed filter surface	=	$4.159 \times 10^4 \text{ mm}^2$
Areal test portion, 2 x 36mm discs	=	$2,036 \text{ mm}^2$
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
Copper concentration, in $\mu\text{g/m}^3$	=	T

$$T = \frac{(X_1 - X_2) \times 20.43 \times 25}{V}$$

10. NOTES ON PROCEDURE

10.1 *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 copper is almost all between 1 and 3 microns according to Lee (12.2).

10.2 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 760mm Hg.

10.3 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 flow rates, 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. The 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.

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

10.5 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 area aliquots can be very easily reproduced with accuracy. In the method described, a punch of stainless steel is used. No copper contamination has been found to result from its use.

10.6 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 and cadmium measured on high volume filters (12.3, 12.4, 12.5). 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 (12.6).

10.7 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 in this series where two calibration curves are given for the flame and one for the furnace (12.7).

10.8 *Operating conditions, flame*

The optimum operating conditions are as given:

Wavelength	=	324.7nm
Spectral band width	=	0.7nm
Source	=	Hollow cathode
Source current	=	As recommended
Oxidant	=	Air
Fuel	=	Acetylene
Flame	=	Oxidizing, lean blue
Sensitivity	=	0.078 µg/ml for 1% absorption

Change the acetylene container before the cylinder pressure drops below 50 psig.

10.9 *Graphite furnace*

The calibration curve for the flame mode obeys Beer's Law up to and beyond 5.0 micrograms of copper per ml of test sample as illustrated by Figure 1. A representative curve for copper, measured by the graphite furnace, is given in Figure 2, which shows greatly increased sensitivity over the flame. Furnace operating conditions:

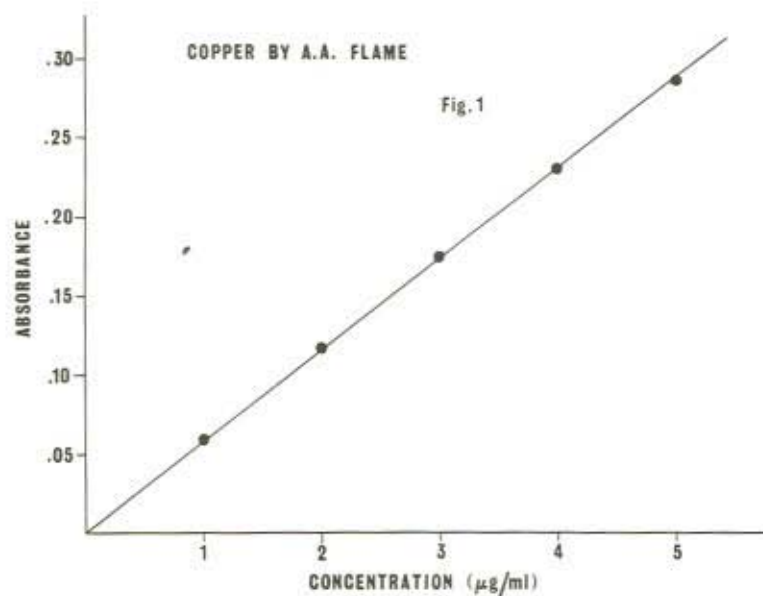
Wavelength	=	324.7nm
Sample size	=	20 microlitres
Purging gas	=	Argon or nitrogen
Thermal decomposition	=	drying (20 sec, 100°C) charring (20 sec, 1,100°C) atomizing (10 sec, 2,400°C)

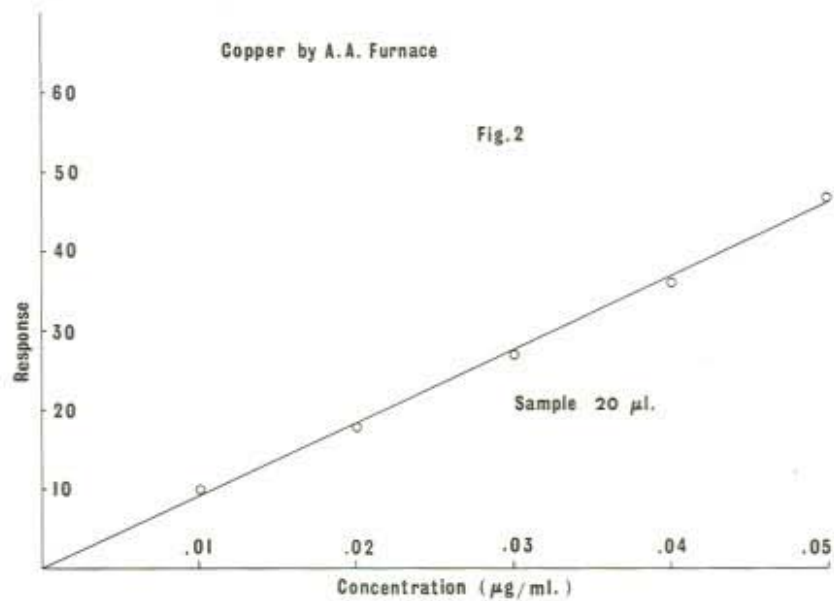
11. SCHEMATIC REPRESENTATION OF PROCEDURE

- 11.1 Draw laboratory air sample.
- 11.2 Cut areal test portion from exposed surface.
- 11.3 Digest areal test portion.
- 11.4 Adjust digest to volume to give test sample.
- 11.5 Aspirate test portion into flame.
- 11.6 Or, add test portion to furnace, measured by microlitre pipette.

12. REFERENCES

- 12.1 West, P. W. Symposium on Air Quality, American Chemical Society, Los Angeles, April 1, 1971.
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- 12.4 Zdrojewski, A., Quickert, N., Dubois, L. and Monkman, J. L. The Accurate Measurement of Lead in Airborne Particulates. *Int. J. Envir. Anal. Chem.* **2**, 63, 1972.
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- 12.7 Monkman, J. L. Determination of Airborne Particulate Lead by Atomic Absorption Spectroscopy, see p.1.





Determination of Airborne Particulate Nickel by Atomic Absorption Spectrophotometry

1. INTRODUCTION

Although nickel is widely distributed over the face of the earth, the igneous rocks, in which it occurs, are not readily susceptible to weathering. The minerals are usually sulfides, oxides and silicates. Nickel is used primarily in the metallurgical industry, particularly in ferro alloys. The amounts of nickel emitted to the air from iron and steel plants are rather low in view of the large quantities of nickel handled.

Nickel in airborne particulates may be measured by conventional polarography, but sample preparation must be meticulous, otherwise the nickel wave may be masked. Methods using anodic stripping voltammetry show promise but more practical experience must be obtained. The sensitivity of methods using emission or X-ray spectrography is low and the accuracy is affected by matrix error. Nickel may be measured on cellulose filter samples to a limit of identification of 0.08 microgram using the Weisz ring oven (12.1).

In the method to be described, airborne particulates are collected by drawing the air through a filter. The filter, or an areal aliquot, with collected particulates, is digested to prepare a test sample. Preparation of this sample is simple and rapid. The aqueous acidic sample is scrutinized by an atomic absorption spectrophotometer at the wavelength of 232.0nm and the nickel is calculated by referring the measured absorbance to the appropriate calibration curve. The nickel values found are expressed in micrograms per cubic metre of air sampled. Some practical details of accuracy and precision obtainable will be found under the section "Expression of Results" (9).

2. FIELD OF APPLICATION

The method is applicable to the measurement of the levels of suspended particulate nickel found in either ambient or industrial atmospheres. Based upon the flame mode, washed glass filters and a nominal air volume of 2,000 cubic metres, one may determine down to 0.0050 micrograms of nickel per cubic metre of air. For the same conditions, but using cellulose filters, nickel may be measured down to $0.0025\mu\text{g}/\text{m}^3$. The greater sensitivity of the flameless mode allows concentrations of $0.00025\mu\text{g}/\text{m}^3$ to be determined.

3. 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.

4. 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.

5. REAGENTS

5.1 *Air, compressed*

In pressure cylinders or online.

5.2 *Acetylene, compressed*

In pressure cylinders

5.3 *Glass filters*

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

5.4 *Cellulose filters*

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

5.5 *Water*

Distilled at least twice from glass or quartz.

5.6 *Hydrofluoric acid*

49%. Reagent grade, in polyethylene containers.

5.7 Nitric acid

71%. Reagent grade.

5.8 Standard solution of nickel

Dissolve 1g of nickel metal in about 3ml concentrated HNO_3 and make up to 1 litre. One ml of this stock solution contains 1,000 micrograms of Nickel, Ni.

6. APPARATUS

6.1 Spectrophotometer, atomic absorption

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

6.2 Pipettes, glass

Millilitre capacities, "to deliver".

6.3 Volumetric flasks

Borosilicate with ground glass stopper, 25ml capacity.

6.4 Bottles, polyethylene

Screw cap, for storage of test samples, 30ml capacity.

6.5 Beakers, teflon

Griffin form, 100ml capacity.

6.6 Beakers, borosilicate

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

6.7 Hot plate

Electric with temperature control, thermostat and ceramic heating surface.

6.8 Büchner funnel

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

6.9 *Graphite furnace*

One suitable instrument is available commercially to the Massmann design.

6.10 *Strip chart recorder*

To display and record the response from the furnace.

6.11 *Pipettes, automatic*

Eppendorf design, with capacities 10 to 100 microlitres.

7. SAMPLING AND SAMPLES

7.1 *Air Sampling*

7.2 *Preparation of the laboratory sample*

Cellulose filters (5.4) may be used without further treatment. Glass fibre filters (5.3) 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 flow rate 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 flow rate and time.

7.3 *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 1ml of hydrofluoric acid (5.6). Gently warm the contents of the beaker, at low heat, until the hydrofluoric acid is almost completely evaporated. At this point add 1 to 2ml of nitric acid (5.7) and continue to heat gently until a few drops of nitric acid are left. Add about 10ml of water, bring nearly to the boil and filter through a Whatman 41 filter into a glass beaker (6.6). Transfer to a 25ml volumetric flask (6.3). Rinse down the teflon beaker with another 10ml quantity of water, warm and filter into the same beaker. Transfer to the 25ml 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 (6.4). The test sample is now ready for analysis. The above procedure applies to the digestion of glass fibre filters. Cellulose filters can be digested or extracted using nitric acid.

8. PROCEDURE

8.1 *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 REPLACED.**

8.2 *Test Portions*

8.2.1 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 the flame, between the introduction of each test portion, to prevent cross contamination.

8.2.2 Test portions, furnace

Measure and insert into the furnace, test portions of 10 to 100 microlitres of the test sample using an automatic pipette (6.11).

8.3 *Calibration Curves*

8.3.1 Calibration curves, flame

Using "to deliver" pipettes, prepare known concentrations of nickel by dilution of standard solution (5.8) to cover the range of 1.0 to 5.0 micrograms of nickel per ml. Install in the spectrophotometer and align, if necessary, the hollow cathode source for nickel. Set the wavelength of the microchromator at 232.0nm. Using an air-acetylene flame, aspirate an unmeasured portion of each dilute standard nickel solution for 10 seconds (8.2.1). At the same time, aspirate into the flame a blank of distilled water. From the instrumental responses obtained, prepare a calibration curve of absorbance against concentration of nickel in micrograms per ml. Such a representative calibration curve is given in Figure 1 (Page 54).

8.3.2 Calibration curves, furnace

By means of an automatic pipette with polyethylene tip, place identical microlitre volumes of the dilute standard nickel 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 2 to 48

12 nanograms nickel in steps of 2 nanograms (0.1 to 0.6 micrograms per ml for a 20 microlitre volume). Prepare a calibration curve of response, in arbitrary units, against concentration of nickel in micrograms per ml. Such a representative calibration curve is given in Figure 2 (Page 54).

8.4 *Determination*

8.4.1 *Determination, flame*

Set the wavelength of the monochromator at 232.0nm. Observing conditions of 8.2.1 and 8.3.1, 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 nickel in all the unknown test samples which can be accommodated to the wavelength of 232.0nm and the corresponding calibration curve.

8.4.2 *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 nickel present in the test sample by referring to the appropriate calibration curve, such as, for example, Figure 2 (Page 54).

8.5 *Blank Tests*

8.5.1 *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.

8.5.2 *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 7.3. Measure nickel and express blanks in micrograms of nickel per ml.

9. EXPRESSION OF RESULTS

9.1 *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. 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. A zero blank has been found for glass fibre filters using the furnace mode.

9.2 Instrumental precision

This is defined as the standard deviation of a number of replicate determinations and is expressed in micrograms per ml. Typical precisions for ten replicate determinations on standard samples are: $3.00 \pm 0.01 \mu\text{g/ml}$ for the flame mode, $0.40 \pm 0.0072 \mu\text{g/ml}$ for the flameless mode, on a $20 \mu\text{l}$ sample.

9.3 Minimum measurable

9.3.1 Concentration in test sample

This is taken as twice the blank deviation, or instrument precision, whichever is larger. This is $0.02 \mu\text{g}$ per ml in the case of nickel for the flame mode, and $0.002 \mu\text{g}$ per ml for the flameless mode.

9.3.2 Concentration in air

This is based on a sample volume of 2,000 cubic metres and two aliquot discs 36mm in diameter. For washed glass filters and the flame mode, this minimum measurable concentration is 0.0050 micrograms of nickel per cubic metre; for cellulose filters the corresponding value is $0.0025 \mu\text{g/m}^3$. The added sensitivity of the graphite furnace lowers this value to 0.0005 micrograms of nickel per cubic metre.

9.4 Calculations

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

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

Total exposed filter surface	=	$4.159 \times 10^4 \text{ mm}^2$
Areal test portion, 2 x 36mm discs	=	$2,036 \text{ mm}^2$
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
Nickel concentration, in g/m	=	T

$$T = \frac{(X_1 - X_2) \times 20.43 \times 25}{V}$$

10. NOTES ON PROCEDURE

10.1 *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 nickel is almost between 1 and 3 microns according to Lee (12.2).

10.2 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 760mm Hg.

10.3 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 flow rates, 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.

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

10.5 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 nickel contamination has been found to result from its use so far. As cellulose is more difficult to cut than glass fibre the die should be exceedingly sharp.

10.6 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 and cadmium measured on high volume filters (12.3, 12.4, 12.5). 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 (12.6).

10.7 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 in this series where two calibration curves are given for the flame and one for the furnace (12.7).

10.8 *Operating conditions, flame*

The optimum operating conditions are as given:

Wavelength	=	232.0nm
Spectral band width	=	0.2nm
Source	=	Hollow cathode
Source current	=	As recommended
Oxidant	=	Air
Fuel	=	Acetylene
Flame	=	Oxidizing, lean, blue
Sensitivity	=	0.15µg/ml for 1% absorption

Change the acetylene container before the cylinder pressure drops below 50 psig.

10.9 *Graphite furnace*

Use of the graphite furnace results in increased sensitivity, as shown by a comparison of Figures 1 and 2. Great care must be taken with the alignment of the furnace so that no response is obtained with a distilled water blank. Furnace operating conditions:

Wavelength	=	232.0nm
Sample size	=	20 microlitres
Purging gas	=	Argon or nitrogen
Thermal decomposition	=	drying (20sec, 100°C) charring (20sec, 1,100°C) atomizing (20sec, 2,400°C)

The use of a deuterium lamp background compensator is recommended.

11. SCHEMATIC REPRESENTATION OF PROCEDURE

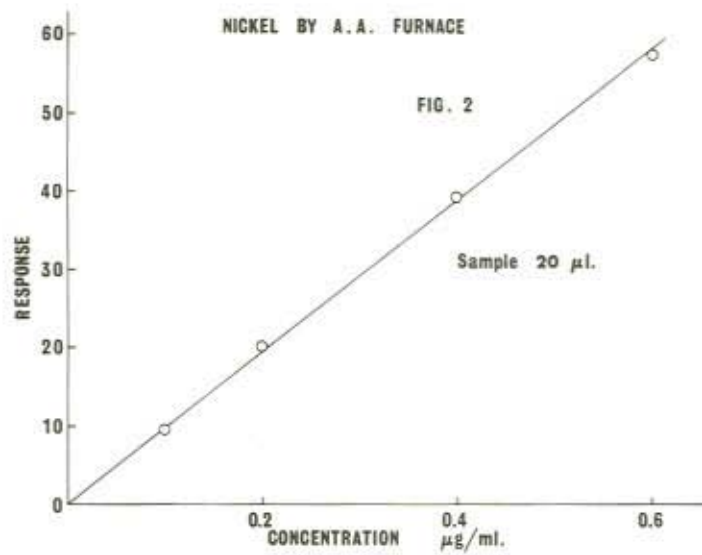
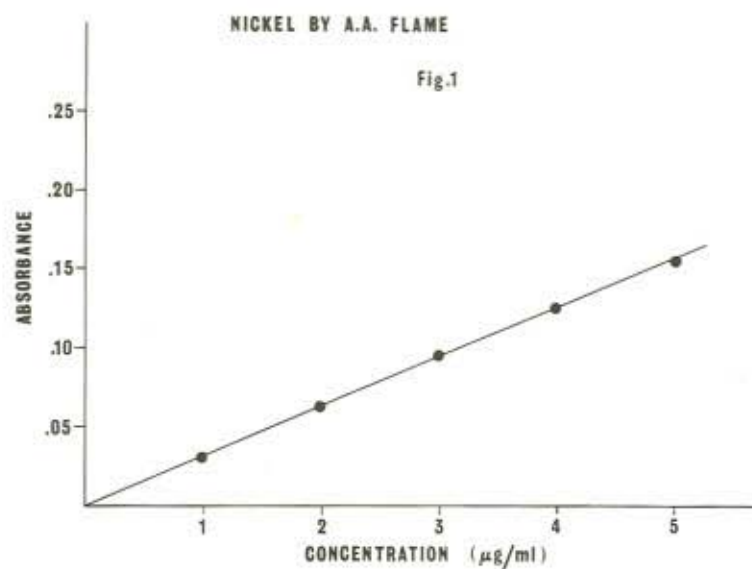
11.1 Draw laboratory air sample.

11.2 Cut areal test portion from exposed surface.

- 11.3 Digest areal test portion.
- 11.4 Adjust digest to volume to give test sample.
- 11.5 Aspirate test portion into flame.
- 11.6 Or, add test portion to furnace, measured by microlitre pipette.

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- 12.7 Monkman, J. L. Determination of Airborne Particulate Lead by Atomic Absorption Spectroscopy, see p.1.



Determination of Airborne Particulate Manganese by Atomic Absorption Spectrophotometry

1. INTRODUCTION

Manganese is widely distributed in nature, always in the combined state. Among the elements in the earth's crust it ranks twelfth in abundance. The manganese mining industry does not constitute a significant source of emission to the air. Manganese compounds found in the air are generated primarily by metallurgical uses in the iron and steel industry. Most of these emissions are in the form of oxides.

In the method to be described, airborne particulates are collected by drawing the air through a filter. The filter, or an areal aliquot, with collected particulates, is digested to prepare a test sample. Preparation of this sample is simple and rapid. The aqueous acidic sample is scrutinized by an atomic absorption spectrophotometer at the wavelength 279.8nm and the manganese is calculated by referring the absorbance found to the appropriate calibration curve. By the use of a graphite furnace, additional sensitivity may be achieved beyond that of the usual flame mode. The manganese levels found are expressed in micrograms per cubic metre of air sampled. Some practical details of accuracy and precision obtainable will be found under the section "Expression of Results" (9).

2. FIELD OF APPLICATION

The method is applicable to the measurement of the levels of suspended particulate manganese found in either ambient or industrial atmospheres. Based upon the flame mode, washed glass filters and a nominal air sample volume of 2,000 cubic metres, manganese is measurable to 0.010 micrograms per cubic metre. The sensitivity is improved four times if the air sample is taken on cellulose. For the flameless mode, the sensitivity is increased only for the cellulose filters, in which case a minimum concentration of 0.0001 micrograms of manganese per cubic metre can be detected.

3. PRINCIPLE

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

4. 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 dissolution, volatility or adsorption must be avoided.

5. REAGENTS

5.1 *Air, compressed*

In pressure cylinders or online.

5.2 *Acetylene, compressed*

In pressure cylinders.

5.3 *Glass filters*

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

5.4 *Cellulose filters*

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

5.5 *Water*

Distilled at least twice from glass or quartz.

5.6 *Hydrofluoric acid*

49%. Reagent grade, in polyethylene containers.

5.7 *Nitric acid*

71%. Reagent grade.

5.8 *Standard solution of manganese*

Dissolve 3.602 grams of manganese chloride tetrahydrate, $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ in dilute HCl and make up to 1 litre. 1ml contains $1,000\mu\text{g}$ per ml of manganese, Mn.

6. APPARATUS

6.1 *Spectrophotometer*

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

6.2 *Pipettes, glass*

Millilitre capacities, "to deliver".

6.3 *Volumetric flasks*

Borosilicate with ground glass stopper, 25ml capacity.

6.4 *Bottles, polyethylene*

Screw cap, for storage of test samples, 30ml capacity.

6.5 *Beakers, teflon*

Griffin form, 100ml capacity.

6.6 *Beakers, borosilicate*

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

6.7 *Hot plate*

Electric, with temperature control, thermostat and ceramic heating surface.

6.8 *Büchner funnel*

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

6.9 *Graphite furnace*

One suitable instrument is available commercially to the Massmann design.

6.10 *Strip chart recorder*

To display and record the response from the furnace.

6.11 *Pipettes, automatic*

Eppendorf design, with capacities 10 to 100 microlitres.

7. SAMPLING AND SAMPLES

7.1 *Air Sampling*

7.2 *Preparation of the laboratory sample*

Cellulose filters (5.4) may be used without further treatment. Glass fibre filters (5.3) 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 flow rate 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 flow rate and time.

7.3 *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 1ml of hydrofluoric acid (5.6). Gently warm the contents of the beaker, at low heat, until the hydrofluoric acid is almost completely evaporated. At this point, add 1 to 2ml of nitric acid (5.7), and continue to heat gently until a few drops of nitric acid are left. Add about 10ml of water, bring nearly to the boil and filter through a Whatman 41 filter into a glass beaker (6.6). Transfer to a 25ml volumetric flask (6.3). Rinse down the teflon beaker with another 10ml quantity of water, warm and filter into the same beaker. Transfer to the 25ml 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 (6.4). The test sample is now ready for analysis. The above procedure is applicable only to the digestion of glass fibre filters. Cellulose filters may be digested or extracted with nitric acid.

8. PROCEDURE

8.1 *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 REPLACED.**

8.2 Test Portions

8.2.1 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.

8.2.2 Test portions, furnace

Measure and insert in the furnace, test portions of 10 to 100 microlitres of the test sample using an automatic pipette (6.11).

8.3 Calibration Curves

8.3.1 Calibration curves, flame

Using "to deliver" pipettes, prepare known concentrations of manganese by dilution of standard solution (5.8) to cover the range of 0.5 to 3.0 micrograms of manganese per ml. Install in the spectrophotometer and align, if necessary, the hollow cathode source for manganese. Set the wavelength of the monochromator at 279.8nm. Using an air-acetylene flame, aspirate an unmeasured portion of each dilute standard manganese solution for 10 seconds (8.2.1). At the same time, aspirate into the flame a blank of distilled water. From the instrumental responses obtained, prepare a calibration curve of absorbance against concentration of manganese, in micrograms per ml. Such a representative calibration curve is given in Figure 1 (Page 64).

8.3.2 Calibration curves, furnace

By means of an automatic pipette with polyethylene tip, place identical microlitre volumes of the dilute standard manganese 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 0.2 to 1.0 nanograms of manganese in steps of 0.2 nanograms (0.01 to 0.05 micrograms per ml for a 20 microlitre sample). Prepare a calibration curve of response, in arbitrary units, against concentration of manganese in micrograms per ml. Such a representative calibration curve is given in Figure 2 (Page 65).

8.4 Determination

8.4.1 Determination, flame

Set the wavelength of the monochromator at 279.8nm. Observing conditions of 8.2.1 and 8.3.1, aspirate an unmeasured test portion of each unknown test sample into the flame. Record the response of each unknown.

Aspirate distilled water into the flame between each unknown test portion to prevent cross contamination. Measure the manganese in all the unknown test samples which can be accommodated to the wavelength of 279.8nm and the corresponding calibration curve.

8.4.2 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 manganese present in the test sample, by referring to the appropriate calibration curve, such as, for example, Figure 2 (Page 65).

8.5 Blank Tests

8.5.1 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.

8.5.2 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 7.3. Measure manganese and express blanks in micrograms of manganese per ml.

9. EXPRESSION OF RESULTS

9.1 Blank

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. It should be also 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. In the case of manganese, the blank problem is much less serious with cellulose.

9.2 Instrumental precision

This is defined as the standard deviation of a number of replicate determinations, expressed in micrograms per ml. For ten repeat measurements on standard samples, the following precision has been obtained: $2.00 \pm 0.01 \mu\text{g/ml}$ for the flame mode and $0.040 \pm 0.00092 \mu\text{g/ml}$ for the flameless mode.

9.3 Minimum measurable

9.3.1 Concentration in test sample

This is taken as twice the blank deviation or instrument precision, whichever is larger. For the flame mode this is 0.01 micrograms per ml for cellulose filter and 0.04 micrograms per ml for glass fibre filters. The larger value for glass fibre filters is caused by the somewhat variable blank reading, which has been found to be in the range of 0.15 to 0.40 micrograms of manganese per ml; for cellulose filters the blank is zero. For the flameless mode an improvement in the minimum measurable is achieved only for cellulose filters and is 0.0004 micrograms per ml.

9.3.2 Concentrations in air

This is based on a sample volume of 2,000 cubic metres and two aliquot discs 36mm in diameter. This minimum measurable concentration is 0.010 micrograms of manganese per cubic metre with glass and 0.0025 micrograms per cubic metre with cellulose for the flame mode. The increased sensitivity of the graphite furnace reduces this to 0.0001 micrograms per cubic metre for cellulose filters.

9.4 Calculations

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

Total exposed filter surface	=	$4.159 \times 10^4 \text{ mm}^2$
Areal test portion, 2 x 36mm discs	=	$2,036 \text{ mm}^2$
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
Manganese concentration, in $\mu\text{g}/\text{m}^3$	=	T

$$T = \frac{(X_1 - X_2) \times 20.43 \times 25}{V}$$

10. NOTES ON PROCEDURE

10.1 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 manganese is almost all between 1 and 3 microns, according to Lee (12.1).

10.2 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 760mm Hg.

10.3 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 flow rates, 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.

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

10.5 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 manganese contamination has been found to result from its use.

10.6 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 and cadmium measured on high volume filters (12.2, 12.3, 12.4). 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 (12.5).

10.7 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 in this series where two calibration curves are given for the flame and one for the furnace (12.6).

10.8 Operating conditions, flame

Wavelength	=	279.8nm
Spectral band width	=	0.2nm
Source	=	Hollow cathode
Source current	=	As recommended
Oxidant	=	Air
Fuel	=	Acetylene
Flame	=	Oxidizing, lean, blue
Sensitivity	=	0.049 μ g/ml for 1% absorption

Change the acetylene cylinder before the pressure drops below 50 psig.

10.9 Graphite furnace

The calibration curve for the flame mode obeys Beer's Law up to and beyond 3.0 micrograms per ml. The considerably enhanced sensitivity for manganese provided by the graphite furnace is illustrated in Figure 2.

Furnace operating conditions:

Wavelength	=	279.8nm
Sample size	=	20 μ l
Purging gas	=	Argon or nitrogen
Thermal decomposition	=	drying (20sec, 100°C) charring (20sec, 1,100°C) atomizing (20sec, 2,500°C)

The use of a deuterium lamp background compensator is recommended.

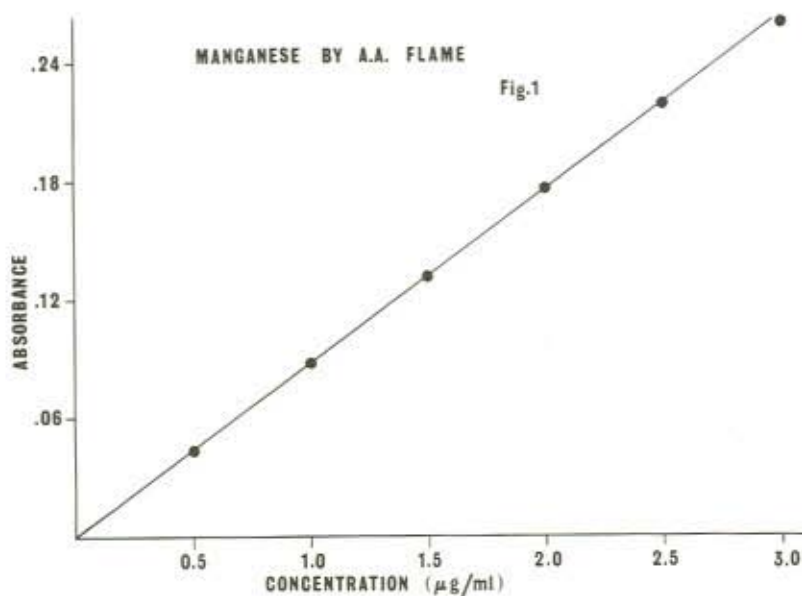
11. SCHEMATIC REPRESENTATIVE OF PROCEDURE

- 11.1 Draw laboratory air sample.
- 11.2 Cut areal test portion from exposed surface.
- 11.3 Digest areal test portion.
- 11.4 Adjust digest to volume to give test sample.
- 11.5 Aspirate test portion into flame.
- 11.6 Or, add test portion to furnace, measured by microlitre pipette.

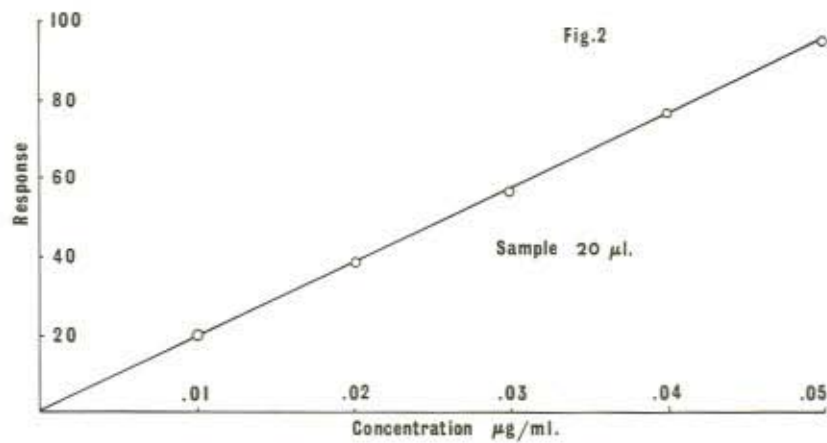
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- 12.6 Monkman, J. L. et al. Determination of Airborne Particulate Lead by Atomic Absorption Spectroscopy, see p.1.



Manganese by A.A. Furnace



Determination of Airborne Particulate Cobalt by Atomic Absorption Spectrophotometry

1. INTRODUCTION

Cobalt in airborne particulates may be measured by conventional polarography but sample preparation must be meticulous or the cobalt wave may be masked. Methods using anodic stripping voltammetry show promise but more practical experience must be obtained. The identification and measurement of cobalt by the Weisz ring oven is simple and sensitive. The identification limit on cellulose filter samples is 0.05 microgram (12.1).

In the method described, airborne particulates are collected by drawing air through a filter. The filter, or an areal aliquot, with collected particulates, is digested to prepare a test sample. Preparation of this sample is simple and rapid. The aqueous acidic sample is scrutinized by an atomic absorption spectrophotometer at the wavelength of 240.7nm and the cobalt is calculated by referring the absorbance found to the appropriate calibration curve. The cobalt values found are expressed in micrograms per cubic metre of air sampled. Some practical details of accuracy and precision obtainable will be found under the section "Expression of Results" (9).

2. FIELD OF APPLICATION

The method is applicable to the measurement of the levels of suspended particulate cobalt found in either ambient or industrial atmospheres. Based upon the flame mode, washed glass filters and a nominal air volume of 2,000 cubic metres, one may determine down to 0.0050 micrograms of cobalt per cubic metre of air. For the same conditions but using cellulose filters cobalt may be measured down to $0.0025\mu\text{g}/\text{m}^3$. The flameless mode allows a determination down to 0.0002 micrograms per cubic metre for either type of filter.

3. PRINCIPLE

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

4. 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.

5. REAGENTS

5.1 *Air, compressed*

In pressure cylinders or online.

5.2 *Acetylene, compressed*

In pressure cylinders.

5.3 *Glass filters*

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

5.4 *Cellulose filters*

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

5.5 *Water*

Distilled at least twice from glass or quartz.

5.6 *Hydrofluoric acid*

49%. Reagent grade, in polyethylene containers.

5.7 *Nitric acid*

71%. Reagent grade.

5.8 *Standard solution of cobalt*

Dissolve 4.037 grams of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in HCl and dilute to 1 litre. 1ml of this stock solution contains 1,000 μg per ml of cobalt, Co.

6. APPARATUS

6.1 *Spectrophotometer, atomic absorption*

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

6.2 *Pipettes, glass*

Millilitre capacities, "to deliver".

6.3 *Volumetric flasks*

Borosilicate with ground glass stopper, 25ml capacity.

6.4 *Bottles, polyethylene*

Screw cap, for storage of test samples, 30ml capacity.

6.5 *Beakers, teflon*

Griffin form, 100ml capacity.

6.6 *Beakers, borosilicate*

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

6.7 *Hot plate*

Electric, with temperature control, thermostat and ceramic heating surface.

6.8 *Büchner funnel*

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

6.9 *Graphite furnace*

One suitable instrument is available commercially to the Massmann design.

6.10 *Strip chart recorder*

To display and record the response from the furnace.

6.11 *Pipettes, automatic*

Eppendorf design, with capacities 10 to 100 microlitres.

7. SAMPLING AND SAMPLES

7.1 *Air Sampling*

7.2 *Preparation of the laboratory sample*

Cellulose filters (5.4) may be used without further treatment. Glass fibre filters (5.3) 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 flow rate 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 flow rate and time.

7.3 *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 1ml of hydrofluoric acid (5.6). Gently warm the contents of the beaker, at low heat, until the hydrofluoric acid is almost completely evaporated. At this point, add 1 to 2ml of nitric acid (5.7) and continue to heat gently until a few drops of nitric acid are left. Add about 10ml of water, bring nearly to the boil and filter through a Whatman 41 filter into a glass beaker (6.6). Transfer to a 25ml volumetric flask (6.3). Rinse down the teflon beaker with another 10ml quantity of water, warm and filter into the same beaker. Transfer to the 25ml 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 (6.4). The test sample is now ready for analysis. The above procedure is applicable to the digestion of glass fibre filters. Cellulose filters may be digested or extracted with nitric acid.

8. PROCEDURE

8.1 *Safety precautions*

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

8.2 Test Portions

8.2.1 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.

8.2.2 Test portions, furnace

Measure and insert in the furnace, test portions of 10 to 100 microlitres of the test sample using an automatic pipette (6.11).

8.3 Calibration Curves

8.3.1 Calibration curves, flame

Using "to deliver" pipettes, prepare known concentrations of cobalt by dilution of standard solution (5.8) to cover the range of 1.0 to 5.0 micrograms of cobalt per ml. Install in the spectrophotometer and align, if necessary, the hollow cathode source for cobalt. Set the wavelength of the monochromator at 240.7nm. Using an air-acetylene flame, aspirate an unmeasured portion of each dilute standard cobalt solution for 10 seconds (8.2.1). At the same time, aspirate into the flame a blank of distilled water. From the instrumental responses obtained, prepare a calibration curve of absorbance against concentration of cobalt in micrograms per ml. Such a representative calibration curve is given in Figure 1 (Page 75).

8.3.2 Calibration curves, furnace

By means of an automatic pipette with polyethylene tip, place identical microlitre volumes of the dilute standard cobalt 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 micrograms of cobalt in steps of 2 nanograms (0.1 to 0.5 micrograms per ml for a 20 microlitre sample). Prepare a calibration curve of response, in arbitrary units, against concentration of cobalt in micrograms per ml. Such a representative calibration curve is given in Figure 2 (Page 76).

8.4 Determination

8.4.1 Determination, flame

Set the wavelength monochromator at 240.7nm. Observing conditions of 8.2 and 8.3, 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 cobalt in all the unknown test samples which can be accommodated to the wavelength of 240.7nm and the corresponding calibration curve.

8.4.2 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 cobalt present in the test sample by referring to the appropriate calibration curve, such as, for example, Figure 2 (Page 76).

8.5 *Blank Tests*

8.5.1 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.

8.5.2 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 7.3. Measure cobalt and express blanks in micrograms of cobalt per ml.

9. EXPRESSION OF RESULTS

9.1 *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. It should also be noted that part of the filter blank value is due to matrix interference from elements present in large amounts in the filter such as Na, Ba, Si, Ca, Zn, K and Al. Both cellulose and glass fibre filters give a zero blank using the furnace mode. Using the flame mode, the glass fibre blank is about 0.13 micrograms per ml.

9.2 *Instrumental precision*

This is defined as the standard deviation of a number of replicate determinations, expressed in micrograms per ml. For ten repeat measurements on standard samples, the following was obtained: $3.00 \pm 0.02 \mu\text{g/ml}$ for the flame mode and $0.40 \pm 0.0048 \mu\text{g/ml}$ for the flameless mode.

9.3 Minimum measurable

9.3.1 Concentration in test sample

This is taken as twice the blank deviation or instrument precision, whichever is larger. This is 0.02 and 0.01 micrograms per ml for glass fibre and cellulose filters, respectively, using the flame mode. For the flameless mode this value is decreased to 0.0007 micrograms per ml.

9.3.2 Concentrations in air

This is based on a sample volume of 2,000 cubic metres and two aliquot discs 36mm in diameter. For the flame mode and washed glass fibre filters this minimum measurable concentration is 0.0050 micrograms of cobalt per cubic metre; for cellulose filters the corresponding value is 0.0025 micrograms per cubic metre. The increased sensitivity of the flameless mode reduced the minimum measurable concentration to 0.0002 micrograms per cubic metre for either type of filter.

9.4 Calculations

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

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

Total exposed filter surface	=	$4.159 \times 10^4 \text{ mm}^2$
Areal test portion, 2 x 35mm discs	=	$2,036 \text{ mm}^2$
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
Cobalt concentration, in $\mu\text{g}/\text{m}^3$	=	T

$$T = \frac{(X_1 - X_2) \times 20.43 \times 25}{V}$$

10. NOTES ON PROCEDURE

10.1 Collection efficiencies

Little is known about actual collection efficiencies and in methods for the analysis of particulate metals, these efficiencies are usually ignored.

10.2 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 760mm Hg.

10.3 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 flow rates, 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.

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

10.5 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 area aliquots can be very easily reproduced with accuracy. In the method described, a punch of stainless steel is used. No cobalt contamination has been found to result from its use. As cellulose is more difficult to cut than glass fibre the die should be exceedingly sharp.

10.6 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 and cadmium measured on high volume filters (12.2, 12.3, 12.4). 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 (12.5).

10.7 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 in this series where two calibration curves are given for the flame and one for the furnace (12.6).

10.8 *Operating conditions, flame*

The optimum operating conditions are as given:

Wavelength	=	240.7nm
Spectral band width	=	0.2nm
Source	=	Hollow cathode

Source current	=	As recommended
Oxidant	=	Air
Fuel	=	Acetylene
Flame	=	Oxidizing, lean, blue
Sensitivity	=	0.15 μ g/ml for 1% absorption

Change the acetylene container before the cylinder pressure drops below 50 psig.

10.9 Graphite furnace

All other conditions remaining the same, the use of the furnace instead of the flame results in greatly increased sensitivity. A representative curve for the measurement of cobalt is given in Figure 2 (Page 76).

Furnace operating conditions are as follows:

Wavelength	=	240.7nm
Sample size	=	20 microlitres
Purging gas	=	Argon or nitrogen
Thermal decomposition	=	drying (20sec, 100°C) charring (20sec, 1,100°C) atomizing (20sec, 2,100°C)

The use of a deuterium lamp background compensator is recommended.

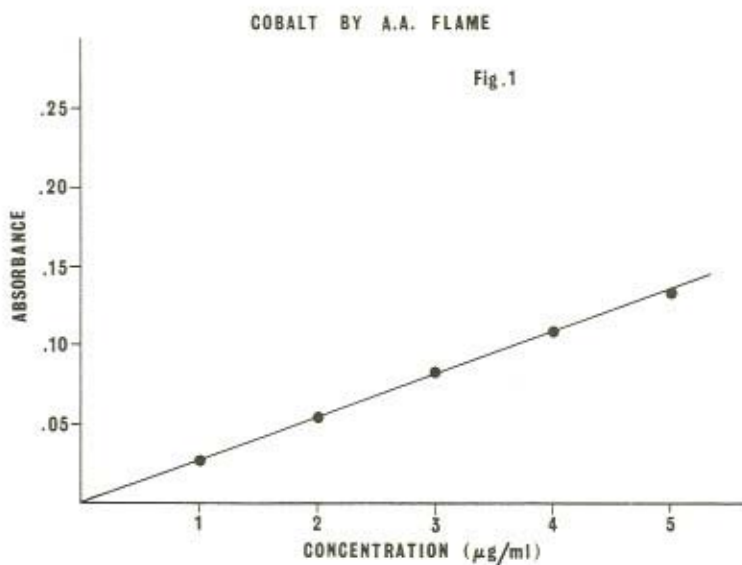
11. SCHEMATIC REPRESENTATION OF PROCEDURE

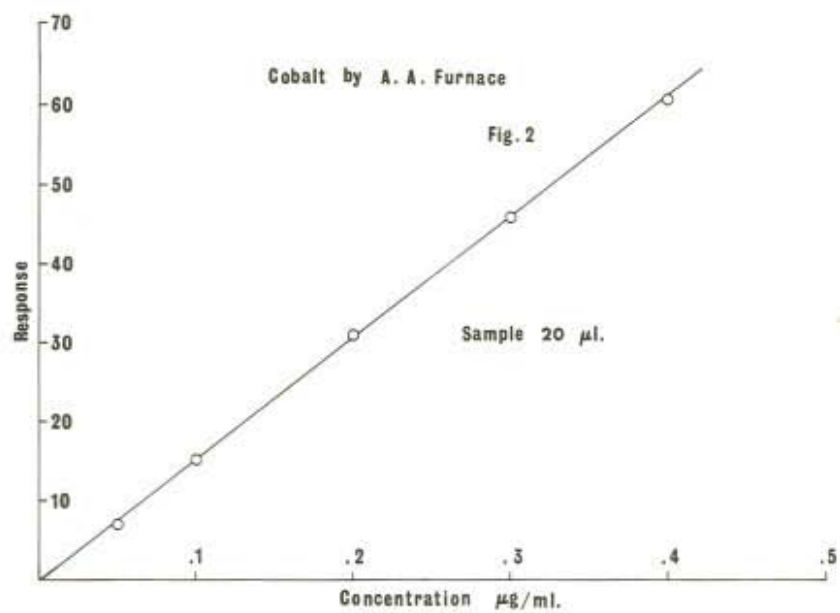
- 11.1 Draw laboratory air sample.
- 11.2 Cut areal test portion from exposed surface.
- 11.3 Digest areal test portion.
- 11.4 Adjust digest to volume to give test sample.
- 11.5 Aspirate test portion into flame.
- 11.6 Or, add test portion to furnace, measured by microlitre pipette.

12. REFERENCES

- 12.1 West, P. W. Symposium on Air Quality, American Chemical Society, Los Angeles, April 1, 1971.
- 12.2 Dubois, L., Teichman, T., Airth, J. M., and Monkman, J. L. The Metal Content of Urban Air. *Journal A.P.C.A.* 16, 2, 77, 1966.

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- 12.4 Zdrojewski, A., Quickert, N. and Dubois, L. The Accurate Measurement of Cadmium in Airborne Particulates. *J. Int. Envi. Anal. Chem.* September 1972.
- 12.5 Pierce, J. O., and Meyer, J. H. Sampling and Analysis Considerations in evaluating levels of atmospheric lead. *Atmospheric Environment* 5, 811, 1971.
- 12.6 Monkman, J. L. et al. Determination of Airborne Particulate Lead by Atomic Absorption Spectroscopy, see p.1.





Determination of Airborne Particulate Beryllium by Atomic Absorption Spectrophotometry

1. INTRODUCTION

Inhalation of beryllium or its compounds can cause a systemic disease in men and animals with associated pulmonary damage. The element is widely distributed but constitutes only 0.006% of the earth's crust. Beryl is the only commercial source of beryllium, but beryl is only obtained as a by-product of the production of other minerals. The processes of extracting, refining and machining of beryllium and its alloys produce considerable quantities of airborne beryllium. Dusts are produced in emitting and grinding operations. These emissions from extractive and metallurgical operations produce the toxic manifestations. Air concentrations at 100 air sampling stations in the USA are said to be of the order of 0.5 nanograms per cubic metre.

Beryllium in suspended particulates may be measured by fluorimetric methods. One of these methods utilizes the fluorescence emitted by beryllium fused into a bead of sodium fluoride. Another method is based upon the bright yellow fluorescence produced when beryllium reacts with morin. The measurement of beryllium by the Weisz ring oven on paper tape samples is simple and sensitive. The morin reaction is used and the limit of identification, per individual assay, is given as 0.01 micrograms of beryllium as the element (12.1).

In the method to be described, airborne particulates are collected by drawing the air through a filter. The filter or an areal aliquot, with collected particulates, is digested to prepare a test sample. Preparation of this sample is simple and rapid. The aqueous acidic sample is scrutinized by an atomic absorption spectrophotometer at the wavelength 234.8nm and the beryllium is calculated by referring the absorbance found to the appropriate calibration curve. By the use of a graphite furnace, additional sensitivity may be achieved beyond that of the usual flame mode. The beryllium values found are expressed in micrograms per cubic metre of air sampled. Some practical details of accuracy and precision obtainable will be found under the section "Expression of Results" (9).

2. FIELD OF APPLICATION

The method is applicable to the measurement of the levels of suspended particulate beryllium found in either ambient or industrial atmospheres. Based upon the flame mode, washed glass filters and a nominal air sample

volume of 2,000 cubic metres, beryllium is measurable to 0.0025 micrograms per cubic metre. The same sensitivity applies if the air sample is taken on cellulose. For the same test sample, the use of the flameless mode increases the sensitivity almost two orders of magnitude, to 0.00005 micrograms per cubic metre.

3. PRINCIPLE

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

4. 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.

5. REAGENTS

5.1 *Air, compressed*

In pressure cylinders or online.

5.2 *Acetylene, compressed*

In pressure cylinders.

5.3 *Nitrous oxide, compressed*

In pressure cylinders.

5.4 *Glass filters*

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

5.5 *Cellulose filters*

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

5.6 *Water*

Distilled at least twice from glass or quartz.

5.7 *Hydrofluoric acid*

49%. Reagent grade, in polyethylene containers.

5.8 *Nitric acid*

71%. Reagent grade.

5.9 *Standard solution of beryllium*

Dissolve 22.757g of beryllium nitrate tetrahydrate in water and make up to 1 litre. One ml of this stock solution contains 1,000 micrograms of beryllium, Be.

6. APPARATUS

6.1 *Spectrophotometer, atomic absorption*

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

6.2 *Pipettes, glass*

Millilitre capacities, "to deliver".

6.3 *Volumetric flasks*

Borosilicate with ground glass stopper, 25ml capacity.

6.4 *Bottles, polyethylene*

Screw cap, for storage of test samples, 30ml capacity.

6.5 *Beakers, teflon*

Griffin form, 100ml capacity.

6.6 *Beakers, borosilicate*

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

6.7 *Hot plate*

Electric, with temperature control, thermostat and ceramic heating surface.

6.8 *Büchner funnel*

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

6.9 *Graphite furnace*

One suitable instrument is available commercially to the Massmann design

6.10 *Strip chart recorder*

To display and record the response from the furnace.

6.11 *Pipettes, automatic*

Eppendorf design, with capacities 10 to 100 microlitres.

7. SAMPLING AND SAMPLES

7.1 *Air Sampling*

7.2 *Preparation of the laboratory sample*

Cellulose filters (5.5) may be used without further treatment. Glass fibre filters (5.4) 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 flow rate 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 flow rate and time.

7.3 *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 1ml of hydrofluoric acid (5.7). Gently warm the contents of the beaker, at low
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heat, until the hydrofluoric acid is almost completely evaporated. At this point, add 1 to 2ml of nitric acid (5.8), and continue to heat gently until a few drops of nitric acid are left. Add about 10ml of water, bring nearly to the boil and filter through a Whatman 41 filter into a glass beaker (6.6). Transfer to a 25ml volumetric flask (6.3). Rinse down the teflon beaker with another 10ml quantity of water, warm and filter into the same beaker. Transfer to the 25ml 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 (6.4). The test sample is now ready for analysis. The above procedure applies to the digestion of glass fibre filters. Cellulose filters may be digested or extracted with nitric acid.

8. PROCEDURE

8.1 *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 REPLACED.

8.2 *Test Portions*

8.2.1 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.

8.2.2 Test portions, furnace

Measure and insert in the furnace, test portions of 10 to 100 microlitres of the test sample using an automatic pipette (6.11).

8.3 *Calibration Curves*

8.3.1 Calibration curves, flame

Using "to deliver" pipettes, prepare known concentrations of beryllium by dilution of standard solution (5.9) to cover the range of 1.0 to 4.0 micrograms of beryllium per ml. Install in the spectrophotometer and align, if necessary, the hollow cathode source for beryllium. Set the wavelength of the monochromator at 234.8nm. Using a nitrous oxide acetylene flame, aspirate an unmeasured portion of each dilute standard beryllium solution for 30 seconds (8.2.1). At the same time, aspirate into the flame a blank of

distilled water. From the instrumental responses obtained, prepare a calibration curve of absorbance against concentration of beryllium, in micrograms per ml. Such a representative calibration curve is given in Figure 1 (Page 87).

8.3.2 Calibration curves, furnace

By means of an automatic pipette with polyethylene tip, place identical microlitre volumes of the dilute standard beryllium 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 0.2 to 1.0 nanograms of beryllium in steps of 0.2 nanograms (0.01 to 0.05 micrograms per ml for a 20 microlitre sample). Prepare a calibration curve of response, in arbitrary units, against concentration of beryllium in micrograms per ml. Such a representative calibration curve is given in Figure 2 (Page 87).

8.4 Determination

8.4.1 Determination, flame

Set the wavelength of the monochromator at 234.8nm. Observing conditions of 8.2.1 and 8.3.1, 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 beryllium in all the unknown test samples which can be accommodated to the wavelength of 234.8nm and the corresponding calibration curve.

8.4.2 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 beryllium present in the test sample by referring to the appropriate calibration curve, such as, for example, Figure 2 (Page 87).

8.5 Blank Tests

8.5.1 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.

8.5.2 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 7.3. Measure beryllium and express blanks in micrograms of beryllium per ml.

9. EXPRESSION OF RESULTS

9.1 *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 beryllium the glass fibre filter blank can vary from 0.01 to 0.05 micrograms per ml using the flame mode, and from 0.001 to 0.009 micrograms per ml using the flameless mode. It should be noted that part of the filter blank value is due to interferences from elements present in large amounts in the filter, such as Na, Ba, Si, Ca, Zn, K and Al; these interferences are usually larger for the flame mode. For any one batch of filters, the blank has been found to be relatively uniform, $\pm 10\%$, and hence causes no difficulty. A considerable number of filters in each batch should be checked, however, to ensure uniformity of the blank.

9.2 *Instrumental precision*

This is defined as the standard deviation of a number of replicate determinations, expressed in micrograms per ml. For ten repeat measurements on standard samples, the following has been found: $3.00 \pm 0.02 \mu\text{g/ml}$ for the flame mode and $0.040 \pm 0.0011 \mu\text{g/ml}$ for the flameless mode.

9.3 *Minimum measurable*

9.3.1 Concentration in test sample

This is taken as twice the blank deviation, or instrument precision, whichever is larger. This is $0.01 \mu\text{g}$ per ml for the flame mode and $0.0002 \mu\text{g}$ per ml for the flameless mode.

9.3.2 Concentration in air

This is based on a sample volume of 2,000 cubic metres and two aliquot discs 36mm in diameter. For the flame mode this minimum measurable concentration is 0.0025 micrograms of beryllium per cubic metre, regardless of whether glass or cellulose filters were used. For the flameless mode, the greatly increased sensitivity reduces this to 0.00005 micrograms per cubic metre (for the case that the blank is small (9.2)).

9.4 Calculations

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

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

Total exposed filter surface	=	$4.159 \times 10^4 \text{ mm}^2$
Areal test portion, 2 x 36mm discs	=	$2,036 \text{ mm}^2$
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
Beryllium concentration, in $\mu\text{g}/\text{m}^3$	=	T

$$T = \frac{(X_1 - X_2) \times 20.43 \times 25}{V}$$

10. NOTES ON PROCEDURE

10.1 Collection efficiencies

Little is known about actual collection efficiencies and in methods for the analysis of particulate metals, these efficiencies are usually ignored.

10.2 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 760mm Hg.

10.3 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 flow rates, 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.

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

10.5 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 beryllium contamination has been found to result from its use.

10.6 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 and cadmium measured on high volume filters (12.2, 12.3, 12.4). 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 (12.5).

10.7 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 in this series where two calibration curves are given for the flame and one for the furnace (12.6).

10.8 *Operating conditions, flame*

The optimum operating conditions are as given:

Wavelength	=	234.8nm
Spectral band width	=	0.7nm
Source	=	Hollow cathode
Source current	=	As recommended
Oxidant	=	Nitrous oxide
Fuel	=	Acetylene
Flame	=	Reducing, rich, red
Sensitivity	=	0.035 μ g/ml for 1% absorption

Change acetylene container before cylinder pressure drops below 50 psig.

10.9 *Graphite furnace*

The calibration curve for the flame mode obeys Beer's Law up to and beyond 4.0 micrograms of beryllium per ml of test sample as illustrated by Figure 1. A representative curve for beryllium measured by the graphite furnace, is given in Figure 2, which shows greatly increased sensitivity over the flame. Furnace operating conditions:

Wavelength	=	234.8nm
Sample size	=	20 microlitres
Purging gas	=	Argon or nitrogen

Thermal decomposition = drying (20sec, 100°C)
= charring (20sec, 1,100°C)
= atomizing (20sec, 2,400°C)

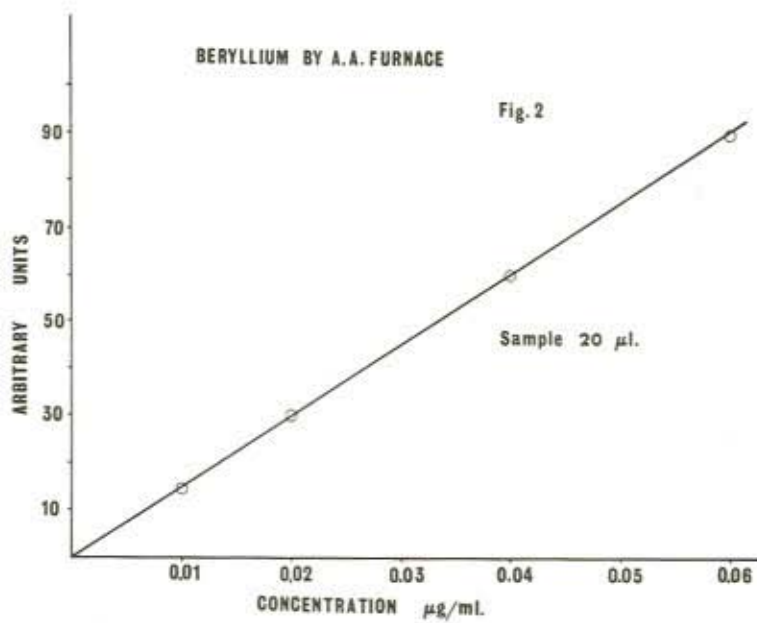
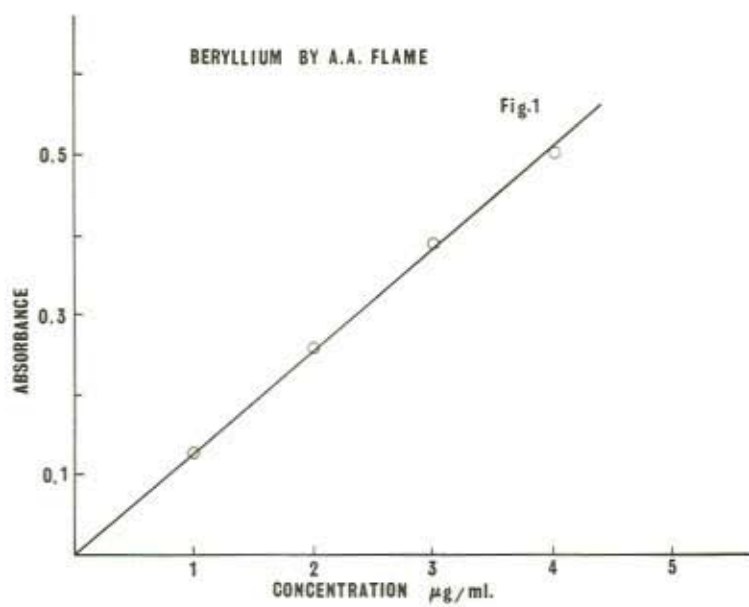
The use of a deuterium lamp background compensator is recommended.

11. SCHEMATIC REPRESENTATIVE OF PROCEDURE

- 11.1 Draw laboratory air sample.
- 11.2 Cut areal test portion from exposed surface.
- 11.3 Digest areal test portion.
- 11.4 Adjust digest to volume to give test sample.
- 11.5 Aspirate test portion into flame.
- 11.6 Or, add test portion to furnace, measured by microlitre pipette.

12. REFERENCES

- 12.1 West, P. W. Symposium on Air Quality, American Chemical Society, Los Angeles, April 1, 1971.
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- 12.5 Pierce, J. O., and Meyer, J. H. Sampling and Analysis Considerations in evaluating levels of atmospheric lead. *Atmospheric Environment* 5, 811, 1971.
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Determination of Airborne Particulate Vanadium by Atomic Absorption Spectrophotometry

1. INTRODUCTION

Vanadium is moderately toxic to humans and animals. Chronic exposure to environmental air concentrations has been statistically associated with the incidence of cardiovascular disease and certain types of cancer. Vanadium is emitted into the atmosphere from industries producing the metal, its chemical compounds, and alloys. Other emitting sources are power plants and utilities consuming residual and crude oils and coals containing vanadium. The industrial uses of vanadium and the consumption of vanadium-containing fuels is increasing markedly. In the past, emission spectrography has been used to measure vanadium in high volume air samples taken on glass filters.

The ring oven has been used and the level of identification is given as 0.01 microgram. Atomic absorption spectroscopy, using the conventional flame mode, is not sufficiently sensitive and there are interferences with the method if the background contains certain elements, e.g. aluminum. The use of the graphite furnace eliminates these interferences and provides greatly increased sensitivity (12.1).

In the method to be described, airborne particulates are collected by drawing the air through a filter. The filter, or an areal aliquot, with collected particulates, is digested to prepare a test sample. Preparation of this sample is simple and rapid. The aqueous acidic sample is scrutinized by an atomic absorption spectrophotometer at the wavelength 318.4nm and the vanadium is calculated by referring the absorbance found to the appropriate calibration curve. The vanadium levels found are expressed in micrograms per cubic metre of air sampled. Some practical details of accuracy and precision obtainable will be found in the section "Expression of Results" (9).

2. 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 2,000 cubic metres, vanadium is measurable to 0.0004 micrograms per cubic metre. For the same test sample, the use of the flame mode decreases the sensitivity to 0.025 micrograms per cubic metre, as well as introducing possible errors.

3. 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.

4. 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.

5. REAGENTS

5.1 *Air, compressed*

In pressure cylinders or online.

5.2 *Acetylene, compressed*

In pressure cylinders.

5.3 *Nitrous oxide, compressed*

In pressure cylinders.

5.4 *Glass filters*

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

5.5 *Cellulose filters*

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

5.6 *Water*

Distilled at least twice from glass or quartz.

5.7 *Hydrofluoric acid*

49%. Reagent grade, in polyethylene containers.

5.8 *Nitric acid*

71%. Reagent grade.

5.9 *Standard solution of vanadium*

Dissolve 1.7856g of vanadium pentoxide (V_2O_5) in 10ml concentrated hydrochloric acid, and dilute to 1 litre with water. 1ml of this stock solution contains 1,000 micrograms of vanadium, V.

6. APPARATUS

6.1 *Spectrophotometer, atomic absorption*

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

6.2 *Pipettes, glass*

Millilitre capacities, "to deliver".

6.3 *Volumetric flasks*

Borosilicate with ground glass stopper, 25ml capacity.

6.4 *Bottles, polyethylene*

Screw cap, for storage of test samples, 30ml capacity.

6.5 *Beakers, teflon*

Griffin form, 100ml capacity.

6.6 *Beakers, borosilicate*

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

6.7 *Hot plate*

Electric, with temperature control, thermostat and ceramic heating surface.

6.8 *Büchner funnel*

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

6.9 *Graphite furnace*

One suitable instrument is available commercially to the Massmann design.

6.10 *Strip chart recorder*

To display and record the response from the furnace.

6.11 *Pipettes, automatic*

Eppendorf design, with capacities 10 to 100 microlitres.

7. SAMPLING AND SAMPLES

7.1 *Air Sampling*

7.2 *Preparation of the laboratory sample*

Cellulose filters (5.5) may be used without further treatment. Glass fibre filters (5.4) 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 flow rate 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 flow rate and time.

7.3 *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 1ml of hydrofluoric acid (5.7). 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% (12.1). Then, add 1 to 2ml of nitric acid (5.8) and continue to heat gently until a few drops of nitric acid are left. Add about 10ml of water, bring

nearly to the boil and filter through a Whatman 41 filter into a glass beaker (6.6). Transfer to a 25ml volumetric flask (6.3). Rinse down the teflon beaker with another 10ml quantity of water, warm and filter into the same beaker. Transfer to the 25ml 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 (6.4). 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.

8. PROCEDURE

8.1 *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 REPLACED.

8.2 *Test Portions*

8.2.1 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.

8.2.2 Test portions, furnace

Measure and insert in the furnace, test portions of 10 to 100 microlitres of the test sample using an automatic pipette (6.11).

8.3 *Calibration Curves*

8.3.1 Calibration curves, flame

Using "to deliver" pipettes, prepare known concentrations of vanadium by dilution of standard solution (5.9) with filter blank solution (8.5.2) to cover the range of 20 to 200 micrograms of vanadium per ml. Install in the spectrophotometer and align, if necessary, the hollow cathode source for vanadium. Set the wavelength of the monochromator at 318.4nm. Using a nitrous oxide-acetylene flame, aspirate an unmeasured portion of each dilute standard vanadium solution for 10 seconds (8.2.1). At the same time, 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 ml. A representative

calibration curve is given in Figure 1 (Page 98). The matrix effect is considerable and is dependent on the concentrations of a number of interfering elements (12.1): Figure 3 illustrates the effect of aluminium (Page 99).

8.3.2 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 ml for a 20 microlitre volume). Prepare a calibration curve of response, in arbitrary units, against concentration of vanadium in micrograms per ml. Such a representative calibration curve is given in Figure 2 (Page 98).

8.4 Determination

8.4.1 Determination, flame

Set the wavelength of the monochromator at 318.4nm. Observing conditions of 8.2.1 and 8.3.1, 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 318.4nm and the corresponding calibration curve.

8.4.2 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.

8.5 Blank Tests

8.5.1 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.

8.5.2 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 7.3. Measure vanadium and express blanks in micrograms of vanadium per ml.

9. EXPRESSION OF RESULTS

9.1 *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. 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, An, K and Al.

9.2 *Instrumental precision*

This is defined as the standard deviation of a number of replicate determinations and is expressed in micrograms per ml. Typical precisions for ten replicate determinations on standard samples are: $100.0 \pm 0.5 \mu\text{g/ml}$ for the flame mode $0.50 \pm 0.012 \mu\text{g/ml}$ for the flameless mode, on a $20 \mu\text{l}$ sample.

9.3 *Minimum measurable*

9.3.1 Concentration in test sample

This is taken as twice the blank deviation, or instrument precision, whichever is larger. This is $0.1 \mu\text{g}$ per ml in the case of vanadium, in the flame mode and $0.0014 \mu\text{g}$ per ml in the flameless mode.

9.3.2 Concentration in air

This is based on a sample volume of 2,000 cubic metres, two aliquot discs 36mm in diameter. This minimum measurable concentration is 0.0250 micrograms of vanadium per cubic metre for the flame mode, regardless of whether glass or cellulose filters are used. The increased sensitivity of the graphite furnace reduces the minimum concentration to 0.0004 micrograms vanadium per cubic metre.

9.4 *Calculations*

The vanadium content of the test portion is expressed in micrograms per ml, 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 254mm:

Total exposed filter surface	=	$4.159 \times 10^4 \text{ mm}^2$
Areal test portion, 2 x 36mm discs	=	2.036 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 $\mu\text{g}/\text{m}^3$	=	T

$$T = \frac{(X_1 - X_2) \times 20.43 \times 25}{V}$$

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.

10. NOTES ON PROCEDURE

10.1 *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 microns, according to Lee (12.2).

10.2 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 760mm Hg.

10.3 Although the method described is normally 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 flow rates 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.

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

10.5 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.

10.6 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 and cadmium measured on high volume filters (12.3, 12.4, 12.5). 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 (12.6).

10.7 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 in this series where two calibration curves are given for the flame and one for the furnace (12.7).

10.8 *Operating conditions, flame*

The optimum operating conditions are as given:

Wavelength	=	318.4nm
Spectral band width	=	0.7nm
Source	=	Hollow cathode
Source current	=	As recommended
Oxidant	=	Nitrous oxide
Fuel	=	Acetylene
Flame	=	Reducing, red
Sensitivity	=	2.2µg/ml for 1% absorption

Change acetylene container before cylinder pressure drops below 50psig.

10.9 *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	=	318.4nm
Sample size	=	20 microlitres
Purging gas	=	Argon or nitrogen

Thermal decomposition = drying (20sec, 100°C)
charring (25sec, 1,100°C)
atomizing (8sec, 2,500°C)

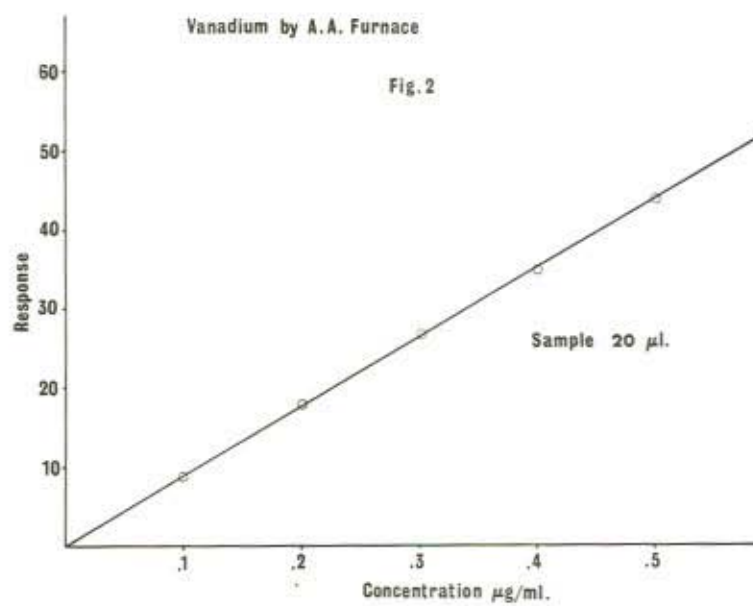
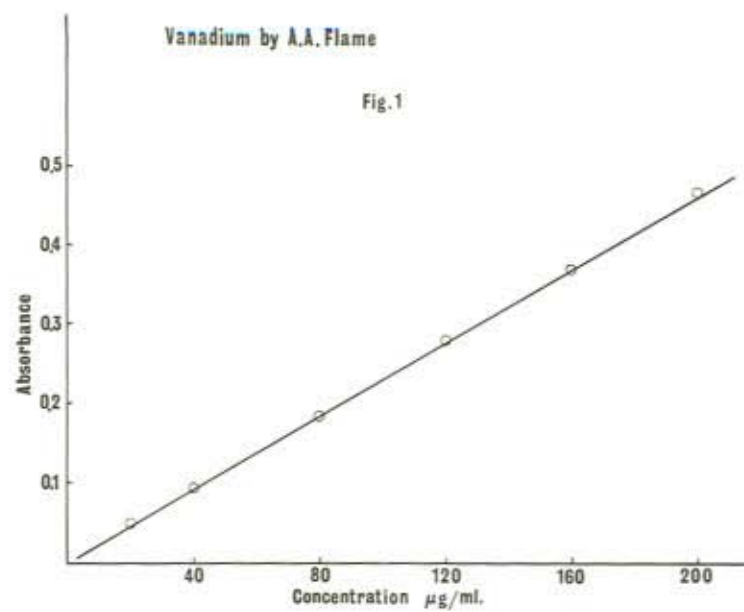
The use of a deuterium lamp background compensator is recommended.

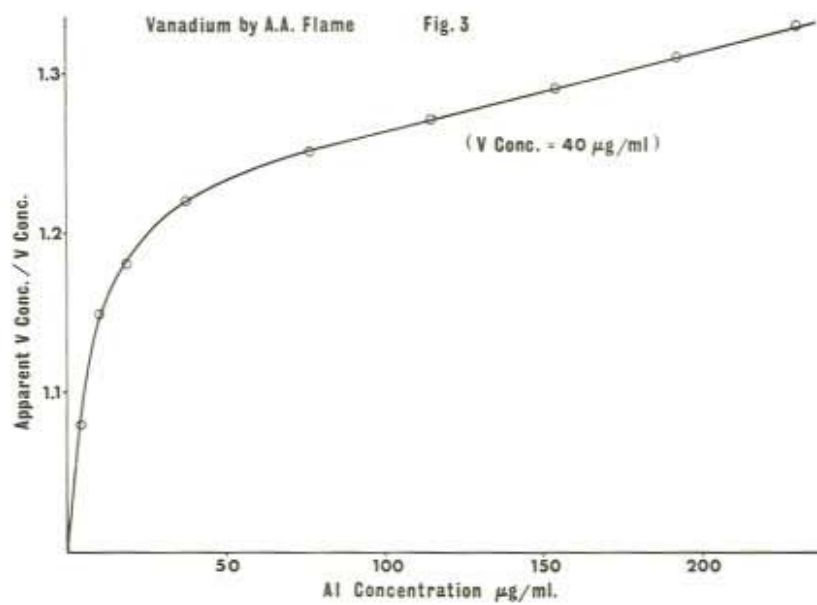
11. SCHEMATIC REPRESENTATION OF PROCEDURE

- 11.1 Draw laboratory air sample.
- 11.2 Cut areal test portion from exposed surface.
- 11.3 Digest and test portion.
- 11.4 Adjust digest to volume to give test sample.
- 11.5 Aspirate test portion into flame.
- 11.6 Alternatively, add test portion to furnace, as measured by microlitre pipette.

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- 12.7 Monkman, J. L. et al. Determination of Airborne Particulate Lead by Atomic Absorption Spectroscopy, see p.1.





Determination of Chromium in Airborne Particulates by Atomic Absorption Spectrophotometry

1. INTRODUCTION

Chromium is used principally in the manufacture of steel and other alloys or for chrome plating. Chromite ore, $\text{FeO} \cdot \text{Cr}_2\text{O}_3$, is the most important source of chromium. The ore, because of its high resistance to heat, is used to manufacture refractories. Chromium, finding its way into the air from the metallurgical industry, is probably in the trivalent or zero state. The toxicity of trivalent chromium has not been demonstrated (12.1). Chromium sesquioxide, an extremely insoluble compound, is probably the most abundant form of airborne trivalent chromium. Divalent chromium compounds are so easily oxidized that they cannot be expected in ambient air. Hexavalent chromium, in the air, probably originates from the production of chromates and dichromates by the chemical industry. The highly colored salts of chromium have been used as pigments and as mordants in the textile industry. Hexavalent chromium compounds are extremely toxic. Contact with the skin should be avoided and inhalation as dust can severely irritate the nasal mucosa and respiratory tract. Ingestion may be fatal.

Gravimetric titrimetric and colorimetric methods for chromium determination have been of limited use in air quality studies. The Weisz ring oven method has been used to measure the chromium content of particulates collected on sample tapes, with a detection limit of $0.15\mu\text{g}$ and a range of $0.3\text{--}1.0\mu\text{g}$. Atomic absorption methods have been widely used to determine chromium because of their sensitivity and speed.

In the method to be described, airborne particulates are collected by drawing the air through a filter. The filter, or an areal aliquot, with collected particulates, is digested to prepare a test sample. Preparation of this sample is simple and rapid. The aqueous acidic sample is scrutinized by an atomic absorption spectrophotometer at the wavelength 357.8nm and the chromium content is calculated by referring the absorbance found to the appropriate calibration curve. By the use of a graphite furnace, additional sensitivity may be achieved beyond that of the usual flame mode. The chromium values found are expressed in micrograms per cubic metre of air sampled. Some practical details of accuracy and precision obtainable will be found under the section "Expression of Results" (9).

2. FIELD OF APPLICATION

The method is applicable to the measurement of the levels of suspended particulate chromium found in either ambient or industrial atmospheres.

Based upon the flame mode, washed glass filters and a nominal air sample volume of 2,000 cubic metres, chromium is measurable to 0.015 micrograms per cubic metre. If the sample is taken on analytical grade cellulose, the minimum quantity measurable is decreased to a point which is dependent upon the chromium content of the reagents used to dissolve the cellulose. Analytical grade cellulose contains less than 0.25 micrograms Cr per aliquot disc 36mm in diameter. As levels of chromium in urban air are low and since the possibility of contamination from chromium-containing metals in the laboratory may be rather high, every care must be taken to ensure that the chromium being measured is actually due to the air sample.

3. 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.

4. REACTIONS

The most important reactions relate to the complete dissolution of the particulate sample in acid 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. If a portion of the airborne chromium to be measured is in the form of Cr_2O_3 , some difficulty may be encountered in solubilizing all the chromium. Using the test sample preparation method outlined in 7.3, only a total of from 5-10 μg of Cr_2O_3 will be solubilized per digestion. This represents a maximum of 0.1 μg per cubic metre, a figure approximately six times the "normal" value expected for the chromium content of urban air.

5. REAGENTS

5.1 *Air, compressed*

In pressure cylinders or online.

5.2 *Acetylene, compressed*

In pressure cylinders.

5.3 *Glass filters*

Commercially available material is exhaustively washed prior to use; in size 203 by 254mm.

5.4 *Cellulose filters*

Ashless, acid washed, analytical grade, in size 203 by 254.

5.5 *Water*

Distilled at least twice from glass or quartz.

5.6 *Hydrofluoric acid*

49%. Reagent grade, in polyethylene containers.

5.7 *Nitric acid*

71%. Reagent grade.

5.8 *Standard solutions of chromium*

Dissolve the amount of chromium salt equivalent to 1 gram of chromium in water and dilute to 1 litre with water. 1ml of this stock solution contains 1,000 micrograms of chromium, Cr. Both trivalent and hexavalent chromium have been found to give equal response using the atomic absorption conditions described in 10.8 and 10.9.

6. APPARATUS

6.1 *Spectrophotometer, atomic absorption*

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

6.2 *Pipettes, glass*

Millilitre capacities, "to deliver".

6.3 *Volumetric flasks*

Borosilicate with ground glass stopper, 25ml capacity.

6.4 *Bottles, polyethylene*

Screw cap, "leak free" for storage of test samples, 30ml capacity.

6.5 *Beakers, teflon*

Griffin form, 100ml capacity.

6.6 *Beakers, borosilicate*

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

6.7 *Hot plate*

Electric, with temperature control, thermostat, and ceramic heating surface.

6.8 *Büchner funnel*

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

6.9 *Graphite furnace*

One suitable instrument is available commercially to the Massmann design.

6.10 *Strip chart recorder*

To display and record the response from the furnace.

6.11 *Pipettes, automatic*

Eppendorf design, with capacities 10 to 100 microlitres.

7. SAMPLING AND SAMPLES

7.1 *Air Sampling*

Draw air through the filter at a flow rate between 1.13 and 1.60 cubic metres per minute if high volume sampling is used. An appropriate time period is 24 hours when glass fibre filters are used. The resistance to flow offered by the cellulose filters is much greater than for glass and an appreciably smaller total volume will be taken with cellulose for a similar sampling time. Calculate and record the total volume of air sampled in cubic metres, as the product of mean flow rate and time.

7.2 *Preparation of the laboratory sample*

As soon as possible after the sampling has been completed, the filter should be carefully removed from the filter head, placed in an envelope with complete documentation and transmitted to the laboratory in the quickest reliable way.

7.3 Preparation of test sample

Cut areal aliquots from the exposed surface of a filter using a circular metal punch. A suitable punch is one made of a material which will not release chromium during the punching process, a criterion which may be determined by establishing the chromium content of filter blanks having no contact with metal during preparation. 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 (5.6). 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 (5.7) 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 (6.6). Transfer to a 25 ml volumetric flask (6.3). 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 (6.4). 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.

8. PROCEDURE

8.1 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 REPLACED.

8.2 Test Portions

8.2.1 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.

8.2.2 Test portions, furnace

Measure and insert in the furnace, test portions of 10 to 100 microlitres of the test sample using an automatic pipette (6.11).

8.3 Calibration Curves

8.3.1 Calibration curves, flame

Using "to deliver" pipettes, prepare known concentrations of chromium by dilution of standard solution (5.8) with filter blank solution prepared as in (7.3) from unexposed filter to cover the range of 1.0 to 5.0 micrograms of chromium per ml. Install in the spectrophotometer and align, if necessary, the hollow cathode source for chromium. Set the wavelength of the monochromator at 357.8nm. Using nitrous oxide-acetylene flame, aspirate an unmeasured portion of each dilute standard chromium solution for 10 seconds (8.2.1). At the same time, aspirate into the flame a solution of filter blank. From the instrumental responses obtained, prepare a calibration curve of absorbance against concentration of chromium, in micrograms per ml. Such a representative calibration curve is given in Figure 1, with the corresponding curve for chromium standards in water (Page 111).

8.3.2 Calibration curves, furnace

By means of an automatic pipette with polyethylene tip, place identical microlitre volumes of the dilute standard chromium 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 0.2 to 1.0 nanogram chromium in steps of 0.2 nanogram; 0.01 to 0.05 micrograms per ml for a 20 microlitre volume. Prepare a calibration curve of response, in arbitrary units, against concentration of chromium in micrograms per ml. Such a representative calibration curve is given in Figure 2. Preparation of standards in filter blank is not necessary for furnace work as the matrix effects observed do not occur with the furnace.

8.4 Determination

8.4.1 Determination, flame

Set the wavelength of the monochromator at 357.8nm. Observing conditions of 8.2.1 and 8.3.1, 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 chromium in all the unknown test samples which can be accommodated to the wavelength 357.8nm and the corresponding calibration curve.

8.4.2 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 chromium present in the test sample by referring to the appropriate calibration curve, such as, for example, Figure 2 (Page 111).

8.5 *Blank Tests*

8.5.1 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.

8.5.2 Filter blanks

In parallel with the preparation of calibration curves and test samples, prepare areal test portions from unexposed filter media as described in 7.3. Measure chromium and express blanks in micrograms of chromium per ml.

9. EXPRESSION OF RESULTS

9.1 *Blanks*

The glass filter blank value for any element may vary considerably with the batch. This has been very noticeable with manganese, beryllium and chromium. For this reason, filter blanks should be determined regularly. It should be noted, however, that the filter blank values for chromium within a given batch of filters are extremely uniform. If, where possible, filters from a known batch are used, detection limits of the method may be lowered.

Extreme care must be taken to isolate and eliminate chromium 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.

9.2 *Instrumental precision*

This is defined as the standard deviation of a number of replicate determinations and is expressed in micrograms per ml. Typical precisions for ten repeat determinations on standard samples are 2.00 ± 0.01 micrograms per ml for the flame mode, against 0.05 ± 0.0008 micrograms per ml for the flameless mode using a 20 μ l sample.

9.3 *Minimum measurable*

9.3.1 Concentration in test sample

This is taken as twice the blank deviation, or instrument precision, whichever is larger. This is 0.06 micrograms per ml in the case of chromium, using the flame mode and glass fibre filters. For the flameless mode the blank deviation is the determining factor and this may vary for different filter batches. Minimum measurable may be as high as 0.04 micrograms per ml for glass fibre filters.

9.3.2 Concentration in air

This is based upon a sample volume of 2,000 cubic metres and two aliquot discs 36mm in diameter. The minimum measurable concentration is 0.015 micrograms per cubic metre for the flame mode and 0.010 micrograms per cubic metre for the flameless mode. These values are lower for cellulose filters as explained in Section 2.

9.4 Calculations

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

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

Total exposed filter surface	=	$4.159 \times 10^4 \text{ mm}^2$
Areal test portion, 2 x 36mm discs	=	$2,036 \text{ mm}^2$
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
Chromium concentration, in $\mu\text{g}/\text{m}^3$	=	T

$$T = \frac{(X_1 - X_2) \times 20.43 \times 25}{V}$$

10. NOTES ON PROCEDURE

10.1 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 chromium is almost all between 0.6 and 4.5 microns according to Lee (12.2).

10.2 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 760mm Hg.

10.3 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 flow rates, 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.

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

10.5 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 made of brass is used. No chromium contamination has been found to result from its use.

10.6 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 (12.3, 12.4, 12.5) and cadmium (one exception was noted in 12.5) 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 (12.6).

10.7 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 in this series where two calibration curves are given for the flame and one for the furnace (12.7).

10.8 *Operating conditions, flame*

The optimum operating conditions are as given:

Wavelength	=	357.8nm
Spectral band width	=	1.4nm
Source	=	Hollow cathode
Source current	=	As recommended
Oxidant	=	Nitrous oxide
Fuel	=	Acetylene
Flame	=	Reducing, rich red
Sensitivity	=	0.026 μ g/ml for 1% absorption

Change acetylene cylinder before pressure drops to 50 psig.

10.9 Graphite furnace

The calibration curve for the flame mode obeys Beer's Law up to 8.0 micrograms of chromium per ml of test sample as illustrated by Figure 1. A representative curve for chromium, measured by the graphite furnace, is given in Figure 2, which shows greatly increased sensitivity over the flame.

Furnace operating conditions:

Wavelength	=	357.8nm
Sample size	=	20 microlitres
Purging gas	=	Argon or nitrogen
Thermal composition	=	drying (15sec, 100°C) charring (15sec, 230°C) atomizing (15sec, 2,400°)

The use of a deuterium lamp background compensator is recommended.

10.10 Most chromium salts, likely to be found in ambient air, will be soluble if the digestion procedure in 8.3 is followed. Complete recovery of added trivalent ($\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$) and hexavalent (K_2CrO_4) chromium has been demonstrated in our laboratory. Chromium compounds which may be difficult to dissolve are chromium sesquioxide (Cr_2O_3), elemental chromium (Cr), chromium arsenide (CrAs), chromium nitride (CrN) and chromium silicide (Cr_3Si_2). The solubility of Cr_2O_3 has been discussed in Section 4. CrAs , CrN , Cr_3Si_2 and elemental chromium are not likely to be found in ambient air. Elemental chromium is not found in nature and airborne chromium in the vicinity of electroplating plants or producers of chromium alloys will likely be in the oxide form. The fluorides of chromium, CrF_2 and CrF_3 , have melting points above 1,000° and loss of chromium during digestion of the glass fibre filter with hydrofluoric acid does not occur.

10.11 The following is an outline of the method for washing glass fibre filters prior to use.

At present, the expedient used is to attempt to leach out the impurities by means of boiling distilled water. A special Büchner funnel, rectangular rather than circular, was constructed of polypropylene by Bel Art Products, Pequannock, New Jersey. This was designed to hold one box of 8 x 10 Gelman A filters. To improve the access of the hot distilled water, spacers are placed in the pile at intervals of every 10 filters. The pile of filters is covered with boiling water, allowed to steep for 30 minutes and the water is withdrawn by suction. This process is repeated. The washed glass filters are allowed to air dry in a dust-free location.

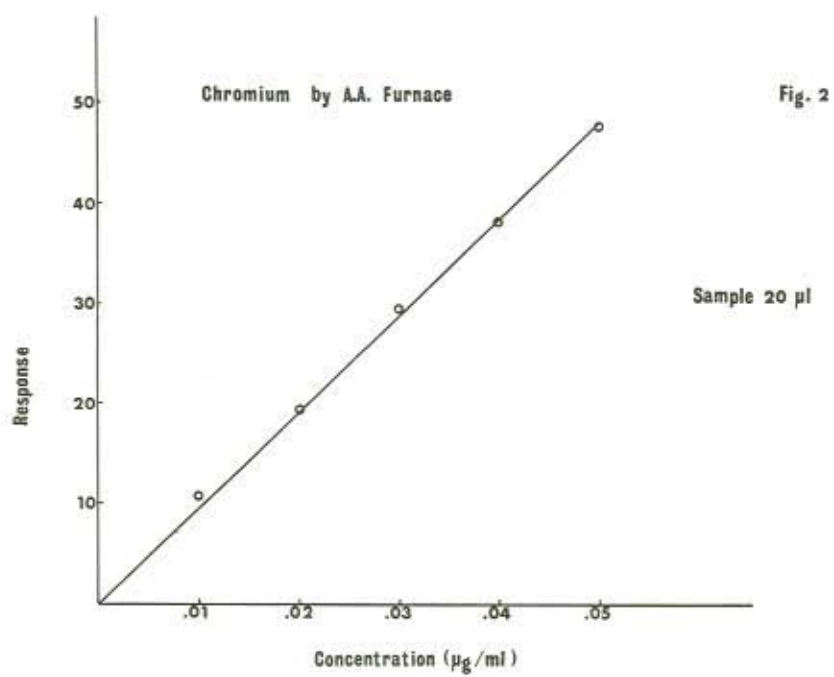
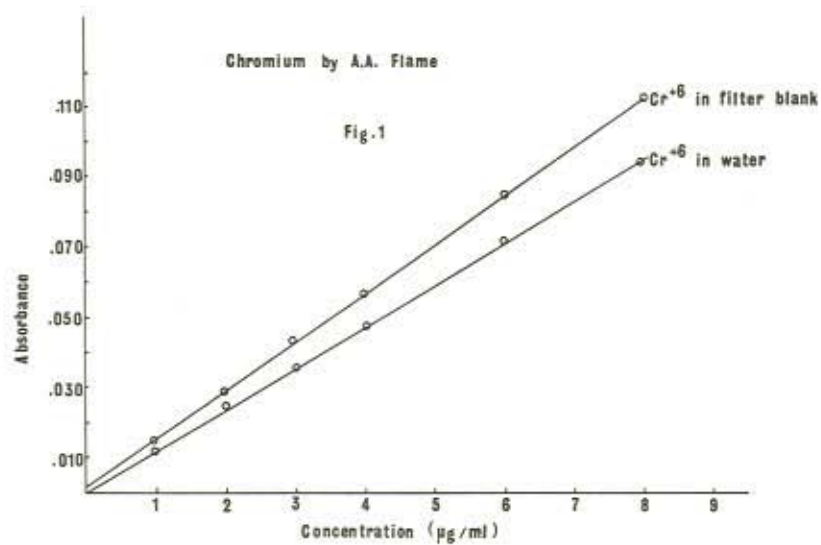
10.12 With the use of flameless atomic absorption, equipped with a background corrector, it was shown that chromium is present in the acid digest of glass fibre filters having no previous contact with metal. Two 36mm discs were shown to contain from 1.64 to 3.35 micrograms of chromium of which 0.3 micrograms were derived from the reagents used to dissolve the two discs. The variability of the chromium content of the glass fibre was less if filters from the same batch were used.

11. SCHEMATIC REPRESENTATION OF PROCEDURE

- 11.1 Draw laboratory air sample.
- 11.2 Cut area test portion from exposed surface.
- 11.3 Digest areal test portion.
- 11.4 Adjust digest to volume to give test sample.
- 11.5 Aspirate test portion into flame.
- 11.6 Or, add test portion to furnace, measured by microlitre pipette.

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Determination of Airborne Particulate Hexavalent Chromium

1. INTRODUCTION

Collection procedures are given for soluble and insoluble chromium compounds. Analytical procedures are given for the determination of hexavalent chromium, total chromium and a fusion technique for chromium ore.

Chromium, finding its way into the air from metallurgical operations, is probably in the trivalent or zero state. The toxicity of trivalent chromium has not been demonstrated. The most abundant form of airborne trivalent chromium is probably chromium sesquioxide, an extremely insoluble compound. Divalent chromium compounds are so easily oxidized that they cannot exist in ambient air. Hexavalent chromium in the air probably originates from the production of chromates and dichromates by the chemical industry. Hexavalent chromium compounds are extremely toxic.

2. FIELD OF APPLICATION

The method is applicable to the measurement of the levels of suspended particulate chromium found in either ambient or industrial atmospheres. Since levels of chromium in urban air are low and the possibility of contamination from chromium containing metals in the laboratory may be rather high, care must be taken to ensure that the chromium being measured is actually due to the air sample.

3. PRINCIPLE

In the method to be described, airborne particulates are collected by drawing air through dry filter media such as a silver membrane filter, by collection on acetate membrane filters, or by the use of an electrostatic precipitator. Suitably prepared samples or aliquots are assayed using *s*-diphenylcarbazide.

4. REACTIONS

The most important reactions relate to the complete dissolution of the particulate sample 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. If a portion of the airborne chromium to be measured is in the form of chromium trioxide, Cr_2O_3 , some difficulty may be encountered in solubilizing all the chromium.

5. REAGENTS

5.1 *Triple-distilled water*

Redistill double-distilled water in an all borosilicate-glass still. Triple-distilled water is used in all steps following the oxidation of chromium to the hexavalent form to avoid possible reduction which might occur from impurities in double-distilled water. In all subsequent references to the use of water, triple-distilled water is meant.

5.2 *Nitric acid, concentrated, redistilled*

Redistill reagent grade acid in an all borosilicate-glass still. Discard the first 50ml distillate.

5.3 *Sodium hydroxide solution, 0.1 N*

Dissolve 4gm sodium hydroxide in water and make up to 1 litre with water.

5.4 *Potassium permanganate, 0.1 N*

Dissolve 3.16gm reagent grade potassium permanganate in water and make up to 1 litre with water.

5.5 *Sodium azide, 5%*

Dissolve 5gm sodium azide in water and make up to 100ml with water. Store in refrigerator. Shelf life: 1 month.

5.6 *Sulfuric acid, 5 N*

Cautiously add 139ml concentrated sulfuric acid to about 800ml water. Add dilute (0.5%) potassium permanganate solution to the hot acid solution until a very faint pink color appears. Cool and dilute to 1 litre with water.

5.7 *Sulfuric acid, 2 N*

Cautiously add 54ml concentrated sulfuric acid to about 800ml water. Add dilute (0.5%) potassium permanganate solution to the hot acid solution until a very faint pink color appears. Cool and dilute to 1 litre with water.

5.8 *Sulfuric acid, 0.5 N*

Cautiously add 13.9ml concentrated sulfuric acid to about 800ml water. Add dilute (0.5%) potassium permanganate solution to the hot acid solution until a very faint pink color appears. Cool and dilute to 1 litre with water.

5.9 Sodium dihydrogen phosphate buffer, 4 M

Dissolve 138.01gm sodium dihydrogen phosphate monohydrate in water and make up to 250ml with water.

5.10 Sodium bisulfate, 40%

Dissolve 20gm sodium bisulfate in water and make up to 50ml with water.

5.11 *s*-Diphenylcarbazide

Dissolve 10.0gm of phthalic anhydride in 175ml redistilled 95% ethyl alcohol, warming to effect solution. Cool, add a solution of 0.625gm of *s*-diphenylcarbazide in about 50ml of redistilled 95% ethyl alcohol, and make up to 250ml with the ethyl alcohol. Keep in a brown bottle in the refrigerator. This solution is stable for several months.

5.12 Stock hexavalent chromium solution (1ml $\approx$ 80 μ g Cr)

Dissolve 0.2263gm reagent grade potassium dichromate in water and make up to 1 litre with water.

5.13 Standard hexavalent chromium solution (1ml $\approx$ 2 μ g Cr)

Dilute 5ml of stock hexavalent chromium solution to 200ml with water. Prepare fresh daily.

5.14 Standard trivalent chromium solution (1ml $\approx$ 2 μ g Cr)

Pipet 5ml of stock hexavalent chromium solution into a Phillips beaker. Reduce the chromium by adding about 15mg sodium sulfite and 0.5ml of nitric acid. Evaporate to dryness gently as strong heating may reoxidize the chromium. Add 0.5ml nitric acid and again evaporate to dryness gently to destroy any excess sulfite. Dissolve in 1ml nitric acid with warming and make up to 200ml with water. Test a portion for the absence of hexavalent chromium by adding some diphenylcarbazide. This solution is stable for 2-3 days.

5.15 Wash acid

Carefully add 50ml concentrated nitric acid to 150ml concentrated hydrochloric acid, mix, and add to 200ml water.

5.16 8-Quinolinol, 1.0% in chloroform

Dissolve 10.0gm 8-hydroxyquinoline in 1 litre chloroform. Store in dark bottle in refrigerator. Shelf life: 3 months.

6. APPARATUS

6.1 *Spectrophotometer*

Able to cover the visible range including wavelength 540nm and with wavelength scale reading to 0.1nm.

6.2 *Laboratory shaking machine*

As available commercially.

6.3 *Muffle furnace*

As available commercially, preferably with temperature programming.

6.4 *Platinum crucibles*

10ml capacity or larger.

6.5 *Steam bath*

Usual laboratory equipment.

6.6 *Glassware*

Beakers, Griffin and Phillips type, volumetric flasks, and cuvettes for spectrophotometer.

6.7 *Silver membrane filters*

These are available from Selas Flotronics, Spring House, Pennsylvania, U.S.A.

6.8 *Acetate membrane filters*

These are available from Millipore Corporation, Bedford, Mass., U.S.A.

6.9 *Electrostatic precipitator*

A suitable instrument is available from Mine Safety Appliances, Pittsburgh, Pennsylvania.

7. SAMPLING AND SAMPLES

7.1 *Soluble chromium*

Particulates should be collected with silver membrane filters. A minimum air volume of 5 cubic feet should be sampled. The silver membrane filters may be submitted to the laboratory in field monitors or in plastic petri dishes. Blank filters should be submitted in duplicate.

7.2 *Insoluble chromium*

Particulates should be collected with acetate membrane filters or by electrostatic precipitator. A minimum volume of 5 cubic feet should be sampled. For submission to the laboratory, seal the ends of the collecting tubes before shipment. Plastic caps or aluminium foil may be used. Acetate membrane filters may be submitted in the field monitors or in plastic petri dishes. Submit filter or tube blanks in duplicate.

8. SAMPLE PREPARATION

8.1 *Glassware (used throughout these procedures)*

Glassware should be thoroughly cleaned with a detergent solution, rinsed well with tap water and then rinsed with "wash acid", followed by tap water and then triple-distilled water. To avoid contamination, chromic-sulfuric acid mixture is not used. When necessary, alcoholic potassium hydroxide is used to remove grease.

8.2 *Silver membrane filters*

Place silver membrane filter in clean wide-mouthed plastic bottle. Add 25ml of 0.1 N sodium hydroxide solution and fasten lid securely on bottle. Place on shaking machine and shake gently for 20 minutes. Extract blank filters with each batch of samples. Transfer extracts into a 50ml volumetric flask and make to volume with 0.1 N sodium hydroxide. Proceed with analysis as directed in Section 9.1.

8.3 *Electrostatic precipitator tubes or acetate membrane filters*

8.3.1 *Chromium compounds (other than chromium ore)*

Dissolve acetate membrane filter in nitric acid in a 250ml Phillips beaker and add 0.25ml of 40% sodium bisulfate solution. Evaporate to dryness at a moderate heat and ash by adding small amounts of nitric acid until a white ash is obtained. Rinse electrostatic precipitator tubes into clean beakers with 2% nitric acid solution containing a wetting agent. Transfer sample to 250ml Phillips beaker and add 0.25ml of 40% sodium bisulfate solution as for acetate filters. Ash with small amounts of nitric acid at a moderate heat until a white ash is obtained. In either case dissolve ash in redistilled nitric

acid, and add 10ml water. Heat to dissolve if necessary. If there is no residue, make to volume of 25ml. Take out aliquot of 20ml and evaporate to dryness on steam bath. Proceed with analysis as directed in Section 9.2. If an insoluble residue is present, filter through Whatman 42 filter paper. Rinse until acid-free with distilled water. Combine filtrate with washings and set aside to be combined later with the leach of melt from the fusion of the residue. Place filter containing residue in platinum crucible. Place uncovered crucible in muffle furnace and slowly raise temperature to 550°C. Hold at this temperature until filter paper is completely ashed. To the residue add 0.05-0.01gm fusion mixture (4 parts by weight magnesium oxide mixed with 1 part by weight sodium carbonate, which is dried and stored in an air-tight container). Stir the residue into fusion mixture with glass rod. Cover crucible and place in muffle furnace. Raise temperature slowly to 900°C and hold there for 1-2 hours. Dissolve cooled melt with hydrochloric acid and water and heat if necessary. Examine leach for unfused particles. If present, they must be filtered and fused again. Filter leachings and combine with acid soluble portions (filtrate plus washings) and adjust to volume of 25ml. Take aliquot of 20ml and evaporate to dryness on the steam bath. Proceed with analysis as directed in Section 9.2.

8.3.2 Chromium ore

8.3.2.1 ORE SAMPLES COLLECTED ON ELECTROSTATIC PRECIPITATOR TUBES

Rinse electrostatic precipitator tubes with 10% hydrochloric acid solution. It may be necessary to rinse the tubes with alcohol to facilitate the acid rinse. If alcohol is used, then it must be evaporated from the acid solution before proceeding. Filter through Whatman 42 filter paper and wash with distilled water until acid-free. Combine filtrate with washing and set aside to be combined later with the leach of the melt from the fusion of the residue. Place filter containing residue in platinum crucible. Place uncovered crucible in muffle furnace and slowly raise temperature to 550°C. Hold at this temperature until filter paper is completely ashed. Proceed with fusion of residue as described in Section 8.3.2.3.

8.3.2.2 ORE SAMPLES COLLECTED ON ACETATE MEMBRANE FILTERS

Wrap filter in a Whatman 42 filter paper and place in a platinum crucible. Place uncovered crucible in muffle furnace and slowly raise temperature to 550°C. Hold at this temperature until filter papers are completely ashed. Proceed with fusion of residue as described in Section 8.3.2.3.

8.3.2.3 FUSION

To the residue add 0.2-0.3gm fusion mixture (4 parts by weight magnesium oxide mixed with 1 part by weight sodium carbonate which is dried and

stored in an air-tight bottle). Stir residue into fusion mixture with glass rod. Cover crucible, and place in muffle furnace. Raise temperature slowly to 900°C and hold there for 1-2 hours. Dissolve cooled melt with hydrochloric acid and water and heat if necessary. Examine leach for unfused particles. If present, they must be filtered and fused again. Combine leachings with acid soluble portions of ore samples and make to 100ml volume (or greater if necessary). Take aliquot for analysis and evaporate to dryness on steam bath. Proceed with analysis as described in Section 9.2.

9. PROCEDURE

9.1 *Silver membrane filters*

9.1.1 Hexavalent chromium

Place 20ml aliquot of the alkaline extract in a small Erlenmeyer flask. At the same time initiate a reagent blank of 20ml of 0.1 N sodium hydroxide. To both sample and blank, add 1.4ml 5 N sulphuric acid. Centrifuge if necessary, or filter through an alundum crucible. Decant supernatant into a 25ml volumetric flask. Add 1ml s-diphenylcarbazide reagent. Mix and make to volume with water. Read absorbance of the solution at 540nm on the spectrophotometer using 1cm cells, against the reagent blank. Colors too intense to read may be diluted to larger volumes using reagents in proportion, or alternatively, take the remaining 5ml aliquot of the original alkaline extract and proceed as described for the 20ml aliquot, except for adding 1.1ml 5 N sulfuric acid instead of 1.4ml.

9.1.2 Total soluble chromium

The following procedure gives a measure of both hexavalent (9.1.1) and trivalent chromium compounds. Place a second 20ml aliquot of the 0.1 N sodium hydroxide extracts in a 125ml Phillips beaker. At the same time, initiate a reagent blank of 20ml of 0.1 N sodium hydroxide. To both sample and blank, add 1.4ml 5 N sulfuric acid. Add 0.5ml of 0.1 N potassium permanganate solution. Cover with a watch glass and heat on a steam bath for 20 minutes. If necessary, add more permanganate to maintain a slight pink color. Decolorize the permanganate by adding 5% sodium azide at the rate of 1 drop every 10 seconds, swirling after each drop. Three to five drops are usually required. Use sufficient azide to destroy any brownish tint of manganese dioxide but avoid excess. Solution may still be colored if interfering substances are present. Promptly cool to room temperature in a tray of cold water. Centrifuge, if necessary, or filter through an alumina crucible. If the supernatant is distinctly colored, extract at pH 4 with 8-quinolinol in chloroform. If solution is only slightly colored, proceed as follows. Decant supernatant into a 25ml volumetric flask. Add 1ml s-diphenylcarbazide reagent. Mix and allow 1 minute for color development. Add 2.5ml of 4 M phosphate buffer. Mix and dilute to mark with water.

Read absorbance (or transmittance) of the solution at 540nm using 1cm cells and against the reagent blank as reference. Colors too intense to read may be diluted to larger volumes using reagents in proportion or by taking the remaining 5ml aliquot of the original alkaline extracts and proceeding as described for the 20ml aliquot, adding, however, 1.1ml of 5 N sulfuric acid instead of 1.4ml.

9.2 *Electrostatic precipitator tubes or acetate membrane filters*

Samples taken by EP or acetate membrane filters are handled as follows:

9.2.1 Hexavalent chromium

No separate determination is made for hexavalent chromium because the ashing and/or fusion steps in sample preparation may alter the valence.

9.2.2 Total chromium

Total chromium is the sum of hexavalent and trivalent forms. Dissolve the residue, obtained from evaporation in the steam bath, in a few ml of water, adding a drop or two of 0.5 N sulfuric acid if necessary. The solution should be approximately pH 7 at this point. Adjust pH with 0.1 N sodium hydroxide in 0.1 N sulfuric acid as required. Initiate a reagent blank of 10ml water. Add 10ml 0.5 N sulfuric acid and 0.5ml 0.1 N potassium permanganate solution. Cover with watch glass and heat in a steam bath for 20 minutes. If necessary, add more permanganate to maintain a slight pink color. Decolorize the permanganate by adding 5% sodium azide at a rate of 1 drop every 10 seconds swirling after each drop. Three to five drops is usually required. Use sufficient azide to destroy any brownish tint of manganese dioxide but avoid excess. Solution may still be colored if interfering substances are present. Promptly cool to room temperature in a tray of cold water. Centrifuge, if necessary, or filter through an alundum crucible. If supernatant is distinctly colored, extract at pH 4 with 8-quinolinol in chloroform. If solution is only slightly colored continue as follows. Decant supernatant into a 25ml volumetric flask. Add 1ml s-diphenylcarbazide reagent. Mix and allow one minute for color development. Add 2.5ml of 4 M phosphate buffer. Mix and dilute to mark with water. Read absorbance (or percent transmittance) of the solution at 540nm using 1cm cells. For reference, use the reagent blank. Colors too intense to read may be diluted to larger volumes using reagents in proportion or take the remaining 5ml aliquot and proceed as described for the 20ml aliquot.

9.3 *Calibration*

9.3.1 Silver membrane samples

9.3.1.1 HEXAVALENT CHROMIUM

Standards in the range of 0 to 40 μ g hexavalent Cr are prepared by adding 0-1-2-5-10-20ml of standard hexavalent chromium solution, 2 μ g/ml, to a series of 25ml volumetric flasks. Add 10ml 0.2 N sodium hydroxide and proceed as directed in 9.1.1. Prepare a standard curve.

9.3.1.2 TOTAL SOLUBLE CHROMIUM

Standards in the range of 0 to 40 μ g chromium are prepared by adding 0-1-2-5-10-20ml of standard trivalent chromium solution; 2 μ g/ml, to a series of 125ml Phillips beakers. Add 10ml 0.2 N sodium hydroxide. Proceed as directed in 9.1.2. Prepare a standard curve.

9.3.2 Electrostatic samples or acetate membrane filters

Standards in the range 0 to 40 μ g chromium are prepared by adding 0-1-2-5-10-20ml of standard trivalent chromium solution, 2 μ g/ml, to a series of small flasks. Add 0.25ml of 40% sodium bisulfate and evaporate to dryness. Proceed as directed under 9.2.2. Prepare a standard curve.

10. EXPRESSION OF RESULTS

10.1 After determining the amount of chromium in the sample or aliquot, from the standard curve, obtain the net amount by subtracting any reading obtained for the blanks. Make allowance for total number of aliquots taken.

10.2 *Silver membrane filters*

Report results as follows: Milligrams chromium trioxide (CrO₃) per cubic metre of air, calculated from hexavalent chromium and milligram soluble total chromium (Cr³ + Cr⁶) per cubic metre of air.

10.3 *Electrostatic samples or acetate membrane filters*

EP tubes or acetate membrane filters should be reported as milligrams total chromium (Cr³ + Cr⁶) per cubic metre of air.

11. NOTES ON PROCEDURE

11.1 *Collection efficiencies*

It is believed that the collection of chromium compounds is quantitative using any of the three sampling methods described.

11.2 *Temperature and pressure*

The effect of these sampling variables has been largely disregarded in the past. Since these factors have an effect upon the value of the measured air volume, it is recommended that these corrections be introduced routinely. There is increasing agreement, at the international level, that the standard conditions of temperature and pressure be 25°C and 760mm Hg.

11.3 *Solubility of chromium salts*

Chromium compounds that may be difficult to dissolve are chromium sesquioxide (Cr_2O_3) and elemental chromium (Cr). Elemental chromium is not found in nature and airborne chromium in the vicinity of electroplating or metallurgical plants is likely to be in the oxide form. The fluorides CrF_2 and CrF_3 have melting points above 1,000°C and loss of chromium during digestion of a glass fibre air sample does not occur on hydrofluoric acid digestion. Complete recovery of added trivalent ($\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$) and hexavalent (K_2CrO_4) chromium has been demonstrated (12.1).

11.4 *Interferences*

Iron and vanadium react with s-diphenylcarbazide to produce yellow-brown colors but the reaction is less sensitive than with chromium. Mercury produces a violet precipitate very slowly. Addition of a small amount of sodium chloride before s-diphenylcarbazide, forms mercuric chloride which eliminates this interference (12.2).

If a distinct color is noted after the oxidation of chromium to the hexavalent form, extraction with 8-quinolinol in chloroform at pH 4 will remove large amounts of iron, molybdenum and copper as well as vanadium. Extract excess 8-quinolinol with chloroform and then adjust pH to 1.0 with sulfuric acid before developing color. Nitrates are detrimental to the stability of the final color in 0.2 N sulfuric acid. It has been found that the interference can be greatly reduced by the addition of buffer to raise the pH to 2. The addition of the phosphate buffer before addition of the color reagent reduces the interference of iron. Fifteen minutes should be allowed for complete color development in this case.

It should hardly be necessary to mention that glassware should not be cleaned with the usual chromsulfuric acid cleaning solution. In fact, only new glassware should be used, which has never been cleaned in this way. Cleaning may be done with alcoholic potassium hydroxide or clean steam.

Care must be taken at all stages of sample preparation to avoid contamination from the stainless steel and chrome plated apparatus so omnipresent in modern laboratories.

11.3 *Sensitivity*

The limit of sensitivity should be so set that the analyst does not have to

work at the extreme lower portion of the calibration curve. A reasonable quantity is 1 microgram. Allowing for a 20/50 aliquot this would correspond to 0.02 milligrams chromium/m³ in a 5 cubic foot air sample.

12. REFERENCES

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Determination of Airborne Particulate Lead by the Ring Oven Technique

1. INTRODUCTION

Airborne particulates containing lead, will generally consist of the metal oxide, chlorides, bromides or chlorobromides. The major source of airborne lead in urban areas is the combustion of leaded gasoline. However, other sources such as manufacturing operations involving lead, use of pesticides, combustion of coal, incineration of refuse, etc., are also significant. The average ambient concentration of the metal in U.S. in 1964-65 was reported as $0.79\mu\text{g}/\text{m}^3$ with the maximum concentration found to be $8.60\mu\text{g}/\text{m}^3$ (9.1). Atomic absorption spectroscopy must be considered the method of choice in critical studies for the determination of lead in airborne particulates. Other methods such as neutron activation, emission spectroscopy, polarography and spectrophotometry may also be used depending on the availability of facilities and equipment and the sophistication of the technical staff. The ring oven technique is recommended for use where circumstances dictate against the use of the more sophisticated techniques. The ring oven technique serves admirably where field methods are required and it is also useful where only occasional samples are to be run and stand-by equipment and personnel are not available.

2. SCOPE AND FIELD OF APPLICATION

The ring oven method for determining traces of lead is well suited for the analysis of airborne particulate samples. It may be applied for determining the quality of the ambient air and it is particularly well suited for field surveys and spot checks. It is not recommended for routine monitoring because of the tedium involved in processing large numbers of samples.

3. PRINCIPLE

The method is based on the application of the ring oven technique to samples collected on filter media such as filter paper tapes. All processing of the collected sample and the determination itself is performed on the same filter paper. The lead in the dust sample is solubilized by treatment with ammonium acetate. The lead acetate pseudo salt formed is washed to the

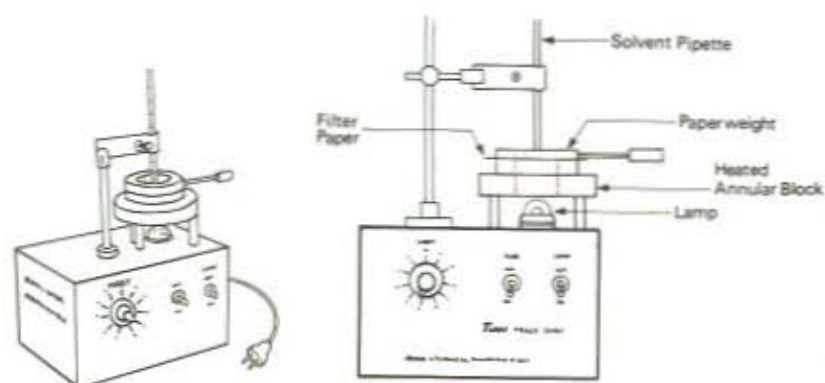


Figure 1. Ring Oven
(Arthur H. Thomas Co., Philadelphia, No. 9430-E10
"Trace Oven")

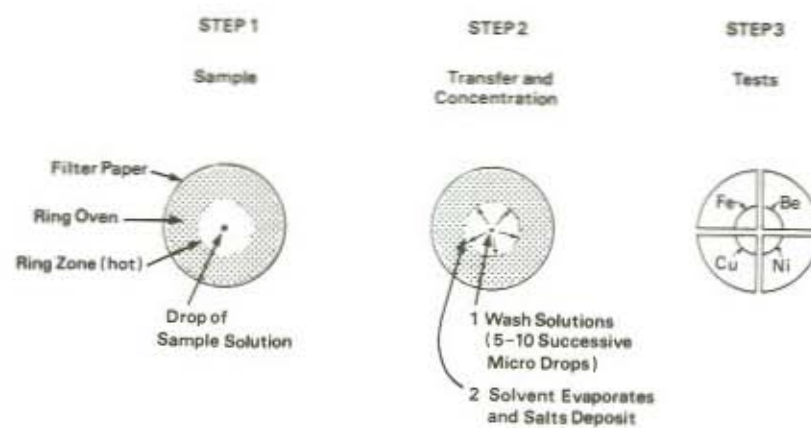


Figure 2.

heated ring zone where it is deposited in a sharply defined ring. Possible interferences due to other pollutants that may be present are masked by the addition of potassium cyanide. The determination of the lead present is performed colorimetrically by spraying dithizone which forms a brick-red colored complex. The excess reagent and other soluble species, are washed off with a wash solution containing cyanide and ammonia. The color so developed is compared against standards prepared in a similar manner.

The ring oven technique was introduced in 1954, as a means for conducting separations and sample concentrations on filter paper (9.2). The technique was a preliminary step for spot test analysis and was used also as a means to provide a complete qualitative scheme of separations and analysis for samples as small as a single drop of unknown (9.3). Recent work has demonstrated the effectiveness of the method for quantitative analyses. In this regard, it is particularly attractive as a means of determining significant metallic species present in samples of airborne particulates (9.4). Preferably, these samples are collected on filter paper tape, using sequential tape samplers. Alternatively, samples can be collected by means of high volume samplers and then a suitable areal aliquot of the sample is placed on filter paper and processed according to appropriate procedures. The ring oven methods are usually selective or even specific. The methods are very sensitive, applying generally to the microgram to nanogram range and accuracies are comparable with those of other standard trace analytical procedures. The general construction and appearance of a ring oven is shown in Figure 1. The steps involved in the preparation and analysis of an airborne particulate sample is summarized in Figure 2. It is often possible to perform four or even more separate determinations on one sample by simply cutting as many sectors of the ring as there are determinations to be performed (Figures 1 and 2, Page 124).

4. REAGENTS

4.1 *Standard lead solution*

Dissolve 1.000g of reagent grade lead metal in minimum amount of nitric acid and evaporate to dryness. Dissolve the residue in distilled water and dilute to 100ml. This gives a lead concentration of 10mg/ml. Suitable dilutions are made from this stock solution to obtain a lead concentration of 100 μ g/ml (or 0.1 μ g/ μ l).

4.2 *Dithizone*

Dissolve 0.005g of reagent grade diphenylthiocarbazone (dithizone) in 100ml of carbon tetrachloride.

4.3 *Ammonium acetate*

Dissolve 15g of reagent grade ammonium acetate in distilled water and dilute to 100ml.

4.4 *Potassium cyanide*

Dissolve 0.5g of reagent grade potassium cyanide in distilled water and dilute to 100ml.

4.5 *Sodium thiosulfate*

Dissolve 5g of reagent grade sodium thiosulfate in 100ml of distilled water.

4.6 *Cyanide wash solution*

Dissolve 0.2g of potassium cyanide in distilled water, add 2ml of concentrated ammonium hydroxide and dilute to 100ml with distilled water.

5. APPARATUS

5.1 *Ring oven*

Preferably with a 33mm ring and an adapter with 22mm ring size for use with 1in and ½in dust spot respectively.

5.2 Sequential tape sampler or high volume sampler.

5.3 Whatman 41 or Munktells 00 filter tapes and filter papers, lambda pipettes and capillary tubes.

6. SAMPLING

Sequential tape samplers are preferred for sample collection. Collect 0.5 to 2m³ of sample (depending on the level of the dust burden) on sample tape. Center dust spot on the ring oven.

In case of samples collected using a high volume sampler, areal samples of suitable sizes are punched out, and placed dust side down on the center of a filter paper and placed on the ring oven.

7. PROCEDURE

7.1 Add 30μl ammonium acetate (15%) and 30μl sodium thiosulfate (5%). Wash to ring zone with distilled water.

7.2 Add 30μl ammonium acetate (15%) and 30μl potassium cyanide (0.5%). Wash to ring zone with distilled water.

7.3 Remove tape from the ring oven and spray ring zone with dithizone (0.005% in carbon tetrachloride).

7.4 Remove excess dithizone by dipping tape in cyanide wash solution for 1 minute. Finally, wash tape in running tap water, press between filter papers to remove excess water. Air dry and compare with standards. Limit of detection: 0.05 μ g. Range: 0.1-1.0 μ g.

8. CALIBRATION AND EXPRESSION OF RESULTS

A set of standard rings, containing 0.1, 0.3, 0.7, 0.9 and 1.0 μ g of lead is prepared by adding appropriate amounts of a standard lead solution containing 100 μ g/ml (or 0.1 μ g/ μ l) of lead and following the above procedure 7. The estimation of an unknown is made by visual comparison of the intensities of the unknown ring to the standard rings.

In the case of the tape samples the μ g/ m^3 of lead is directly obtained by dividing the estimated microgram value by the volume of air sampled. For the high volume samples, it is given by the following relation:

$$\begin{aligned} \mu\text{g}/m^3 \text{ of lead} &= \text{Estimated } \mu\text{g} \\ &\times \frac{\text{Total area of high volume sample filter}}{\text{Area of disc}} \\ &\times \frac{1}{\text{Volume of air}} \end{aligned}$$

assuming uniform deposition of the pollutants on the filter. Very often this is not the case. Therefore, a suitable number of discs should be punched out of the large filter at random, each disc analyzed as above for the lead content and mean value of μ g/ m^3 should be calculated. The error for the determination varies between 10 to 20%.

9. REFERENCES

- 9.1 Cleaning Our Environment. The Chemical Basis for Action. A Report by American Chemical Society, 1969.
- 9.2 Weisz, H. *Mikrochim. Acta*, 1954, 140.
- 9.3 West, P. W., and Mukherjee, A. K. *Anal. Chem.*, 31, 947-50, (1959).
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Determination of Airborne Particulate Cadmium by the Ring Oven Technique

1. INTRODUCTION

Airborne particulates containing cadmium will generally consist of the metal oxide but occasionally cadmium sulfide or other cadmium salts may be present, depending on the sources. Manufacturing operations involving cadmium, serve as the principal pollutant sources. Cadmium is quite widely used in pigments, semi-conductors, storage batteries and in electroplating. The average concentration of the metal in ambient atmospheres was given as $0.002\mu\text{g}/\text{m}^3$ in 1964, with the maximum concentration found to be $0.350\mu\text{g}/\text{m}^3$ (9.1). The determination of cadmium in airborne particulate samples is best made using atomic absorption spectroscopy. Neutron activation, X-ray fluorescence, emission spectroscopy, polarography, and spectrophotometry may also be used depending on the availability of facilities and trained personnel. The ring oven technique serves admirably where field methods are required or where availability of facilities and technical staff imposes restrictions.

2. SCOPE AND FIELD OF APPLICATION

The ring oven method for determining traces of cadmium is well suited for the analysis of airborne particulate samples. It may be applied for determining the quality of the ambient air and it is particularly well suited for use in field surveys and spot checks. Where large numbers of samples must be processed, the method becomes tedious and this imposes some restriction on its use for routine studies.

3. PRINCIPLE

The method is based on the application of the ring oven technique to samples collected on filter media such as filter paper tapes. All processing of the collected sample and the determination itself is performed on the filter paper. The dust sample is processed by treatment with potassium cyanide which dissolves the cadmium as the cyano complex. The complex is washed to the heated ring zone where it is deposited as a sharply defined ring.

Possible interferences due to other pollutants that may be present are masked by the addition of sodium phosphate. The determination of the amount of cadmium present is performed by adding ferrous dipyrldyl iodide which forms a highly colored addition complex. After excess reagent is washed out, the color is compared against standards prepared in a similar manner.

The ring oven technique was introduced in 1954, as a means for conducting separations and sample concentrations on filter paper (9.2). The technique was a preliminary step for spot test analysis and was used also as a means to provide a complete qualitative scheme of separations and analysis for samples as small as a single drop of unknown (9.3). Recent work has demonstrated the effectiveness of the method for quantitative analyses. In this regard, it is particularly attractive as a means of determining significant metallic species present in samples of airborne particulates (9.4). Preferably, these samples are collected on filter paper tape, using sequential tape samplers. Alternatively, samples can be collected by means of high volume samplers and then a suitable areal aliquot of the sample is placed on filter paper and processed according to appropriate procedures. The ring oven methods are usually selective or even specific. The methods are very sensitive, applying generally to the microgram to nanogram range and accuracies are comparable with those of other standard trace analytical procedures. The general construction and appearance of a ring oven is shown in Figure 1. The steps involved in the preparation and analysis of an airborne particulate sample is summarized in Figure 2. It is often possible to perform four or even more separate determinations on one sample by simply cutting as many sectors of the ring as there are determinations to be performed (Figures 1 and 2, Page 124).

4. REAGENTS

4.1 *Standard cadmium solution*

Dissolve 1.00g of reagent grade cadmium metal in minimum amount of nitric acid, evaporate to dryness, dissolve the residue in distilled water and dilute to 100ml. This gives a cadmium solution of concentration 10mg/ml. Appropriate dilutions are made from this cadmium stock solution to obtain working standard solution of concentration 100 μ g/ml (or 0.1 μ g/ μ l).

4.2 *Ferrous dipyrldyl iodide solution*

0.25g α, α' -dipyrldyl and 0.146g ferrous sulfate are dissolved in 50ml of distilled water, 10g potassium iodide is added and after shaking vigorously for 3 minutes the solution is filtered. The $[\text{Fe}(\alpha, \alpha'\text{-dip})_3 \cdot \text{I}_2]$ solution contains excess iodide ions to accomplish the formation of the $[\text{CdI}_4]^-$ ions essential to the cadmium test. The reagent is stable for 5 days. If it becomes turbid on long standing, it should be filtered before use.

4.3 *Ammonium acetate*

Dissolve 15g of reagent grade ammonium acetate in 100ml of distilled water.

4.4 *Potassium cyanide*

Dissolve 0.5g of reagent grade potassium cyanide in 100ml of distilled water.

4.5 *Sodium phosphate*

Dissolve 10g of reagent grade trisodium phosphate in 100ml of distilled water.

4.6 *Ammonium hydroxide*

Use concentrated ammonium hydroxide solution. Approximately 58% solution.

5. APPARATUS

5.1 *Ring oven*

Preferably with a 33mm ring and an adapter of 22mm ring size for use with 1in and ½in dust spot respectively.

5.2 Sequential tape sampler or high volume sampler.

5.3 Whatman 41 or Munktells 00 filter tapes and filter papers, lambda pipettes and capillary tubes.

6. SAMPLING

Sequential tape samplers are preferred for sample collection. Collect 0.5 to 2m³ of sample (depending on the level of the dust burden) on sample tape. Center dust spot on the ring oven.

In case of samples collected using a high volume sampler, areal samples of suitable sizes are punched out and placed dust side down on the center of a filter paper and placed on the ring oven.

7. PROCEDURE

7.1 Add 30μl ammonium acetate (15%). Wash to ring zone with distilled water.

7.2 Add 30 μ l ammonium acetate (15%) and 30 μ l potassium cyanide (0.5%) wash to ring zone with distilled water.

7.3 Add 30 μ l of 10% trisodium phosphate and wash it to the ring zone.

7.4 Dry the ring and expose it to ammonia fumes.

7.5 Add the reagent (ferrous dipyridyliodide) to the ring using a capillary pipet. After ten seconds, wash in a jet of distilled water for 30 seconds. Dry in a current of warm air. Compare against standards. Limit of identification: 0.08 μ g. Optimum range: 0.1 μ g-2.0 μ g.

8. CALIBRATION AND EXPRESSION OF RESULTS

A set of standard rings, containing 0.1, 0.3, 0.7, 0.9 and 1.0 μ g of cadmium is prepared by adding appropriate amounts of a standard cadmium solution containing 100 μ g/ml (or 0.1 μ g/ μ l) of cadmium and following the above procedure 7. The estimation of an unknown is done by visual comparison of the intensities of the unknown ring to the standard rings.

In the case of the tape samples, the μ g/ m^3 of cadmium is directly obtained by dividing the estimated microgram value by the volume of air sampled. For the high volume samples, the μ g/ m^3 of cadmium is given by the following relation:

$$\begin{aligned} & \mu\text{g}/m^3 \text{ of Cd} = \text{Estimated } \mu\text{g} \\ & \times \frac{\text{Total area of high volume sample filter}}{\text{Area of disc}} \\ & \times \frac{1}{\text{Volume of air}} \end{aligned}$$

assuming uniform deposition of the pollutants on the filter. Very often this is not the case. Therefore, a suitable number of discs should be punched out of the large filter at random, each disc analyzed as above for the cadmium content and a mean value of μ g/ m^3 should be calculated. The error for the determination varies between 10 to 20%.

9. REFERENCES

- 9.1 Preliminary Air Pollution Survey of Cadmium and Its Compounds, A Literature review U.S. Dept. of HEW, Public Health Service, Consumer Protection and Environmental Health Service National Air Pollution Control Administration, Raleigh, North Carolina, 1969.

- 9.2 Weisz, H. *Mikrochim. Acta*, 1954, 140.
- 9.3 West, P. W. and Mukherjee, A. K. *Anal. Chem.*, **31**, 947-50, (1959).
- 9.4 Dharmarajan, V., and West, P. W. *Anal. Chim. Acta*, **57**, 469 (1971).

Determination of Airborne Particulate Zinc by the Ring Oven Technique

1. INTRODUCTION

Zinc is mainly present in airborne particulates as the metal oxide. Metallic Zn fumes, and some common salts of Zn have also been often detected in the airborne particulate samples. The primary sources of emissions of zinc compounds into the atmosphere are zinc, lead and copper smelting operations and possibly the incineration of zinc bearing materials. Zinc is very widely used in galvanising of iron and steel and also in producing alloys of brass. The average concentration of zinc in the ambient atmospheres in the U.S. in 1964-65 has been reported as $0.67\mu\text{g}/\text{m}^3$ and the maximum concentration was found to be $58.00\mu\text{g}/\text{m}^3$ (9.1). The best accepted method for the determination of zinc in airborne particulates is atomic absorption spectroscopy. Other instrumental methods such as emission spectroscopy, spectrophotometry, polarography, X-ray fluorescence and neutron activation can also be adapted for the determination of Zn in air samples depending upon the availability of trained personnel and the equipments. The ring oven methods serve admirably where field methods are required for occasional spot checks.

2. SCOPE AND FIELD OF APPLICATION

The ring oven method is sensitive and reliable. It is well suited for the determination of zinc in airborne particulate samples. It can be applied for determining the quality of ambient air and because the equipment is portable, it is particularly well suited for use in field surveys and spot checks. It is not recommended for routine analysis, where large numbers of samples must be processed, because of the tedium involved in sample processing.

3. PRINCIPLE

The method is based on the application of the ring oven technique to airborne particulate samples collected on filter media, such as filter paper tapes. The collection, dissolution of the desired metal species, concentration and the final colorimetric determination can all be performed on the same filter paper. The zinc in the dust sample is solubilized by addition of

potassium cyanide, whereby the zinc forms the soluble tetracyanate complex. The complex is washed to the ring zone with distilled water, and when the solvent evaporates, it is deposited in a sharply defined ring. A solution of ammonium thiosulfate is also washed to the ring zone. Possible interferences that may be present along with zinc in the dust sample, are masked by the presence of cyanide and thiosulfate ions. The determination of zinc present is performed colorimetrically by spraying the ring zone with a dilute solution of dithizone in carbontetrachloride. An intense purple red ring develops, which can be compared against standards prepared in a similar manner.

The ring oven technique was introduced in 1954, as a means of conducting separations and sample concentrations on filter paper (9.2). The technique was a preliminary step for spot test analysis and was used also as a means to provide a complete qualitative scheme of separations and analysis for samples as small as a single drop of unknown (9.3). Recent work has demonstrated the effectiveness of the method for quantitative analysis. In this regard, it is particularly attractive as a means of determining significant metallic species present in samples of airborne particulates (9.4). Preferably, these samples are collected on filter paper tape, using a sequential tape sampler. Alternatively, samples can be collected by means of high volume samples and then a suitable areal aliquot of the sample is placed on a filter paper and processed according to appropriate procedures. The ring oven methods are usually selective or even specific. The methods are very sensitive, applying generally to the microgram to nanogram range and accuracies are comparable with those of other standard trace analytical procedures. The general construction and appearance of a ring oven is shown in Figure 1. The steps involved in the preparation and analysis of an airborne particulate sample is summarized in Figure 2. It is often possible to perform four or even more separate determinations on one sample by simply cutting as many sectors of the ring as there are determinations to be performed (Figures 1 and 2, Page 124).

4. REAGENTS

4.1 *Standard zinc solution*

Dissolve 1.000g of reagent grade zinc metal in minimum amount of nitric acid and evaporate to dryness carefully. Dissolve the residue in distilled water and dilute to 100ml. This gives a zinc concentration of 10mg/ml. Suitable dilutions are made from this stock solution to obtain a zinc concentration of 100 μ g/ml.

4.2 *Dithizone*

Dissolve 0.005g of reagent grade diphenylthiocarbazone (dithizone) in 100ml of carbon tetrachloride.

4.3 *Ammonium acetate*

Dissolve 15g of reagent grade ammonium acetate in distilled water and dilute to 100ml. It has been our experience in this laboratory, that all reagent grade ammonium acetates commercially available are contaminated with traces of zinc, thereby, giving objectionably high blanks for zinc. The ammonium acetate solution can be purified by first extracting it with a 5ml aliquot of dithizone solution and then repeated extractions with only carbon tetrachloride to remove the traces of dithizone dissolved in the aqueous phase.

4.4 *Potassium cyanide*

Dissolve 0.5g of reagent grade potassium cyanide in distilled water and dilute to 100ml.

4.5 *Ammonium thiosulfate*

Dissolve 5g of reagent grade ammonium thiosulfate in distilled water and dilute to 100ml. This solution should also be purified as described in 4.3.

5. APPARATUS

5.1 *Ring oven*

Preferably with a 33mm ring zone and an adapter with 22mm ring size for use with 1in and ½in dust spot respectively.

5.2 Sequential tape sampler on high volume sampler.

5.3 Whatman 41 or Munktells 00 filter tapes and filter papers, lambda pipettes and capillary tubes.

6. SAMPLING

Sequential tape samplers are preferred for sample collection. Collect 0.5 to 2m³ of sample (depending on the level of the dust burden) on sample tape. Center dust spot on the ring oven.

In case of samples collected using a high volume sampler, areal samples of suitable sizes are punched out and placed dust side down on the center of a filter paper and placed on the ring oven.

7. PROCEDURE

7.1 Add 30μl of ammonium acetate (15%) and wash it to the ring zone with deionized water.

7.2 Add 30 μ l ammonium acetate (15%) and 30 μ l potassium cyanide (0.5%), and wash to the ring zone using ammonium thiosulfate (5%).

7.3 Remove tape from the ring oven and allow it to air dry. Add 30 μ l of dithizone solution allowing the reagent to diffuse to the ring zone by capillary action. Wash the reagent to the ring zone using only carbon tetrachloride. An intense purple-red ring develops. Compare against standard rings made by the same procedure. Limit of detection: 0.05 μ g. Range: 0.1-2.0 μ g.

8. CALIBRATION AND EXPRESSION OF RESULTS

A set of standard rings containing 0.1, 0.3, 0.7, 0.9, and 1.0 μ g of zinc is prepared by adding appropriate amounts of a standard zinc solution containing 100 μ g/ml (or 0.1 μ g/ μ l) of zinc and following the above procedure 7. The estimation of an unknown is made by visual comparison of the intensities of the unknown ring to the standard rings.

In the case of the tape samples, the μ g/m³ of zinc is directly obtained by dividing the estimated microgram value by the volume of air sampled. For the high volume samples, it is given by the following relation:

$$\begin{aligned} \mu\text{g/m}^3 \text{ of zinc} &= \text{Estimated } \mu\text{g} \\ &\times \frac{\text{Total area of high volume sample filter}}{\text{Area of disc}} \\ &\times \frac{1}{\text{Volume of air}} \end{aligned}$$

assuming uniform deposition of the pollutants on the filter. Very often, this is not the case. Therefore, a suitable number of discs should be punched out of the large filter at random, each disc analyzed as above for the zinc content and a mean value of μ g/m³ should be calculated. The error for the determination varies between 10 to 20%.

9. REFERENCES

- 9.1 Air Quality Data from the National Air Sampling Networks and Contributing State and Local Networks 1964-1965, U.S. Dept. of Health, Education and Welfare, 1966.
- 9.2 Weisz, H. *Mikrochim. Acta*, 140, (1954).
- 9.3 West, P. W. and Mukherjee, A. K. *Anal. Chem.*, 31, 947-950 (1959).
- 9.4 Dharmarajan, V. Ph.D. Dissertation, Louisiana State University, Baton Rouge, Louisiana, 70803, August, 1972.

Determination of Airborne Particulate Copper by the Ring Oven Technique

1. INTRODUCTION

Airborne particulates containing copper will generally consist of the metal oxide but occasionally other copper salts may be present depending on the sources. Manufacturing operations involving copper, serve as the principal sources of particulate copper in ambient air. Incineration of copper-bearing materials can also be an emission source. The average concentration of the metal in ambient atmospheres was given as $0.09\mu\text{g}/\text{m}^3$ in the U.S. in 1964-1965 and the maximum concentration reported during the same period was $10\mu\text{g}/\text{m}^3$ (9.1). Atomic absorption spectroscopy must be considered the method of choice in critical studies for the determination of copper in airborne particulates. Other methods such as neutron activation, emission spectroscopy, polarography and spectrophotometry may also be used, depending on the availability of facilities and equipment and the sophistication of the technical staff. The ring oven technique serves admirably where field methods are required or where circumstances dictate against the use of the more sophisticated techniques.

2. SCOPE AND FIELD OF APPLICATION

The ring oven method for determining traces of copper is well suited for the analysis of airborne particulate samples. It may be applied for determining the quality of the ambient air and it is particularly well suited for field surveys and spot checks. It is not recommended for routine monitoring because of the tedium involved in processing large numbers of samples.

3. PRINCIPLE

The method is based on the application of the ring oven technique to samples collected on filter media such as filter paper tapes. All processing of the collected sample and the determination itself is performed on the filter paper. The dust sample is processed by treatment with potassium cyanide which dissolves copper as the cyano complex. The complex is washed to the heated ring zone where it is deposited as a sharply defined ring. Possible interferences due to other pollutants that may be present are masked by cyanide and malonic acid which is present in the reagent itself. The

determination of the amount of copper present is performed by adding a saturated solution of dithiooxamide in ethanol containing 20% malonic acid which reacts specifically with copper to produce a dark greenish-black ring. The intensity of the sample ring is compared against a set of standards prepared in a similar manner.

The ring oven technique was introduced in 1954, as a means of conducting separations and sample concentrations on filter paper (9.2). The technique was a preliminary step for spot test analysis and was used also as a means to provide a complete qualitative scheme of separations and analysis for samples as small as a single drop of unknown (9.3). Recent work has demonstrated the effectiveness of the method for quantitative analyses. In this regard, it is particularly attractive as a means of determining significant metallic species present in samples of airborne particulates (9.4). Preferably, these samples are collected on filter paper tape, using sequential tape samplers. Alternatively, samples can be collected by means of high volume samplers and then a suitable areal aliquot of the sample is placed on filter paper and processed according to appropriate procedures. The ring oven methods are usually selective or even specific. The methods are very sensitive, applying generally to the microgram to nanogram range and accuracies are comparable with those of other standard trace analytical procedures. The general construction and appearance of a ring oven is shown in Figure 1. The steps involved in the preparation and analysis of an airborne particulate sample is summarized in Figure 2. It is often possible to perform four or even more separate determinations on one sample by simply cutting as many sectors of the ring as there are determinations to be performed (Figures 1 and 2, Page 124).

4. REAGENTS

4.1 *Standard copper solution*

Dissolve 1.000g of electrolytically pure copper metal in minimum amount of nitric acid and evaporate to dryness. Dissolve the residue in distilled water and dilute to 100ml. This gives a copper concentration of 10mg/ml. Suitable dilutions are made from this stock solution to obtain a copper concentration of 100 μ g/ml (or 0.1 μ g/ μ l).

4.2 *Dithiooxamide reagent*

Make a saturated solution of dithiooxamide in absolute ethanol and add enough malonic acid so that the final solution will have 20% w/v of malonic acid. All chemicals used should be reagent grade.

4.3 *Ammonium acetate*

Dissolve 15g of reagent grade ammonium acetate in distilled water and dilute to 100ml.

4.4 *Potassium cyanide*

Dissolve 0.5g of reagent grade potassium cyanide in distilled water and dilute to 100ml.

5. APPARATUS

5.1 *Ring oven*

Preferably with a 33mm ring and an adapter with 22mm ring size for use with 1in and ½in dust spot respectively.

5.2 Sequential tape sampler or high volume sampler.

5.3 Whatman 41 or Munktells 00 filter tapes and filter papers, lambda pipettes and capillary tubes.

6. SAMPLING

Sequential tape samplers are preferred for sample collection. Collect 0.5 to 2m³ of sample (depending on the level of the dust burden) on sample tape. Center dust spot on the ring oven.

In case of samples collected using a high volume sampler, areal samples of suitable sizes are punched out, and placed dust side down on the center of a filter paper and placed on the ring oven.

7. PROCEDURE

7.1 Add 30μl ammonium acetate (15%) and wash to the ring zone with distilled water.

7.2 Add 30μl ammonium acetate (15%) and 30μl potassium cyanide (0.5%). Wash to the ring zone with distilled water, remove from ring zone and let it dry at room temperature.

7.3 Spray ring zone with reagent (saturated solution of dithiooxamide in 20% malonic acid in ethanol). Dry in a jet of cold air. Compare against standards. Limit of identification: 0.08μg. Optimum range: 0.1-1.8μg.

8. CALIBRATION AND EXPRESSION OF RESULTS

A set of standard rings, containing 0.1, 0.3, 0.7, 0.9 and 1.0μg of copper is prepared by adding appropriate amounts of a standard copper solution

containing 100 $\mu\text{g}/\text{ml}$ (or 0.1 $\mu\text{g}/\mu\text{l}$) of copper and following the above procedure 7. The estimation of an unknown is made by visual comparison of the intensities of the unknown ring to the standard rings.

In the case of the tape samples the $\mu\text{g}/\text{m}^3$ of copper is directly obtained by dividing the estimated microgram value by the volume of air sampled. For the high volume samples, it is given by the following relation:

$$\begin{aligned} \mu\text{g}/\text{m}^3 \text{ of copper} &= \text{Estimated } \mu\text{g} \\ &\times \frac{\text{Total area of high volume sample filter}}{\text{Area of disc}} \\ &\times \frac{1}{\text{Volume of air}} \end{aligned}$$

assuming uniform deposition of the pollutants on the filter. Very often this is not the case. Therefore, a suitable number of discs should be punched out of the large filter at random, each disc analysed as above for the copper content and a mean value of $\mu\text{g}/\text{m}^3$ should be calculated. The error for the determination varies between 10 to 20%.

9. REFERENCES

- 9.1 Cleaning Our Environment, The Chemical Basis for Action. A report by the Subcommittee on Environmental Improvement, Committee on Chemistry and Public Affairs, American Chemical Society, Washington, D.C., 1969.
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- 9.4 West, P. W. and Pitombo, L. R. M. *Anal. Chim. Acta*, **37**, 374-8 (1967).

Determination of Airborne Particulate Nickel by Ring Oven Technique

1. INTRODUCTION

Airborne nickel particulates consist usually of the oxide or sulfide. Sources of nickel in the atmosphere include metallurgical operations, exhausts from engines burning nickel containing fuels, burning oil and coal and the incineration of various nickel containing products. Nickel concentrations in urban air in the United States was reported to average $0.032\mu\text{g}/\text{m}^3$ in 1964. The maximum concentration reported was $0.690\mu\text{g}/\text{m}^3$ (9.1). Atomic absorption spectroscopy must be considered the method of choice for critical studies of airborne particulates for nickel content. Other methods such as neutron activation, emission spectroscopy, polarography, and spectrophotometry may be used depending on the availability of facilities and equipment and the sophistication of the technical staff. The ring oven technique is recommended for use where circumstances dictate against the use of the more sophisticated techniques. The ring oven method compares favorably with other methods in regard to reliability and accuracy. It is more sensitive than most methods, it is far cheaper than other available methods, it is easy to apply and may be used for field studies. It is particularly effective for use where only occasional samples are to be run and stand-by equipment and personnel are not available.

2. SCOPE AND FIELD OF APPLICATION

The ring oven method for determining traces of nickel in samples of airborne particulates is suitable for determining ambient air quality for spot checks and field surveys. It is not recommended for routine monitoring because of the tedium involved in processing large numbers of samples. Reliable results can be obtained over the range of 0.1 to $1.0\mu\text{g}$ of nickel. Errors for the method should run no more than 10 to 20% and the method can be considered specific for nickel.

3. PRINCIPLE

The method is based on the use of the ring oven which serves as a means for completely processing the sample as collected, on a filter medium such as filter paper tape. The nickel in the dust species is made soluble by treatment

with cyanide. The resultant nickel complex is washed to the heated ring zone where it is deposited as a sharply defined ring. The nickel complex is treated with formaldehyde which releases (demasks) the nickel which is then determined colorimetrically by the addition of dimethylglyoxime and exposure to ammonia fumes.

The ring oven technique was introduced in 1954, as a means for conducting separations and sample concentrations on filter paper (9.2). The technique was a preliminary step for spot test analysis and was used also as a means to provide a complete qualitative scheme of separations and analysis for samples as small as a single drop of unknown (9.3). Recent work has demonstrated the effectiveness of the method for quantitative analyses. In this regard, it is particularly attractive as a means of determining significant metallic species present in samples of airborne particulates (9.4). Preferably, these samples are collected on filter paper tape, using sequential tape samplers. Alternatively, samples can be collected by means of high volume samplers and then a suitable areal aliquot of the sample is placed on filter paper and processed according to appropriate procedures. The ring oven methods are usually selective or even specific. The methods are very sensitive, applying generally to the microgram to nanogram range and accuracies are comparable with those of other standard trace analytical procedures. The general construction and appearance of a ring oven is shown in Figure 1. The steps involved in the preparation and analysis of an airborne particulate sample is summarized in Figure 2. It is often possible to perform four or even more separate determinations on one sample by simply cutting as many sectors of the ring as there are determinations to be performed (Figures 1 and 2, Page 124).

4. REAGENTS

4.1 *Standard nickel solution*

Dissolve 1.00g of reagent grade nickel metal in minimum amount of nitric acid and evaporate to dryness. Dissolve the residue in distilled water and dilute to 100ml. This gives a nickel concentration of 10mg/ml. Suitable dilutions are made from this stock solution to obtain a nickel concentration of 100 μ g/ml (or 0.1 μ g/ μ l).

4.2 *Dimethylglyoxime*

Dissolve 1g of reagent grade dimethylglyoxime in 100ml of absolute ethanol.

4.3 *Ammonium acetate*

Dissolve 15g of reagent grade ammonium acetate in distilled water and dilute to 100ml.

4.4 *Potassium cyanide*

Dissolve 0.5g of reagent grade potassium cyanide in distilled water and dilute to 100ml.

4.5 *Formaldehyde solution*

Use a reagent grade chemical of approximately 37%.

4.6 *Ammonium hydroxide*

Use a reagent grade concentrated solution of approximately 58%.

5. APPARATUS

5.1 *Ring oven*

Preferably with 33mm ring and an adapter of 22mm ring size for use with 1in and ½in dust spot.

5.2 Sequential tape sampler or high volume sampler.

5.3 Whatman 41 or Munktells 00 filter tapes and filter papers, lambda pipettes and capillary tubes.

6. SAMPLING

Sequential tape samplers are preferred for sample collection. Collect 0.5 to 2m³ of sample (depending on the level of the dust burden) on sample tape. Center dust spot on the ring oven.

In case of samples collected using a high volume sampler areal samples of suitable sizes are punched out, placed dust side down on the center of a filter paper and placed on the ring oven.

7. PROCEDURE

7.1 Add 30μl ammonium acetate (15%), wash to ring zone with distilled water.

7.2 Add 30μl ammonium acetate (15%) and 30μl potassium cyanide (0.5%), wash to ring zone with distilled water.

- 7.3 Expose ring zone to formaldehyde fumes for two minutes.
- 7.4 Add or spray dimethylglyoxime (1% in ethanol) to the test ring.
- 7.5 Expose to ammonia fumes. A brilliant red ring develops. Compare against standards.

8. CALIBRATION AND EXPRESSION OF RESULTS

A set of standard rings, containing 0.1, 0.3, 0.5, 0.7, 0.9, and 1.0 μg of nickel is prepared by adding appropriate amounts of a standard nickel solution containing 100 $\mu\text{g}/\text{ml}$ (or 0.1 $\mu\text{g}/\mu\text{l}$) of nickel, and following the above procedure 7. The estimation of an unknown is done by visual comparison of the intensities of the unknown ring to the standard rings.

In the case of the tape samples the $\mu\text{g}/\text{m}^3$ of nickel is directly obtained by dividing the estimated microgram value by the volume of air sampled. For the high volume samples it is given by the following relation:

$$\begin{aligned} \mu\text{g}/\text{m}^3 \text{ of Ni} &= \text{Estimated } \mu\text{g} \\ &\times \frac{\text{Total area of high volume sample filter}}{\text{Area of disc}} \\ &\times \frac{1}{\text{Volume of air}} \end{aligned}$$

assuming uniform deposition of the pollutants on the filter. Very often this is not the case. Therefore, a suitable number of discs should be punched out of the large filter at random, each disc analysed as above for the nickel content and a mean value of $\mu\text{g}/\text{m}^3$ should be reported. The error for the determination varies between 10 and 20%.

9. REFERENCES

- 9.1 Preliminary Air Pollution Survey of Nickel and Its Compounds. A Literature Review. U.S. Dept. of HEW, Public Health Service, Consumer Protection and Environmental Health Service National Air Pollution Control Administration, Raleigh, North Carolina, 1969.
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- 9.4 Dharmarajan, V. Ph.D. Dissertation, Louisiana State Univ., August, 1972.

Determination of Airborne Particulate Cobalt by the Ring Oven Technique

1. INTRODUCTION

Airborne particulates containing cobalt will generally consist of the metal oxide, but occasionally the sulfides and other salts of cobalt are also encountered. The major sources of cobalt in the atmosphere are the industrial processing plants engaged in the extraction, refining and alloying of the metal. The average ambient concentration of the metal in U.S. in 1964-65 was reported at less than $0.0005\mu\text{g}/\text{m}^3$ with the maximum concentration found to be $0.06\mu\text{g}/\text{m}^3$ (9.1). The determination of cobalt is best made using atomic absorption spectroscopy. Other methods such as spectrophotometry, emission spectroscopy and neutron activation may be used depending upon the availability of facilities and trained personnel. The ring oven method is recommended for use where circumstances dictate against the use of more sophisticated techniques. The ring oven technique serves admirably where field methods are required and it is also useful where only occasional samples are to be run and standby equipment and personnel are not available.

2. SCOPE AND FIELD OF APPLICATION

The ring oven method for determining traces of cobalt is well suited for the analysis of airborne particulate samples. It may be applied for determining the quality of the ambient air and it is particularly well suited for use in field surveys and spot checks. Where large numbers of samples must be processed the method becomes tedious and this imposes restrictions on its use for routine studies.

3. PRINCIPLE

The method is based on the application of the ring oven technique to samples collected on filter media, such as filter paper tapes. All processing of the collected sample and the determination itself is performed on the filter paper. The dust sample is processed by treatment with potassium cyanide which dissolves cobalt compounds by the formation of cyano complex. The complex is washed to the heated ring zone with deionized water, where it is deposited in a sharply defined ring. Possible interferences due to other pollutants that may be present are masked by the addition of disodium hydrogen phosphate. The determination of cobalt present is performed by adding 1-nitroso-2-naphthol in acetone to the ring zone.

Cobalt reacts with 1-nitroso-2-naphthol to form a brown colored product, the intensity of which can be compared against those of the standards.

The ring oven technique was introduced in 1954, as a means for conducting separations and sample concentrations on filter paper (9.2). The technique was a preliminary step for spot test analysis and was used also as a means to provide a complete qualitative scheme of separations and analysis for samples as small as a single drop of unknown (9.3). Recent work has demonstrated the effectiveness of the method for quantitative analyses. In this regard, it is particularly attractive as a means of determining significant metallic species present in samples of airborne particulates (9.4).

Preferably, these samples are collected on filter paper tape, using sequential tape samplers. Alternatively, samples can be collected by means of high volume samplers and then a suitable areal aliquot of the sample is placed on filter paper and processed according to appropriate procedures. The ring oven methods are usually selective or even specific. The methods are very sensitive, applying generally to the microgram to nanogram range and accuracies are comparable with those of other standard trace analytical procedures. The general construction and appearance of a ring oven are shown in Figure 1. The steps involved in the preparation and analysis of an airborne particulate sample are summarized in Figure 2. It is often possible to perform four or even more separate determinations on one sample by simply cutting as many sectors of the ring as there are determinations to be performed (Figures 1 and 2, Page 124).

4. REAGENTS

4.1 *Standard cobalt solution*

Dissolve 1.000g of reagent grade cobalt metal in minimum amount of nitric acid and dilute to 100ml with deionized water. This gives a concentration of 10mg/ml of cobalt. Suitable dilutions are made from this stock solution to obtain cobalt concentrations of 100 μ g/ml (or 0.1 μ g/ μ l).

4.2 *1-Nitroso-2-naphthol*

Dissolve 0.1g of reagent grade 1-nitroso-2-naphthol in 100ml of acetone.

4.3 *Ammonium acetate*

Dissolve 15g of reagent grade ammonium acetate in deionized water and dilute to 100ml.

4.4 *Potassium cyanide*

Dissolve 0.5g of reagent grade potassium cyanide in deionized water and dilute to 100ml.

4.5 *Disodium hydrogen phosphate*

Dissolve 5.0g of reagent grade disodium hydrogen phosphate in 100ml of deionized water.

5. APPARATUS

5.1 *Ring oven*

Preferably with a 33mm ring and an adapter with 22mm ring size for use with 1in and ½in dust spot respectively.

5.2 Sequential tape sampler or high volume sampler.

5.3 Whatman 41 or Munktells 00 filter tapes and filter papers, lambda pipettes and capillary tubes.

6. SAMPLING

Sequential tape samplers are preferred for sample collection. Collect 0.5 to 2m³ of sample (depending on the level of the dust burden) on sample tape. Center dust spot on the ring oven.

In case of samples collected using a high volume sampler, areal samples of suitable sizes are punched out, and placed dust side down on the center of a filter paper and placed on the ring oven.

7. PROCEDURE

7.1 Add 30μl ammonium acetate (15%) and wash to the ring zone with deionized water.

7.2 Add 30μl ammonium acetate (15%) and 30μl of potassium cyanide (0.5%) and wash to the ring zone with deionized water.

7.3 Expose the ring zone to ammonia fumes.

7.4 Add 30μl disodium hydrogen phosphate and wash to the ring zone with deionized water.

7.5 Add or spray with reagent (0.1% 1-nitroso-2-naphthol in acetone). Compare against standards. Limit of identification: 0.05μg. Range: 0.1-3.0μg.

8. CALIBRATION AND EXPRESSION OF RESULTS

A set of standard rings, containing 0.1, 0.3, 0.7, 0.9 and 1.0 μg cobalt is prepared by adding appropriate amounts of a standard cobalt solution containing 100 $\mu\text{g}/\text{ml}$ (or 0.1 $\mu\text{g}/\mu\text{l}$) of cobalt and following the above procedure 7. The estimation of an unknown is made by visual comparison of the intensities of the unknown ring to the standard rings.

In the case of the tape samples the $\mu\text{g}/\text{m}^3$ of cobalt is directly obtained by dividing the estimated microgram value by the volume of air sampled. For the high volume samples, it is given by the following relation:

$$\begin{aligned} & \mu\text{g}/\text{m}^3 \text{ of cobalt} = \text{Estimated } \mu\text{g} \\ & \times \frac{\text{Total area of high volume sample filter}}{\text{Area of disc}} \\ & \times \frac{1}{\text{Volume of air}} \end{aligned}$$

assuming uniform deposition of the pollutants on the filter. Very often this is not the case. Therefore, a suitable number of discs should be punched out of the large filter at random, each disc analyzed as above for the cobalt content and mean value of $\mu\text{g}/\text{m}^3$ should be calculated. The error for the determination varies between 10 to 20%.

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- 9.4 Dharmarajan, V. Ph.D. Dissertation, Louisiana State University, August, 1972.

Determination of Airborne Particulate Beryllium by the Ring Oven Technique

1. INTRODUCTION

Airborne particulates containing beryllium, will generally consist of the metal oxides, fluorides, chlorides, sulfates, and the metal fumes itself. Beryllium is commonly encountered as an atmospheric pollutant within the confines and in the proximity of industrial plants producing or using beryllium substances. The major sources of beryllium in the atmosphere are the industrial processing plants engaged in the extraction, refining, machining and alloying of the metal. The combustion of coals containing small quantities of beryllium and the proposed use of beryllium as an additive in rocket fuels, are also possible sources. The average ambient concentration of the metal in U.S. in 1964-65 was reported as less than $0.0005\mu\text{g}/\text{m}^3$ with the maximum concentration found to be $0.010\mu\text{g}/\text{m}^3$ (9.1). The determination of beryllium in airborne particulates is best made by using atomic absorption spectroscopy. Other methods such as fluorimetry, spectrophotometry, emission spectroscopy and neutron activation may be used depending upon the availability of facilities and trained personnel. The ring oven method is recommended for use where circumstances dictate against the use of more sophisticated techniques. The ring oven technique serves admirably where field methods are required and it is also useful where only occasional samples are to be run and standby equipment and personnel are not available.

2. SCOPE AND FIELD OF APPLICATION

The ring oven method for determining traces of beryllium is well suited for the analysis of airborne particulate samples. It may be applied for determining the quality of the ambient air and it is particularly well suited for use in field surveys and spot checks. Where large numbers of samples must be processed the method becomes tedious, and this imposes some restrictions on its use for routine studies.

3. PRINCIPLE

The method is based on the application of the ring oven technique to samples collected on filter media such as filter paper tapes. All processing of

the collected sample and the determination itself is performed on the filter paper. The dust sample is processed by treatment with ammonium acetate which dissolves beryllium compounds by the formation of polynuclear acetate complexes. The complex is washed to the heated ring zone with deionized water, where it is deposited in a sharply defined ring. Possible interferences due to other pollutants that may be present are masked by the addition of EDTA solution. The determination of beryllium present is performed by applying morin reagent to the ring zone and washing it in a bath containing ammonia and methanol. Beryllium reacts with morin to form a yellow-green fluorescent product, the intensity of which can be compared against those of standard under a UV lamp.

The ring oven technique was introduced in 1954, as a means for conducting separations and sample concentrations on filter paper (9.2). The technique was a preliminary step for spot test analysis and was used also as a means to provide a complete qualitative scheme of separations and analysis for samples as small as a single drop of unknown (9.3). Recent work has demonstrated the effectiveness of the method for quantitative analyses. In this regard, it is particularly attractive as a means of determining significant metallic species present in samples of airborne particulates (9.4).

Preferably, these samples are collected on filter paper tape, using sequential tape samplers. Alternatively, samples can be collected by means of high volume samplers and then a suitable areal aliquot of the sample is placed on filter paper and processed according to appropriate procedures. The ring oven methods are usually selective or even specific. The methods are very sensitive, applying generally to the microgram to nanogram range and accuracies are comparable with those of other standard trace analytical procedures. The general construction and appearance of a ring oven is shown in Figure 1. The steps involved in the preparation and analysis of an airborne particulate sample is summarized in Figure 2. It is often possible to perform four or even more separate determinations on one sample by simply cutting as many sectors of the ring as there are determinations to be performed (Figures 1 and 2, Page 124).

4. REAGENTS

4.1 *Standard beryllium solution*

Dissolve 10.4g of $\text{Be}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ in deionized water, acidify with 1ml of nitric acid and dilute to 50ml. This gives a solution containing 10mg/ml of beryllium. Suitable dilutions are made from this stock solution to obtain beryllium concentration of $10\mu\text{g/ml}$ (or $0.01\mu\text{g}/\mu\text{l}$).

4.2 *Morin reagent crayon*

Melt a mixture of 1.5g of paraffin wax and 3.5g of glyceryl stearate in a test tube. Slowly add 50mg of morin (3,5,7,2,4-pentahydroxyflavone) into the

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hot melt, with constant agitation until the morin dissolves in the melt and becomes homogenous and transparent. Pour the melt into a plastic straw. After the wax is cooled and solidified, it is exposed as needed, by peeling off the protective plastic, and used by rubbing its tip on the deposit in the ring.

4.3 *Ammonium acetate*

Dissolve 15g of reagent grade ammonium acetate in distilled water and dilute to 100ml.

4.4 *Potassium cyanide*

Dissolve 0.5g of reagent grade potassium cyanide in distilled water and dilute to 100ml.

4.5 *Ethylenediaminetetraacetic acid (EDTA)*

Dissolve 3g of reagent grade EDTA in 100ml of distilled water (0.1M).

4.6 *Ammonia – Methanol wash solution*

Mix 50ml of concentrated ammonium hydroxide (approximately 58%) and 50ml of methanol and stir well.

5. APPARATUS

5.1 *Ring oven*

Preferably with a 33mm ring and an adapter with 22mm ring size for use with 1in and ½in dust spot respectively.

5.2 Sequential tape sampler or high volume sampler.

5.3 Whatman 41 or Munktells 00 filter tapes and filter papers, lambda pipettes and capillary tubes.

6. SAMPLING

Sequential tape samplers are preferred for sample collection. Collect 0.5 to 2m³ of sample (depending on the level of the dust burden) on sample tape. Center dust spot on the ring oven.

In case of samples collected using a high volume sampler, areal samples of suitable sizes are punched out, and placed on the ring oven.

7. PROCEDURE

7.1 Add 30 μ l of ammonium acetate (15%) and wash to the ring zone with distilled water.

7.2 Add 30 μ l ammonium acetate (15%) and 30 μ l potassium cyanide (0.5%) and wash to the ring zone with distilled water.

7.3 Add 30 μ l of EDTA (0.1M) and wash to the ring zone with distilled water and dry it.

7.4 Place the dried paper on the oven surface and carefully apply a thin coating of the reagent crayon to the ring.

7.5 Soak the sector in the ammonia-methanol bath for about 5 minutes. Dry the sector in a current of warm air. Examine the intensity of fluorescence under a UV lamp and compare against standards prepared in a similar way. Limit of identification: 0.01 μ g. Range: 0.03-0.2 μ g.

8. CALIBRATION AND EXPRESSION OF RESULTS

A set of standard rings, containing 0.03, 0.05, 0.07, 0.09, 0.1 and 0.3 μ g of beryllium is prepared by adding appropriate amounts of a standard beryllium solution containing 10 μ g/ml (or 0.01 μ g/ μ l) of beryllium and following the above procedure 7. The estimation of an unknown is made by visual comparison of the fluorescent intensities of the unknown ring to the standard rings, under a UV lamp.

In the case of the tape samples, the μ g/m³ of beryllium is directly obtained by dividing the estimated microgram value by the volume of air sampled. For the high volume samples, it is given by the following relation:

$$\begin{aligned} & \mu\text{g/m}^3 \text{ of beryllium} = \text{Estimated } \mu\text{g} \\ & \times \frac{\text{Total area of high volume sample filter}}{\text{Area of disc}} \\ & \times \frac{1}{\text{Volume of air}} \end{aligned}$$

assuming uniform deposition of the pollutants on the filter. Very often this is not the case. Therefore, a suitable number of discs should be punched out of the large filter at random, each disc analyzed as above for the beryllium content and a mean value of μ g/m³ should be calculated. The error for the determination varies between 10 to 20%.

9. REFERENCES

- 9.1 Preliminary Air Pollution Survey of Beryllium and Its Compounds. A Literature Review. U.S. Dept. of HEW, Public Health Service, Consumer Protection and Environmental Health Service National Air Pollution Control Administration, Raleigh, North Carolina, 1969.
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Determination of Selenium in Air

1. INTRODUCTION

Selenium is an air pollutant that has been generally overlooked in spite of the fact that its distribution is widespread. It is significant that selenium is considered to be an essential trace element as well as a toxin and possible carcinogen. Unfortunately, most data available on the distribution and amount of selenium present in the atmosphere are misleading because of erroneous sampling methods used. Because selenium in the air probably exists as SeO_2 or H_2SeO_3 , it is important that the volatility of these species are kept in mind. These, and most other selenium compounds, are so volatile that filtration by means of high-volume samplers cannot be used because the selenium is vaporized as fast as it is collected. Sampling should be done by impingement into water or an aqueous solution of Na_2SO_3 , Na_2S or NaOH . If the one of the latter is used, care must be taken to assure that there is no appreciable amount of selenium in the chemicals used for preparing the trapping solution.

Selenium can be determined by neutron activation (11.1), atomic absorption (11.2), gas chromatography, spectrophotometry (11.3), fluorimetry (11.4, 5), ring oven technique (11.6), or by catalytic methods (11.7). Atomic absorption and gas chromatography hold promise. Fluorometric and spectrophotometric methods, based on the reaction of selenium with 1, 2-diamino compounds to form selenenols, are sensitive and selective but require meticulous technique. The synthesis of selenenols is the basis of the ring oven method and thus may be used for field studies.

The catalytic method, based on the catalysis of the sulfide reduction of methylene blue, is very sensitive and selective. It is rapid, uncomplicated and accurate.

2. SCOPE AND FIELD OF APPLICATION

The method can be used for any air samples for which a sensitive, rapid and simple determination is required. It measures total selenium regardless of oxidation state. It works satisfactorily in the range of 0.1 to $1.0\mu\text{g}$ of selenium. When present in excess of $10\mu\text{g}$, copper interferes seriously; however, this interference, can be eliminated as described in Section 10, Special Case.

3. PRINCIPLE

The determination is based on the catalytic effect of selenium in the reduction of methylene blue by sodium sulfide (11.8). Any deleterious

effect caused by polysulfide is readily overcome by the addition of sodium sulfite to form thiosulfate which, like sodium sulfite, has no interfering actions on the reduction of methylene blue. Formaldehyde is added to stabilize the blank. EDTA is used as a general masking agent for metal ions, and iron (III) has an inducing effect on the reaction. Triethanolamine is included because of its stabilizing effect on the blank, particularly in the presence of large concentrations of iron, perhaps by maintaining the higher oxidation state of iron.

4. REACTIONS

The decoloration of methylene blue by excess alkali sulfides is shown by the following equation:

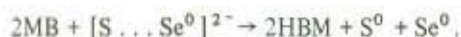


where MB represents methylene blue and HBM represents the leuco form of methylene blue.

The free sulfur is dissolved by formation of polysulfide:



When selenium is present, it is dissolved by alkali sulfides to form selenosulfides, $[\text{S} \dots \text{Se}^0]^{2-}$, which react with methylene blue according to the equation:



The elemental sulfur and selenium formed are redissolved by the excess of sodium sulfide with the formation of polysulfides or selenosulfides.

5. REAGENTS

5.1 *Stock selenium solution*

Dissolve 50mg of pure selenium metal in a minimum amount of concentrated nitric acid; boil gently to expel brown fumes and make up to 100ml with distilled water. This solution contains 0.5mg/ml of selenium. Standard working solutions are prepared by appropriate dilutions.

5.2 *Alkaline sodium sulfide solution*

Dissolve 2.4g of sodium sulfide, 2.4g of sodium sulfite and 4g of sodium hydroxide in 100ml of distilled water. This solution is stable for 2 days.

5.3 *Conditioner solution*

Prepare 1 litre of solution containing 25g of the disodium EDTA, 0.4g of ferric chloride, and 50ml of triethanolamine; dilute to the mark with distilled water.

5.4 *Methylene blue solution*

Prepare a 0.05% solution in distilled water.

5.5 *Formaldehyde solution*

Use reagent grade (assay 36-38%).

6. APPARATUS

6.1 *Absorber*

A standard all-glass, impinger, multi-jet or fritted bubbler may be used.

6.2 *Air pump*

It should be capable of maintaining an air pressure differential greater than 0.5 atmosphere at the desired flow rate.

6.3 *Air flowmeter*

This metering device should be capable of controlling and measuring flows with an accuracy of $\pm 2\%$.

7. SAMPLING

Use a glass bubbler containing 10ml of distilled water as the trapping solution. Keeping the flow rate constant, collect approximately 30 liters of sample. Measuring the time accurately, record the actual volume of air by multiplying the flow rate by the time in minutes.

8. PROCEDURE

Use a ml sample or an aliquot containing 0.1 to 1.0 μ g of selenium diluted to 10ml with distilled water. Transfer this solution to a test tube and add 5ml of conditioner solution, 5ml of formaldehyde solution, and 1ml of alkaline

sulfide solution. Mix the contents of the tube well after each addition. Add 2 drops of methylene blue solution and shake briefly to ensure complete mixing. By using a stop watch, measure the time required for complete decolorization of the methylene blue. Obtain the amount of selenium present from the calibration curve. To prepare blank solutions, substitute distilled water for the sample or solutions containing selenium.

9. CALIBRATION CURVE

From the stock selenium solution, prepare solutions containing 0.2, 0.4, 0.6, 0.8 and 1.0 μ g of selenium. Carry out the instructions in Section 9, Procedure. Plot the reciprocal of time (min^{-1}) versus micrograms of selenium. A linear curve is obtained.

10. SPECIAL CASE

If more than 10 μ g of copper are present, interference is observed. This can be eliminated by separating the copper from the selenium, by passing the solution through a 10cm column prepared by filling a 25ml buret with Dowex 50 W-X2, 50 to 100 mesh, cation exchange resin. The flow rate should be 0.5ml/min.

11. REFERENCES

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Determination of Particulate Arsenic in Air

1. INTRODUCTION

Arsenic compounds in environmental samples, have been measured in the past by variations of the Gutzeit procedure or the molybdenum blue method. Because the former procedure is not reproducible from one test run to another, much analytical effort is lost in the need for calibration of each run. The molybdenum blue method is seriously affected if the arsenic should not be pentavalent at the stage of color development. Serious errors are often occasioned by the interfering presence of oxidizing or reducing agents. The method of Vasak and Sedivec makes use of the arsine generation procedure, associated with the name Gutzeit. The arsine evolved is trapped in a silver organic reagent with stoichiometric replacement of the silver by arsenic (11.1). Dubois et al have worked out the optimum operating conditions for the method (11.2). The Vasak and Sedivec method, in various forms, is perhaps the most generally accepted method for arsenic and its compounds at present, being reliable, sensitive, accurate and fulfilling the requirements of a reference method (11.3).

There must be a clear understanding of the difficulties associated with the sampling of arsenic compounds, as found in air. Volatile compounds, such as arsine, will not be trapped on dry filter media. Particulate arsenic compounds, such as arsenic trioxide, have an appreciable volatility and this must be taken into account in any sampling procedure. Arsenic oxide, as a vapor in air, is in the form As_4O_6 and the saturated concentration at 25°C is calculated to be 0.6 micrograms per cubic metre (11.4). If this equilibrium concentration is comparable to or higher than the amount of particulate As_2O_3 , collected on the filter, the filtration sampling procedure is unsatisfactory. Sample collection and arsenic analysis, based upon such collection, cannot be accurate. The low concentrations of "arsenic oxide" in air 0.01 to $1.0\mu\text{g}/\text{m}^3$, reported by various monitoring networks, may well be indicative of poor collection efficiency (11.5).

The same remarks on sampling and volatility apply equally to compounds of mercury and selenium as well as the large number of polycyclic aromatic hydrocarbons found in air.

2. FIELD OF APPLICATION

The method is applicable to the measurement of arsenic compounds, as found in ambient air. The compound encountered most commonly is arsenic trioxide which may be in vapor or solid form, depending upon the concentration present and the temperature. The measuring range of the method is 1 to 15 micrograms of arsenic (As). As little as 0.1 micrograms per determination may be measured with accuracy.

3. PRINCIPLE

A prepared test sample containing the arsenic compound in aqueous solution is put through an arsine generation procedure, the arsenic evolved is trapped in a solution of silver diethyldithiocarbamate in pyridine. A pink to red color is developed in this reagent, the intensity being proportional to the amount of arsine reacting with the reagent. The absorbance is measured with a spectrophotometer and the amount of arsenic in the sample is read from the calibration curve (11.1, 11.2, 11.3).

4. REACTIONS

Arsenic or arsenic compounds, in the form of arsine, displace an equivalent amount of silver from silver diethyldithiocarbamate.

5. REAGENTS

5.1 *Silver diethyldithiocarbamate*

Reagent grade, very pale yellow in color. If yellowish brown, discard or purify by crystallization, at reduced temperature, in the absence of light.

5.2 *Pyridine*

Reagent grade. It is usually necessary to purify before use by passing through a column of activated alumina.

5.3 *Arsine absorbing solution*

Dissolve 0.5 gram silver diethyldithiocarbamate (5.1) in purified pyridine. Dilute with pyridine to final volume of 200ml. Store in an amber glass bottle, with ground stopper, in the refrigerator.

5.4 *Sulfuric acid*

Reagent grade, concentrated, low in arsenic.

5.5 *Hydrochloric acid*

Reagent grade, concentrated, low in arsenic.

5.6 *Potassium iodide 15%*

Dissolve 15 grams of reagent grade material in distilled water, making up solution to 100ml with distilled water.

5.7 Stannous chloride 40%

Dissolve 15 grams of reagent grade stannous chloride in 75ml of hydrochloric acid (5.5) making up solution to 100ml with concentrated hydrochloric acid.

5.8 Zinc metal

Granular, 20 mesh, low in arsenic.

5.9 Lead acetate solution

Dissolve 10 grams reagent grade lead acetate in distilled water and make up to 100ml with distilled water.

5.10 Nitric acid

Reagent grade, concentrated, low in arsenic.

5.11 Sodium hydroxide 40%

Dissolve 40 grams of reagent grade sodium hydroxide in distilled water and dilute to 100ml with distilled water.

5.12 Sodium hydroxide 1%

Dissolve 5 grams reagent grade sodium hydroxide in distilled water and dilute to 500ml with distilled water.

5.13 Stock arsenic solution

Dissolve 1.32 grams of reagent grade arsenic trioxide in 10ml of sodium hydroxide (5.13). Dilute to 1 litre with distilled water. One ml of this solution contains 1,000 micrograms arsenic, as the element.

5.14 Standard arsenic solution A

Dilute 10ml of arsenic solution (5.14) to 100ml with distilled water. 1ml = 100 μ g arsenic (As). Prepare fresh daily.

5.15 Standard arsenic solution B

Dilute 1ml of standard solution A (5.14) to 100ml with distilled water. 1ml = 1 μ g arsenic (As). Prepare fresh daily.

5.16 *Nonaq stopcock grease*

Water soluble stopcock grease. Available from Fisher Scientific Co., Pittsburgh, Pa.

6. APPARATUS

6.1 *Spectrophotometer*

Able to make measurements in the visible, between 500-600nm.

6.2 *Arsine generation apparatus*

An assembly in three pieces, as described (11.2).

6.3 *Support rack*

The above (6.2) should be firmly supported by the neck of the generation flask. A convenient arrangement has been described (11.6). This permits the installation of a complete generation assembly at every four inches of fume hood frontage.

6.4 *Hydrogen sulfide absorbent*

The scrubber section of the glassware (6.2) should contain a *dry* absorbent which might be glass beads, or cotton balls which have been soaked in lead acetate solution and dried (5.9).

6.5 *Miscellaneous*

Reagent bottles, volumetric flasks, cuvettes, etc., as required.

7. SAMPLING AND SAMPLES

7.1 *Air sampling*

The collection of arsine is being excluded from consideration, because it is a gaseous compound associated with specific industrial processes. In volatile compounds of arsenic such as arsenopyrite, FeAsS_2 may be sampled on dry filter media by conventional methods. Special attention has to be given to the sampling of arsenic trioxide because of its volatility at sampling temperatures (11.4). If the temperature at the time of sampling is very low and if the concentration of arsenic in the air being sampled is very high, one may consider the use of dry filter media. As a general rule, it is better to take samples by impinger in dilute aqueous sodium hydroxide.

7.2 Preparation of test sample

Inspect impinger sample to ensure absorbing solution is colorless, transparent and free from turbidity or suspended matter. If amount of arsenic is known to be high, take an aliquot of suitably low volume. If concentration of arsenic is known to be low, it may be necessary to use the entire sample, evaporating carefully to 30ml or less so that all sample may be used.

8. PROCEDURE

8.1 Calibration curve

Prepare a series of arsenic standards in the range of 0.15 micrograms of arsenic, in 1 or 2 microgram intervals, by pipetting suitable volumes of the arsenic working standard B into 125ml Erlenmeyer flasks. Add sufficient distilled water to each flask to make a total liquid volume of 35ml. To each flask add 5ml concentrated hydrochloric acid (5.5), 2ml of potassium iodide solution and 8 drops stannous chloride solution. Swirl the flasks and allow to stand for 15 minutes to ensure reduction of all arsenic to the trivalent form. Place 3ml of the silver absorbing reagent in the receiver and attach to scrubber tube with clamp. Lubricate the ground glass joint with Nonaq stopcock grease or water, add 3 grams of granulated zinc to flask and quickly connect scrubber joint to flask. At room temperature, arsine evolution is completed in about 30 minutes. Transfer the absorbing solution to a 1cm cell and measure the absorbance at 560nm against the absorbing reagent as reference. Prepare calibration curve by plotting measured absorbance against micrograms of arsenic taken.

8.2 Air samples

Treated in the same manner as standards. Depending upon the analyst's knowledge of the sampling conditions, all or part of the sample may be taken for analysis. From previous experience with known amounts of arsenic, the analyst will be able to decide from the color of the absorbing solution, whether the sample (or aliquot) taken is within the range of the calibration curve. Smaller or larger aliquots may be taken and the determination repeated.

9. EXPRESSION OF RESULTS

If a 25ml aliquot of a 50ml prepared sample is taken for analysis and 3ml of absorbing solution has been used, the arsenic concentration, in milligrams element per cubic metre is:

$$\frac{\text{Micrograms arsenic from curve XZ}}{1,000 \times \text{volume air in m}^3}$$

10. NOTES ON PROCEDURE

10.1 *Collection efficiencies*

Little is known about collection efficiencies of arsenic trioxide on dry filter media. It is known that collection is incomplete and for this reason airborne particulates containing arsenic compounds should be sampled by impinger, in dilute acid or alkali solutions (11.5).

10.2 *Temperature and pressure*

The effect of these sampling variables has been largely disregarded in the past. Since these factors have an effect upon the accuracy of the measured air volume, it is recommended that these corrections be introduced routinely. There is increasing agreement, at the international level, that the standard conditions of temperature and pressure should be 25°C and 760mm Hg.

11. REFERENCES

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- 11.2 Dubois, L., Teichman, T. and Monkman, J. L. Etude sur la Méthode de Vasak et Sedivec. *Mikrochim Acta*, 9, 3, 415, 1966.
- 11.3 Monkman, J. L. Determination of Arsenic in Air, Manual of Recommended Analytical Methods. American Conference of Governmental Industrial Hygienists, Cincinnati, 1958.
- 11.4 Lao, R. C., Teichman, T. and Dubois, L. Efficiency of Collection of Arsenic Trioxide in High Volume Sampling. In press. I. Science. Total Environment, November 1973.
- 11.5 Air Quality Data, US Public Health Service, Cincinnati, 1966.
- 11.6 Monkman, J. L. Versatile Laboratory Clips. *Chemist-Analyst*, 5 (2), 54, 1962.

Determination of Mercury in Air

1. SCOPE

This method is applicable to elementary mercury present in air.

2. PRINCIPLES OF METHOD

Elementary mercury is taken up from the air by amalgamating with silver gauze. When heated, the mercury liberated is then flushed through the cell of a spectrophotometer.

3. REAGENTS

3.1 *Silver gauze*

The material used consisted of 24 wires per cm, each wire having a diameter of 0.165mm, the total surface area, per sq cm of gauze, being approximately 2.45 sq cm.

3.2 Magnesium perchlorate.

3.3 Mercury.

3.4 *Palladium chloride absorbent*

20 grams of 10-20 mesh firebrick is impregnated with a solution of 0.5 grams of palladium chloride and dried.

4. APPARATUS

4.1 Spectrophotometer with gas cell.

4.2 Recorder.

4.3 Gastight syringe, graduated in μl , 1,000 μl total capacity.

4.4 Silver absorber, see Figure 1. A piece of silver gauze, forming a double cylinder, mounted in a finger condenser of borosilicate glass or quartz (Page 168).

4.5 Muffle furnace.

5. PROCEDURE

5.1 *Sampling of air*

Before using the absorber, heat activate by means of a gas micro burner, meanwhile purging the silver element with a constant flow of clean air. Cool the absorber and seal the side arms with PVC tubing; the absorber can be stored for 10-20 days before sampling. Connect the absorber to the portable air sampler as shown in Figure 2. Direct the side arms downwards to avoid intake of dust. Start the pump, the flow rate of which has been adjusted to the desired value by calibration with a rotameter. Allow a known volume of air to pass through the silver absorber (Page 169).

Note: The sampling interval of the pump can be operated by a clockwork timer. If simultaneous sampling with several absorbers is desired, this can be effected by means of radio assemblies with remote control operation.

If the concentration of mercury in the air is high, the sampling method can be modified, see Figure 3. Draw air, purified by passage through a palladium chloride scrubber, through the silver absorber by means of a portable air sampler. Collect the air sample in an airtight disposable polyethylene syringe and inject into the air stream (Page 170).

5.2 *Determination of mercury*

Connect the silver absorber to the spectrophotometer (setting 253.7nm) as shown in Figure 4. Start the pump so that air flows into the apparatus through a palladium chloride scrubber, then through the silver absorber and then to the gas cell. Adjust the flow to 1,500ml/min. With the use of heating tape, heat the cell to 80°C continuously in order to prevent condensation of water or mercury vapour. Heat the silver absorber to 800°C so that the mercury vapour is transferred to the gas cell. The light absorption is registered by the recorder. Alternatively, by the use of a digital integrator as used in gas chromatography, offscale readings may be avoided. The accuracy of the measurement can be increased considerably, using the integrator, and the capacity of the silver absorber can be increased from 10ng to 100ng mercury.

5.3 *Calibration*

Store mercury metal in pyrex reagent bottles, fitted with serum caps, in a thermostated water bath, maintained at $\pm 0.1^\circ\text{C}$. After equilibration,

withdraw a volume of saturated mercury vapour by a gastight syringe. Inject the mercury vapour into the apparatus through the septum situated in front of the silver absorber. Heat the absorber to 800°C and record the light absorption. Cool the silver absorber and inject a new volume of mercury vapour. Convert the peak heights obtained into absorbance units. Plot the absorbance against mercury content to obtain a calibration graph. Convert the peak height obtained from the sample and determine the mercury content from the calibration graph.

6. EXPRESSION OF RESULTS

Using the spectrophotometer-integrator assembly it is possible to measure as little as 0.1 nanogram of mercury. Some values of precision obtainable are presented below:

<i>Mercury nanograms</i>	<i>Precision percent</i>
4.0	±2.29
1.0	±2.50
0.4	±6.90

MERCURY VAPOUR SAMPLER

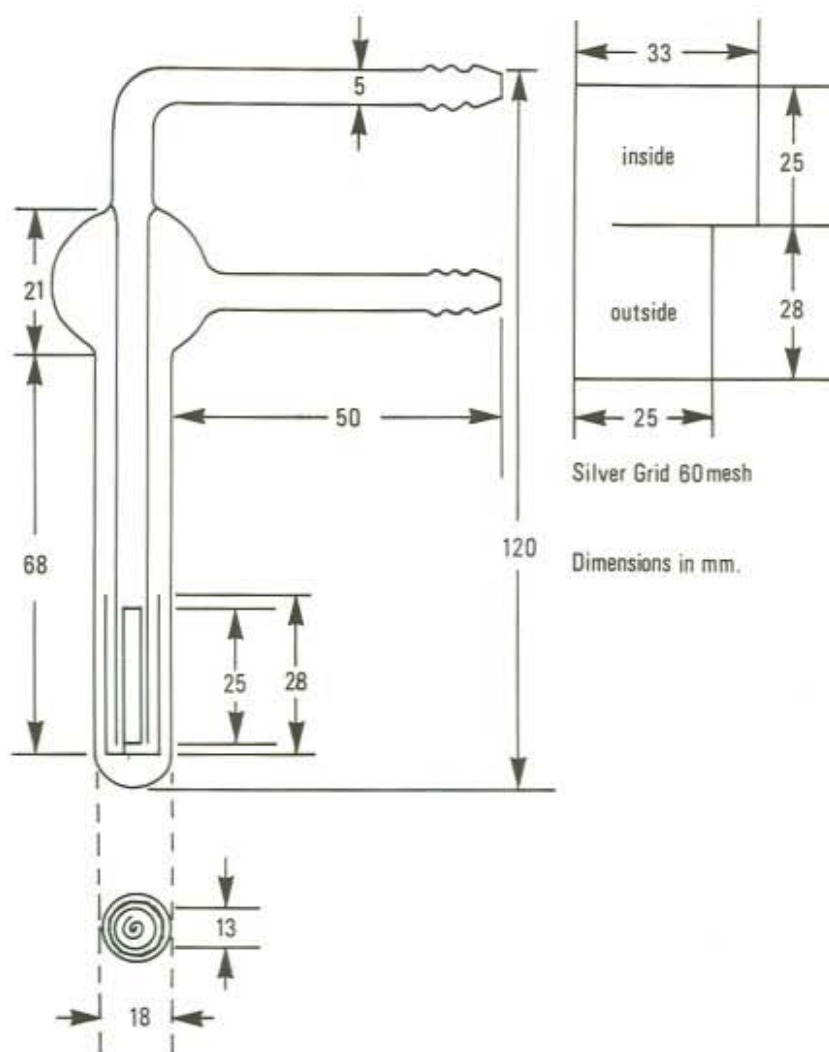


Fig. 1

AIR SAMPLER

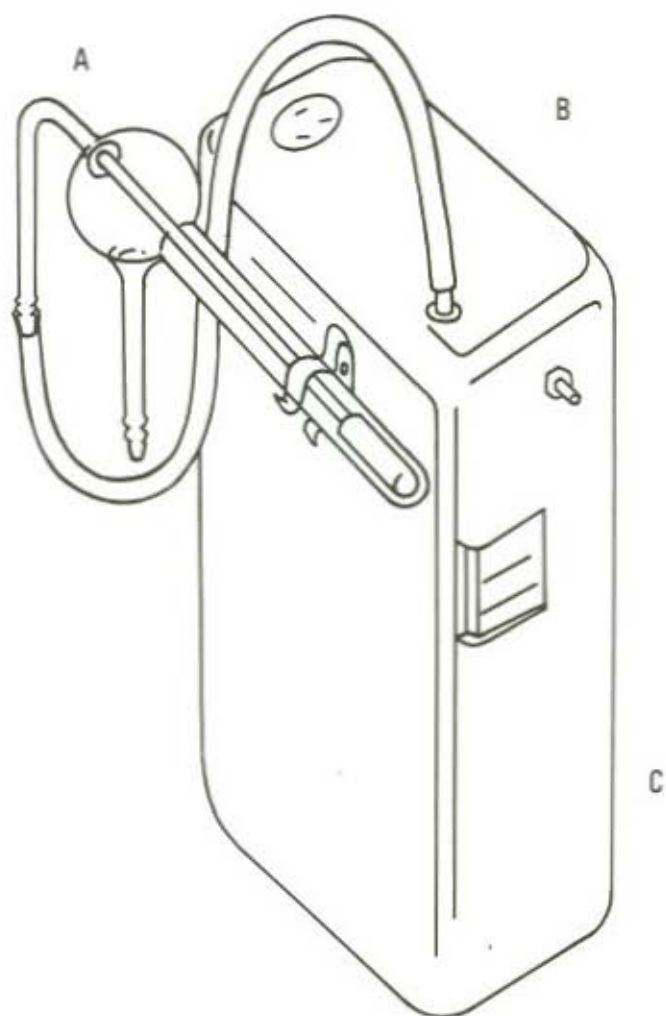
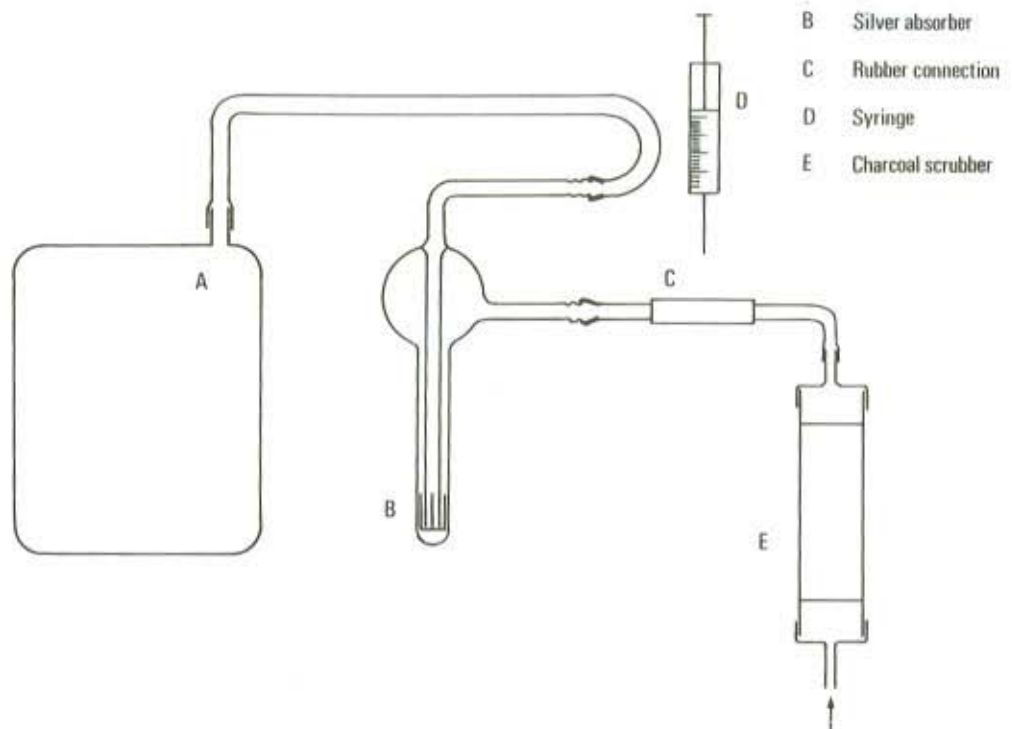


Fig. 2

- A Silver absorber
- B PVC tubing
- C Portable air sampler

SAMPLING FOR HIGH CONCENTRATIONS OF MERCURY

Fig. 3



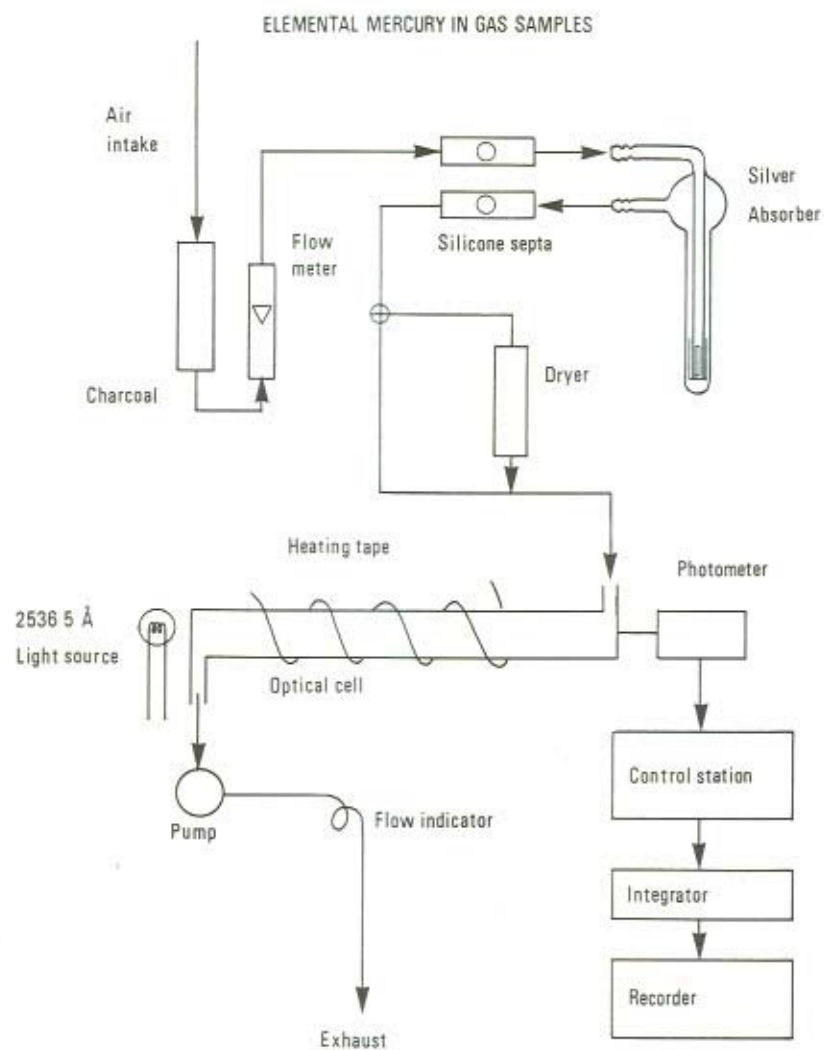


Fig. 4

Determination of Mercury in Water

1. SCOPE

This method is applicable to the determination of the total content of organic and inorganic mercury in water.

2. PRINCIPLE OF METHOD

Addition of strong acid and oxidising agent converts all forms of mercury into mercuric ion. An excess of a reducing agent then liberates elementary mercury which is carried by a stream of air through the cell of flameless atomic absorption instrument.

3. REAGENTS

3.1 Sulphuric acid, concentrated.

3.2 Sulphuric acid, 3 M.

3.3 Hydrogen peroxide, 30%.

3.4 Potassium permanganate solution, 6% w/v.

3.5 Hydroxylamine hydrochloride solution, 20% w/v.

3.6 Tin (II) chloride solution, 20% w/v.

4. APPARATUS

4.1 Spectrophotometer fitted with 10cm cylindrical glass cell, about 18mm ID, with quartz glass windows and energy recording adaptor.

4.2 Recorder.

4.3 Source, mercury discharge lamp.

4.4 Digestion tubes, 100 x 16mm.

4.5 Burettes.

Note: Alternative to 4.1-4.3, an atomic absorption spectrophotometer with a hollow-cathode mercury lamp, and a recorder read-out can be used. The burner head is removed, and the gass cell placed in the light path, the latter determining the maximum length of cell to be used.

5. PROCEDURE

5.1 *Cleaning of glassware*

Clean all glassware by washing in dilute HNO_3 , followed by water and distilled water.

5.2 *Instrument preparation*

Set up the apparatus as described in method for mercury in air.

5.3 *Instrument settings*

As for method for mercury in air.

5.4 *Sample preparation*

Make duplicate tests on each sample. Include two water blanks and standard mercury solutions.

5.4.1 For samples which must be stored before analysis, acidify with sulphuric acid and add a few drops of permanganate. Store in glass bottles.

5.4.2 To 10ml water sample in a 100ml measuring flask add a few drops of hydrogen peroxide and acidify with 3 M sulphuric acid. Add permanganate solution dropwise from a burette until the solution has a faint pink colour. Cool in a water bath and add 10ml permanganate solution and 1.5ml sulphuric acid. Leave overnight at room temperature. The following day, dilute with distilled water to 100ml and transfer 3ml to a digestion tube.

5.5 *Determination of mercury*

Determine the mercury content as described in method for mercury in air.

Determination of Mercury in Biological Media

1. SCOPE

By this method the total content of mercury – inorganic and organic – can be determined in any easily homogenated biological sample. Detection limit 0.02mg/kg for a one gram sample.

2. PRINCIPLES OF METHOD

When homogenated with an oxidising agent and acid the different forms of mercury in the sample are all converted into mercuric ion. Reducing agent then added in excess liberates elementary mercury, which by a stream of air is carried through the cell of a flameless atomic absorption instrument.

3. REAGENTS

3.1 Sulphuric acid, concentrated.

3.2 Potassium permanganate solution, 6% w/v.

3.3 Hydroxylamine chloride solution, 20% w/v.

3.4 Tin (II) chloride solution, 20% w/v.

3.5 Distilled water deionised by passing through mixed cation/anion exchange column.

4. APPARATUS

4.1 Spectrophotometer fitted with 10cm cylindrical gas cell, about 18mm ID, with quartz glass windows, and energy recording adaptor.

4.2 Recorder.

4.3 Source, mercury discharge lamp.

4.4 Macerator.

4.5 Digestion tubes, 100 x 16mm.

4.6 Burettes.

Note: Alternative to 4.1-4.3, an atomic absorption spectrophotometer with a hollow-cathode mercury lamp, and a recorder read-out can be used. The burner head is removed, and the gas cell placed in the light path.

5. PROCEDURE

5.1 *Cleaning of glassware*

Clean all glassware by washing in dilute HNO_3 , followed by water, distilled water and deionized water.

5.2 *Instrument preparation*

Set up the apparatus as shown in the diagram. Switch on the photometer and allow the mercury lamp to warm up for 20min. With the aid of the potentiometer, adjust the sensitivity so that the full deflection of the recorder (20mV) corresponds to 100% light absorption. Control this sensitivity at intervals during analysis. The air is pumped through the apparatus by a respirator or electrical pump. Before entering the apparatus, the air is filtered through a tube containing active carbon and gold sand. Place a small plug of cotton wool between the sample tube and the gas cell to filter off any possible droplets carried by the air stream. Adjust the flow of air with the flow meter, (250ml/min) allowing the air to bubble through a digestion tube containing 3ml water.

5.3 *Instrument settings*

Wavelength: 253.7nm.

Slit width: 0.66mm.

Recorder chart speed: 1cm/min.

Air velocity: 250ml/min.

5.4 *Sample preparation*

Make duplicate tests on each sample. Include two water blanks and standard mercury solutions in each series of test.

5.4.1 *Digestion of biological fluids*

Pipette 1ml of the sample (e.g. urine, diluted blood) into a digestion tube, place the tube in a plastic covered wire test tube rack, and cool in a water bath. Add 0.2ml sulphuric acid from a burette and mix contents by swirling. Leave in water bath for a few minutes, and add 1.5ml potassium

permanganate solution from a burette. Shake carefully, and leave the tubes loosely stoppered overnight at room temperature. The following day, reduce the excess of permanganate with 0.3ml hydroxylammonium chloride solution from a burette. Determine the mercury content as below.

5.4.2 Digestion of biological tissue

Weigh 1g sample into a test tube large enough to accommodate the rotor of the macerator. Add 5(10)ml deionised water and homogenise. Rinse the rotor in several quantities of water before treating next sample. Weigh 1g homogenate into a 10ml bottle and digest as for the fluid samples, using 2ml sulphuric acid and 15ml permanganate solution. Reduce excess permanganate with 3ml hydroxylammonium chloride solution. Pipette 3ml into a digestion tube, and determine the mercury content.

5.4.3 Determination of mercury

Introduce 10 drops of tin (II) chloride solution into the small funnel over the air inlet tube (stopcock closed). Remove the digestion tube containing water, replace with a tube containing sample or standard; connect loosely to the glass joint. Introduce tin (II) chloride solution into the tube by opening the stopcock for a few seconds, then press the tube firmly against the joint. Air now bubbles through the solution, transferring the free mercury formed by reduction to the gas cell. The light absorption is registered by the recorder, rises rapidly to a maximum, and falls slowly. When the recorder pen has returned to the base line, remove the digestion tube, and rinse both sides of the gas inlet tube using a wash bottle. Place the digestion tube containing the next sample solution in position. If rapid speed of analysis is desired, the gas inlet tube can be rinsed before the recorder pen has reached the base line.

Note: An automatic method using an automatic sample changer has been devised by Lind and Skare (Analyst, 1971, 96 223-229), allowing analysis of 60 samples in two hours.

5.5 Calibration graph

Convert the peak heights obtained with standard mercury samples into absorbance units, and plot absorbance against mercury content, giving a calibration graph, which should be linear within the interval 0 to 0.3 μ g mercury. The reagent blank (2 to 5ng mercury) is included in the absorbance read on the calibration graph, and is automatically accounted for.

Convert peak heights obtained with the samples into absorbance units, and determine the mercury contents from the calibration graph. If necessary, dilute samples containing more than 0.3 μ g/ml mercury and repeat analysis.

Determination of Methylmercury Compounds in Fish

1. SCOPE

The method is designed for methylmercury compounds in fish and other marine organisms at levels down to about 0.01mg/kg* but can also be used, with modifications where necessary having regard to recovery levels, for other foods. Normally, the sample is first examined for total mercury residues. Examination for methylmercury compounds is unnecessary if no residues are found.

2. FIELD OF APPLICATION

The procedure has been mainly designed for a variety of fish, including tuna, salmon, pike, cod and herring and is capable of estimating 0.02mg/kg of methylmercuric chloride in a 2g sample.

3. PRINCIPLE OF METHOD

Methylmercury compounds are extracted with benzene, extracted into aqueous cysteine solution, acidified, back extracted into benzene and the benzene extract is examined gas chromatographically.

4. REAGENTS

Alkaline sodium sulphate solution, 2N Sodium hydroxide in 10% w/v sodium sulphate solution. Benzene, redistilled from charcoal. Hydrochloric acid, concentrated. Cysteine solution, 1% w/v—dissolve 0.5g cysteine hydrochloride and 0.4g sodium acetate in 50ml 10% sodium sulphate solution. Methylmercuric chloride, standard solutions in benzene.

5. APPARATUS

Conical flasks, 100ml; Steam bath; Separators, 100ml; Büchner filter, 10cm; Kuderna-Danish evaporator; Gas chromatographic column; Polyethylene glycol succinate; Chromosorb G, acid-washed DCMS treated, 80-100 mesh; Nitrogen carrier gas, oxygen-free,

*Based on a sample weight of 5g.

6. PROCEDURE

6.1 *Extraction*

Place 2g of homogenized sample in a 100ml conical flask, add 10ml 2N sodium hydroxide in 10% sodium sulphate solution and disperse on a steam bath (up to 20min). Transfer to 100ml separator, add 25ml benzene, 6ml concentrated hydrochloric acid, shake for 2min. Centrifuge, or filter under suction through a 10cm Whatman 1 paper; transfer to another 100ml separator, warming on the steam bath gently as necessary to break any stable emulsion. Separate the aqueous layer, extract with 20ml benzene, combine the benzene extracts and concentrate to not less than 4ml in a Kuderna-Danish evaporator in the steam bath. Extract.

6.2 *Clean-up (7.1)*

Extract with 2 x 1.5ml cysteine solution, combine the extracts, add 1ml concentrated hydrochloric acid and extract with a measured volume (5.0 or 10.0ml) of benzene.

6.3 *Gas chromatography*

Prepare a glass column 1.5m x 3mm (internal diameter) by packing with 2% diethylene glycol succinate on 80-100 mesh chromosorb G for operation at 160°C, using nitrogen carrier gas at a flow rate adjusted to give a retention time of about 3min for methylmercuric chloride. Examine 5 microlitre portions of the purified benzene extract obtained above. Prepare a calibration curve using standard methylmercuric chloride solutions. A peak height of about 5% full scale deflection should be obtained with 0.05 methylmercuric chloride in a 5ml volume.

7. REFERENCES

- 7.1 Westöö, G. *Acta Chem. Scand.*, **21**, 1,790, 1967.

Determination of Traces of Lead and Cadmium in Water

1. SCOPE

The methods are suitable for samples containing up to 10 micrograms per litre of dissolved cadmium or 100 micrograms per litre of dissolved lead.

2. PRINCIPLE OF METHOD

Lead and cadmium are selectively complexed by chelation with ammonium pyrrolidine dithiocarbamate, extracted into 4-methylpentan-2-one and estimated by direct aspiration of the organic phase in an atomic absorption spectrometer (8.1).

3. REAGENTS

Deionised water; Nitric acid, concentrated; Standard cadmium solutions, 0.5 to 10 micrograms per litre; Standard lead solutions, 5 to 100 micrograms per litre; Hydrochloric acid 1N or 6N; Ammonium pyrrolidine dithiocarbamate solutions, 4% w/v; 4-Methylpentan-2-one.

4. APPARATUS

Atomic absorption spectrophotometer; Burner suitable for air-acetylene flame; Centrifuge, Separating funnels, 250ml.

5. SAMPLING PRECAUTION

Samples should be examined as soon as possible after being taken. Steps must be taken to ensure that traces of lead or cadmium are not lost by absorption on the surface of sampling vessels (2). Soft glass or polyvinyl chloride vessels should not be used.

6. PROCEDURE

Adjust the pH of 200ml of sample to 2.2-2.8 with hydrochloric acid. Add 1ml ammonium pyrrolidine dithiocarbamate solution, mix and add 5ml

4-methylpentan-2-one and shake for 2min. If an emulsion forms at the interface of the two layers, centrifuge for 10min. Repeat the extraction with a second 5ml 4-methylpentan-2-one and combine the two extracts. If a precipitate forms in the solvent phase during the first extraction, add an additional 5ml 4-methylpentan-2-one and repeat the extraction with a second 10ml. Since the extra solvent reduces the concentration factor and sensitivity of the method, do not apply unless necessary. Determine the metal in the organic phase by comparison with standards that have similarly been extracted. Aspirate the organic phase into the flame, reducing the fuel-to-air ratio as necessary, using the 283.3nm line for lead and the 228.8nm line for cadmium.

7. EXPRESSION OF RESULTS

Results should be expressed as micrograms of cadmium (Cd) or lead (Pb) per litre and should indicate whether filtered or unfiltered samples have been used.

8. REFERENCES

8.1 Standard Methods for the Examination of Water and Wastewater, 13th Edn, pp. 211-215, American Public Health Association, 1971.

Determination of Total Lead and Cadmium in Biological Media

1. SCOPE

The method is applicable to homogenised samples. The method of sample digestion may depend on the exact nature of the sample: the validity of the procedure used should be checked by recovery experiments on similar samples.

2. PRINCIPLE OF METHOD

The sample is ashed or wet oxidised under controlled conditions, taking care to avoid losses of trace metal by volatilisation or absorption (6). Lead and cadmium are removed from interfering matter as dithiocarbamate complexes and estimated by atomic absorption spectrophotometry.

3. REAGENTS

3.1 *For wet oxidation*

Nitric acid, concentrated; sulphuric acid, concentrated.

3.2 *For ashing*

Hydrochloric acid solution, 5N.

3.3 *For end method*

Ammonium pyrrolidine dithiocarbamate solution, 2% w/v 4-methylpentan-2-one.

4. APPARATUS

4.1 *For wet oxidation*

Silica digestion (Kjeldahl) flasks; volumetric flasks, 50ml.

4.2 *For ashing*

Platinum dishes; infra-red drying lamps; muffle furnace; volumetric flasks, 50ml.

4.3 *For end method*

Separating funnels, 100ml; filter papers, siliconised; atomic absorption spectrophotometer with air-acetylene burner.

5. SAMPLES AND SAMPLING

The sample is thoroughly mixed by shaking, kneading, mashing or passing through a mincer with non-metallic implements. Subsamples for digestion should be 15-20g for most solid materials (5-10g for fatty materials), 50ml for liquids.

6. PROCEDURE

6.1 *Preparation of sample*

The sample is digested either by wet oxidation or (lead only) by ashing.

6.1.1 Wet oxidation

Transfer the sample to a silica digestion flask, disperse as necessary with added water, Add 10ml concentrated nitric acid and heat (if necessary) to initiate oxidation. Allow initial reaction to subside, heat to boiling, cool. Add 10ml concentrated sulphuric acid and heat gently until charring *just* commences: continue with stronger heating adding concentrated nitric acid carefully, dropwise as charring occurs; avoid excessive charring. When solution fails to darken on prolonged heating, cool (if not colourless when cold, further digestion is necessary), carefully add 50ml water, boil gently to fuming. Cool, add carefully 10ml water, boil gently to fuming to remove last traces of nitric acid; cool, add carefully 20ml water, cool, transfer quantitatively to 50ml volumetric flask, dilute to mark with water; mix.

6.1.2 Ashing (lead only)

Place the sample in a platinum dish and dry carefully under infra-red lamp, burning off fats as necessary. Transfer to muffle furnace, hold at 490°C for 12-15hr, cool; dampen with water and reheat in muffle furnace at 490°C, if necessary until the ash is completely white. Cool. Add 5ml water, simmer with 10ml 5N hydrochloric acid to dissolve and transfer quantitatively to 50ml standard flask, dilute to mark with water; mix.

6.2 *End method*

Transfer a suitable aliquot of the prepared digest to a 100ml separating funnel, dilute (as necessary) to 50ml, ensure that the solution is thoroughly

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cool, and add 2ml 2% ammonium pyrrolidine dithiocarbamate solution. Mix thoroughly, stand for 3-5 minutes, add by pipette 5 or 10ml 4-methylpentan-2-one, stopper flask and shake for 30secs. Allow phases to separate, discard aqueous phase, filter ketone phase through siliconised paper to remove last traces of water into a small plastic bottle. Aspirate in air-acetylene flame using 283.3nm line for lead, 228.8nm line for cadmium. Prepare standard and blank solutions in the same way by extracting aqueous solutions of the same acidity as the sample solution.

7. EXPRESSION OF RESULTS

For solid and semi-solid samples, results are expressed in mg per kg, for liquid samples in mg or micrograms per litre (according to the amount present) to one, or at the most two, significant digits.

8. NOTES ON PROCEDURE

Samples should be stored in acid-washed pyrex glassware or high density polyethylene containers. A reflux system similar to that described by Smith may be used for the wet digestion procedure (10.1, 10.2).

Cadmium analyses by atomic absorption spectrophotometry at low levels can be improved by using a deuterium background detector to compensate for molecular absorption. Alternative methods for cadmium are based on polarography, spectrophotometry (10.3) or spectrofluorimetry (10.4). An alternative method for lead is the colorimetric dithizone procedure (10.5) although difficulty may be encountered due to instability of the coloured complex.

9. SCHEMATIC REPRESENTATION OF PROCEDURE

Sample preparation; ashing or wet oxidation; adjustment of volume of digest to 50ml; separation from interfering materials by extraction of dithiocarbamates with 4-methylpentan-2-one; examination for lead, cadmium by atomic absorption spectrophotometry.

10. REFERENCES

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Determination of Selenium in Biological Media

1. SCOPE

The method is suitable for the determination of total selenium in biological tissue at levels of the order of 0.01-0.03mg/kg.

2. PRINCIPLE

The sample is digested under strongly oxidising conditions with nitric and perchloric acids, a fluorescent selenium complex (naphtho[2,3-d]-2-seleno-1,3-diazole) formed with 2,3-diaminonaphthalene, extracted into cyclohexane, back-extracted into 0.1 M hydrochloric acid and compared with standard selenium solutions spectrofluorimetrically.

3. REAGENTS

Perchloric acid, 72%; Hydrochloric acid, concentrated; Nitric acid, concentrated—redistilled; Ammonium hydroxide solution, 7 M; Cyclohexane; dekalin (decahydronaphthalene); Light petroleum—boiling range 100-120°C; EDTA solution—0.04 M diammonium salt prepared from EDTA and ammonium hydroxide solution; 2,3-Diaminonaphthalene (DAN)—recrystallised from water in diffuse daylight with a little sodium sulfite and activated charcoal.

DAN solution—0.1% in 0.1 M hydrochloric acid, prepared immediately before use in yellow light. Dissolve 0.05g 2,3-diaminonaphthalene in 50ml 0.1 N hydrochloric acid, heat at 50°C for 20 minutes, cool to 20°C: extract twice with 10ml dekalin, centrifuge (10.1).

Cresol Red Solution—0.02% w/v in water.

Standard Se solution—Dissolve an accurately weighed amount of selenium (Se) in a minimum amount of concentrated nitric acid, evaporate off the excess nitric acid in the presence of a little perchloric acid and add a trace of hydrochloric acid to give a solution containing 0.1 N acid. Dilute to 0.1 microgram Se per ml with 0.1 N hydrochloric or perchloric acid.

4. APPARATUS

Filter fluorimeter; digestion tubes, 2.5 x 20cm, fitted with 15cm air condensers; evaporator-manifold connected to centrifugal pump, connected to digestion tubes immersed in a water bath; separatory funnels—100ml; centrifuge.

5. PROCEDURE

Digest ca. 1.0 gram of sample with 5ml nitric acid, adding more nitric acid then 2ml perchloric acid when the initial vigorous reaction ceases. Reflux, fume and boil strongly for 15 minutes before cooling. Add 2ml water, evaporate, add 2ml hydrochloric acid, heat in boiling water bath for 5 minutes, rinse internally with 4ml water, cool.

To each tube (including blanks and standards) add 2ml EDTA solution, one drop of cresol red solution and adjust to pH 1.0 with 7 M ammonium hydroxide solution (or dilute perchloric acid solution). Dilute to 50ml with 0.1 M hydrochloric acid, add 5ml DAN solution, stopper, shake and leave in a water bath at 50°C in the dark for 20 minutes. Cool in a water bath at room temperature in diffuse daylight, run into a 100ml separatory funnel containing 10ml cyclohexane, shake for one minute, discard the aqueous phase. Extract the cyclohexane phase twice with 25ml 0.1 M hydrochloric acid, separate and centrifuge (2,000rpm for 2 minutes) in polypropylene centrifuge tubes, measure fluorescence (6.2).

Notes: Oxygen flask combustion may also be used (6.2).

6. REFERENCES

- 6.1 Parker, C. A. and Harvey, L. G., *Analyst*, 1962, 87, 558.
- 6.2 Watkinson, J. H., *Anal. Chem.*, 1966, 38, 92-97.

Determination of Sulfur Dioxide by the West-Gaeke Method

1. INTRODUCTION

The determination of sulfur dioxide in air is complicated by the presence of oxygen and the coexistence of other pollutants, such as the oxidants (ozone; oxides of nitrogen) or reductants (hydrogen sulfide; disulfide) that either react with the sulfur dioxide itself during sampling and storage or interfere with subsequent analytical processes. Acidic and/or basic substances in air further contribute to the complexity of the determination. The techniques employed for the determination include conductometry; polarography, iodimetry, acidimetry, gas chromatography, flame photometry, coulometry and spectrophotometry. Of all the methods proposed, the spectrophotometric method introduced by West and Gaeke in 1956 (12.1) remains the choice for critical studies because of its relative freedom from interferences, its sensitivity and its accuracy.

The spectrophotometric method has been subjected to exhaustive study by many laboratories and responsible agencies throughout the world. In general, collaborative studies have completely verified the reliability of the method. A number of minor modifications of the original procedure have been proposed mainly in the form of concentration changes of reagents. However, the modifications have generally introduced complications and have done little to improve the method. The procedure recommended is, therefore, the original one modified only in minor details.

2. SCOPE AND FIELD OF APPLICATION

This is the reference method for the determination of sulfur dioxide. It should be used for critical studies of air quality and, when suitably modified, it can be used for determining base-line values for "unpolluted" atmospheres. It is a preferred method for continuous air monitoring, provided the instrumentation employed is of sound design and construction.

The method can be used for spot checks, monitoring, field surveys, methods and instrument calibration and such other applications as require a sensitive, accurate and reliable method for the determination of sulfur dioxide.

3. PRINCIPLE OF THE METHOD

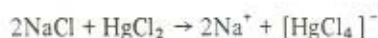
The West-Gaeke method is based on the absorption and stabilization of sulfur dioxide from air by a solution of sodium (or potassium) tetrachloro-

mercurate II, to form the dichlorosulfitomercurate II complex. The sulfito complex resists oxidation by atmospheric oxygen and is even stable in the presence of small amounts of strong oxidants such as ozone and the oxides of nitrogen.

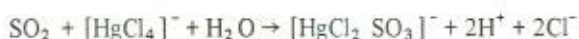
Quantitative determinations of the collected sulfur dioxide is accomplished by adding acid-bleached pararosaniline hydrochloride and formaldehyde to the sulfito complex and measuring the intensely colored pararosaniline methylsulfonic acid so produced.

4. REACTIONS

4.1 Tetrachloromercurate II is produced by adding 2 moles of NaCl (or KCl) to 1 mole of HgCl_2



4.2 Sulfur dioxide is trapped and stabilized through complexation



4.3 Formation of the color product, pararosaniline methylsulfonic acid. See 12.2.

5. REAGENTS

5.1 *Distilled water (or deionized water)*

Must be Cl_2 free.

5.2 *Tetrachloromercurate II, TCM, 0.1 M*

Dissolve 0.1 mole of mercury II chloride (27.2g) mole of sodium chloride (11.7g) in water and dilute to 1 liter.

5.3 *Formaldehyde, 0.2%*

Dilute 5ml of 37% formaldehyde to 1 liter with water. Prepare daily.

5.4 *Pararosaniline stock solution*

Mix 0.64g of pararosaniline hydrochloride with 240ml of concentrated hydrochloric acid, dilute to 1 liter with water and stir until dissolved. This solution is stable for at least 2 years and improves with age but a new calibration should be carried out at least once each year.

5.5 *Pararosaniline reagent*

Dilute stock solution 1:4 with water as needed. Stable at least 2 months.

5.6 *Sulfamic acid, 0.5%*

Dissolve 0.5g sulfamic acid in water and dilute to 100ml. Stable for several days at room temperature or several weeks if refrigerated.

6. APPARATUS

6.1 *Absorber*

A midget or other fritted bubbler should be used.

6.2 *Air monitoring equipment*

A suitable metering valve in conjunction with a wet or dry test gas meter or rotameter may be used to measure and control the air flow. With rotameters the metering valve should be placed downstream of the flowmeter. Alternatively calibrated hypodermic needles may be used as critical orifices with a pump that can maintain greater than a 0.5 atmospheric differential across the orifice. A membrane filter should be placed upstream of the critical orifice to protect the orifice from plugging and the filter should be changed at regular intervals.

A 22-gauge hypodermic needle will deliver a flow of about 1 liter/min while a 27-gauge needle 5/8in long will deliver a flow of 150 to 200ml/min (12.3).

7. SAMPLING AND SAMPLES

Add 10ml TCM to a midget bubbler. Insert the bubbler into the sampling system upstream of the air metering equipment. The sampling probe may consist of glass or TFE-Teflon and should be as short as possible. Collect about 30 liters of sample at a flow of between 0.5 and 2.5 liters/min typically 1 liter/min for 30 minutes. Twenty-four hour samples may be collected using 20ml of TCM and a flow rate of about 200ml/min. Water lost by evaporation should be replaced.

The TCM solution should be shielded from sunlight during and after sampling and extended exposure to temperatures above 30°-35°C should be avoided. If stored for more than 1 to 2 days the sample should be refrigerated. At 25°, 30° and 40°C, losses of sulfur dioxide occur at the respective rates of 1.0, 2.5 and 12% per day.

8. PROCEDURE

If a precipitate is observed in the sample, it should be removed by centrifugation or filtration. Allow 20 minutes between sampling and analysis to ensure decomposition of any ozone that may be present. To the sample and a 10.0ml TCM blank add 1.0ml each of the pararosaniline and the formaldehyde solutions and mix. Allow to stand for 30 minutes and read the absorbance relative to the blank at 560nm. If shortly after the addition of formaldehyde and pararosaniline an absorbance value above the analytical range appears likely, the sample should be diluted with an additional 10ml of TCM together with 1.0ml portions of pararosaniline and formaldehyde.

9. CALIBRATION CURVES

Permeation tubes containing liquid sulfur dioxide may be used (12.4) to prepare calibration curves (available from the U.S. Bureau of Standards, also Metronics, Inc., 3201 Porter Drive, Palo Alto, California, 94304 and Polyscience Corp., P.O. Box 791, Evanston, Illinois 60204). The permeation tube should be maintained under a stream of clean dry air or nitrogen ($\approx 100\text{ml/min}$) with the temperature controlled to $\pm 0.1^\circ\text{C}$. Conveniently, the permeation tube may be placed in a 250ml bubbler and the bubbler may then be immersed in a constant temperature bath. Calibrate the tube gravimetrically at the intended operating temperature (to a precision of $\pm 2\%$) by weighing the tube about every four days. The tube which should emit sulfur dioxide at a rate of 2 to $5\mu\text{g/min}$ should be weighed to $\pm 0.1\text{mg}$. Note the time to the nearest 5 minutes. The rate of permeation will be given by the equation.

$$\text{Rate} = \frac{\text{Weight Loss } (\mu\text{g})}{\text{Time (min)}}$$

Increase the flow rate over the tube to 1 liter/min and allow to equilibrate for 5 minutes. Absorb the emitted sulfur dioxide in 10 to 15ml TCM with a midjet bubbler while maintaining the same flow rate. Remove the bubbler after absorbing $250\mu\text{g}$ of sulfur dioxide. Quantitatively transfer the solution to a 100ml volumetric flask. Rinse the bubbler twice with unexposed TCM and dilute to volume with this reagent. Dilute 2, 4, 6 and 8ml aliquots of this standard which contains $2.5\mu\text{g/ml}$ sulfur dioxide to 10ml with fresh TCM. Also take 10ml of the undiluted standard. Analyse the solutions by the method given in the procedure section (8) and plot μg sulfur dioxide per 10ml solution versus absorbance. Alternatively, anhydrous reagent grade sodium sulfite may be used to standardize the method.

10. EXPRESSION OF RESULTS

Convert the volume of air sampled to the volume at standard conditions of 25°C, 760mm Hg;

$$V_R = V \times \frac{P}{760} \times \frac{298}{(t + 273)}$$

V_R = volume of air at 25°C and 1 atmosphere

V = volume of air sampled, liters

P = barometric pressure, mm Hg

t = temperature of air sampled, °C

Ordinarily, the correction for pressure is slight and may be neglected.

Determine the concentration of sulfur dioxide in the sample by the following formula:

$$SO_2, \mu g/m^3 = \frac{W}{V_R}$$

Where $W = \mu g SO_2/10ml$ found from calibration curve

$10^3 =$ Conversion of liters to m^3 .

Where desired, values may be reported in ppm,

$ppm SO_2 = \mu g SO_2/m^3 \times 3.82 \times 10^{-4}$.

11. SPECIAL CASES

If high levels of nitrogen oxides (2 ppm or above) are expected 1ml of sulfamic acid may be added to the sample 10 minutes prior to analysis (12.5, 6). Large amounts of some heavy metal may interfere, these interferences may be eliminated by the addition of 0.07g of EDTA (ethylenediaminetetraacetate, tetrasodium salt) per liter of TCM prior to sampling (12.7, 8). If these modifications are to be used, calibration curves employing them should also be made.

12. REFERENCES

- 12.1 West, P. W. and Gaeke, G. C. *Anal. Chem.*, **28**, 1,816, 1956.
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- 12.3 Lodge, J. P. Jr., Pate, J. B., Ammons, B. E. and Swanson, G. A. *J. Air Pol. Control Assoc.*, **16**, 197, 1966.
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Collection and Determination of Sulfur Dioxide Incorporating Permeation and the West-Gaeke Procedure

1. SCOPE AND FIELD OF APPLICATION

1.1 This method (9.1) provides a technique for sampling and determining the average concentration of sulfur dioxide (SO_2) in the ambient atmosphere for periods from 6 hours to 1 week. The method is selective, sensitive, reproducible and suitable for field use. Sampling is accomplished by permeation through a silicone membrane with subsequent determination by the West-Gaeke Method (9.2).

1.2 The lower limit of detection for a 24hr sampling period is $5\mu\text{g}/\text{m}^3$ (based on twice the standard deviation of the blank) while the analytical range is from 5 to $1,000\mu\text{g}/\text{m}^3$.

1.3 The precision is 2 to 3% when repetitive samples are run by the same operator under laboratory conditions. The accuracy under field conditions is primarily limited by variations of ambient temperature. Variations of $\pm 10^\circ\text{C}$ will cause errors no greater than 5%.

1.4 The method is particularly well suited for taking 24hr averages which are often stipulated by various regulating bodies.

1.5 At concentrations of $600\mu\text{g}/\text{m}^3$ of hydrogen sulfide, $500\mu\text{g}/\text{m}^3$ ozone and $300\mu\text{g}/\text{m}^3$ nitrogen dioxide, no significant interferences occur. Particulates should not interfere since they cannot permeate the membrane. At $4,500\mu\text{g}/\text{m}^3$ of hydrogen sulfide darkening of the silicone membrane occurs. This is accompanied by the formation of yellow spots on the membrane and pinholes through which liquid may leak. Permeation devices with darkened membranes should, therefore, be discarded.

2. PRINCIPLE

2.1 Sampling is accomplished with a permeation device consisting of a glass tube with a silicone membrane across one end. Sodium tetrachloromercurate (II) is placed inside the tube in contact with the membrane. When the tube is exposed, SO_2 after permeating the silicone membrane is absorbed and stabilized as the dichlorosulfitomercurate (II) complex (9.3). The amount of SO_2 absorbed in a given amount of time can then be related to the average concentration because the rate of permeation of SO_2 is directly proportional to the concentration of SO_2 to which the device is exposed.

2.2 The absorbed sulfur dioxide is analyzed by the traditional West-Gaeke method by addition of acidified pararosaniline and formaldehyde. The absorbance of the magenta colored product is then read at 575nm and the amount of SO₂ in the absorbing solution is found on a calibration chart. The ambient concentration can be calculated from the amount of SO₂ absorbed by use of a calibration constant that has been previously determined for the particular permeation device used. The device is calibrated by exposing it to a known concentration of SO₂.

2.3 The dichlorosulfitomercurate (II) decomposes on exposure to direct sunlight. A light shielding box is used to mount the permeation device to protect the solution.

3. REAGENTS

3.1 Reagent grade chemicals shall be used in all tests and shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society,¹ where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

3.2 *Purity of water*

High quality deionized water should be used in all test solutions. Water must be free of oxidants.

3.3 *Sodium tetrachloromercurate (II), 1.0 M*

Dissolve 272g of mercuric chloride (HgCl₂) (*Caution: Highly poisonous*), and 117g sodium chloride (NaCl) in water and dilute to 1 liter.

3.4 *Pararosaniline hydrochloric solution*

Dissolve 0.7g of pararosaniline in 240ml of concentrated hydrochloric acid and water and dilute to 1 liter. Dilute 20ml of this concentrate to 100ml with water. This solution is stable for at least three months. The concentrate is stable for at least a year. The use of impure pararosaniline may result in high reagent blanks. Blanks (vs. water) of approximately 0.02 absorbance units should be obtained for 1cm cells if the reagent is of acceptable quality.

3.5 *Formaldehyde, 0.2%*

Dilute 0.5ml of 37% formaldehyde to 100ml with deionized water. This solution should be prepared daily.

4. APPARATUS

4.1 *Permeation device*

The permeation device is prepared by sealing a 0.0025cm thick film of single backed (polyester) silicone rubber² to the end of a 41mm O.D x 80mm long glass tube using silicone rubber cement. The membrane backing should be on the exterior of the finished device. For calibration, the device is inserted into a rubber stopper. After calibration, the glass tube is wrapped with tape to help protect absorbed SO₂ from sunlight. A one hole rubber stopper with an 8cm long 1mm I.D. capillary inserted into it is installed in the top of the device to eliminate internal pressures.

4.2 *Shelter*

A light shielding box is used to mount the permeation device. There should be free movement of air through the box and the permeation device should be mounted near the top of the center of the box.

4.3 *Flowmeters*

Dry test meters or rotameters with an accuracy of $\pm 2\%$ should be used for calibrating membranes.

4.4 *Calibration chamber*

A calibration chamber into which the permeation device can be placed must be used.

4.5 *Photometer*

Most spectrophotometers, colorimeters and filter photometers are satisfactory. The precision of the photometric readout should be better than 2% between 0.3 and 0.5 absorbance units.

5. SAMPLING

5.1 *Collection of sample*

Place 10ml of 1 M sodium tetrachloromercurate (II) in the permeation device. Expose the device to the ambient atmosphere in the shelter designed for the device. Normal exposures vary from 6 hours to 7 days (see clause 8.1). If more than half the solution evaporates during the exposure period, the loss should be made up with deionized water.

5.2 At the end of the exposure period transfer the sample to a container suitable for transporting the sample. During this step, and succeeding steps, the sodium tetrachloromercurate (II) must be protected from sunlight.

6. PROCEDURE

6.1 *Safety precautions*

If solutions containing sodium tetrachloromercurate (II) are spilled on skin, flush with water immediately. Mercury wastes should be recovered when possible by addition of 100g of zinc to 1 liter of the spent sodium tetrachloromercurate (II) solution or by other procedures (9.7, 9.8) and sent to a reprocessor (9.8).

6.2 *Determination*

Adjust the volume of the trapped sample to 10.0ml by adding an appropriate amount of water. Add 1ml each of the pararosaniline and formaldehyde solutions and stir vigorously. Read the absorbance at 575nm after 40 ± 10 minutes versus a reagent blank treated identically as the sample and find the total $\mu\text{g (w)}$ of SO_2 in the sample from a calibration plot. Samples above the range of calibration can be diluted several times with the reagent blank to obtain absorbance readings on scale, but this exercise should be carried out only to save a sample.

6.3 *Calibration and standards*

6.3.1 Preparation of standard sulfur dioxide concentrations

Calibrate permeation tubes that contain liquified SO_2 gravimetrically and use to prepare standard concentrations of SO_2 in air (9.4, 9.5, 9.6). Use these standard concentrations of SO_2 to calibrate the permeation device and prepare known solutions of SO_2 in sodium tetrachloromercurate (II).

Prepare or obtain³ an FEP fluorocarbon tube that emits at a rate of 3 to $6\mu\text{g/min}$. Larger tubes or a group of tubes may be used for calibration of several of the permeation devices at one time. Maintain the tube under a stream of clean dry air or nitrogen (100ml/min) with the temperature controlled to $\pm 0.1^\circ\text{C}$. The permeation tube may then be immersed in a constant temperature bath. Calibrate the tube (to a precision of $\pm 2\%$) by weighing the tube about every four days. The tube should be weighed to $\pm 0.1\text{mg}$ and the time recorded to the nearest 10min. The rate of permeation will be given by the equation.

$$\text{Rate} = \frac{\text{Weight Loss } (\mu\text{g})}{\text{Time (min)}}$$

For use as a standard source of SO₂ increase the flow rate to between 1 and 2 l/min and allow to equilibrate for 5min. A concentration of about 3,000µg/m³ should be produced.

6.3.2 Calibration curves for sodium tetrachloromercurate (II)

Absorb 500µg of SO₂ from the standard source into 150ml of 1 M sodium tetrachloromercurate (II) using a 250ml bubbler equipped with an extra coarse frit. After collection, transfer the sample quantitatively to a 250ml volumetric flask using two 10ml portions of unexposed sodium tetrachloromercurate (II) and dilute to volume with this same reagent. This solution is stable for 1 month if refrigerated.

Pipet graduated amounts (such as 0, 2, 4, 6, 8, and 10ml) of the above standard and corresponding amounts of unexposed tetrachloromercurate (II) into a series of 25ml Erlenmeyer flasks or test tubes to give a total volume of 10ml. Then add the remaining reagents as described in the procedure (see clause 6.2) and plot absorbance (vs. blank) against the total micrograms of SO₂. The plot is not linear above about 8µg SO₂.

6.3.3 Calibration of permeation device

Flow standard SO₂ in air through the calibration chamber for 5 minutes. Add 10ml of sodium tetrachloromercurate (II) to the permeation device. Insert the device into the calibration chamber and note the time. Remove after 2 hours and analyze as described in the procedure (see clause 6.2).

7. EXPRESSION OF RESULTS

7.1 Calculation of calibration constant

Calculate the calibration constant as follows:

$$k = \frac{Pt}{rw}$$

where: k = calibration constant.

t = exposure time, hr.

w = weight of SO₂ absorbed, µg.

P = rate of emission SO₂ by permeation tube µg/min.

r = flow rate of air at calibration temperature and pressure.

7.2 Calculation of results

Calculate the concentration of SO₂ in air as follows:

$$\text{SO}_2, \mu\text{g}/\text{m}^3 = \frac{wk}{t}$$

where: t = exposure time, hr.

w = weight of SO_2 absorbed, μg .

k = calibration constant.

The constant k , increases 0.5% for a 1°C increase in temperature, therefore, if the average temperature that the device is exposed to varies greatly from the temperature that the calibration was carried out it should be corrected for temperature. A compensation to relate data to the standard 760mm of Hg may also be made by the following equation:

$$k_p = \frac{760 k}{p}$$

where: k_p = calibration constant at pressure, p .

p = average atmospheric pressure at sampling location.

8. NOTES ON PROCEDURES

8.1 *Solution containing SO_2*

Sampling solutions of dichlorosulfitomercurate (II) are somewhat unstable when stored at elevated temperatures. Therefore, long exposure periods at high temperatures should be avoided. A 24-hour sampling period can, in general, be tolerated except under extremely harsh conditions (temperatures greater than 40°C). At 40° and 30° the losses of sulfur dioxide are 3.0 and 0.5% per day. At lower temperatures the rate of SO_2 loss is practically negligible. For extended storage (more than 1 week) the samples should be refrigerated.

8.2 *Precision and accuracy*

The precision is 2 to 3% when repetitive samples are run by the same operator under laboratory conditions. The accuracy under field conditions is primarily limited by variations of ambient temperature. Variations of $\pm 10^\circ\text{C}$ will cause errors no greater than 5%.

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FOOTNOTES

1. "Reagent Chemicals, American Chemical Society Specifications", Am. Chemical Soc., Washington, D.C. For suggestions on the testing of reagents not listed by the American Chemical Society, see "Reagent Chemicals and Standards", by Joseph Rosin, D. Van Nostrand Co., Inc., New York, N.Y., and the "United States Pharmacopeia".
2. Silicone rubber film obtained from General Electric Co. has been found to be satisfactory.
3. Permeation tubes are available from the U.S. Bureau of Standards, Metronics, Inc., 3201 Porter Drive, Palo Alto, California, 94304 and Polyscience Corp., P.O. Box 791, Evanston, Illinois, 60204.

Determination of Atmospheric Sulfur Dioxide by Coulometric Titration

1. INTRODUCTION

Sulfur dioxide monitors have been designed that utilize conductivity or acidity produced through its oxidation to form sulfuric acid. In general, such instruments lack specificity. Colorimetric methods such as the West-Gaeke procedure, have been adapted for use in continuous monitors. Although this approach may provide excellent sensitivity and selectivity, the instruments require considerable maintenance. Monitors utilizing coulometry for the measurement step, although subject to some interferences, offer advantages of general instrument reliability. Such instruments may be quite sensitive and precise.

2. SCOPE AND FIELD OF APPLICATION

The method is applicable to most urban or industrial atmospheres provided particulates and the interfering species such as O_3 , halogens, H_2S , and strong oxidants are removed by suitable scrubbing (11.5). The response time is 3-5 minutes to reach 95% of the final value. Sulfur dioxide levels as low as $10.5\mu g/m^3$ (4ppb) can be detected, but the normal working range is $262\mu g/m^3$ to $104,800\mu g/m^3$ (0.1 ppm to 40 ppm).

3. DEFINITIONS

3.1 *Cell electrolyte*

The solution with appropriate buffers containing the titrant ion.

3.2 *Supporting electrolyte*

All chemical species in the cell electrolyte except the titrant.

3.3 *Titrant*

Species in the electrolyte which is depleted by the introduction of SO_2 . Normally it is I_3^- or Br_2 .

4. PRINCIPLE

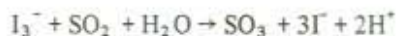
An air sample of known volume is pulled through suitable filters to remove particulates and interferences. The resultant gas stream is fed into an enclosed coulometric cell. The SO_2 reacts with the titrant in the cell electrolyte causing a decrease in the titrant, and the amount of current required to bring the titrant back to its original level is measured on a recorder. By Faraday's law the number of microequivalents of SO_2 can be determined and the SO_2 level expressed in the $\mu\text{g}/\text{m}^3$.

In the method described no sample preparation is required. The air stream of approximately 150ml/min is pulled through a dust filter covered with a stainless steel mesh (to prevent the intake of large objects or insects) (11.5) and a scrubbing filter (11.5) into the cell electrolyte. Two electrodes measure the redox potential originating from either Br_2/Br^- or I_3/I^- couple depending on the commercial system employed. As SO_2 is drawn into the enclosed coulometric cell, the titrant's concentration is lowered. The new potential is compared to an internal reference and the difference is converted into a current between two other electrodes (generating electrodes) in the coulometric cell. The amount of current required to bring the titrant concentration back to its original value (potential) is monitored. The amount of SO_2 titrated is found from a calibration curve, and related to the atmospheric concentration by noting the time interval of measurement and the flow rate.

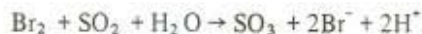
5. REACTIONS

Depending on the commercial coulometric cell employed, the supporting electrolyte composition will vary. Several typical half reactions are:

Cell reaction:



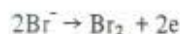
or



Generation anode reaction:



or



6. REAGENTS

As specified by manufacturer for the cell electrolyte.

7. APPARATUS

Many coulometric titration systems for SO_2 are available. Beckman, Dohrman and Phillips instruments are representative of this field.

8. SAMPLING AND SAMPLES

Atmospheric air requires no preparation other than passing it through a dust and scrubbing filter.

9. PROCEDURE

9.1 *Safety precautions*

Follow normal precautions for handling of caustic materials (cell electrolyte).

9.2 *Calibration curve*

A SO_2 permeation tube of known capacity is employed to provide a source of SO_2 . To set up a calibration curve atmospheric air is pulled through the dust filter, an activated charcoal filter, past the permeation tube, through the scrubbing filter and into the coulometric cell at a constant flow rate. The cell electrolyte is stirred to disperse the SO_2 uniformly and thus increase the mass transfer.

Due to evaporation in the course of analysis a certain amount of titrant is lost and this produces a small current. To compensate for this evaporation current, atmospheric air is pulled through a dust filter, activated charcoal filter, scrubbing filter and into the coulometric cell. Since this air is free of reactants, the evaporation current can be determined and subtracted from the gross SO_2 current providing a net current curve.

9.3 *Determination*

An air sample is pulled through a dust filter and scrubbing filter. The resultant air stream is passed into the coulometric cell and the current recorded.

Using the same flow rate and time interval of measurement the evaporation current can be determined and subtracted from the gross current leaving the net current due to SO_2 . By comparison to the net current curve the amount of SO_2 titrated can be found, and expressed as $\mu\text{g}/\text{m}^3$.

9.4 Blank tests

Since the cell is reset to its original state in the course of measurement, no blank tests are necessary.

10. EXPRESSION OF RESULTS

$$\mu\text{g}/\text{m}^3 = \frac{(Q_G - Q_E)k}{v \times t} \times 10^{-6}$$

- where Q_G = Number of coulombs in sample titration at standard flow rate & time
 Q_E = Number of coulombs due to evaporation current during standard flow rate & time
 v = flow rate, ml/min
 t = time in min of test sample
 k = constant from net calibration curve;
 $\mu\text{g SO}_2/\text{coulomb}$

11. NOTES ON PROCEDURE

11.1 The filtering system employed in the measurement process ensures that most interfering species are removed. Of those that remain in NO_x is the most prevalent. By using a buffered solution ($\text{pH} = 7$) the NO_x effect can be minimized. In the I_3^-/I^- system sodium azide has been used to selectively react with any Cl_2 or NO_x reaching the supporting electrolyte.

11.2 Temperature control is necessary in the coulometric cell. Most cells are kept at approximately 35° .

11.3 Air flow can be varied while a normal flow is approximately 150ml/min. A representative system is capable of titrating $5\mu\text{g}$ of SO_2 in 3 to 5 minutes.

11.4 Precision of titration is limited by the precision of sample introduction. Constant flow rate is thus very important.

11.5 A heated glass fiber filter can be used as the dust eliminator. In this way all gaseous components are allowed to flow through. The silver filter would remove the ozone, halogen, and H_2S interferences, and in some systems it is used as the scrubbing filter. In the I_3^-/I^- system only the strong oxidant methyl hydroperoxide and peroxyacetic acid interfere, but the probability of finding these compounds in the atmosphere is low.

12. SCHEMATIC REPRESENTATION

- 12.1 Pull the atmospheric sample through heated glass fiber filter.
- 12.2 Pull resultant gas stream through Ag scrubbing filter.
- 12.3 Pull resultant stream into stirred coulometric cell.
- 12.4 Record flow rate, time interval, and current.

13. REFERENCES

- 13.1 Bremanis, E., et al. *Mat. Res. and Std.*, 7, 459, 1967.
- 13.2 Brewer, A. W. and Milford, J. R. *Proc. Roy. Soc.*, A 256, 470, 1960.
- 13.3 Gluckauf, E., et al. *J. Chem. Soc.*, 1, 1, 1944.
- 13.4 Wartburg, A. F., Brewer, A. W. and Lodge, J. P. *Int. J. of Air and Water Pollution*, 8, 21, 1964.

Method for the Continuous Determination of Carbon Monoxide in the Atmosphere by Non-dispersive Infrared Spectrometry

1. FIELD OF APPLICATION

1.1 This method is applicable to the determination of carbon monoxide in ambient air and to the analysis of gases under pressure.

1.2 *Range and sensitivity*

Instruments are commercially available that measure in the range of 0 to 58mg/m³, which includes the concentrations most commonly encountered in ambient urban air.

1.3 *Interferences*

Interferences vary according to the nature of the sample. The interference caused by carbon dioxide is minimal at normal atmospheric concentrations. On the other hand, water vapor can produce an interference equivalent to 12 milligrams of carbon monoxide per cubic metre, if this is not corrected. Water vapor interference can be minimized by (a) passing the air sample through silica gel or similar drying agents, (b) maintaining constant humidity in the sample and calibration gases by refrigeration, (c) saturating the air sample and calibration gases to maintain constant humidity or (d) using narrowband optical filters in combination with some of these measures. Hydrocarbons at the levels found in ambient air do not ordinarily interfere.

1.4 A statement from the manufacturer should be obtained as to the specifications for discrimination against expected interfering substances.

2. PRINCIPLE

This method is based on the absorption of infrared radiation by carbon monoxide. Energy, from a source emitting radiation in the infrared region, is split into two parallel beams, one passing through the sample compartment. The two beams finally pass the detector which consists of two matched cells each containing carbon monoxide. These two cells are separated by a diaphragm. The carbon monoxide in the detector cells only absorbs radiation corresponding to its characteristic frequencies. With a

non-absorbing gas in the reference cell and with no carbon monoxide in the sample cell, the signals from both detectors are balanced electronically. Any carbon monoxide introduced into the sample cell will absorb radiation, which reduces the temperature and pressure in the detector cell and displaces a diaphragm. This displacement is detected electronically and amplified to provide an output signal (10.1).

3. DEFINITIONS

Range – The minimum and maximum measurement limits.

Output – Electrical signal which is proportional to the measurement. Usually expressed as millivolts or milliamps full scale at a given impedance.

Full scale – The maximum measuring limit for a given range.

Minimum detectable sensitivity – The smallest amount of input concentration that can be detected.

Lag Time – The time interval from a step change in input concentration at the instrument inlet to the first corresponding change in instrument output.

Time to 90% response – The time interval from a step change in the input concentration at the instrument inlet to a reading of 90% of the ultimate recorded concentration.

Rise time – The interval between 10% response time and time to 90% response after a step increase in the inlet concentration.

Fall time – The interval between 90% response time and time to 10% response after a step increase in the inlet concentration.

Zero drift – The change in instrument output over a stated time period, usually 24 hours, of unadjusted continuous operation, when the input concentration is zero; usually expressed as percent full scale.

Span drift – The change in instrument output over a stated time period, usually 24 hours, of unadjusted continuous operation, when the input concentration is a stated upscale value; usually expressed as percent full scale.

Operational period – The period of time over which the instrument can be expected to operate unattended within specifications.

Noise – Deviations from the mean output not caused by input concentration changes.

Accuracy — The degree of agreement between a measured value and the true value; usually expressed as $\pm$ percent of full scale.

Precision — The degree of agreement between repeated measurements of the same concentration, expressed as the average deviation of the single results from the mean.

Interference — An undesired positive or negative output caused by a substance other than the one being measured.

Interference equivalent — The portion of indicated input concentration due to the presence of an interfering substance or signal.

Operating temperature range — The range of ambient temperatures over which the instrument will meet all performance specifications.

Operating humidity range — The range of ambient relative humidity over which the instrument will meet all performance specifications.

Overload recovery time — The time required for the instrumental system to recover from an overload signal equal to the maximum input of the system.

Linearity — The maximum deviation between an actual instrument reading and the reading predicted by a straight line drawn between upper and lower calibration points.

4. SUGGESTED PERFORMANCE SPECIFICATIONS

Minimum range: 0-58mg/m³.

Minimum output: 0-10, 0-100, 0-1,000 or 0-5,000mV full scale.

Minimum detectable sensitivity: 0.6mg/m³.

Lag time: 15 seconds, maximum.

Time to 90% response: 30 seconds, maximum.

Rise time, 90%: 15 seconds, maximum.

Fall time, 90%: 15 seconds, maximum.

Maximum zero drift: 3% per week — less than 1% in 24 hours.

Maximum span drift: 3% per week — less than 1% in 24 hours.

Precision: Not more than $\pm 0.5\%$.

Minimum operational period: 3 days.

Noise: Not more than $\pm 0.5\%$.

Maximum interference equivalent: 1% of full scale.

Minimum operating temperature range: 5-40°C.

Minimum operating humidity range: 10-100%.

Warm-up time: Not more than 1 hour.

Overload recovery time: 30 seconds.
Deviation from linearity: Not more than 1% of full scale.

5. REAGENTS

5.1 *Zero gas*

Nitrogen or helium in pressure cylinders provided with two-stage regulator valves is required. These gases should contain less than 0.1 milligram carbon monoxide per cubic metre.

5.2 *Calibration gases*

Calibration gases corresponding to 10, 20, 40 and 80% of full scale are used. These should be provided in pressure cylinders equipped with two-stage regulator valves. Zero and calibration gases should be supplied with certification or guaranteed analysis of carbon monoxide content. Regardless of whether guaranteed analyses are provided or obtained, the user, in his own interest, must check that the degree of linearity of the four standards is sufficient. If this degree of linearity is not obtained during calibration some or all of the calibration gases should be returned to the supplier for correction.

6. APPARATUS

6.1 *Carbon monoxide analyzer*

Commercially available instruments should be installed on location and demonstrated, preferably by the manufacturer, to meet or exceed manufacturer's specifications and those described in this method. A typical analyzer system is illustrated in Figure 1 (Page 212).

6.2 *Sample introduction system*

Pump, flow control valve and flowmeter.

6.3 *Filter*

A filter with a porosity of 2 to 10 microns should be used to prevent large particles from entering the sample cell.

6.4 *Moisture control*

Refrigeration units are provided with some commercial instruments for maintaining constant humidity. Drying tubes containing indicating

anhydrous calcium sulphate or indicating silica gel may be used. These should be of large capacity, such as 72 hours or more, so that too frequent changing may be avoided. These filters must be changed before strike through of water. In addition, suitable filters must be installed downstream from the drying cartridge to prevent the entry, to the optical cells, of particulate dust from the drying material.

7. OPERATING PROCEDURE

7.1 Specific operating procedures must be supplied by manufacturer in a detailed manual which corresponds in every detail with the instrument under test.

7.2 The first step common to all analyzers is to turn on the power supply and allow the necessary warm-up time before actual operation is begun using standard or sample gases. This time varies among analyzers and the length of time the analyzer has spent without power applied. It should not be more than 30 minutes. In any case, warm-up time should be long enough to stabilize drift.

7.3 Several classifications of procedures are actually involved. First is preliminary or initial setup; second, routine operation; and third, trouble shooting. The first and third classifications should be carried out by a competent technician. They involve use of internal adjustments, and often require special electronic instrumentation. Routine operations involve the use of external controls only and require relatively little training.

7.4 Typical initial or start-up procedures are setting of electrical zero, making coarse adjustments of infrared sources, oscillator tuning, if used, signal phase adjusting, amplifier gain adjusting, and initial span and zero adjusting.

7.5 Routine operations that might ordinarily be involved are described in the sequence below:

7.5.1 Turn power on.

7.5.2 Allow analyzer to warm up for time period earlier found to be necessary.

7.5.3 Introduce "zero" gas and adjust zero control to proper reading.

7.5.4 Introduce "span" gases and adjust span control to proper reading.

7.5.5 Check sample flow rate. This must not be in excess of rate found to cause pressure effects. Minimum rate is adjusted on the requirement for the resolution of fine sample structure.

7.5.6 Log all operations, control settings, adjustments, and the time of these operations.

7.6 Trouble shooting and maintenance must be carried out routinely and may be required without notice. The principal routine servicing includes replacement of particle filter, water removal check and recorder servicing. Other servicing that can be expected includes sensitivity checks, analyzer signal output determination, infrared source check, amplifier servicing, sample cell cleaning, phase adjustments, and servicing or changing detector. Recorder service requirements are the same as for any similar null-balancing instrument used for signal recording.

8. CALIBRATION

8.1 *Calibration curve*

Determine the linearity of the detector response at the operating flow rate and temperature. Prepare a calibration curve and check against the curve furnished with the instrument. Introduce zero gas and set the zero control to indicate a recorder reading of zero. Introduce span gas and adjust the span control to indicate the proper value. On the scale of 0 to 58mg/m³, set the 46mg/m³ standard at 80% of full scale on the recorder chart. Recheck zero and span until adjustments are no longer necessary. Introduce intermediate calibration gases and plot the values obtained. If a straight line is not obtained, or if deviation from linearity is not acceptable, the accuracy of the calibration gases should be questioned and some or all of these calibration gases should be returned to the supplier.

9. EXPRESSION OF RESULTS

9.1 *Calculations*

Determine the concentrations directly from the calibration curve. No calculations are necessary. Carbon monoxide concentrations in mg/m³ are converted to ppm as follows:

$$\text{ppm CO} = \text{mg CO/m}^3 \cdot 0.873 \text{ at } 25^{\circ}\text{C and } 760\text{mm mercury}$$

9.2 *Precision and accuracy*

Precision determined with calibration gases is $\pm 0.5\%$ full scale in the 0-58mg/m³ range. Precision is not dependent upon accuracy and precision can be obtained without the values being accurate. Perfect linearity of the calibration curve, for example, may only indicate precision.

A large scale collaborative study of such carbon monoxide measurements has been made (10.2). Carbon monoxide was determined in both dry and humidified air. Using the terminology of Mandel, values for "repeatability" or intralaboratory precision and "reproducibility" or interlaboratory precision, have been established (10.3). For concentrations of carbon monoxide in air up to 60 milligrams per cubic metre, these values are illustrated graphically in Figure 2, taken from the study above cited (Page 212).

From this figure, it is evident that repetition or replication of analyses will not materially assist in increasing the precision of the measurements. It will, in fact, generally be a waste of time and effort. Reproducibility is seen to be optimal at a concentration of 20 milligrams per cubic metre.

The limits of accuracy of such measurements are also given in this study, to which reference should be made. In general terms, the accuracy of the measured carbon monoxide value depends upon *both* the overall instrumental accuracy and the accuracy with which the known concentrations of carbon monoxide have been made up in the calibration gases. An accuracy of $\pm 1\%$ of full scale recorder chart can be obtained in the range of 0-58mg/m³ of carbon monoxide. Variations in the temperature, ambient to the analyzer, can cause changes equivalent to as much as 0.5mg CO/m³ per °C. This effect can be minimized by operating the analyzer in a temperature-controlled room. Pressure changes between span checks will cause momentary changes in instrument response. Zero drift is usually less than $\pm 1\%$ of full scale per 24 hours, if cell temperature and pressure are maintained constant.

10. REFERENCES

- 10.1 Tentative Method of Continuous Analyses for Carbon Monoxide Content of the Atmosphere. Methods of Air Sampling and Analysis, Intersociety Committee, page 233. 1972.
- 10.2 Collaborative Study of Reference Methods for the Continuous Measurement of Carbon Monoxide in the Atmosphere. McKee, H. C., and Childers, R. E. Southwest Research Institute, Houston, Texas. May 1972.
- 10.3 Repeatability and Reproducibility. Mandel, J. Materials Research and Standards. Am. Soc. Testing and Materials, Vol. 11, 8, 8. August 1971.

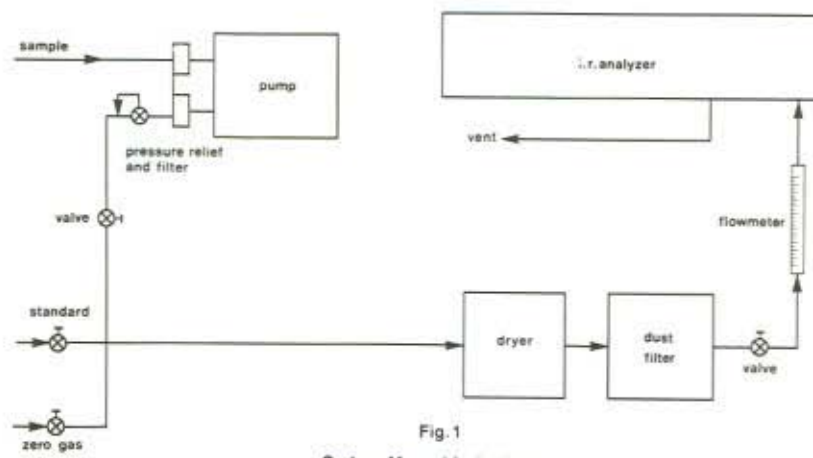


Fig. 1
Carbon Monoxide Analyzer

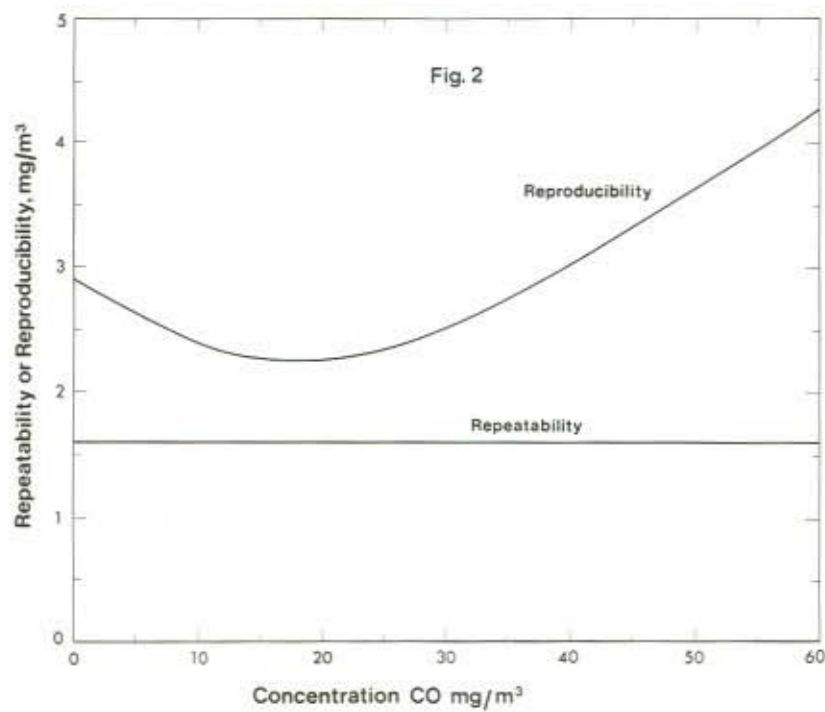


Fig. 2

Determination of Carbon Monoxide in the Atmosphere using Flame Ionization Detection

1. PRINCIPLE

By employing the correct adsorbants, an air sample may be freed of all components which can give a response in a flame ionization detector, except methane. Carbon monoxide must pass unaltered through the adsorbant. Carbon monoxide and methane are then easily separated chromatographically and carbon monoxide can be conveniently reduced catalytically to methane and measured with a flame ionization detector. The method is semi-continuous, with analysis rate selectable from 4 to 15 samples per hour. Between analyses, the sample stripper column is backflushed.

The instrument should have two modes of operation. One mode should provide for a complete visual display of electrometer output on a meter or strip chart recorder. The second mode should incorporate an automatic zeroing system which switches off when a predetermined change in electrometer output is anticipated, and remains off until the event of interest has passed.

2. APPLICABILITY

The method is applicable to the determination of carbon monoxide in ambient air and to the analysis of gases under pressure. Instruments are commercially available that measure in ranges selectable to a maximum of 6-300ppm (7.344mg/m^3) which includes the concentrations most commonly encountered in ambient urban air and the concentrations likely to be found in localized areas and potentially detrimental to health. The extreme sensitivity of the flame ionization detector is essential for accurate measurement of low levels of carbon monoxide (10.1). Instruments are available which have a 0.02-1ppm range (10.2). Changes in temperature and pressure which could alter the density of the sample must be compensated for by recalibration. Interferences may be examined by directing a stripped, chromatographed sample directly into the flame, by-passing the catalytic converter. Instruments should be equipped to do this. The manufacturer should provide some data on interferences. Conversion of carbon monoxide to methane should be quantitative to achieve maximum sensitivity and reliability.

3. DEFINITIONS

Range – The minimum and maximum measurement limits.

Output – Electrical signal which is proportional to the measurement. Usually expressed as millivolts or milliamps full scale at a given impedance.

Full Scale – The maximum measuring limit for a given range.

Minimum detectable (sensitivity) – The smallest amount of input concentration, significantly greater than zero, that can be detected.

Lag time – The time interval from a step change in input concentration at the instrument inlet to the first corresponding change in instrument output.

Time to 90% response – The time interval from a step change in the input concentration at the instrument inlet to a reading of 90% of the ultimate recorded concentration.

Rise time – The interval between 10% response time and time to 90% response after a step increase in the inlet concentration.

Fall time – The interval between 90% response time and time to 10% response after a step decrease in the inlet concentration.

Zero drift – The change in instrument output over a stated time period, usually 24 hours, of unadjusted continuous operation, when the input concentration is zero; usually expressed in percent.

Span drift – The change in instrument output over a stated time period, usually 24 hours, of unadjusted continuous operation, when the input concentration is a stated upscale value; usually expressed in percent.

Operational period – The period of time over which the instrument can be expected to operate unattended within specifications.

Noise – Spontaneous deviations from the mean output not caused by input concentration changes.

Accuracy – The degree of agreement between a measured value and the true value; usually expressed as $\pm$ percent of the true value after the effects of interfering substances have been eliminated (physically or mathematically).

Precision – The degree of agreement between repeated measurements of the same concentration, expressed as the average deviation of the single results from the mean.

Specificity – Degree to which the mean measurement is due only to the substance being determined.

Interference — An undesired positive or negative output caused by a substance other than the one being measured.

Interference equivalent — The portion of indicated input concentration due to the presence of an interfering substance or signal.

Operating temperature range — The range of ambient temperatures over which the instrument will meet all performance specifications.

Operating humidity range — The range of ambient relative humidity over which the instrument will meet all performance specifications.

Overload recovery time — The time required for the instrumental system to recover from an overload signal equal to 10 times the maximum input of the system.

Linearity — The maximum deviation between an actual instrument reading and the reading predicted by a straight line drawn between calibration points.

4. SUGGESTED PERFORMANCE SPECIFICATIONS

Minimum range: 0.02-1 ppm (0.023-1.15mg/m³).

Maximum range: 6-300ppm (7-344mg/m³).

Output (selectable): 0-10, 0-100, 0-1,000 or 0-5,000mV full scale.

Minimum detectable (sensitivity): 0.02ppm (0.023mg/m³).

Lag time: 4 minutes, maximum.

Time to 90% response: 4 minutes, maximum.

Rise time: 2 seconds, maximum.

Fall time: 2 seconds, maximum.

Maximum zero drift: Automatic zeroing.

Maximum span drift: 3% per week — less than 1% in 24 hours.

Precision: Not more than $\pm 0.5\%$.

Minimum operational period: 3 days.

Specificity: Manufacturer's statement of substances in ambient air other than carbon monoxide which can induce instrument response and the degree of response for each.

Noise: Not more than $\pm 0.5\%$.

Maximum interference equivalent: 1% of full scale.

Minimum operating temperature range: 5-40°C.

Minimum operating humidity range: 10-100%.

Warm-up time: Not more than 1 hour.

Overload recovery time: 30 seconds.

Deviation from linearity: Not more than 1% of full scale.

Safety features: Automatic fuel shut-off and flame-out indicator.

5. REAGENTS

5.1 *Zero gas*

A sample of CO-free air or air having a low (<0.1 ppm) but accurately known CO concentration. This gas is not necessarily for zeroing as calibration is done with automatic zero on. However, suspected interfering gases may be diluted with this zero gas and tested with the instrument.

5.2 *Calibration gases*

Calibration gases corresponding to 10, 20, 40 and 80% of full scale are used. These should be provided in pressure cylinders equipped with two-stage regulator valves. Zero and calibration gases should be supplied with certification or guaranteed analysis of carbon monoxide content. Regardless of whether guaranteed analyses are provided or obtained, the user, in his own interest, must check that the degree of linearity of the four standards is sufficient. If this degree of linearity is not obtained during calibration some or all of the calibration gases should be returned to the supplier for correction. If possible, these gases should be purchased from at least two different suppliers.

5.3 *Flame air*

Compressed air in cylinders, dry and clean enough that any response of the flame ionization detector to contaminants in this air can easily be eliminated electronically. Air containing less than 2ppm hydrocarbon expressed as methane is suitable.

5.4 *Hydrogen*

Compressed hydrogen in cylinders, with a toggle valve in-line for emergency shut-off. The hydrogen should contain less than 0.1ppm hydrocarbon expressed as methane.

6. APPARATUS

6.1 *Carbon monoxide analyzer*

Commercially available instruments should be installed on location and demonstrated, preferably by the manufacturer, to meet or exceed manufacturer's specifications and those described in this method.

6.2 *Sample introduction system*

A vacuum pump to pull the sample through the instrument.

6.3 Filter

A filter with a porosity of 2 to 10 microns should be used to prevent large particles from entering the instrument.

6.4 Moisture control

When sampling ambient air, care should be taken to ensure that moisture does not enter the tube leading from sampling site to burner manifold. An inverted funnel on the sampling site end of this tube has proved useful in keeping rainwater from entering the tube.

7. OPERATING PROCEDURE

7.1 Specific operating procedures must be supplied by the manufacturer in a detailed manual which corresponds in every detail with the instrument under test.

7.2 The first step common to all analyzers is to turn on the power supply and allow the necessary warm-up time before actual operation is begun using standard or sample gases. This time varies among analyzers and the length of time the analyzer has spent without power applied. It should not be more than 30 minutes. In any case, warm-up time should be long enough to stabilize drift.

7.3 Several classifications of procedures are actually involved. First is preliminary or initial setup; second, routine operation; and third, trouble shooting. The first and third classifications should be carried out by a competent technician. They involve use of internal adjustments, and often require special electronic instrumentation. Routine operations involve the use of external controls only and require relatively little training.

7.4 Typical initial or start-up procedures are leak testing gas connections, setting cylinder and instruction gas pressure regulators, flame ignition, zero and span adjusting and connecting the sample pump and inlet tube.

7.5 Routine operations that might ordinarily be involved are described in the sequence below:

7.5.1 Verify the stability of the oven temperature.

7.5.2 Verify calibration with span gases.

7.5.3 Look for signs of column deterioration by examining retention times.

7.5.4 Check for abnormalities in the chromatograms, i.e. negative excursions, excessive noise, etc.

7.5.5 Check sample flow rate. This must not be in excess of rate found to cause pressure effects.

7.5.6 Log all operations, control settings, adjustments, and the time of these operations.

7.6 Trouble shooting and maintenance must be carried out routinely and may be required without notice. The principal routine servicing includes replacement of particle filter, replacement of compressed gases and recorder servicing. Other servicing that can be expected includes reactivating chromatography and stripper columns. Recorder service requirements are the same for any similar null-balancing instrument used for signal recording.

8. CALIBRATION

8.1 *Calibration curve*

Determine the linearity of the detector response at the operating flow rate and temperature. Prepare a calibration curve and check against the curve furnished with the instrument. Introduce zero gas and set the zero control to indicate a recorder reading of zero. Introduce span gas and adjust the span control to indicate the proper value. On the scale 7 to 344mg/m³ set the 275 mg/m³ standard at 80% of full scale on the recorder chart. Recheck zero and span until adjustments are no longer necessary. Introduce intermediate calibration gases and plot the values obtained. If a straight line is not obtained, or if deviation from linearity is not acceptable, the accuracy of the calibration gases should be questioned and some or all of these calibration gases should be returned to the supplier.

9. EXPRESSION OF RESULTS

9.1 *Calculations*

Determine the concentrations directly from the calibration curve. No calculations are necessary. Carbon monoxide concentrations in ppm are converted to mg/m³ as follows:

$$\text{mg CO/m}^3 = 1.145 \cdot \text{ppm CO}$$

at 25° and 760mm mercury.

9.2 *Precision and accuracy*

Precision determined with calibration gases is ±0.5% full scale in the 7-344mg/m³ range. Precision is not dependent upon accuracy and precision can be obtained without the values being accurate. Perfect linearity of the

calibration curve, for example, may only indicate linearity of detector response, not accuracy. In general terms, the accuracy of the measured carbon monoxide value depends upon *both* the overall instrumental accuracy and the accuracy with which the known concentrations of carbon monoxide have been made up in the calibration gases. An accuracy of $\pm 1\%$ can be obtained in the range of 0.58mg/m^3 of carbon monoxide.

10. REFERENCES

- 10.1 Stevens, R. K. and O'Keefe, A. E. Modern Aspects of Air Pollution Monitoring. *Analytical Chemistry* **42**, 143A 1970.
- 10.2 Air Sampling Instruments: For Evaluation of Atmospheric Contaminants. 4th Edition 1972. American Conference of Governmental Industrial Hygienists, Cincinnati, Ohio.

Estimation of Nitrogen Dioxide and Nitric Oxide in Air

In addition to the method described below, a number of instruments have recently become available based on chemiluminescence: these are currently being evaluated and may be of considerable value.

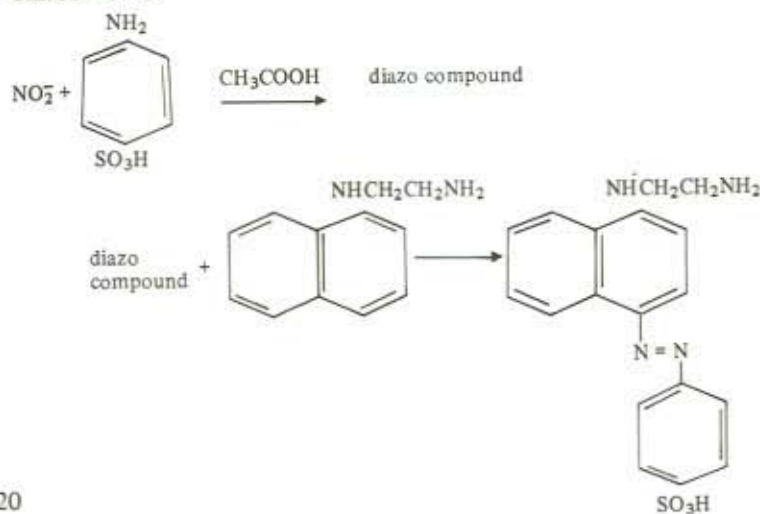
1. SCOPE

The method is applicable to nitrogen dioxide concentrations in the atmosphere from a few parts per thousand million to about 5 parts per million, with only slight interference from other gases.

2. PRINCIPLE OF METHOD

Nitrogen dioxide is absorbed in a solution of sulphanilic acid which is thereby diazotised; the diazonium salt is coupled with N-(1-naphthyl)-ethylenediamine and the azo-dye formed measured spectrophotometrically. The same process can be used for nitric oxide after oxidation to nitrogen dioxide by first passing the sample through an oxidising solution: this gives a measure of total nitrogen dioxide and nitric oxide, the latter being estimated by difference. The method is basically that of Saltzman (9.1) as recommended by the American Society for Testing Materials.

3. REACTIONS



4. REAGENTS

The reagents are made from analytical-grade chemicals in nitrite-free water prepared, if necessary, by redistilling distilled water in an all-glass still after adding a crystal of each of potassium permanganate and barium hydroxide. Unless otherwise stated, solutions are stable for several months if stored in well-stoppered, amber glass bottles at low temperature. The absorbing solution should be warmed to room temperature before use. Acetic acid, glacial; sodium nitrite; sulphanilic acid; N-(1-naphthyl)-ethylenediamine hydrochloride stock solution: dissolve 0.2 gram of the reagent in 100ml of water.

4.1 *Absorbing solution*

Dissolve 5 gram of sulphanilic acid in about 900ml of water containing 140ml of glacial acetic acid. Cool, add 20ml of the stock solution of N-(1-naphthyl)-ethylenediamine hydrochloride and dilute to 1 litre with water. Avoid lengthy exposure to air during preparation and use. Sodium nitrite stock solution: dissolve 2.03 gram of sodium nitrite in water and dilute to 1 litre. Solution stable for about 90 days.

4.2 *Sodium nitrite standard solution*

Dilute 10ml of the stock solution to 1 litre with water. Prepare fresh just before use. One ml of this solution produces a colour equivalent to that of 10 μ l of nitrogen dioxide (10ppm in 1 litre of air at 760mm Hg and 25°C). This is based on the empirical determination that 0.72 mole of sodium nitrite produces the same colour as 1 mole of nitrogen dioxide. There is some controversy concerning this stoichiometric factor which has ranged from 0.5 to 1.0 (9.2-9.5). For this reason for work of the highest accuracy the calibration graph should be prepared using standard atmospheres of nitrogen dioxide.

4.3 *Potassium permanganate (for determination of nitric oxide)*

Dissolve 2.5 gram of potassium permanganate in about 90ml of water, add 0.75ml of concentrated sulphuric acid (SG = 1.84), cool and dilute to 100ml with water. This solution has poor keeping properties and is preferably prepared fresh as required.

5. APPARATUS

5.1 *Bubblers*

These should be of the miniature fritted type. Alternatively all-glass midjet impingers (which may be obtained commercially, eg from Mine Safety

Appliances Limited) may be used. It should be noted that if the latter are used, absorption efficiency may be lower than with the fritted type and it may be necessary to use more than two in series to ensure complete collection of sample.

6. SAMPLING AND PROCEDURE

6.1 *Nitrogen dioxide only*

Transfer, by means of a pipette, 10ml of the absorbing solution to two bubblers connected in series. By means of a suitable pump draw the atmosphere through the absorbing solution at the rate of 400ml/min until a reasonable red-violet colour has developed in the first bubbler. Note the volume of air sampled and the temperature and pressure. After a further 15min the optical density of each solution is measured in 20mm cells at 550nm using unexposed reagent as reference and the concentration of nitrogen dioxide determined from the prepared calibration graph. Correction for pressure and temperature may be made if necessary by means of the usual gas equation.

6.2 *Nitric oxide only*

Transfer 10ml of the absorbing solution to three suitable small bubblers and 10ml of the potassium permanganate solution to a fourth bubbler. Connect in series – bubblers 1 and 2 containing absorber, bubbler 3 containing oxidant and bubbler 4 absorber. Proceed as for nitrogen dioxide and measure optical density of the solution in bubbler 4 which will be a measure of the nitric oxide concentration in terms of nitrogen dioxide. Conversion of nitric oxide to nitrogen dioxide by acid permanganate is variable and can be as low as 70%, hence the method will give only an approximate value for nitric oxide concentration. Conversion efficiencies of 95 to 100% have been reported using other oxidants (9.6).

6.3 *Nitrogen dioxide and nitric oxide*

If a simultaneous estimation of these gases is required then the optical densities of solutions in bubblers 1 and 2, as described under nitric oxide, may also be measured.

7. SPECIAL CASES

Instruments for automatic continuous monitoring of oxides of nitrogen in the atmosphere utilising the Saltzman method are available commercially.

Their bulk, however, might preclude the use of such instruments in the upper atmosphere and no information is available regarding the availability of miniature models. Coulometric and non-dispersive infra-red spectroscopic methods which lend themselves to miniaturisation have been described. The former is however non-specific for nitrogen oxides being subject to interference from oxidants and water vapours. The latter in its present form is seriously affected by the presence of water vapour and is relatively insensitive below about 10ppm.

8. NOTES ON PROCEDURE

8.1 *Preparation of calibration graph*

Add known volumes, up to 1ml, of the standard nitrite solution to a series of 25ml volumetric flasks and dilute to volume with the absorbing solution. Mix well and after 15min measure the optical density of the solution in 20mm cells at 550nm using the reagent as reference and plot graph of optical density against concentration.

8.2 *Interferences*

The effect of interfering gases is relatively unimportant unless present in quantities much higher than that of nitrogen dioxide. Ozone in amounts greater than 5 times that of nitrogen dioxide cause a small interference imparting a slight orange tint to the reagent. A 10-fold ratio of sulphur dioxide produces no interference, but a 30-fold ratio slowly bleaches the colour to a slight extent. Interferences from other gases is negligible.

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Determination of Ozone in the Atmosphere

1. SCOPE

The method is simple, sensitive and specific for the determination of ozone in air. It responds only to ozone and is not affected by other oxidizing or reducing agents.

2. FIELD OF APPLICATION

The method is useful for the determination of ozone in the ambient or polluted air. Ozone can be monitored continuously when this method is used in combination with a formaldehyde monitor. This method has proved to be very useful for determining low concentrations of ozone in ozonized air produced in laboratories where the air used is not very pure.

3. PRINCIPLE OF THE METHOD, REACTIONS AND SPECIFICITIES

The method presented here is based on the reaction of ozone with 4-allyl-2-methoxy phenol (eugenol). Ozone preferentially attacks the olefinic bond in allyl group and releases an equivalent amount for formaldehyde. The resultant formaldehyde is collected in distilled water and determined by a slight modification of West-Gaeke method for sulfur dioxide (9.1).

4. REAGENTS AND MATERIALS

Para-rosaniline hydrochloride (Fisher Scientific Co., Catalog No. 42500). Mercuric chloride, sodium chloride, sodium hydroxide, potassium iodide, sulfamic acid and standard formaldehyde solution (1,000mg/l).

4.1 *Sodium tetrachloromercurate II solution*

This solution was prepared by dissolving 13.6g of mercuric chloride and 5.8g of sodium chloride per liter of distilled water.

4.2 *Sodium dichloro-sulfite mercurate II solution*

Dissolve 0.25g of sodium sulfite in 50ml of sodium tetrachloromercurate II solution. (This reagent is unstable and should not be used over 24hrs).

4.3 *Para-rosaniline reagent*

Prepared by dissolving 0.16g of para-rosaniline hydrochloride in 24ml of concentrated HCl, then diluting to 100ml with distilled water.

4.4 *Alkaline iodide solution*

Ten grams of KI and 40g of NaOH were dissolved per liter of water.

4.5 *Acidifying reagent*

Five g of sulfamic acid were dissolved in 100ml of water, then 84ml of 85% phosphoric acid were added and the mixture was made up to 200ml.

4.6 *Preparation of ozonized air*

The ozonized air used in laboratory was produced by passing pre-purified air through a brown glass aspirator bottle of 5 liter capacity in which a germicidal lamp (4W Germicidal Lamp, G.E. 024511) was fixed. The mouth of the bottle was sealed with a cork through which the leads of the lamp and an outlet tube were passed as shown in Figure 1. Initially, the lamp was kept on for a week so that it could generate enough ozone to react with any of the organic matter that might be present in the aspirator. After this equilibration, the lamp was turned on every morning at least an hour before any samples were ozonized. An ozone concentration of 0.5 to 10ppm was obtained as desired by controlling the flow of air through the aspirator. Lower concentrations, down to 0.05ppm, were obtained by partially covering the lamp with aluminum foil and keeping it on for ten days to equilibrate for any possible reaction of ozone with aluminum foil.

4.7 *Purification of eugenol*

Eugenol as well as all other l-alkenes tried were found to contain formaldehyde as impurity. This may be due to the exposure of the compounds to atmospheric ozone. Each compound was purified just before use, by passing it over 3in column of pure dry sodium sulfite crystals.

4.8 *Apparatus*

Gas samplers (described by Wartburg, Pate and Lodge, 1969), midget impingers (MSA Catalog No. 46984); air flow meters (Fisher and Porter Co., Catalog No. 450-015); Dyna-vac pump (Cole-Parmer, Catalog No. 7064); Beckman D.B. Spectrophotometer.

5. SAMPLING AND SAMPLES

The sampling equipment was set up as shown in Figure 1. The gas samples shown were obtained from the National Center for Atmospheric Research, Boulder, Colorado. Midget impingers were also tried and found to be satisfactory. Two sampling bubblers were used in series. One was used as an impinger in which air containing ozone was impinged upon the surface of eugenol placed in the container; the second, containing 10ml of distilled water, was used as an absorber for formaldehyde. Air in the first impinger was passed through an orifice of 1mm diameter at a rate of 2l/m. The jet velocity has been estimated to be 44m/sec. With 1ml of eugenol in the tube, the spacing tip and the surface of the eugenol was 5min. In the second bubbler the orifice may be replaced by a frit which must be completely immersed in the water for absorbing the formaldehyde (Page 229).

6. PROCEDURES

6.1 *Determination of formaldehyde*

Two reliable methods are available for the determination of formaldehyde: (1) The method developed by Lyles et al. (9.1), and (2) By the use of chromotropic acid (9.2). The chromotropic acid method was tried, but some vapors of eugenol were carried into the air along with the formaldehyde formed and interfered with the determination of formaldehyde. Moreover, the sampling solution used in the latter method (0.1% chromotropic acid in concentrated sulfuric acid) is certainly not a desirable one to work with. The method of Lyles et al., which is based on the reverse of the West-Gaeke method for sulfur dioxide, has been found to be simple, reliable, and satisfactory for the determination of formaldehyde formed by the ozonolysis of eugenol. To ten milliliters of aqueous solution of formaldehyde, add one milliliter of sodium dichloro-sulfito-mercurate II solution and mix thoroughly. Add one milliliter of para-rosaniline solution, mix and allow to stand for 20min. Determine absorbance at 560mm, and by the use of standard calibration curve determine the total amount of formaldehyde in 10ml of sampling solution.

7. CALCULATIONS

Convert the volume of air sampled to the volume at standard conditions of 25°C, 760mm Hg:

$$V_R = V \times \frac{P}{760} \times \frac{298}{(t + 273)}$$

V_R = volume of air at 25°C and 1 atmosphere.
 V = volume of air sampled, liters.
 P = barometric pressure, mm Hg.
 t = temperature of air sampled, °C.

Ordinarily, the correction for pressure is slight and may be neglected.

If we assume 1:1 stoichiometry for the 1% neutral buffered KI method (10.6) for ozone, the following expression should be used for determining ozone concentrations:

$$\text{ppm ozone} = \frac{\mu\text{g HCHO found} \times 224}{30 \times \text{volume of air sampled (liters)}} \times 1.54$$

8. STOICHIOMETRY OF THE REACTION

Ozone concentration in an air containing about 2ppm of ozone was determined by the formaldehyde method, the neutral iodide method and the alkaline iodide method. The same ozonized air under exactly similar conditions was used in all three determinations. The following results were obtained:

<i>Method Used</i>	<i>Ozone Concentration (ppm)</i>
Neutral iodide	2.3
Alkaline iodide	1.55
Eugenol-formaldehyde	1.50

A recent report on stoichiometry of iodide method, by Boyd et al. (9.4), provided evidence that the alkaline iodide method to yield one iodine molecule for every one molecule of ozone absorbed and that the neutral iodide method actually yields 1.54 molecules of iodine for every one molecule of ozone absorbed. On the contrary, the results obtained by Kopczynski and Bufalini (9.5) show that in neutral iodide method one mole of iodine is released per mole of ozone. Results of this study are in complete agreement with the alkaline iodide method (9.6). Because of unavailability of standard ozone concentrations it is difficult to decide as to which method yields true results. Obviously, a standard method of generating known concentration of ozone is badly needed.

8.1 Determinations of ozone at different concentration levels

Ozone was determined in several samples of air containing ozone in the range of 0.05 to 2.0ppm. Each concentration level was determined three times by alkaline iodide method as well as by eugenol-formaldehyde. Results are given in Table I.

TABLE 1

Comparative study of eugenol-formaldehyde method and alkaline iodide method.

Ozone concentration (ppm)*	
Alkaline iodide method	Eugenol-formaldehyde method
0.045	0.050
0.11	0.10
0.18	0.17
0.25	0.25
0.99	0.92
1.20	1.15
1.50	1.45
1.90	1.80

*Results tabulated are averages of three samples.

The eugenol-formaldehyde method yields comparable results to those obtained by alkaline iodide method of Byers and Saltzman (9.6), at all concentrations with the range of 0.05 to 2ppm ozone concentration. Since ozone is not likely to exist in concentrations higher than 2.0ppm in ordinary atmospheres, higher concentrations were not studied. A few higher concentrations, in the range of 2-5ppm of ozone, were determined by eugenol-formaldehyde method, but no comparison was made with iodide method.

8.2 Sensitivity of the method

The sensitivity of the method is exactly the same as that for formaldehyde method of Lyles et al. (9.1), since each molecule of ozone yields proportional amounts of formaldehyde. Ozone concentration of 0.02ppm can be easily determined by sampling the air for 40 minutes at a rate of two liters per minute.

8.3 Selectivity of the method

The eugenol-formaldehyde method described seems to be specific for ozone; only formaldehyde will interfere. Simultaneous determination of formaldehyde must be carried out and the concentration of formaldehyde must be subtracted from the concentration of ozone obtained.

Since formaldehyde can be determined with the same technique by removing the first impinges, this would present no difficulty whatsoever. Interference effects of hydrogen peroxide (3%) and peracetic acid were studied by spraying the two solutions into the air being sampled. Neither

hydrogen peroxide nor peracetic acid gave any formaldehyde when reacted with eugenol. Sulfur dioxide and other reducing agents present in the air do not interfere.

8.4 Field studies

The method is now being tested for on-site determinations of ozone. Preliminary studies indicate that the method would be quite suitable for field studies (9.7). Any formaldehyde monitoring equipment can be easily adopted for monitoring ozone. A midget impinger containing 1ml of eugenol is all that need be connected to the equipment to convert it to an ozone monitor.

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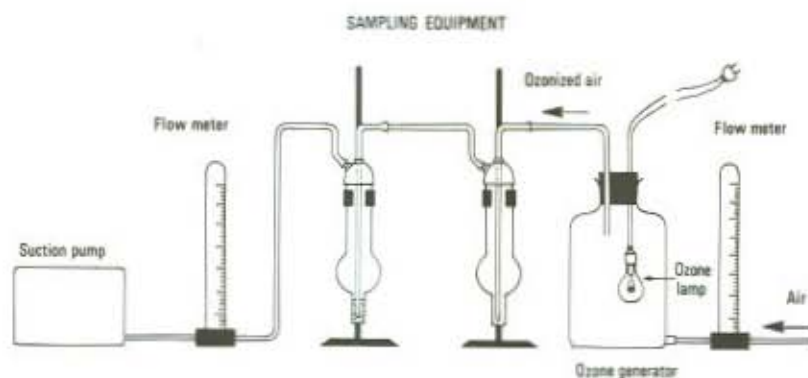


Fig. 1

Spectrophotometric Determination of Atmospheric Fluorides

1. INTRODUCTION

Fluoride is a special hazard to vegetation where as little as 0.1ppb may affect certain species such as Chinese apricot and some varieties of gladiolus. Although most plants can tolerate many times this concentration and animals are generally unaffected by two or three orders of magnitude higher concentrations than this, it is important that the analytical method used for determining fluorides be capable of great sensitivity and applicable over a wide range of concentrations. A critical problem presented in the determination of atmospheric fluorides is that of sampling. The usual sampling procedures involve trapping the fluoride in an aqueous system whereby not only fluoride but also other pollutants are captured. Although fluoride can co-exist in dilute atmosphere with iron, aluminum, manganese, calcium, magnesium and lead, aqueous solutions of the respective ions react to form insoluble salts and stable complexes. Particularly in the case of the slightly dissociated iron, aluminum and manganese complexes, steps must be taken to isolate the fluoride before final analysis because determinative procedures are incapable of measuring undissolved fluoride.

Many methods have been evolved for the determination of fluoride. The fluoride electrode is excellent for determining fluoride activities in the microgram per milliliter range but is not sufficiently sensitive for air pollution studies except where large volumes of air are being sampled or very high concentrations of fluoride are anticipated. Many spectrophotometric methods have been proposed, most of which are based on the bleaching of a colored species of a chelated metal. The fluoride in such procedures complex the metal responsible for the colored species, thus destroying the color. In 1959, Belcher and Leonard introduced the first reagent for fluoride that produced a color rather than destroying one (11.2). A modification of this sensitive and highly selective reagent (11.2) is utilized together with a unique sampling technique to provide a sensitive, rapid, and specific method for fluoride monitoring (11.4).

A number of approaches have been used to remove interferences or isolate fluoride so that final analytical measurement can be made reliable. Ion exchange has found some use but most monitoral work has relied on distillation. The classic Willard-Winter distillation effectively breaks down stable fluoride compounds and liberates the fluoride from interfering materials. The method is laborious, however, and the use of microdiffusion provides an attractive alternate approach (11.1). The method of dynamic volatilization has advantages of flexibility and rapidity and is described below.

2. SCOPE AND FIELD OF APPLICATION

The lanthanide-alizarin complexan-fluoride reaction is the basis for the spectrophotometric determination of atmospheric fluorides. Optimum reaction conditions have been established and the sampling procedure eliminates the interference of diverse ions and molecules that are commonly present in the atmosphere. The method has a sensitivity of $0.0019\mu\text{g}$ fluoride per sq. cm. and is reproducible within $\pm 0.003\mu\text{g}$, per ml at the 95% confidence level for known concentrations of fluoride of $0.400\mu\text{g}$ per ml. The procedure is uniquely suitable for the determination of actual fluoride concentrations in ambient atmospheres at parts per billion levels. It is well suited for use in mobile laboratories and fixed base monitoring stations.

3. PRINCIPLE OF THE METHOD, REACTION, AND SPECIFICITY

The method involves the elimination of interfering species by use of a pre-scrub through hot (70°C) sulfuric acid, followed by the trapping of liberated HF in an aqueous system with subsequent spectrophotometric determination with lanthanum-alizarin complexan. The final trapping solution contains sulfamic acid which reacts with any nitrite that might be present, converting it to non-interfering nitrogen gas. All interferences that are likely to be present in the atmosphere are thus eliminated, either by the initial H_2SO_4 trap or by the reaction in the final absorbing system.

4. REAGENTS AND MATERIALS

4.1 *Standard fluoride solution ($5\mu\text{g}$ per ml)*

Dissolve 0.221 gram of reagent grade NaF in distilled water and dilute to 1 liter. This solution contains $100\mu\text{g}$ fluoride per ml. Dilute 1 to 20 to obtain the working solution.

4.2 *Buffer solution*

Combine 188 grams of anhydrous NaOAc with 336ml of glacial HOAc and dilute to 1 liter with distilled water. When this solution is diluted to 1 to 10 with distilled water, the pH should be 4.3.

4.3 *Alizarin complexan ($1 \times 10^{-3} \text{ M}$)*

Dissolve 0.385 gram of reagent in a minimum amount of dilute NaOH. Dilute to 1 liter with a buffer solution containing 34ml of glacial HOAc and 18.8 grams of anhydrous NaOAc per liter.

4.4 Lanthanum nitrate-buffer (2×10^{-3} M)

Dissolve 0.866 grams of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and 102 grams of anhydrous NaOAc in 400ml of distilled H_2O . Add 222ml of glacial HOAc and 890 milliequivalents of HCl. Dilute to 1 liter. The pH of this solution, when diluted 1 to 10 and containing acetone to the extent of 25% (v/v) should be 4.1-4.2.

5. APPARATUS

5.1 Spectrophotometer — Beckman DU, or equivalent.

5.2 Heating mantel, with powerstat.

5.3 Glass scrubbers — Fritted glass, 30ml.

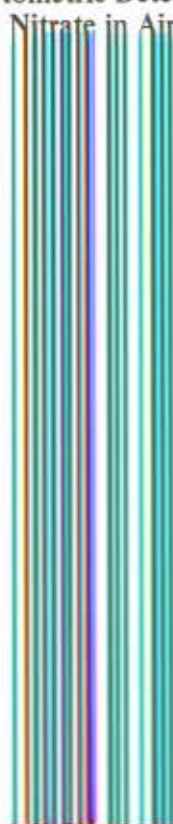
6. SAMPLING

When fluorides are scrubbed from the atmosphere prior to analysis, a number of species containing iron, aluminum, calcium magnesium, and lead are also trapped and thus put into solution along with the isolated fluorides. The resultant formation of insoluble substances such as calcium fluoride, and lead fluoride introduces potential interference and certainly the formation of extremely stable complexes such as the hexafluoroaluminate and the hexafluoroferrate (III) must mask fluorides so that subsequent analytical determination gives values representing fluoride activities after sampling rather than the significant fluoride concentrations of the atmosphere before sampling. The following analytical procedure takes these and other potential interferences into consideration.

The majority of the interferences can be eliminated quite readily while the air sample is being collected. This is accomplished by placing a pre-scrubber containing concentrated sulfuric acid between the sample source and the absorption solution. If the pre-scrubber is heated to approximately 70°C , the volatile acids will pass over into the absorbing solution leaving any interfering cation in the sulfuric acid. It is assumed that particulates and aerosols are immediately dissolved in the hot acid, thus liberating the F^- .

Samples should be collected in a sample train consisting of an inlet tube made of stainless steel or Tygon tubing connected to a 30ml fritted glass bubbler containing approximately 20ml. of concentrated H_2SO_4 maintained at 70°C by an appropriate heating mantel. The scrubbed sample is next led directly into a second fritted glass bubbler containing 30ml of 0.05% sulfamic acid.

Spectrophotometric Determination of



1. INTRODUCTION

Nitric acid and nitrates in air can be measured conveniently by means of the chromotropic acid (9.1) or brucine (9.2) methods. Likewise, mixtures of nitric oxide, nitrous anhydride and nitrogen tetroxide can be converted to equivalent nitrate and estimated as such (9.3). Other methods such as the phenol-disulfonic acid procedure, reduction to nitrite with subsequent measurement by means of a modified Griess reaction or the use of ultra-violet spectrophotometry have been proposed but are not recommended for general use because of lack of specificity or sensitivity or both. The chromotropic acid method is chosen in preference to the brucine procedure because the latter may suffer from interferences due to oxidants, other than nitrate, that may be present in the air.

2. SCOPE AND FIELD OF APPLICATION

This is a method for determining trace quantities of nitrate in the air suitable for establishing ambient air quality for spot checks, monitoring, or field surveys. Reliable results can be obtained over the range of 0.5-50 μ g of nitrate. Interferences due to substances such as nitrite, oxidizing agents, chloride and iron (III) which normally interfere in nitrate determinations have been eliminated.

3. PRINCIPLE

The method is based on the reaction of nitrate with chromotropic acid. The absorbance of the resulting yellow solution is proportional to the nitrate concentration. Potential interferences have been eliminated. Addition of excess sodium sulfite removes the interference due to oxidizing agents, and addition of urea eliminates nitrite as nitrogen gas. Chloride is masked by the addition of antimony (III).

4. REAGENTS

4.1 Standard nitrate solution

Dissolve 1.371g of reagent grade sodium nitrate in distilled water and dilute to one liter. This gives a nitrate concentration of 1mg/ml. A series of standards can be prepared by suitable dilutions.

4.2 Sulfuric acid

Use analytical reagent grade concentrated acid which is free from nitrate. (Readily checked by adding 1ml reagent to 10ml sulfuric acid. No color should be formed.)

4.3 Purified chromotropic acid

Prepare a saturated solution of the disodium salt of 1,8-dihydroxy-3,6-naphthalene disulfonic acid. Process twice using decolorizing charcoal. Crystallize the reagent from the filtered solution by adding sulfuric acid. Filter; wash several times with ethanol; and dry below 80°C. Prepare a 0.1% solution of the reagent in concentrated sulfuric acid. The reagent solution is colorless and is stable for two weeks.

4.4 Sulfite – urea solution

Dissolve 5g of urea and 4g of reagent grade anhydrous sodium sulfite and dilute to 100ml with distilled water.

4.5 Antimony solution

Heat 0.5g of antimony metal in 80ml of concentrated sulfuric acid until all the metal is dissolved. Cool the solution and add to 20ml of ice water. When kept overnight, if any salt crystallizes, redissolve by heating.

5. APPARATUS

5.1 High volume sampler

Spectrophotometer suitable for measurement of absorbance at 410nm and equipped with matched quartz cells.

6. SAMPLING

A high volume sampler is used for sample collection. Since nitrates are soluble in water, they can be eluted from the filter paper by repeated washing with a small amount of distilled water. Combine the washings and make up to 100ml with distilled water.

7. PROCEDURE

Pipet 2.5ml of each sample or standard solution into dry 10ml volumetric flasks. To each flask add 1 drop of sulfite-urea solution; place the flasks in a

co-pollutants during sampling and if fiber glass filters are used, the acid is partially neutralized by alkaline sites present on the filter surface.

The method chosen for recommendation here is simple, sensitive and rapid. It is based on stoichiometric reactions of dissociated protons and employs the use of an inexpensive ring oven for processing the samples and reaction products (11.8).

2. SCOPE AND FIELD OF APPLICATION

The ring oven method for the determination of sulfuric acid aerosol is sensitive, rapid and easy to perform. It is based on the measurement of dissociated protons and by slight alteration in procedure, can be used either for determination of total non-volatile acid (H_2SO_4) or for total protons from dissociated acids and from the hydrolysis of salts such as ammonium sulfate, ammonium chloride, and zinc sulfate, which react with moisture to produce protons. The method is readily employed for field studies as well as for determinations made on collected samples and returned to the laboratory.

3. PRINCIPLE

This method combines the sampling and determination of sulfuric acid aerosol so that the process is essentially analysis *in situ*. A relatively small sample is collected on quantitative filter paper using a sequential tape sampler or other suitable device that will collect the acid on a spot one inch (or one-half inch) in diameter. The filter itself is then used as the reaction medium for the analytical measurement which is based on the stoichiometric release by acid protons of bromine from a mixture of bromide and bromate. The liberated bromine is reacted with fluoroscein to produce eosin, the color of which is measured against standard colors as a direct determination of proton concentration. The measurement steps are performed using a ring oven.

If non-volatile acid (H_2SO_4) is to be measured the filter on which the sample has been collected should be heated at 100-105°C for 4 or more hours to eliminate any volatile acids.

4. REACTIONS

The determination is based on the stoichiometric release by protons of bromine from a mixture of bromide and bromate as depicted by the following equation:



7. SAMPLING

Collect 0.1-2.0m³ of air sample (depending on anticipated acid levels) with a sequential tape sampler providing either a one inch spot or a one-half inch sample spot. The sample spot is transferred in place on the tape to a ring oven for analysis.

8. PROCEDURE

Place the filter tape on the ring oven with the sample spot centered exactly over the annular space of the heated (90°C) surface. If a one-inch sample spot is taken, a ring oven with a 33mm diameter opening must be used. If a one-half inch sample spot is processed, a ring oven with a 22mm diameter ring should be employed. The following steps apply to the processing of the large sample spots. If the half-inch samples are being processed, then use only one-half the volume of reagents and solutions mentioned in the following procedure.

Add to the exact center of the sample spot 30μl of potassium bromide and wash to the ring zone with distilled water. Allow the ring to dry completely and then add 6μl of fluorescein. Wash the dye to the ring zone with methanol. Remove the tape from the ring oven and add potassium bromate solution around (from the outside!) the ring zone using a capillary tube. Return the tape to the hot ring oven with the spot centered as before and wait three minutes for full color development. Compare the color intensity of the ring with standard rings.

9. CALIBRATION CURVE

Standard rings are conveniently prepared by using 0, 2, 4, 6, 8, and 10μl of standard sulfuric acid solution. After the addition of the known amounts of standard acid, each spot is processed as described above. The resultant standard rings are stable for at least one month.

10. SPECIAL CASES

10.1 The procedure described anticipates the collection of samples by means of a paper tape sequential sampler. It is possible also to collect samples using high-volume samplers by processing only an aliquot of the total sample. For example, a one-half inch spot can be stamped out of the filter using a cork borer. With the dust spot down and centered on a piece of Whatman 41 filter paper (or S&S 495) the regular procedure described above can be followed. Calculations should take into account the fraction of the total sample being processed.

10.2 The procedure for sulfuric acid aerosol can be modified slightly to apply for the determination of total protons. Thus, not only are sulfuric acids measured, but protons from volatile acids, such as hydrochloric and nitric acids, and acid salts, such as ammonium sulfate, ammonium chloride and zinc sulfate, are included. The procedure in this case is as follows: Add to the center of the sample spot 30 μ l of potassium bromide and wash to the ring zone with distilled water. Allow the ring to dry completely and then add 6 μ l of fluorescein. Wash the dye to the ring zone area with methanol. Remove the tape from the ring oven and add potassium bromate solution around (from the outside) the ring zone using a capillary tube. Return the tape to the hot ring oven and wait three minutes for full color development. Compare the color intensity of the ring with standard rings.

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Determination of Fluoride in Water

The ion-selective electrode method has been selected for the determination of fluoride in water because of its practical convenience and reliability. Others also available include the lanthanum alizarin complexone colorimetric method but some involve appreciable practical experience in, for example, special distillation techniques.

1. SCOPE

Waters containing soluble uncomplexed ionic fluoride at levels down to 0.1mg per litre. The total soluble fluoride can be obtained by use of a citrate total ionic strength buffer (8.2).

2. PRINCIPLE OF METHOD

Direct reading of response of a fluoride ion-selective electrode immersed in the sample, without need for preliminary distillation.

3. APPARATUS

Fluoride ion-selective electrode. Available commercially and normally consisting of an electrode made from a single crystal of lanthanum fluoride (in the form of a disc or plug) cemented into the end of a polyvinyl chloride or other suitable plastic tube, in combination with a reference calomel electrode. Expanded-scale pH meter.

4. REAGENTS

Stock fluoride solution, 1ml = 100 micrograms F. Dissolve 221mg anhydrous sodium fluoride in water and make up to 1,000ml. Standard fluoride solution, 1ml = 10 micrograms F. Dilute 100ml of stock fluoride solution to 1,000ml. Total ionic strength adjustment buffer solution.

Place approximately 500ml distilled water in a 1-litre beaker. Add 57ml glacial acetic acid, 58g sodium chloride and 12g sodium citrate dihydrate,

dissolve. Cool, insert a calibrated pH electrode and reference electrode into the solution and slowly add approximately 6 N sodium hydroxide (about 125ml) until the pH is between 5.0 and 5.5. Cool to room temperature, transfer to a 1 litre volumetric flask and add distilled water to the mark.

5. PROCEDURE

Follow the instructions provided by the electrode supplier. Normally the electrode should be inserted into the sample and the sample agitated for 3min until a steady meter reading is obtained, using an ionic strength adjustment buffer where necessary. A typical procedure is as follows: Calibrate the instrument using a series of standard solutions containing respectively 0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.6 and 2.0mg per litre fluoride (prepared by adding 0, 1.0, 2.0 . . . 10.0ml of standard fluoride into a series of 100ml volumetric flasks, adding to each 50ml of total ionic strength adjustment buffer solution and making each up to 100ml). Place 50ml of sample in a 100ml volumetric flask, dilute to 100ml with total ionic strength adjustment buffer solution.

Transfer each standard and sample to a series of 150ml beakers. Immerse the electrode and measure the developed potential while agitating. Allow the electrode to remain in the solution 3min before taking a final reading. Rinse the electrode with distilled water and blot dry between each reading. When using an expanded-scale pH meter (or specific-ion meter) calibrate the electrode frequently by checking the potential reading of the 1.0mg/l (50µgF) standard and adjust the calibration control (if necessary) until the meter reads as before. Confirm the calibration after reading each unknown and also after reading each standard when preparing the standard curve. Using the potential measurement for each unknown sample, read the corresponding fluoride concentration from the standard curve.

6. EXPRESSION OF RESULTS

Results should be expressed in mg F per litre of sample.

7. SPECIAL CASES

Special buffer solutions, to be added to the sample, may be necessary in the presence of aluminium in amounts up to 0.5 (8.1) or 5.0mg per litre (8.2). Interference may also arise from the presence of other polyvalent cations which form complexes with fluoride ions such as Fe^{+3} , Th^{+4} . The addition of a polyvalent anion such as citrate or phosphate has been used to avoid such interferences.

8. REFERENCES

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Spectrophotometric Determination of Nitrate in Water

1. INTRODUCTION

Nitrate in water has been determined by the phenol-disulfonic acid method since 1863. Unfortunately, the method suffers from a number of interferences, the most significant being due to chlorides. The method lacks sensitivity and requires evaporation to dryness of relatively large samples of water. Ultraviolet spectrophotometry has been proposed (10.1) as an alternate method which is free from chloride interference. However, nitrite, chromium and organic matter do interfere unless compensated for through use of special correction curves. Reduction of nitrate to nitrite with subsequent measurement using a modified Griess reaction has been widely used. Although such methods are quite sensitive, a number of significant interferences detract from their appeal. Brucine produces an intense yellow with nitrate in the presence of acid. Chloride does not interfere and other constituents likely to be present in water have little or no effect (10.2). The method of choice for most applications is the chromotropic acid procedure (10.3) which is both sensitive and free from critical interferences. This latter method is accurate and the technique involved is straightforward.

2. SCOPE AND FIELD OF APPLICATIONS

This method is suitable for determining nitrate concentrations in natural waters and it can be applied directly to the analysis of water without recourse to evaporation or precipitation steps. No sample preparation is required unless suspended material is present; in which case the impurities can be removed by centrifugation or filtration. Reliable results can be obtained over the range 0.2-20mg/l of nitrate. Interferences due to substances such as nitrite, oxidizing agents, chloride and iron (III) which normally interfere in nitrate determinations have been eliminated.

3. PRINCIPLE

The method is based on the reaction of nitrate with chromotropic acid. The absorbance of the resulting yellow solution is proportional to the nitrate concentration. Potential interferences have been eliminated through the addition of excess sodium sulfite which removes interferences due to oxidizing agents, and addition of urea which eliminates nitrite interference. Reactions of chloride are masked by the addition of antimony (III).

4. REAGENTS

4.1 *Standard nitrate solution*

Dissolve 1.371g of reagent grade sodium nitrate in distilled water and dilute to one liter. This gives a nitrate concentration of 1mg/ml. A series of standards can be prepared by suitable dilutions.

4.2 *Sulfuric acid*

Use analytical reagent grade concentrated acid which is free from nitrate.

4.3 *Purified chromotropic acid*

Prepare a saturated solution of the disodium salt of 1,8-dihydroxy-3,6-naphthalene disulfonic acid. Process twice using decolorizing charcoal. Crystallize the reagent from the filtered solution by adding sulfuric acid. Filter, wash several times with ethanol and dry below 80°C. Prepare a 0.1% solution of the reagent in concentrated sulfuric acid. The reagent solution is colorless and is stable for two weeks.

4.4 *Sulfite – urea solution*

Dissolve 5g of urea and 4g of reagent grade anhydrous sodium sulfite and dilute to 100ml with distilled water.

4.5 *Antimony solution*

Heat 0.5g of antimony metal in 80ml of concentrated sulfuric acid until all the metal is dissolved. Cool the solution and add to 20ml of ice water. When kept overnight, if any salt crystallizes, redissolve by heating.

5. APPARATUS

Spectrophotometer suitable for measurement of absorbance at 410nm and equipped with matched quartz cells.

6. SAMPLING

Any acceptable procedure for obtaining representative samples from natural waters may be used. The samples to be analyzed are transferred by pipet to volumetric flasks and are treated according to Section 7, Procedure.

7. PROCEDURE

Pipet 2.5ml of sample into dry 10ml volumetric flasks. To each flask add 1 drop of sulfite-urea solution; place the flasks in a tray of cold water (10-20°C) and add 2ml of the antimony sulfate solution. Swirl the flasks during the addition of each solution. After the mixtures have stood in the bath for about 4 minutes, add 1ml of chromotropic acid reagent; swirl the flasks again and allow them to stand in the cooling bath for an additional 3 minutes. Add concentrated sulfuric acid to adjust the volume to the 10ml mark; stopper the flasks and invert 4 times in order to ensure adequate mixing. Finally, allow the solutions to stand for 4-5 minutes at room temperature and again adjust the volume to the 10ml mark with concentrated sulfuric acid. Mix carefully in order not to introduce gas bubbles. After waiting at least 15 minutes, read the absorbance at 410nm. For running blank experiments, substitute double-distilled water for sample or nitrate solutions.

8. CALIBRATION CURVE

By diluting the standard solution, prepare a series of standards containing 0.1, 0.4, 0.7, 1.0, 2.0, 4.0 and 8.0mg/l of nitrate. Carry out the instructions in Section 7, Procedure. Plot absorbance versus nitrate concentration; a linear plot should be obtained.

9. REPRODUCIBILITY

The method is a reliable one. At the 1mg/l level for nitrate the coefficient of variation at the 95% confidence limit is 4%.

10. REFERENCES

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Determination of Phosphate in Water – Method 1 (High Level)

1. SCOPE

The method can be used for water samples up to 75ml in size containing from 100 to 1,000 micrograms of phosphate (PO_4). Method 2 should be used for smaller concentrations of phosphate.

2. PRINCIPLE

The method is based on the formation of a yellow vanadomolybdi-phosphoric acid from orthophosphates. Total phosphate is determined after hydrolysis of polyphosphates to orthophosphate.

3. REAGENTS

Molybdate-vanadate reagent. Dissolve 20g of ground ammonium molybdate, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, in 400ml of warm water (Solution A). Dissolve 1g of ammonium metavanadate in about 300ml of warm water, cool and slowly add, with stirring, 140ml of concentrated nitric acid (Solution B). Add Solution A to Solution B, stirring continuously, and dilute to 1 litre with water. Store in a polyethylene bottle. The reagent is stable for at least 1 month. Dilute nitric acid. Dilute 200ml of concentrated nitric acid ($d_{20} = 1.42$) to 1 litre with water. Store in a polyethylene bottle. Phosphate standard solution. Dry a sufficient quantity of potassium dihydrogen orthophosphate for one hour at 100-105°C. Cool in a desiccator, weigh out 1.433g, dissolve in water and dilute to 1 litre. Store in a polyethylene bottle. Phosphate working solution. Dilute 10ml of the phosphate standard solution to 100ml in a one mark volumetric flask. 1ml contains 100 micrograms of phosphate (PO_4).

4. APPARATUS

100ml volumetric flasks; 150ml beakers; spectrophotometer for operation at 420nm; 4cm spectrophotometer cells.

5. PROCEDURE

5.1 *Preparation of calibration graph*

Into each of a series of 100ml volumetric flasks measure volumes of the phosphate working solution containing 0, 200, 400, 600, 800 and 1,000 μ g. Dilute each to about 50ml with water, add 5ml of the dilute nitric acid and mix. Add 10ml of the molybdate vanadate reagent to each, dilute to the 100ml mark and mix well. Adjust the temperatures of the flasks to a known temperature in a spectrophotometer with the wavelength set at 420nm, using a 4cm cell. Use water in the compensating cell. Correct the readings for the blank with no added phosphate and from the net absorbance obtained and the known phosphate contents of the solutions plot the calibration graph. The absorbance given by 1,000 μ g of phosphate in 100ml is approximately 0.7.

5.2 *Determination of orthophosphate*

Transfer a suitable volume (not exceeding 75ml) of the filtered sample to a 100ml of volumetric flask, neutralise any alkalinity with dilute nitric acid and add 5ml in excess. Mix. Add 10ml of the molybdate-vanadate reagent, dilute to the 100ml mark and mix well. Treat 75ml of water in a similar manner. Adjust the temperature of the flasks to within 1°C of the temperature of calibration and allow to stand for 20 minutes, measure the optical densities in the spectrophotometer with the wavelength set at 420nm and using 4cm cells. Use water in the compensating cell. If it is necessary to compensate for colour in the sample under test, measure an equal volume of the sample and proceed as before but using 7ml of dilute nitric acid instead of the molybdate-vanadate reagent. Measure the optical density against water, deduct the readings obtained on the blank and the colour compensating solutions and read off the phosphate content in microgrammes in the sample from the calibration graph.

5.3 *Determination of total phosphate*

Transfer a suitable volume (not exceeding 75ml) of the filtered sample to a 150ml beaker and dilute, if necessary, to about 75ml with water.

Neutralise any alkalinity with the dilute nitric acid and add 5ml in excess. Then boil gently for 30 minutes covering the beaker with a watch glass to prevent undue evaporation. Cool, transfer completely to a 100ml volumetric flask, add 10ml of the molybdate-vanadate reagent, dilute to the mark and mix well. Treat 75ml of water in a similar manner. Adjust the temperature of the flasks to within 1°C of the temperature of calibration and allow to stand for 10 minutes. Then measure the optical densities in the spectrophotometer with the wavelength set at 420nm and using 4cm cells. Use water in the compensating cell.

If it is necessary to compensate for colour in the sample under test, measure an equal volume of the sample and proceed as before but using 7ml

of dilute nitric acid instead of the molybdate-vanadate reagent. Measure the optical density against water, deduct the readings obtained on the blank and the colour compensating solutions and read off the phosphate content in microgrammes in the sample from the calibration graph.

6. EXPRESSION OF RESULTS

Results are expressed as mg of phosphate (PO_4) per litre.

7. REFERENCES

British Standard 2690, Part 3, p.12, 1966.

Determination of Phosphate in Water – Method 2 (Low Level)

1. SCOPE

The method can be used for water samples up to 50ml in size containing from 5 to 100 micrograms. Method 1 should be used for higher concentrations of phosphate.

2. PRINCIPLE OF METHOD

The method is based on the reaction of orthophosphate in acid solution with ammonium molybdate to form phosphomolybdic acid and the subsequent reduction of this by stannous chloride to the molybdenum blue complex. Total phosphate is determined after hydrolysis of polyphosphates to orthophosphates.

3. REAGENTS

3.1 *Ammonium molybdate sulphuric acid mixed reagent*

Dissolve 25g of ground ammonium molybdate in approximately 200ml of water without heating (Solution A). Add 280ml of concentrated sulphuric acid to 400ml of water and cool (Solution B). Add Solution A to Solution B, cool, and dilute to 1 litre. Store in a polyethylene bottle.

3.2 *Stannous chloride*

Dissolve 2.5g of stannous chloride in glycerol and dilute to 100ml with glycerol. The solution is stable for several weeks. Phosphate standard solution. Dry a sufficient quantity of potassium dihydrogen orthophosphate for one hour at 100-105°C. Cool in a dessicator, weight out 1.433g, dissolve in water and dilute to 1 litre. Store in a polyethylene bottle.

3.3 *Phosphate working solution*

Dilute 5ml of the phosphate standard solution to 500ml in a volumetric flask. 1ml contains 10 micrograms of phosphate (PO_4).

3.4 *Dilute nitric acid*

Dilute 200ml of concentrated nitric acid to 1 litre with water. Store in a polyethylene bottle.

3.5 Sodium hydroxide

5% w/v solution. Store in a polyethylene bottle.

4. APPARATUS

100ml standard flasks; spectrophotometer for operation at 690nm; 4cm spectrophotometer cells.

5. PROCEDURE

5.1 Preparation of calibration graph

Measure accurately volumes of the phosphate working solution containing 0, 10, 20, 40, 60, 80 and 100 μ g phosphate into a series of 100ml standard flasks and add water to make the volume of solution in each flask 50ml. Add 2.5ml of the ammonium molybdate reagent and mix. Add 4 drops of stannous chloride from a dropping pipette, mix and dilute to the mark. Allow to stand for 10 to 12 minutes. Measure the absorbance of the solution at a known temperature between 20°C and 25°C in a spectrophotometer at the wavelength corresponding to maximum absorption (approximately 690nm, but the exact wavelength should be checked for each spectrophotometer) using a 4mm cell. Use water in the compensating cell. Deduct the reading for the blank with no added phosphate and plot a calibration graph of optical density against known phosphate content. The absorbance given by 100 μ g in 100ml is approximately 1.1 and increases by about 1% per 1°C temperature rise.

5.2 Determination of orthophosphate

Transfer a suitable volume (containing less than 100 μ g phosphate) of the filtered sample into a 100ml volumetric flask and dilute to 50ml if necessary. To a second 100ml volumetric flask add 50ml of water. Treat both in a similar manner. Add 2.5ml of ammonium molybdate reagent and mix. Add 4 drops of stannous chloride reagent from a dropping pipette, mix and dilute to the mark. Allow to stand for 10 to 12 minutes. Measure the absorbances of the solutions at a temperature within 1°C of that at which the calibration graph is prepared in the spectrophotometer using the wavelength already determined and 4cm cells. Use water in the compensating cell. If it is necessary to compensate for colour of the sample under test, measure an equal volume of the sample and proceed as before but using 5ml of dilute nitric acid instead of the molybdate sulphuric acid reagent. Measure the absorbance of the solution against water, deduct the readings obtained on the blank and the colour compensating solutions and read off the phosphate content in microgrammes from the calibration graph.

5.3 *Determination of total phosphate*

Transfer a suitable volume (containing not more than 100 μ g PO₄) of the filtered sample to a 150ml beaker. Dilute to 50ml if necessary. To a second 150ml beaker add 50ml of water. Treat both in a similar manner. Add 5ml of dilute nitric acid and boil gently for 30 minutes covering the beaker with a watch glass to prevent undue evaporation. Cool and neutralise with sodium hydroxide, 5% w/v, to pH7. Transfer the solution to a 100ml volumetric flask. Dilute to about 50ml if necessary. Add 2.5ml of ammonium molybdate and proceed as given for orthophosphate.

6. EXPRESSION OF RESULTS

Results are expressed as mg of phosphate (PO₄) per litre.

7. REFERENCES

British Standard 2690 Part 3, p.14, 1966.

Determination of Dissolved Oxygen in Water

INTRODUCTION

Difficulties have been experienced in the use of the Winkler method (6.1) for the estimation of dissolved oxygen in the presence of reducing agents such as sulfur dioxide or sulfites. In addition to the method described below there are procedures for measuring biochemical oxygen demand (BOD), and total organic carbon (TOC).

1. SCOPE

Dissolved oxygen present at normal concentrations in waters.

2. PRINCIPLE OF METHOD

A "diffusion current" is established when a solid electrode system sensitive to oxygen concentration is immersed in the test sample. It is linearly proportional to the concentration of molecular oxygen in the test sample.

3. APPARATUS

3.1 *Sensor*

This is composed of two solid metal electrodes electrically connected by a suitable electrolyte and separated from the sample by a membrane permeable to molecular oxygen. Electrode systems of this type exhibit a relatively high temperature coefficient, but most commercially available instruments are temperature-compensated.

3.2 *Amplifier*

This is a meter for amplification of the signal received from the sensor and conversion to suitable concentration read-out.

4. PROCEDURE

4.1 *Calibration*

Follow the manufacturer's procedure. Generally, calibrate the electrode by immersion in a saturated solution of oxygen in water at a known

temperature, then by reference to suitable tables (6.2), the concentration of oxygen present in oxygen-saturated water at that temperature is found.

4.2 *Sample measurement*

Follow the manufacturer's recommended procedure, ensuring that no air bubbles are trapped against the membrane.

5. EXPRESSION OF RESULTS

Results should be reported as milligrams of dissolved oxygen per litre.

6. REFERENCES

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- 6.2 Truesdale, G. A., Downing, A. L., and Lowden, G. F. *J. Appl. Chem.*, **5**, 53-62, 1955.
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Estimation of DDT and Related Compounds Together with Polychlorobiphenyl Compounds, in Biological Media

1. INTRODUCTION

DDT, its various isomers and degradation products (including DDE) are detected and measured in biological media by multi-detection systems based on chromatography. The systems used also respond to polychlorobiphenyl (PCB) compounds (which represent a complication in DDT residue analysis): where these are encountered they usually comprise a complex mixture of many different PCB compounds of varying composition according to nature of the particular technical material (or materials) from which they derive and possibly in addition varying on account of subsequent weathering procedures which may have removed or degraded some individual constituents at differing rates. There is no single analytical procedure which is applicable to all substrates; or to a single substrate for all possible residue patterns (9.1).

By way of example, the pattern of PCB isomers from samples of wildlife as judged from their gas chromatograms is not identical to that observed in commercial PCB preparations, some of the isomers having apparently been wholly or partly metabolised. Consequently the amount of PCB in a wildlife sample cannot be estimated by direct comparison with a standard substance and some further form of approximation must be used. By injecting known amounts of PCB on to an Apiezon L column it can be shown that the ratio of the Total Peak Area to the Total Weight Injected for most of the higher chlorinated commercial preparations is roughly the same as that for pp'-DDE, and all calculations can be based on this compound as standard.

The procedure outlined below must be regarded only as illustrative of the approach to DDT and PCB residue analysis. Individual analytical procedures must be verified in the light of the considerations outlined above and with due regard to the general points set out in the introduction to this volume.

2. SCOPE

Provided due regard is had to the matters outlined in the introduction above, this method is applicable to biological tissues which can be sufficiently comminuted to allow quantitative extraction of the compounds analysed.

3. PRINCIPLE OF METHOD

The sample is comminuted with a solvent at room temperature in a glass filter column, from which the extract is obtained by pressure. It is then

subjected to clean-up and examined quantitatively by gas chromatographic analysis using an electron capture detector. Measurements are made relative to standard solutions analysed at the same time.

Some of the alternative clean-up methods may be adequate for certain samples, but the more drastic procedures may remove some of the less stable organochlorine compounds by decomposition.

4. REAGENTS

Acetone, column distilled; magnesium sulphate, washed with anhydrous ether; light petroleum boiling range 69°-71°C, treated with conc. sulphuric acid, washed with water, dried over magnesium sulfate and column distilled; ether; dichloromethane (column distilled); acetonitrile (column distilled), saturated with light petroleum; sodium sulphate, anhydrous; florisil, activated at 600°C, add 2% water w/w; silica gel, Kieselgel G (Stahl); sulfuric acid mixture, 38ml fuming (20% SO₃), sulfuric acid 62ml conc. sulfuric acid; sodium chloride solution, 2% w/v; aldrin standard solution, 0.02ng/μl.

5. APPARATUS

Homogeniser, 20,000rpm; glass extraction column with G3 sinter glass filter and polytetrafluoroethylene stopcock, 150mm x 11mm; centrifuge; gas chromatograph, with electron capture detector. Column, all glass, 1.6m x 3mm OD; evaporation manifold; column packings (1) 5.1% QF + 1.4% SF - 96 on 100/120 mesh Gaschrom P silanized; (2) 4.0% SF - 96 on 100/120 mesh Gaschrom P silanized.

6. PROCEDURE

6.1 Estimations are usually made on a series of samples, one of which is a blank (usually a previously analysed sample shown to be satisfactory for this purpose) and one a standard. The standard is also prepared from a blank sample by adding a standard solution containing known amounts of the compounds to be analysed. At intervals in between the gas chromatographic analyses, standard injections of aldrin, or similar low retention compound, are made to check sensitivity.

6.2 *Cleaning of glassware*

Clean all smaller glassware items by heating in a special detergent solution. Rinse with water, then with distilled water and dry. Clean extraction

columns with the detergent, then heat to 70°C in a 4 + 1 mixture of conc. sulfuric and nitric acids, rinse with water, then with distilled water. After drying, rinse once with acetone and twice with light petroleum (boiling range 60°-70°C). From the final solvent rinse, remove a sample for examination by gas chromatography.

6.3 *Sample preparation*

Weigh between one and three grams of sample directly into the extraction column. Add 5ml acetone and comminute using the homogeniser. Rinse the homogeniser rotor in 5ml light petroleum in a centrifuge tube, and transfer the solvent to the column. Cover the top of the column with aluminium foil. Rinse the rotor once in water then in two tubes containing acetone and two tubes light petroleum before comminuting the next sample. Leave the columns to stand 2.5 hours or overnight. Place a 25ml measuring cylinder under the column and run the liquid into the flask, applying pressure to the column with a handpump until all the liquid has run out. Fill the measuring flask with sodium chloride solution until the level is about 2cm above the mark, invert carefully a few times. Remove the stopper and centrifuge slowly at first and finally at 2,000rpm. Transfer the upper layer, after freezing out if necessary, with a pipette to a weighed, graduated 10ml centrifuge tube. Add further small quantities of light petroleum to the flask and transfer to the tube. Place the centrifuge tube in a water bath at 45°C and reduce to 2ml (or some other convenient volume) with a stream of air or nitrogen.

6.4 *Clean-up*

A number of procedures, of which the following examples are typical, may be used according to the nature of the sample and the extract obtained. Special procedures may be necessary for samples with a high moisture content or for those high in sulfur (which gives a false positive response).

6.4.1 *Column clean-up*

Place 5.0g florisil in a chromatographic column, add a 2cm layer of oven-dried sodium sulphate. Rinse the column with about 40ml light petroleum before adding 1ml of solvent extract. When the meniscus has almost reached the column, add light petroleum + ethyl ether (4 + 1) initially only in small portions. Collect 50ml eluate in a weighed ground glass stoppered flask and evaporate to less than 5ml. Adjust the solution volume with light petroleum to 5ml by weighing. Remove an aliquot for analysis by gas chromatography.

6.4.2 *Thin layer clean-up*

Carefully apply a small amount, about 100µl, of solution containing not more than 20mg fat, spotwise to form a band on a small silica gel plate

(28 x 98mm) coated with 1.2g silica gel which has previously been rinsed with methanol and water and heated to 200°C before and after application to the plate. Develop with dichloromethane until the solvent reaches the top of the plate. Dry quickly and examine in UV light. Scrape the layer 5mm above the fat zone into a small packed column (internal diameter 7mm), and add light petroleum + ethyl ether (3 + 2) dropwise until 1.0ml eluate is collected. Remove an aliquot for analysis by gas chromatography.

6.4.3 Acetonitrile partition clean-up

To 1-5ml of light petroleum extract in a glass stoppered tube add an equal volume of acetonitrile. Agitate, transfer the acetonitrile phase with a pipette to a separating funnel. Repeat three times. Dilute the combined extracts with the same volume of light petroleum and six times the volume of water. Shake carefully and discard the water phase. Wash the solvent phase with a few portions of sodium chloride solution, dry by pouring through a short column of sodium sulphate; wash the column with a few ml light petroleum. Concentrate by evaporation and adjust to 5.0ml. Remove an aliquot for analysis by gas chromatography.

6.4.4 Acid treatment

Transfer 1ml light petroleum solution to a 5ml stoppered tube, add 1ml sulfuric acid mixture and invert the tube carefully a few times with adjustment of the glass stopper. Centrifuge 10min, freeze out in solid carbon dioxide-acetone, decant the upper layer into a 3ml tube and stopper. Use an aliquot for gas chromatography.

6.4.5 Alkali treatment

Add 1.0-1.5ml potassium hydroxide solution in ethanol to 1ml solvent extract (or a cleaned up solution) in a centrifuge tube. Mix carefully, avoid wetting the stopper. Place the tube in a water bath at 55° adding additional light petroleum if necessary. Fill the tube with 2% sodium chloride solution (about 11ml) and invert several times. Centrifuge and place tube in a freezing mixture. Decant the upper layer into a 3ml tube, make up to 1.0ml with light petroleum; use an aliquot for gas chromatography.

6.5 Gas chromatography

Examine a suitable aliquot by at least two different gas chromatographic systems. Those indicated above are, typically, operated at 180°C with a gas flow-rate of about 25ml per min, giving a retention time for pp'-DDT of 20min.

CALCULATION OF RESULTS

7.1 The gas chromatograms obtained are evaluated by comparison with those of standard solutions of the pure compounds sought. If, as suggested above, the gas chromatographic conditions are adjusted to give standard retention times, peak heights are measured and used for the evaluation. Variations in sensitivity (more than 30% during a day) and a limited linear dose-response relationship of the electron-capture detector may be taken into account by correction factors calculated from frequent analysis of an external standard compound having a short retention time and by consideration only of peak heights which fall into the linear range of each compound. Whenever the chromatographic pattern allows the use of an internal standard this will simplify the calculations and usually improve somewhat the quality of the analysis.

7.2 Only an approximate result can be calculated since commercial PCB preparations differ and the composition of individual preparations "age" in different ways on exposure. When the pp'-DDE and PCB's have been separated from the other chlorinated residues by silica gel column, examine the concentrated extract by GLC, preferably on an Apiezon column. Insofar as their retention times are identical with those of a standard preparation, all the peaks following that of pp'-DDE are assumed to be PCB compounds. If pp'-DDE appears to be present and it is thought that there may be a peak due to a PCB compound at exactly the same retention time which will significantly affect the calculated amount of pp'-DDE, then oxidise the pp'-DDE to pp'-DCBP (9.2). On chromatography, the pp'-DDBP will give an earlier retention time peak and leave the PCB's unaffected. Calculate the amount of PCB's in the sample injection in the following manner:

- Determine the retention time (Rt) and peak heights (Ht) of all the compounds which appear to be PCB compounds.
- Multiply the individual retention times (Rt) by the peak heights (Ht) and sum all the products so obtained:
$$Rt_n \cdot Ht_n = Rt_1 \cdot Ht_1 + Rt_2 \cdot Ht_2 + Rt_3 \cdot Ht_3 + \dots \text{etc.}$$
- Divide this sum by the product of the peak height x retention time for 1 ng pp'-DDE. This will give an estimate of the total amount of PCB (in ng) in the sample injection.

If a silicone column has to be used for the estimation, divide the sum of the Rt's x Ht's by the product of Rt x Ht for 1 ng dieldrin. Because it is usual for the chromatographic patterns of the PCB compounds eluted from samples to be different from those of the manufacturers' preparations, it is impossible to use individual peaks in the standard material and determine the amount of PCB by simple proportion. A determination of the area per nanogram for the whole range of PCB preparations gives a figure which is very close to that determined for 1 nanogram of pp'-DDE on an Apiezon column, i.e. the *mean* electron-capture response for PCB's is very similar to that for pp'-DDE. If only single PCB compounds are being determined, there will in some cases be a large error. On silicone columns, the mean electron-capture response is nearer to that of dieldrin. This is because the

PCB compounds produce different peak patterns on this liquid phase. The view that the mean electron-capturing power of PCB's is similar to that of pp'-DDE is confirmed by Zitko et al. (9.3).

8. SPECIAL CASE

8.1 *Separation of PCB's from DDT and other pesticides*

Prepare a column with silica gel such as Hopkin & William, MFC which has been heated to 110°C for at least 2hr and to which when cool has been added 2.5% v/w of distilled water. Weigh out 5.0g of the prepared gel and cover it immediately with hexane. Shake the mixture to release any air bubbles and wash the preparation into a narrow glass chromatographic column (7mm I.D.), using hexane. Run the surplus hexane through the column until its meniscus is just touching the surface of the silica gel.

Add the sample extract to the column in about 2.0ml of solvent. Allow the solution to run into the column until the meniscus is just touching the top of the gel. Wash the sample container with 1.0ml of hexane and transfer this washing to the column. Elute the column with 45ml of hexane at the rate of 1 drop per second, stopping the elution when the meniscus just reaches the gel. Concentrate the eluate and examine it by GLC. It should contain all PCB-type compounds, pp'-DDE and HCB. After changing the receiver under the gel column, further elute the silica gel with 50ml of hexane containing 10% v/w of diethyl ether. Concentrate this second eluate and examine it by GLC. It should contain pp'-DDT and all the more polar residues as far as dieldrin.

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Estimation of Traces of Polychlorobiphenyl Compounds (PCB)

1. SCOPE

The method is applicable to water. A modification applicable to fish is described and a reference given to a modification applicable to sediments.

2. PRINCIPLE OF METHOD

PCB's are extracted with hexane, the extract clean-up from interfering co-extractives by column chromatography or solvent partition and the PCB's estimated gas chromatographically by reference to standard materials (8.1).

3. REAGENTS

Hexane; sodium sulfate, anhydrous; silica gel.
Also, for fish; acetone; dimethylformamide; alumina.

4. APPARATUS

Gas chromatograph; Kuderna-Danish evaporators; chromatographic columns; Soxhlet extraction apparatus (for fish).

5. PROCEDURE

5.1 Water

Shake ca. 2l water with 100ml of hexane for 15mins. Allow the mixture to stand until the two phases have completely separated. Run off the lower water layer and pass the hexane through a short column of granular, anhydrous sodium sulfate into a Kuderna-Danish evaporator. Wash the sodium sulfate column with hexane and concentrate the combined washings and sample extract to 1.0ml. Inject 5 μ l of this final solution into two different GLC columns. Compare the retention times of the chromatographic peaks with those obtained from a standard PCB preparation. If there are a number of peaks with retention times equivalent to that of pp'-DDT and longer and which agree with those of PCB, then the presence of PCB can be suspected and a separation of the PCB from other pesticide residues must be carried out by column chromatography on silica gel as described in para. 7.2.

5.2 Fish

Finely comminute 10g of sample and dry it with granular anhydrous, sodium sulfate. Place the prepared material in a preextracted Soxhlet thimble and then extract for 3hr with a 2+1 mixture of hexane and acetone in the Soxhlet apparatus. Pass the extract through a short column of granular, anhydrous sodium sulfate into a Kuderna-Danish evaporator. Wash the sodium sulfate well with more hexane and then concentrate the combined extract and washings to ca. 5ml. Transfer the concentration solution to a 100ml volumetric flask and make up to the mark with hexane. Clean up 25ml of this solution by dimethyl formamide partition and alumina column chromatography in the manner detailed by de Faubert Maunder et al (8.2). Examine the cleaned-up extract on two different GLC columns. If there is a series of peaks, with retention times corresponding to ca. pp'-DDT and longer, then the presence of PCB is indicated. Use the method given in para. 7.2 to separate the PCB from the other pesticide residues.

5.3 Sediment

Holden (8.3) uses a mixture of hexane and propan-2-ol for extraction.

6. CALCULATION OF RESULTS

6.1 Only an approximate result can be calculated since commercial PCB preparations differ and the composition of individual preparations "age" in different ways on exposure.

When the pp'-DDE and the PCB's have been separated from the other chlorinated residues by silica gel column, examine the concentrated extract by GLC, preferably on an Apiezon column. Insofar as their retention times are identical with those of a standard preparation, all the peaks following that of pp'-DDE are assumed to be PCB compounds. If pp'-DDE appears to be present and it is thought that there may be a peak due to a PCB compound at exactly the same retention time which will significantly affect the calculated amount of pp'-DDE, then oxidise the pp'-DDE to pp'-DCBP. On chromatography, the pp'DDBP will give an earlier retention time peak and leave the PCB's unaffected. Calculate the amount of PCB's in the sample injection in the following manner:

- Determine the retention times (Rt) and peak heights (Ht) of all the compounds which appear to be PCB compounds.
- Multiply the individual retention times (Rt) by the peak heights (Ht) and sum all the products so obtained:

$$\Sigma Rt_n \cdot Ht_n = Rt_1 \cdot Ht_1 + Rt_2 \cdot Ht_2 + Rt_3 \cdot Ht_3 + \dots \text{etc.}$$

- Divide this sum by the product of the peak height x retention time for 1 ng pp'-DDE. This will give an estimate of the total amount of PCB (in ng) in the sample injection.

If a silicone column has to be used for the estimation, divide the sum of the R_t 's x H_t 's by the product of R_t x H_t for 1 ng dieldrin.

6.2 Because it is usual for the chromatographic patterns of the PCB compounds eluted from samples to be different from those of the manufacturers' preparations, it is impossible to use individual peaks in the standard material and determine the amount of PCB by simple proportion.

6.3 A determination of the area per nanogram for the whole range of PCB preparations gives a figure which is very close to that determined for 1 nanogram of pp' -DDE on an Apiezon column, i.e. the *mean* electron-capture response for PCB's is very similar to that for pp' -DDE. If only single PCB compounds are being determined, there will in some cases be a large error. On silicone columns, the mean electron-capture response is nearer to that of dieldrin. This is because the PCB compounds produce different peak patterns on this liquid phase. The view that the mean electron-capturing power of PCB's is similar to that of pp' -DDE is confirmed by Zitko et al (8.4).

7. SPECIAL CASES

7.1 *Separation of PCB's from DDT and other pesticides*

7.1.1 Preparation of the column

Use either silica gel, BDH (material for chromatographic adsorption) or silica gel, Hopkin & Williams, MFC. Dry the silica gel at 110°C for at least 2hr, place the material in a desiccator and when cooled, quickly weigh out the required amount of adsorbent into a tared, stoppered bottle or flask. Add 2.5% v/w of distilled water and shake the material for 1½hr or shake for ¾hr and leave the material in the stoppered bottle until next day. Weigh out 5.0g of the prepared gel and cover it immediately with hexane. Shake the mixture to release any air bubbles and wash the preparation into a narrow, glass chromatographic column (7mm I.D.), using hexane. Run the surplus hexane through the column until its meniscus is just touching the surface of the silica gel.

7.1.2 Separation of pesticide residue

Add the sample extract to the column in about 2.0ml of solvent. Allow the solution to run into the column until the meniscus is just touching the top of the gel. Wash the sample container with 1.0ml of hexane and transfer this washing to the column. Elute the column with 45ml of hexane at the rate of 1 drop per second, stopping the elution when the meniscus just reaches the gel. Concentrate the eluate and examine it by GLC. It should contain all

PCB-type compounds, pp'-DDE and HCB. After changing the receiver under the gel column, further elute the silica gel with 50ml of hexane containing 10% v/v of diethyl ether. Concentrate this second eluate and examine it by GLC. It should contain pp'-DDT and all the more polar residues as far as dieldrin.

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Determination of Benzo[a]pyrene and Benzo[k]fluoranthene in Airborne Particulates

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 ultraviolet absorption (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 (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 ultraviolet 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 x 30 grade, 6.0cm in diameter and at least 45cm 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, Ottawa, 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 ml 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 ml of final solution.

7. APPARATUS

7.1 *Soxhlet extractors*

Extractors with a nominal solvent volume of 30ml and a cycling time of 2 minutes are used (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 10.0mm over a length of 30cm.

7.3 *Fluorimeter*

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

8. SAMPLING AND SAMPLES

Air samples are taken by drawing air at known flow rate 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 x 10 inches in overall size. If the hydrocarbon-in-air concentrations are high enough, smaller volumes of air may be taken on 4inch or 2inch filter circles.

9. PROCEDURE

Using a clean circular metal punch, cut 4 to 10 circles of 36mm 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 one-tenth 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 carryover of carbon particles into the extract. After 6 hours extraction with cyclohexane, evaporate the solvent extract carefully to 2ml, 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 slurring the alumina with toluene and filling the tube to a depth of 12.0cm. Place the concentrated extract, no more than 2ml, carefully on top of the alumina which has been covered with a 1cm depth of glass beads. Elute, using toluene. Discard the first 25ml of eluate and collect 3ml fractions, thereafter, up to a total of about 30 fractions, or about 90ml. 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 30-45ml 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 5ml volume is satisfactory. Determine the fluorescence emission at 410nm by using the height-above-baseline technique, while exciting at wavelengths 309 and 385nm. These "optimum" wavelengths were selected by running the excitation spectrum of the 0.015µg/ml standards for both BaP and BkF. Four curves are obtained for solutions in toluene as shown in Figure 2 (Pages 276, 277).

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 309nm, 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 385nm, after which the BaP concentration may be calculated in micrograms per ml, as follows:

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

$$\text{conc. BaP} = \frac{\text{Emission at 395} - \text{conc. BkF} \cdot \text{slope BkF curve 385}}{\text{Slope of BaP curve at 385 exc.}}$$

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

$$\text{BkF (309)} = 8,800$$

$$\text{BkF (385)} = 1,850$$

$$\text{BaP (385)} = 3,850$$

$$\text{From which the concentration of BkF} = \frac{38.5}{8,800} = 0.0044\mu\text{g/ml}$$

$$\text{And the concentration of BaP} = 14.8 - \frac{(0.0044 \times 1,850)}{3,850} = 0.0039\mu\text{g/ml}$$

Concentration of Hydrocarbon, $\mu\text{g/gram}$ =

$$\frac{\mu\text{g/ml} \times 5 \times 10.5}{\text{particulate weight, grams}}$$

Concentration of hydrocarbon, $\mu\text{g/1,000m}^3$ =

$$\frac{\mu\text{g/ml} \times 5 \times 10.5 \times 1,000}{\text{air volume, m}^3}$$

10.3 *Accuracy*

0.250 $\mu\text{g/ml}$ of BaP can be measured with an accuracy of better than ± 0.002 microgram. 0.250 $\mu\text{g/ml}$ of BkF can be measured with an accuracy of better than $\pm 0.001\mu\text{g}$. If the concentration of BaP found is more than twice the BkF concentration, the BkF results will be in error by a factor of 10%.

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 760mm Hg.

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 flow rates, 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 flow rate during sampling is linear and for usual purposes of calculation, the mean value of initial and final flow rates 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 (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 case, it is necessary to use the complete filter (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 (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

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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.

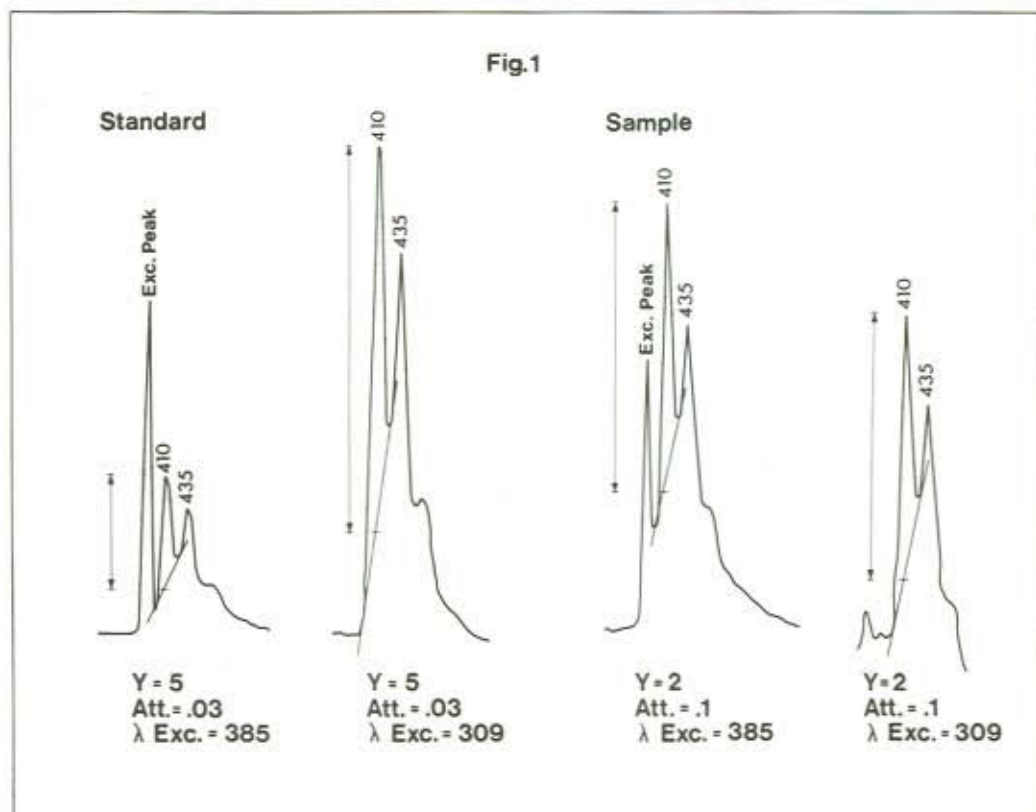
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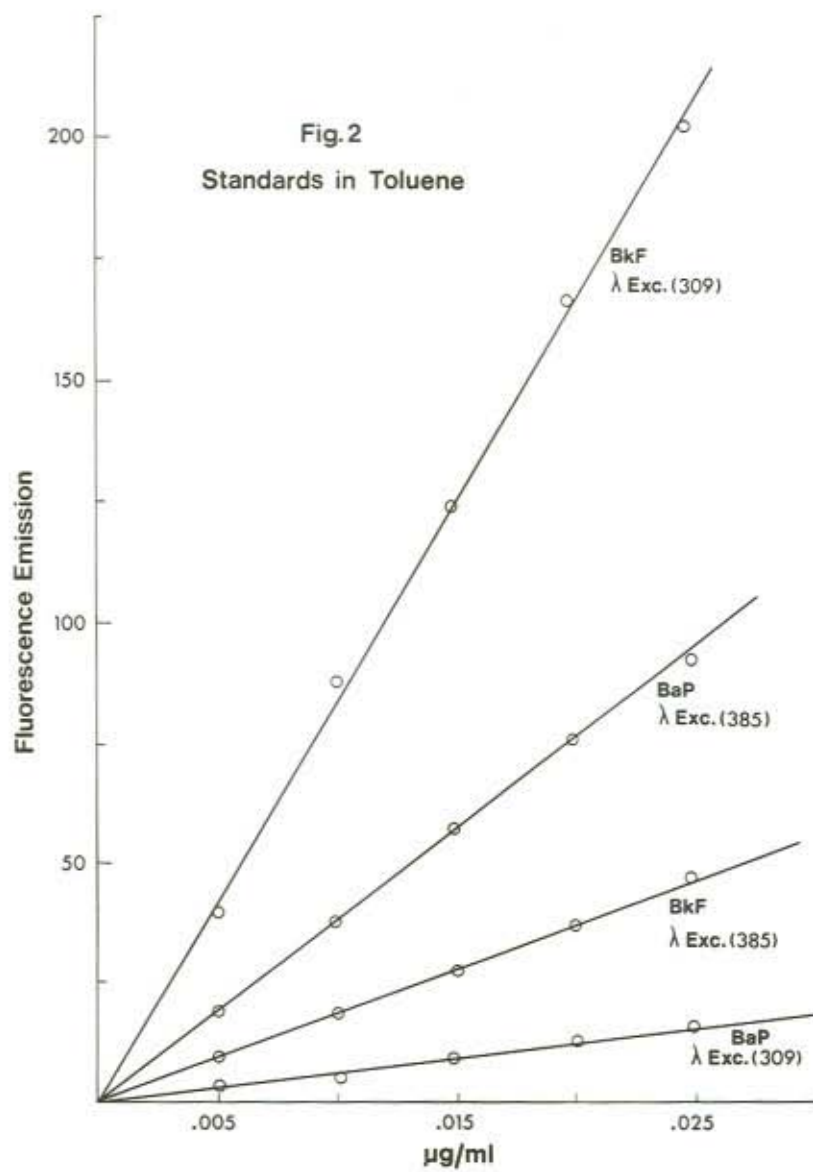
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13. ANNEXES

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 (Page 276).

Figure 2. Four standard curves are given for benzo[a]pyrene and benzo[k]fluoranthene solutions in toluene as each standard solution is extracted using the extraction wavelengths 309 and 385nm (Page 277).





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