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May, 1993

Dear Sir/Madam:

RE: Fourth Edition of the "Methods Manual for Chemical Analysis of Atmospheric Pollutants

Enclosed is a package containing the 4th Edition of the "Methods Manual for Chemical Analysis of Atmospheric Pollutants" issued by the Air Analysis Branch of the Physical & Engineering Sciences Division, Alberta Environmental Centre.

This edition includes a number of newly adapted methods, and some methods have been replaced by more recent ones. Some of the methods have been revised with respect to better sampling procedures, and better accuracy and precision. Please replace all the loose-leaf pages with the new package in the existing binder. A "Quality Assurance Manual" has been added to the Methods Manual under the Appendix.

Please direct any questions you may have regarding this edition to me at the above address.

Yours truly,

N.C. Das, Ph.D.
Head
Air Analysis Branch

NCD/uah/clj
M2D00425.MML

enclosures

FOURTH EDITION

ALBERTA ENVIRONMENT

ALBERTA ENVIRONMENTAL CENTRE

PHYSICAL & ENGINEERING SCIENCES DIVISION

METHODS MANUAL FOR CHEMICAL ANALYSIS OF ATMOSPHERIC POLLUTANTS

1993

AIR & WASTE RESEARCH PROGRAM

AIR ANALYSIS BRANCH

ALBERTA ENVIRONMENTAL CENTRE

VEGREVILLE, AB T9C 1T4

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FOREWORD AND ACKNOWLEDGEMENTS

The "Methods Manual for the Chemical Analysis of Atmospheric Pollutants" contains analytical methodology and procedures for the examination of ambient air, source emission, and precipitation for a variety of parameters. Methods for lead in soil and sulphur in vegetation are also included. All methods and procedures are used by the Assessment & Pollution Control Divisions in obtaining samples and by the Air Analysis Branch in analyzing samples.

The manual was developed to provide a consolidated reference for determining air quality in Alberta. It is the responsibility of the Alberta Environmental Centre to provide chemical analysis in support of the water and air quality control programs of Alberta Environment.

The manual is published in loose-leaf form. The intention is to update it by adding new methods and revising old ones. Comments and suggestions to improve the methods and procedures are most welcome.

Recognition and appreciation is due to all staff members at the Air Analysis Branch, who assisted and contributed in the preparation of the manual. Appreciation is extended to Ursula Horbachewsky-Gough, Lorraine Robert, Brenda Dziwenka, and Debbie Kriaski for typing the manuscript for the Fourth Edition.

Acknowledgements are expressed to authors of references quoted in this manual.

INTRODUCTION

This manual is the Fourth Edition of documented methodology for the chemical analysis of atmospheric pollutants, published by the Physical & Engineering Sciences Division, Alberta Environment. The manual is divided into four parts, as follows:

Part A - Ambient Air Test Methods
Part B - Source Emission Test Methods
Part C - Precipitation Test Methods
Part D - Soil and Vegetation Test Methods

Part A has been subdivided into three sections depending on the types of pollutants, such as gases, suspended particulate matter and dustfall.

The Physical & Engineering Sciences Division attempts to use the best available methodology for the analysis of atmospheric pollutants. Such methods and procedures were carefully selected from many sources and have been described in the manual. Some of them were modified, and some were developed in the Physical & Engineering Sciences Division to meet special needs of Alberta air quality programs.

Accuracy and precision data were established for some procedures and are included. In some cases, two methods have been described for a particular parameter to cover a wide range of concentration. For some parameters, both manual as well as automated methods have been described to give the analyst optional test methods.

Each method has a five-figure code number. The first digit signifies the type of air pollutant, the second and third denote the parameter and the last two digits specify the analytical method.

For descriptive purposes, reference is occasionally made to specific reagents and instrumentation. This does not constitute an endorsement, or recommendation for use by Alberta Environment.

ABBREVIATED REFERENCE TITLES

Std. Meth.	Standard Methods for the Examination of Water and Wastewater 1989, 17th Edition. American Public Health Association, Water Pollution Control Federation.
ASTM	1989 Annual Book of ASTM standards for Atmospheric Analysis, Vol. II. 03.
Source Sampling Code	Source Sampling Code. Reference Methods for Source Sampling and Analysis of Particulates, Sulphur Oxides and Oxides of Nitrogen; Publication SSC-1/76 Standards and Approvals Division, Alberta Environment.
Air Monitoring Directive	Air Monitoring Directive AMD-86-1. Monitoring of Reporting procedures for Industry, Alberta Environment.
Methods of Air Sampling	Methods of Air Sampling and Analysis, 1977, 2nd Edition, APHA Intersociety Committee, American Health Association.

CONTENTS

AMMONIA-NITROGEN

(Phenate, Colorimetric)

1. Introduction

1.1 Ammonia is present in ambient air as ammonia gas or as ammonium chloride and sulphate particulates.

2. Principle

2.1 The sample is collected in impingers containing 0.02N H_2SO_4. Ammonia forms a blue compound--indophenol--with alkaline phenol and hypochlorite. The intensity of the blue colour, which is proportional to the ammonia concentration, is measured at 630 nm. Sodium nitroprusside is added to increase the sensitivity of the reaction.

3. Scope

3.1 The detection limit is 0.1 mg/L NH_3-N in the test solution.

4. Interference

4.1 Colour and turbidity interfere.

5. Apparatus

5.1 Sampling train consisting of 4 impingers, a rotameter and a vacuum pump.
5.2 Spectrophotometer, 1-cm cells.

6. Reagents

6.1 Ammonia-free water: slowly pass distilled water through a 25-cm column of glass tubing (1.2 to 2.5 cm diameter) which has been charged with 2 parts by volume of a strongly basic anion-exchange resin and 1 part by volume of a strongly acidic cation-exchange resin.
6.2 Silica gel.

6.3 Sulphuric acid solution (0.02N): dilute 0.6 mL conc. H_2SO_4 to one litre with ammonia-free distilled water.

6.4 Sodium phosphate buffer (11% w/v): dissolve 11 g of trisodium phosphate, $Na_3PO_4.12H_2O$, in 100 mL of ammonia-free distilled water.

6.5 Phenate reagent: dissolve 340 g phenol in 500 mL of absolute methanol. Dissolve 0.1 g sodium nitroprusside in 15 mL ammonia-free distilled water, add 75 mL of phenol solution and dilute the solution to 100 mL with ammonia-free distilled water.

6.6 Sodium hydroxide solution (5M): dissolve 20 g sodium hydroxide in 100 mL ammonia-free distilled water.

6.7 Basic sodium hypochlorite solution: mix 11.5 mL commercial bleach (2.5% Cl) and 20 mL 5M NaOH in a 100 mL volumetric flask and dilute to volume with ammonia-free distilled water.

6.8 Stock ammonia solution (1000 mg/L NH_3-N): dissolve 3.8190 g anhydrous NH_4Cl (dried at 100°C for 2 hours) in ammonia-free distilled water in a 1000 mL volumetric flask and dilute to volume.

6.9 Standard ammonia solution (10 mg/L NH_3-N): dilute 10.0 mL stock ammonia solution to 1000 mL with ammonia-free distilled water.

6.10 Working standards - prepare as follows:

mL std. sol/100 mL	conc. mg/L NH_3-N
2.5	0.25
5.0	0.50
7.5	0.75
10.0	1.00
20.0	2.00

7. Procedure

7.1 Sampling

7.1.1 Assemble, in order, four fritted impingers, the rotameter and the pump.

7.1.2 Collect an air sample in the first two impingers, each containing 20 mL of 0.02N H_2SO_4. Draw air sample at the rate of 0.2-0.4 litre/min for 60 minutes. Place silica gel in the third impinger and keep the fourth impinger empty. Place the impingers in an ice bath.

7.1.3 Transfer the sample from the two impingers into a polyethylene bottle. Store the sample at 5°C.

7.1.4 Record the total air volume sampled. Measure and record air temperature and pressure.

7.2 Analysis

7.2.1 Rinse all glassware with ammonia-free distilled water.

7.2.2 Measure the sample volume.

7.2.3 Pipet a 10.0 mL sample, a blank and a standard into 25 mL volumetric flasks.

7.2.4 Add 6 mL sodium phosphate buffer, 1 mL phenate reagent and 5 mL basic sodium hypochlorite solution to each flask and dilute to volume with ammonia-free distilled water.

7.2.5 Allow 30 minutes to develop colour.

7.2.6 Set the sprectrophotometer to 100 percent transmittance with the blank at 630 nm and read the percent transmittance for the sample and standards in a 1cm cell.

8. Calculation

8.1 Prepare a calibration curve by plotting percent transmittance vs mg/L NH_3-N. Read the sample concentration from the graph in units of mg/L NH_3-N.

$$mg\ NH_3\text{-}N = \frac{mg/L\ NH_3\text{-}N \times total\ sample\ volume\ in\ mL}{1000}$$

8.2 The final result is expressed as

$$\mu g\ NH_3\text{-}N/m^3 = \frac{mg\ NH_3\text{-}N \times 10^3}{m^3\ of\ collected\ air\ at\ STP}$$

9. References

9.1 Std. Meth., for Water and Wastewater, 17th Ed., p. 4-120.

9.2 H.D. Axelrod and J.P. Greenberg, Atmos. Environ., Vol.10, 1976, p. 495.

CHLORINE, FREE

(Colorimetric)

1. Introduction

1.1 Free chlorine is present in ambient air, mainly in the vicinity of pulp and paper plants.

2. Principle

2.1 When free chlorine is absorbed in an alkaline solution of 4-nitroaniline, an orange-brown colour is developed. The intensity of the colour, which is proportional to the concentration of chlorine, is measured at 485 nm.

3. Scope

3.1 The method is suitable for the determination of chlorine in the range between 0.2 and 50 µg/mL in the absorbing solution.

4. Interference

4.1 Sulphur dioxide interferes. A chromic acid scrubber is used during sampling to remove SO_2.

5. Apparatus

5.1 Spectrophotometer, 1-cm cells.

5.2 A sampling train consisting of 3 impingers, a chromic acid scrubber, rotameter and vacuum pump.

5.3 Chromic acid scrubber: dissolve 6.5 g of chromic oxide in 40 mL of distilled water and 2 mL of conc. H_2SO_4. Add this solution dropwise onto a glass fibre paper of approximately 1000 cm^2 area. Dry the paper in an oven at 80 - 90°C for 1 hour and store in a tightly capped container.

5.4 Chlorine permeation tube.

5.5 Permeation chamber.

6. Reagents

6.1 Absorbing reagent: dissolve 0.4 g of 4-nitroaniline in 1 litre of distilled water. Dilute this solution with an equal volume of a 3N solution of KOH (pH of the solution should be 14). Store this solution in a dark bottle. The reagent is stable for several weeks. On the day of sampling, add 2 g of barbitone sodium to 1 litre of the stock solution.

6.2 Potassium hydroxide (3N): dissolve 170 g of KOH in 1 litre of distilled water.

6.3 Silica gel.

6.4 Standard sodium thiosulphate (0.025N): weigh 12.41 g of $Na_2S_2O_3.5H_2O$ into a 2000 mL volumetric flask and dilute to volume with distilled water.

6.5 Potassium dichromate (0.100N): dissolve 4.904 g of potassium dichromate (previously dried for 2 hours at 103°C) in distilled water and dilute to 1000 mL.

6.6 Starch solution: prepare a paste by adding 10 g of starch to 20 mL of distilled water. Add 2 litres of boiling water to the paste and stir until all starch dissolves. Add a small amount of salicylic acid to prevent mold formation.

6.7 Standardization of sodium thiosulphate: pipet 10.0 mL of 0.100N potassium dichromate solution into a 400 mL beaker containing 25 mL of water, 2 g KI and 5 mL of (1+5) HCl. Allow the reaction to proceed in the dark for 5 minutes, dilute to approximately 200 mL and titrate with 0.025N $Na_2S_2O_3$, adding 0.5 mL of starch near the end point. At the end point, the colour changes from opaque blue to colorless.

$$\text{Normality of } Na_2S_2O_3 = \frac{10.0 \times 0.100}{\text{mL of } Na_2S_2O_3 \text{ consumed}}$$

6.8 Stock chlorine solution: use commercial bleach (NaOCl) as chlorine stock solution or prepare the stock by passing chlorine from a chlorine permeation tube through 100 mL of an ice-cold 3N KOH solution. Standardize the solution by iodometric titration as follows:

6.8.1 Transfer 10.0 mL stock and blank to Erlenmeyer flasks and dilute to 50 mL with distilled water.

6.8.2 Adjust the pH to 3-4 with conc. acetic acid.

6.8.3 Add about 1 g potassium iodide and mix with a stirring rod.

6.8.4 Titrate against 0.025N thiosulphate until the yellow colour of the liberated iodine is almost discharged. Add 1 mL starch solution and titrate until the blue colour is discharged.

The amount of chlorine in the stock solution is expressed as

$$mg/L\ Cl = \frac{(A-B) \times N \times 35,450}{mL\ sample\ used\ for\ titration}$$

where

A = mL of thiosulphate required for sample titration.

B = mL of thiosulphate required for the titration of blank.

N = normality of thiosulphate.

6.9 Standard chlorine solution (1 mg/L Cl): pipet an appropriate volume of the stock and dilute to 100 mL with absorbing solution.

6.10 Working standards: prepare working standards by diluting the following volumes of standard solution to 50 mL with absorbing solution as follows:

mL std. solution/50 mL	conc. µg Cl/50 mL
0.5	0.5
1.0	1.0
2.0	2.0
4.0	4.0
8.0	8.0
10.0	10.0

7. Procedure

7.1 Sampling

7.1.1 Assemble in order, the chromic acid scrubber, three midget impingers, a rotameter and a pump.

7.1.2 Bubble air through the first two impingers (each containing 20 mL of absorbing reagent) at a rate of 0.5-2 litres per minute. Put silica gel in the third impinger.

7.1.3 Adjust the sampling time and flow rate so as to give a chlorine concentration of 1-10 µg/mL in the absorbing solution. Record the total air volume sampled. Measure and record air temperature and atmospheric pressure.

7.1.4 Transfer the absorbing solution from the impingers to a polyethylene bottle and store the sample at 5°C in the dark. Perform analysis within 24 hours.

7.2 Analysis

7.2.1 Transfer the sample to a 50 mL volumetric flask and dilute to 50 mL with absorbing agent. Allow 15 minutes to complete the colour development.

7.2.2 Measure the absorbance of the sample at 485 nm using unexposed absorbing reagent as a blank.

7.2.3 Prepare working standards as described in 6.10. Allow 15 minutes for colour development and read the absorbance at 485 nm.

8. Calculation

8.1 Prepare a calibration curve by plotting absorbance vs microgram chlorine. Read the concentration of chlorine in the sample in units of micrograms from the graph.

$$\mu g\ Cl/m^3 = \frac{\mu g\ Cl}{m^3\ of\ collected\ air\ at\ STP}$$

9. Reference

9.1 J. Geabbay, M. Davidson and A.E. Donagi, Analyst, Vol. 101, Feb. 1976, p. 128.

FLUORIDE, WATER SOLUBLE

(Specific-Ion Electrode)

1. Introduction

1.1 During the combustion of coal and phosphate rocks, fluorine compounds, such as hydrofluoric acid and silicon tetrafluoride, are released.

1.2 In the process of industrial operations to produce phosphate fertilizer, iron and steel, glass and ceramics, fluorine compounds are set free as gaseous and/or particulate fluoride.

2. Principle

2.1 Fluoride is collected by exposing a filter paper soaked with saturated CaO solution. Fluoride is determined using a fluoride specific-ion electrode in conjunction with a standard calomel reference electrode. The potential developed by the presence of fluoride ions is measured by an expanded-scale pH/mV meter.

3. Scope

3.1 The range is 0.05 mg/L to 2 mg/L fluoride in the test solution.

4. Interference

4.1 Polyvalent cations such as Si, Fe and Al interfere. A buffer prevents these interferences.

5. Apparatus

5.1 pH meter with expanded mV scale.

5.2 Fluoride electrode (Orion 94-09, or equivalent).

5.3 Magnetic stirrer and Teflon-coated stirring bar.

6. Reagents

6.1 Saturated CaO solution in distilled water.

6.2 Total ionic strength adjustment buffer (TISAB): add 57 mL of glacial acetic acid, 58 g of sodium chloride and 2 g CDTA (1,2-diamino-cyclohexane-tetra acetic acid) to

approximately 500 mL of distilled water. Stir to dissolve and cool to room temperature. Adjust the pH of the solution to between 5.0 and 5.5 with 5N NaOH. Transfer the solution to a 1000 mL volumetric flash and dilute to volume with distilled water.

6.3 Stock fluoride solution (100 mg/L F): dissolve 0.221 g anhydrous sodium fluoride in distilled water and dilute to 1000 mL.

6.4 Working Standards - prepare as follows:

mL stock/1000 mL	conc. mg/L F
1.0	0.10
2.5	0.25
5.0	0.50
10.0	1.00
15.0	1.50
20.0	2.00

7. Procedure

7.1 Sampling

7.1.1 Immerse 5cm x 60cm filter strips in saturated CaO solution in a plastic tray for 16 hours with occasional shaking.

7.1.2 After 16 hours, remove the filter paper and allow to dry to a slightly damp condition. Then wrap filter strip around a 2¼" diameter by 3¾" long PVC tube. Tie with a strip and place in a plastic bag.

7.1.3 Expose the fluoride paper in the field for approximately 4 weeks, then return it to the laboratory in the plastic bag.

7.2 Analysis

7.2.1 Immerse each fluoride paper sample and blank strip in 50 mL water and 50 mL buffer in a beaker overnight. A tilting dispenser or pipet is used to deliver the 50 mL quantities into the beaker.

7.2.2 Next day, remove the filter paper from the beakers.

7.2.3 Add 50 mL of buffer solution to 50 mL of each standard in 200 mL beakers.

7.2.4 Insert the fluoride specific-ion electrode into the beaker and stir the solution magnetically for 2 minutes and record the potential when the reading is stable. Run the samples, blanks, and standards at the same temperature.

8. Calculation

8.1 Using two-cycle semi-log graph paper, prepare a calibration curve by plotting mg/L F on the log scale vs the mv readings on a linear scale. A straight line should be obtained. Read the fluoride concentration from the graph in units of mg/L F.

$$mg\ F = \frac{mg/L\ F \times total\ sample\ volume\ in\ mL}{1000}$$

The final result is expressed as:

$$mg\ F/cm^2/day = \frac{mg\ F}{a \times d}$$

where

a = area of the fluoride paper.

b = number of days exposed.

Note:

Maintenance of Electrodes:

- The electrodes may be stored in water for short time periods between measurements or may be dried for longer storage. Refer to the electrode manuals.
- The fluoride electrode, whose response may become sluggish with time, can be restored to working order by brushing the sensing element on the flat tip of the electrode with a fluoride tooth paste and a soft brush.

9. References

9.1 Std. Meth. Water and Wastewater. 17th Ed., p. 4-87.

9.2 Orion Application Information Procedure No. 504.

9.3 Methods of Air Sampling and Analysis. APHA Intersociety Committee. M. Katz, Editor; 2nd Ed., p. 417.

FORMALDEHYDE

(Chromotropic acid, Colorimetric)

1. Introduction

1.1 The main sources of formaldehyde are fibreglass, acetic acid and formaldehyde-resin manufacturing plants.

2. Principle

2.1 Formaldehyde is collected in a 1% sodium bisulphite solution to form an addition compound. The addition compound is treated with chromotropic acid in the presence of sulphuric acid. Sulphuric acid releases formaldehyde. Chromotropic acid reacts with free formaldehyde to form a violet complex which is measured at 580 nm.

3. Scope

3.1 The detection limit is 0.1 mg/L in the test solution.

4. Interference

4.1 No significant interference from other aldehydes. Methanol and formic acid interfere.

5. Apparatus

5.1 Sampling train consisting of 4 impingers, a rotameter and a vacuum pump.
5.2 Spectrophotometer, 1-cm cells.

6. Reagents

6.1 Chromotropic acid solution (0.5%): dissolve 0.5 g chromotropic acid (di-sodium salt) in 100 mL of distilled water and filter it before use. The acid is stable in solution for one week if stored in a refrigerator.
6.2 Starch solution (1%): prepare a paste by adding 1 g of starch to 5 mL of distilled water. Add 95 mL of boiling water to the paste and stir until all starch dissolves.

6.3 Sodium bisulphite solution (1%): dissolve 1 g of sodium bisulphite in 100 mL of distilled water.

6.4 Standard sodium thiosulphate solution (0.050N): dissolve 12.41 g of sodium thiosulphate, $NA_2S_2O_3.5H_2O$, in 1000 mL of distilled water. Standardize the solution against potassium dichromate after at least two weeks storage. Use boiled distilled water and add 2 mL of chloroform to minimize bacterial decomposition of the thiosulphate solution.

6.5 Standard potassium dichromate solution (0.50N): dissolve 2.452 g anhydrous potassium dichromate, $K_2Cr_2O_7$, in distilled water and dilute to 1000 mL.

6.6 Standardization of sodium thiosulphate: to 80 mL distilled water add with stirring, 1 mL conc. H_2SO_4, 10 mL 0.050N $K_2Cr_2O_7$ and 0.5 g potassium iodide. Allow the reaction mixture to stand 6 minutes in the dark before titration with the 0.050N $Na_2S_2O_3$ titrant, adding 0.5 mL of starch near the end point. At the end point, the colour changes from blue to colorless.

$$Normality\ of\ Na_2S_2O_3 = \frac{10 \times 0.050}{mL\ Na_2S_2O_3\ consumed}$$

6.7 Stock iodine solution (0.100N): place 12.8 g or iodine in a 250 mL beaker, add 40 g of KI and 25 mL of water. Stir until all is dissolved and then dilute to 1000 mL with water.

6.8 Standard iodine solution (0.010N): dilute 100.0 mL of the 0.100N iodine solution to 1000 mL with distilled water. Standardize against 0.050N sodium thiosulphate solution as follows:

Pipet 50.0 mL standard iodine solution and 50 mL of distilled water into 125 mL Erlenmeyer flasks.

Add 50 mL distilled water, 5 mL (1+5) HCl and mL starch solution to both the flasks. Titrate with 0.050N sodium thiosulphate until the blue colour disappears.

$$Normality\ of\ iodine\ solution = \frac{(a-b) \times N}{50.0}$$

where

N = normality of $Na_2S_2O_3$ solution.

a = mL of $Na_2S_2O_3$ solution consumed by the iodine standard.

b = mL of $Na_2S_2O_3$ solution consumed by the blank.

6.9 Buffer solution: dissolve 80 g of anhydrous sodium carbonate in 500 mL of distilled water. Adjust the pH of this solution to 9.6 ± 0.1 using glacial acetic acid and monitor with a pH meter. Dilute to one litre with distilled water.

6.10 Silica gel.

6.11 Stock formaldehyde solution (1000 mg/L): pipet 3 mL of 37-39% formaldehyde into a 1000 mL volumetric flask and dilute to volume with distilled water.

6.12 Standard formaldehyde solution (100 mg/L): dilute 100.0 mL of the stock solution to 1000 mL with distilled water in a volumetric flask. Standardize this solution as follows: Pipet 10.9 mL of the standard formaldehyde solution and 10 mL of distilled water into 250 mL Erlenmeyer flasks. Add 25 mL of 1% sodium bisulphite and 1 mL of 1% starch solution into each flask. Titrate these solutions with 0.100N iodine until a dark blue colour persists. Bubble air through the solutions for several minutes to remove SO_2 resulting from the decomposition of bisulphite. Add 0.050N sodium thiosulphate dropwise to decolourize the solutions, then add a few drops of 0.010N iodine solution to give a faint blue colour. Cool the solutions in an ice bath and add 50 mL of chilled buffer. Keep the flasks in the ice bath for 10-15 minutes. Titrate the liberated bisulphite with 0.010N iodine solution to the same faint blue colour. The concentration of the standard formaldehyde is then given by

$$\mu g\ formaldehyde/mL = \frac{(V_s - V_b) \times 150}{10} \times \frac{N}{0.010}$$

where

v_s = mL of 0.010N iodine used to titrate the standard.

v_b = mL of 0.010N iodine used to titrate the blank.

N = exact normality of the 0.010N iodine solution.

150 = 1 mL of 0.010N iodine solution is equivalent to 150 µg of formaldehyde.

6.13 Working standards: pipet standard formaldehyde solution and dilute to volume with 1% $NaHSO_3$ as follows:

mL standard/100 mL	conc. µg/mL
20.0	20.0
15.0	15.0
10.0	10.0
5.0	5.0
2.5	2.5

7. Procedure

7.1 Sampling

7.1.1 Collect the sample in the first two impingers, each containing 10 mL of 1% sodium bisulphite solution. Put silica gel in the third impinger and keep the fourth impinger empty.

7.1.2 Pass air at the rate of 0.5 to 2 litres/minute for 30-60 minutes. Record the total air volume sampled. Measure and record air temperature and atmospheric pressure.

7.1.3 Transfer the sample to a polyethylene bottle and preserve it at 5°C.

7.2 Analysis

7.2.1 Measure the sample volume.

7.2.2 Into separate 25 mL volumetric flasks, pipet a 10.0 mL sample; a 1% sodium bisulphite blank; and the working standards.

7.2.3 Add 1 mL chromotropic acid slowly, followed by 5 mL conc. sulphuric acid to each flask Mix well.

7.2.4 Heat the flasks in a boiling water bath for 30 minutes. Cool the flasks and dilute to volume with distilled water.

7.2.5 Set the spectrophotometer to 100 percent transmittance with the blank at 580 nm. Measure the percent transmittance.

8. Calculation

8.1 Prepare a calibration curve by plotting µg/mL formaldehyde vs percent transmittance. Read the concentration of the sample from the graph in units of µg/mL formaldehyde.

$$\mu g\ formaldehyde = mg/mL\ formaldehyde \times sample\ volume\ in\ mL$$

The final result is expressed as:

$$\mu g\ formaldehyde/m^3 = \frac{\mu g\ formaldehyde}{m^3\ of\ collected\ gas\ at\ STP}$$

9. References

9.1 Health Laboratory Science, Method 43501-02-74T, 1975, p. 163.

9.2 Methods of Air Sampling and Analysis. APHA Intersociety Committee, M. Katz, Editor; 2nd Edition, p. 303.

HYDROGEN SULPHIDE

(Iodometric Titration)

1. Introduction

1.1 Hydrogen sulphide is a toxic and malodorous air pollutant. It has adverse effects on lead-based paints and is corrosive to certain metals. It originates from pulp and paper plants, and oil and gas refineries.

2. Principle

2.1 A 5-cm wide tape of filter paper, impregnated with a 5% solution of zinc acetate, is exposed to the atmosphere for approximately 4 weeks. Hydrogen sulphide present in the ambient air reacts with zinc acetate and forms zinc sulphide. The sample is analyzed by decomposing zinc sulphide to hydrogen sulphide with hydrochloric acid, and the sulphide is determined by iodometric titration.

3. Scope

3.1 The method is applicable only to ambient air on a cumulative basis. The detection limit in the test solution is 2 mg/L sulphide.

4. Interference

4.1 Sulphur dioxide and mercaptans interfere.

5. Apparatus

5.1 Jars (20 cm circumference).
5.2 Filter paper tape (Whatman No. 2, 60 x 5 cm, or equivalent).

6. Reagents

6.1 Zinc acetate/glycerine solution: dissolve 5 g zinc acetate and 5 mL glycerine in 100 mL distilled water.

6.2 Sodium thiosulphate solution (0.025N): dissolve 12.41 g of sodium thiosulphate, $Na_2S_2O_3.5H_2O$, in distilled water and dilute to 2000 mL with distilled water. Standardize against standard potassium dichromate.

6.3 Potassium dichromate solution (0.100N): dissolve exactly 4.904 g of potassium dichromate (dried for 2 hours at 103°C) in distilled water in a 1000 mL volumetric flask and dilute to volume.

6.4 Starch solution: prepare a paste by adding 10 g of starch to 20 mL of distilled water. Add 2 litres of boiling water to the paste and stir until all starch dissolves. Add a small amount of salicylic acid to prevent mold formation.

6.5 Standardization of sodium thiosulphate: pipet 10.0 mL of 0.100N potassium dichromate solution into a 400 mL beaker containing 25 mL of water, 2 g KI and 5 mL of (1+5) HCl. Allow the reaction to proceed in the dark for 5 minutes, dilute to approximately 200 mL and titrate with 0.025N $Na_2S_2O_3$, adding 0.5 mL of starch near the end point. At the end point, the colour changes from opaque blue to colorless.

$$\textit{Normality of } Na_2S_2O_3 = \frac{10.0 \times 0.100}{\textit{mL of thiosulphate consumed}}$$

6.6 Stock iodine solution (0.100N): dissolve 40 g KI in 800 mL distilled water in a 1000 mL volumetric flask, add 12.8 g of iodine and dilute to volume.

6.7 Standard iodine solution (0.025N): dilute 125.0 mL of stock solution to 500 mL using distilled water in a 500 mL volumetric flask.

6.8 Standardize the 0.025N iodine solution against the above standard $Na_2S_2O_3$ solution, as follows:

In separate 250 mL Erlenmeyer flasks, pipet 10.0 mL standard iodine solution and 50 mL distilled water. Add 50 mL distilled water, 5 mL (1+5) HCl and 1 mL starch solution to both flasks. Titrate with 0.025N sodium thiosulphate until the blue color disappears.

$$\textit{Normality of iodine solution} = \frac{(a-b) \times N}{50.0}$$

where

N = normality of $Na_2S_2O_3$ solution.

a = mL of $Na_2S_2O_3$ solution consumed by the iodine standard.

b = mL of $Na_2S_2O_3$ solution consumed by the blank.

7. Procedure

7.1 Sampling

7.1.1 Preparation of hydrogen sulphide candle: impregnate 60 x 5 cm filter paper tapes with zinc acetate/glycerine solution by soaking them for 15 to 20 hours in the acetate solution in a plastic tray. Remove the tapes and allow them to dry until they are just slightly damp. Wrap each tape around a jar and tie it with thread. Expose the candle in the field for approximately 4 weeks.

7.2 Analysis

7.2.1 Measure the exposed surface area of the tape in cm^2 before removing it from the jar.

7.2.2 Remove the tape from the jar.

7.2.3 Fold the tape to fit in the bottom of a 600 mL beaker.

7.2.4 Add 150 mL of distilled water, thoroughly immersing the tape. Allow it to stand overnight at room temperature.

7.2.5 Add 10.0 mL of 0.025N iodine solution, followed by 5 mL of conc. HCl. After stirring, if the brown colour of the solution disappears, immediately add more iodine solution in 10 mL portions until the brown colour persists. Record the mL of iodine solution added.

7.2.6 Titrate with 0.025N sodium thiosulphate solution adding 0.5 mL of starch towards the end point. The end point is reached when the blue colour disappears. Record the titrated volume to the nearest 0.10 mL.

7.2.7 Run an iodine blank initially and after every tenth sample.

Calculation:

$$mg\ sulphide = \frac{(C-D) \times 0.4 \times 0.025}{N}$$

where

C = mL of $Na_2S_2O_3$ solution used for blank.

D = mL of $Na_2S_2O_3$ solution used for sample.

0.4 = mg of sulphide, equivalent to 1 mL of 0.025N iodine solution.

N = Normality of $Na_2S_2O_3$ solution.

The final result is expressed as:

$$mg\ SO_3/day/100\ cm^2 = \frac{mg\ sulphide \times 2.497 \times 100}{a \times d}$$

where

$$2.497 = \frac{mol.\ weight\ of\ SO_3}{mol.\ weight\ of\ sulphide}$$

a	=	area of the exposed tape in cm^2.
d	=	no. of days exposed.
100	=	conversion to 100 cm^2.

8. References

8.1 H.P. Sanderson, R. Thomas and M. Katz, J. Air Poll. Control Assoc., Vol. 16, 1966, p. 328.

8.2 H.C. Wohlers and M. Feldstein; J. Air. Poll. Control Assoc., Vol. 16, 1966, p. 19.

NITROGEN DIOXIDE

(Triethanolamine, Colorimetric)

1. Introduction

1.1 Nitrogen dioxide in ambient air originates from combustion systems, such as motor vehicles, furnaces and industrial processes. Nitrogen dioxide is not only toxic to living organisms, but also plays an important role in photochemical smog-forming reactions.

2. Principle

2.1 The triethanolamine exposure method is based on the accumulation of NO_2 over a certain period of time, providing an average NO_2 concentration in ambient air. Nitrogen dioxide is absorbed on triethanolamine-impregnated paper which is exposed in the field for approximately 4 weeks. The filter paper is extracted with Saltzman reagent, and the intensity of colour is measured at 550 nm.

3. Scope

3.1 The detection limit is 2 mg/L NO_2 in the test solution.

4. Interference

4.1 Nitric oxide and ozone do not interfere. Sulphur dioxide interferes to some extent, but the addition of 1% acetone to the Saltzman reagent can avoid any interference from SO_2.

5. Apparatus

5.1 Whatman #1 filter paper.
5.2 Huey plates.
5.3 O-rings.
5.4 Spectrophotometer, 1-cm cells.

6. Reagents

6.1 Triethanolamine solution: dissolve 25 g triethanolamine and 4 g glycerol in 50 mL acetone and dilute the solution to 100 mL with distilled water.

6.2 N-(1-naphthyl)-ethylenediamine dihydrochloride (0.1%): dissolve 100 mg of the reagent in 100 mL of distilled water. Preserve the solution in a brown bottle in a refrigerator.

6.3 Saltzman reagent: dissolve 5.0 g of anhydrous sulphanilic acid, $NH_2C_6H_4SO_3H$, in a solution of 140 mL glacial acetic acid and 800 mL distilled water. Heat gently, if necessary, for complete solution. To the cooled solution add 20 mL of the 0.1% solution of N-(1-naphthyl)-ethylenediamine dihydrochloride and 10 mL acetone. Dilute the solution to one litre with distilled water. The solution is preserved in a well-stoppered brown bottle in a refrigerator.

6.4 Stock sodium nitrite solution (2.160 g/L $NaNO_2$): dissolve 2.160 g sodium nitrite in distilled water in a 1000 mL volumetric flask and dilute to volume with distilled water. Store the stock solution in a refrigerator.

6.5 Standard sodium nitrite solution (0.0216 g/L $NaNO_2$): dilute 10.0 mL of the stock solution to 1000 mL with distilled water. One mL of this standard solution of sodium nitrite produces a colour equivalent to that of 20 µg of NO_2 in the test solution.

6.6 Working standards - prepare working standards by diluting the standard solution to 25 mL with Saltzman reagent as follows:

mL standard solution/25 mL	conc. µg NO_2
0.10	2
0.25	5
0.50	10
0.75	15
1.00	20

Note: Absorbance of standards must be read within 15 minutes of preparation.

7. Procedure

7.1 Sampling

7.1.1 Preparation of plates: soak Whatman #1 filter paper discs (45 mm diameter) in the triethanolamine solution for ½ hour. Dry them in an oven at 50°C for two hours and store in a dessicator.

7.1.2 Place one disc on a Huey plate and hold it in position with a rubber o-ring. Expose it in the field for a period of approximately 4 weeks.

7.2 Analysis

7.2.1 Measure the area of the exposed disc in cm^2.

7.2.2 Remove the exposed disc from the Huey plate and extract it with 200 mL of Saltzman reagent for 60 minutes at room temperature.

7.2.3 Dilute a 10 mL aliquot of this solution to 25 mL with additional Saltzman reagent. Allow 15 minutes to complete the colour development.

7.2.4 Transfer a portion of the sample to a stoppered cell and read the absorbance in a spectrophotometer at 550 nm using unexposed reagent as reference.

7.2.5 Prepare working standards as described in 6.6.

7.2.6 Allow 15 minutes for complete colour development and read absorbance at 550 nm.

8. Calculation

8.1 Prepare a calibration curve by plotting the absorbances vs µg NO_2. Read the concentration of sample from the graph in units of µg NO_2.

$$\mu g\ NO_2 = \frac{\mu g\ NO_2\ in\ the\ aliquot \times total\ sample\ volume\ in\ mL}{aliquot\ volume\ in\ mL}$$

The final result is expressed as

$$\mu g\ NO_2/cm^2/day = \frac{\mu g\ NO_2}{a \times d}$$

where

a = area of the disc in cm^2.

b = no. of days exposed.

9. References

9.1 1989 Annual Book of ASTM Standards, Vol.11.03, p. 28.

9.2 S.C. Barton and H.G. McAdie "A Cumulative Survey Technique for Atmospheric Nitrogen Dioxide": Ontario Reserach Foundation, Sheridan Park, Ontario, Canada, presented at the 67th Annual Meeting of the Air Pollution Control Association, Denver, Colorado, June 9-13, 1974.

9.3 Methods of Air Sampling and Analysis. APHA Intersociety Committee. M. Katz, Editor; 2nd Ed., p. 829.

September 1992

Method No. 14040

PESTICIDES IN AIR

(Gas Chromatography)

1. Introduction

1.1 Pesticides are widely used for the control of weeds and insects. Their occurrence in air is mainly from the application process, i.e., crop spraying. They are also present in the vicinity of manufacturing plants.

2. Principle

2.1 Organo-chlorine and organo-phosphorus pesticides are collected on polyurethane foam plugs. Polyurethane foam, being polar and hydrophobic, is not affected by the water vapour in the air. A glass fibre filter is used before the polyurethane foam plug to remove particulate matter. The adsorbed pesticides are extracted by soxhlet extraction procedure. The extract is analyzed by gas chromatography, using an electron capture detector.

3. Scope

3.1 pg/m^3 to ng/m^3 of air.

4. Interference

4.1 Other organics in air have similar retention times. This can usually be overcome by using 2 different columns and 2 different detectors.

5. Apparatus

5.1 Air sampling train (see Fig. 1) consisting of:

- 5.1.1 Vacuum pump, 8 L/min capacity
- 5.1.2 Extraction thimble (25 x 85 mm)
- 5.1.3 Extraction thimble holder
- 5.1.4 Polyurethane foam plug (poly ether type) 28 x 35 mm
- 5.1.5 Glass fibre filter holder
- 5.1.6 Glass fibre filter (Gelman GE)

5.2 Extraction apparatus consisting of:

5.2.1 Soxhlet extraction apparatus with 250 mL R.B. flasks

5.2.2 Rotary evaporator

5.2.3 Sample vials, 2 mL

5.3 Gas Chromatograph equipped with:

5.3.1 Ni^{63} electron capture detector

5.3.2 Direct injection system for ¼" packed column

5.3.3 Column 1.5% OV 17/1.95% OV 210, 2 metres long

5.3.4 Carrier gas (argon 95%/methane 5%)

6. Reagents

6.1 Hexane (residue analyzer Baker)

Standards	Stock Standards (ng/µL)	Intermediate Standard (pg/µL)	Working Standard Mixtures (pg/µL)			
			1	2	3	4
2,4-D Methyl ester	11.2	336	67.2	33.6	20.2	6.7
2,4,5-T Methyl ester	10.8	108	21.6	10.8	6.5	2.2
Heptachlor	10.8	65	13.0	6.5	3.9	1.3
Methyl Parathion	9.8	235	47.0	23.5	14.1	4.7
p.p'-DDE	10.0	100	20.0	10.0	6.0	2.0
o,p-DDT	10.0	200	40.0	20.0	12.0	4.0

Working standards are prepared by transferring the appropriate amount of stock solution into a volumetric flask and diluting to volume.

7. Procedure

7.1 Preparation of the Absorbent, Polyurethane Foam (PUF)

7.1.1 Place 2 PUF plugs in an extraction thimble and soxhlet extract for 24 h using n-hexane or 5% ether-hexane. Dry the PUF plugs under vacuum and store in washed aluminum foil for shipping.

7.2 Sampling

7.2.1 Place the clean and dry sampling plug in the holder and connect to the pump as shown in figure 1. Install a glass fibre filter before the PUF to eliminate the

collection of unwanted particulate matter. Adjust the air flow to 3-4 L/min by means of a bubble meter or a wet test meter. Allow the sampler to run for a 24-h period. After the sampling period, remove the sampling plug and wrap it in clean aluminum foil and send it to the laboratory for analysis

7.2.2 Calibration Standards

7.2.2.1 The sampling efficiency of the PUF can be measured using a calibration apparatus as shown in figure 2. Adjust the air flow to 3-4 L/min. by means of a bubble meter or a wet test meter. Heat the water bath temperature to 50°C. Inject 100 µL to 1000 µL of intermediate standard into the bottom of the impinger. Allow the sampling pump to run for a 24-h period. After the sampling period, remove the PUF plugs for soxhlet extraction.

7.3 Extraction and Concentration

7.3.1 Place the foam plugs in an extraction thimble and extract by means of a soxhlet apparatus with n-hexane. The extraction should be carried out for 5-6 cycles, approximately for 1 h. Cool the extraction flask and concentrate the extract by means of a rotary evaporator operating at 35°C and 21" Hg, until the volume remaining is approximately 1 mL. Chill and remove the final volume of solvent with a dry N_2 stream. Add 5 mL of hexane and swirl to dissolve the residue. Transfer the sample to amber vials and store in a fridge.

7.4 Gas Chromatographic Analysis

7.4.1 Standardize the GC by injecting an appropriate volume (3 µL) of working standard. When the instrument is stable and the results are reproducible, inject the sample. Instrument conditions found suitable for the Varian 6000 GC were:

Injector Temperature:	225°C
Column Temperature:	195°C
ECD Detector Temperature:	325°C
Carrier Gas Flow:	42 mL/min (58.2 psi)
Detector Attenuation:	8
Detector Range:	10
Integrator Attenuation:	4, 8, 16

8. Calculation

8.1 Calculate the concentration of a particular pesticide in a sample by comparing its peak area with that of the standard.
The concentration is expressed as follows:

$$\mu g/m^3 \text{ of air at STP} = \frac{\text{Peak area of the compd.} \times \text{wt of the std in } \mu g}{\text{Peak area of the std} \times \text{total } m^3 \text{ of air at STP}}$$

The results can also be expressed as ppm (µL/L) by using the following expressions.

$$ppm = \frac{\mu g/m^3 \times MV \times 10^{-3}}{MW}$$

where

MW = molecular weight of the compound.
MV = Molar volume in L at 20°C and 760 mm Hg.

9. Precision and Accuracy

9.1 In a single laboratory (Alberta Environmental Centre), using standards in the concentration range of 1.3 to 67.2 pg/µL, the coefficient of variation for each compound was as follows.

2,4-DME	2.25%-3.42%
2,4,5-TME	2.50%-3.51%
Heptachlor	2.89%-3.05%
Me-Parathion	1.22%-3.56%
p,p'-DDE	2.83%-3.83%
o,p-DDT	1.81%-2.81%

9.2 In a single laboratory (AEC), using standards in the concentration range of 1.3 to 67.2 pg/µL, the recovery for each compound was as follows.

2,4-DME	84-90%
2,4,5-TME	91-95%
Heptachlor	88-91%
Me-Parathion	92-97%
p,p'-DDE	88-92%
o,p-DDT	91-94%

NOTE: The following pesticides can be analyzed by this method, but have not been tested for their adsorption-desorption efficiency on PUF.

Lindane
Aldrin
Parathion
Dieldrin
p,p'-DDT
Diazinon
Methyl-Trithion
Ethion
CDEC Sulfallate
Benefin, Benfluralin, Balan
DMPA Zytron
DCPA, Chlorthal, Dachthal
Nitrogen, TOK
Phorate (thimet)
Disulfoton
Malathion
Heptachlor Epoxide
(BHC) mixed isomers
MDE (DDMU)
TDE (p,p'-isomers)
Carbophenothion
Methoxychlor

10. References

10.1 EPA Manual of Analytical Methods for the Analysis of Pesticides in Humans and Environmental Samples.

10.2 EPA 600/4-80-008, Jan. 1980, Polyurethane foam as Trapping Agent for Airborne Pesticides.

10.3 Analysis of Air Pollutants by H. Leithe, Publisher Ann Arbor Science, 1971.

Figure 1. Apparatus For Sampling of Pesticides From Air

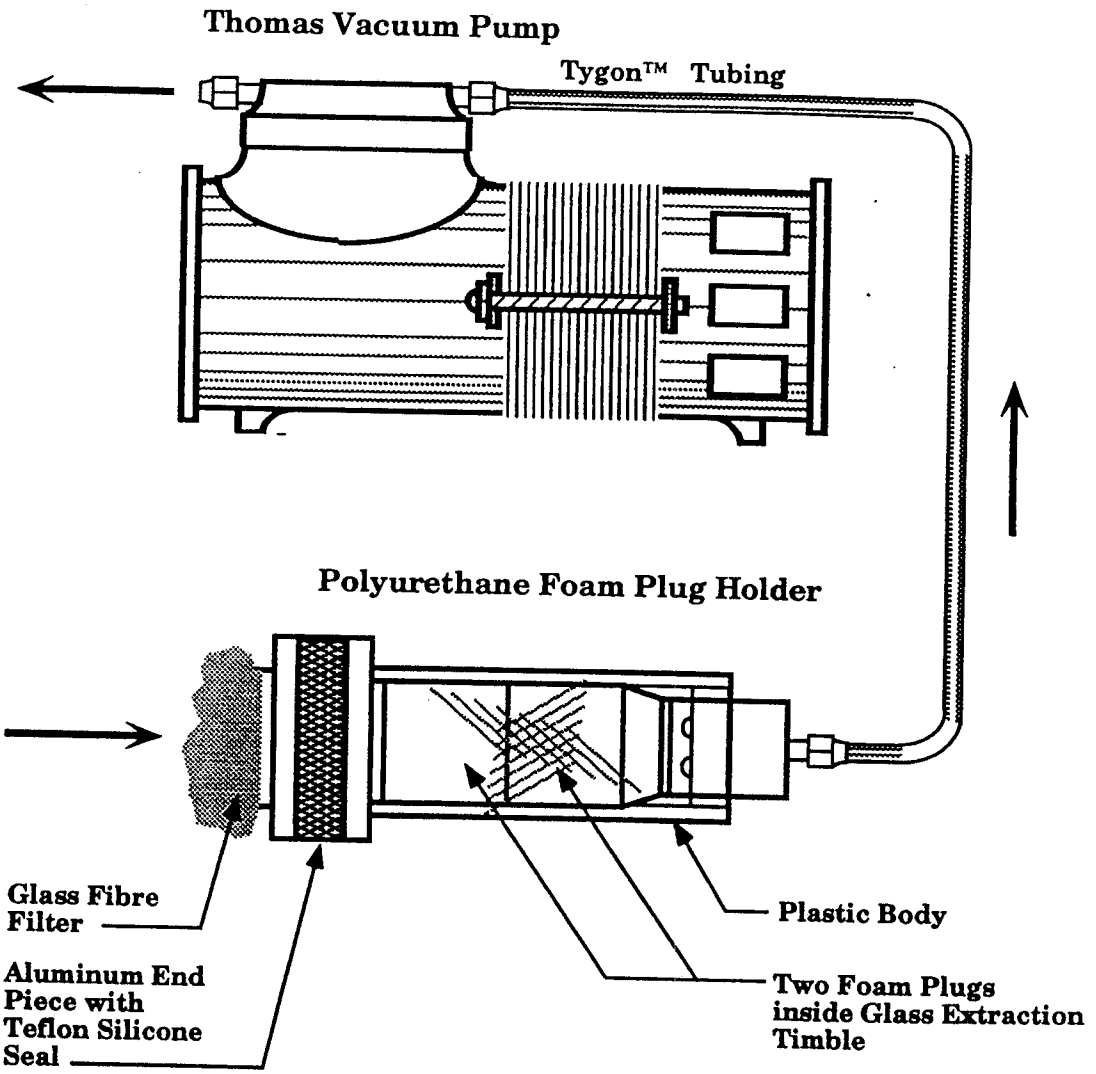


Figure 2. Calibration Apparatus For Collection Efficiency Studies

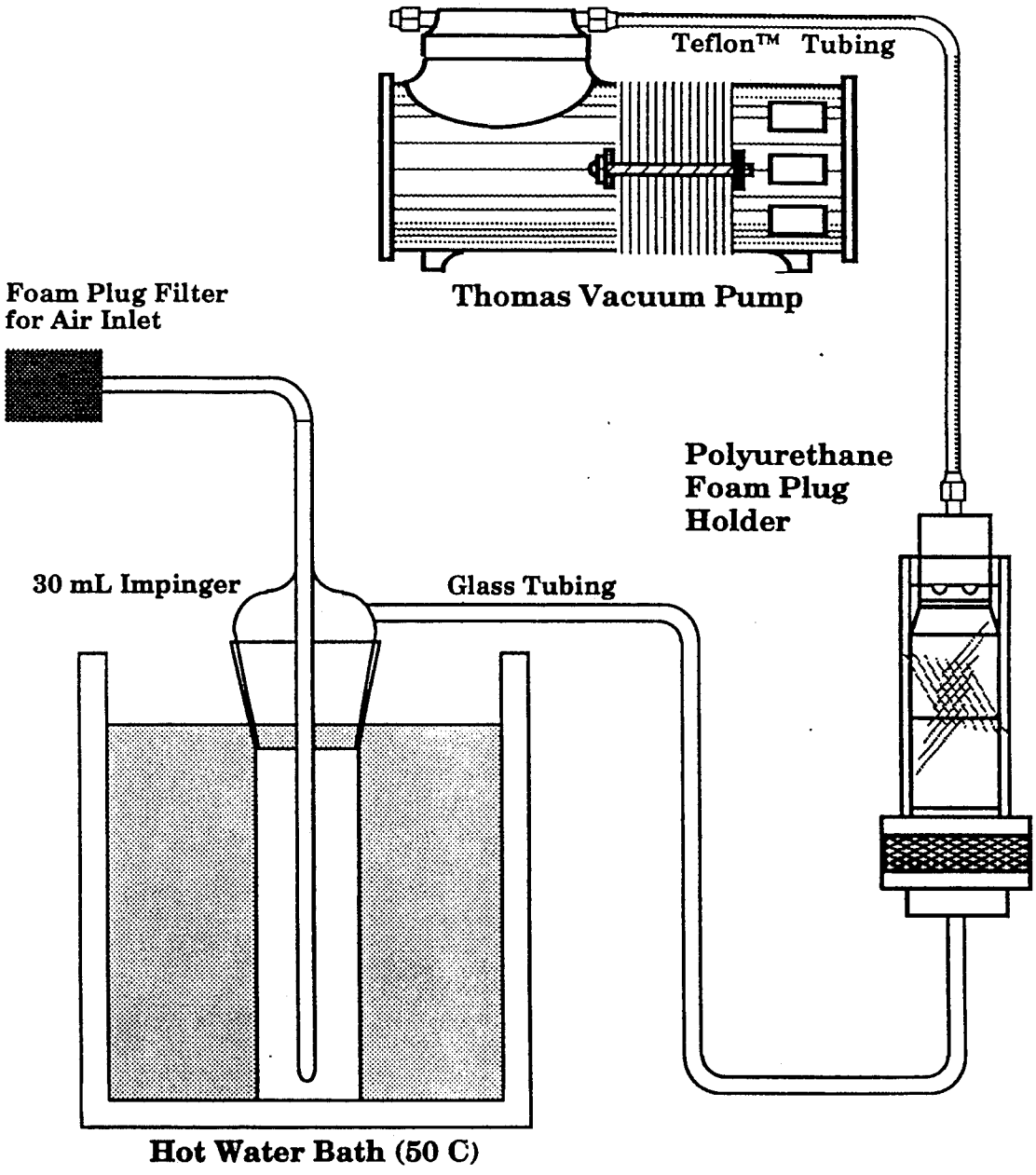


Figure 3. GC-ECD Chromatogram of a Pesticide Standard

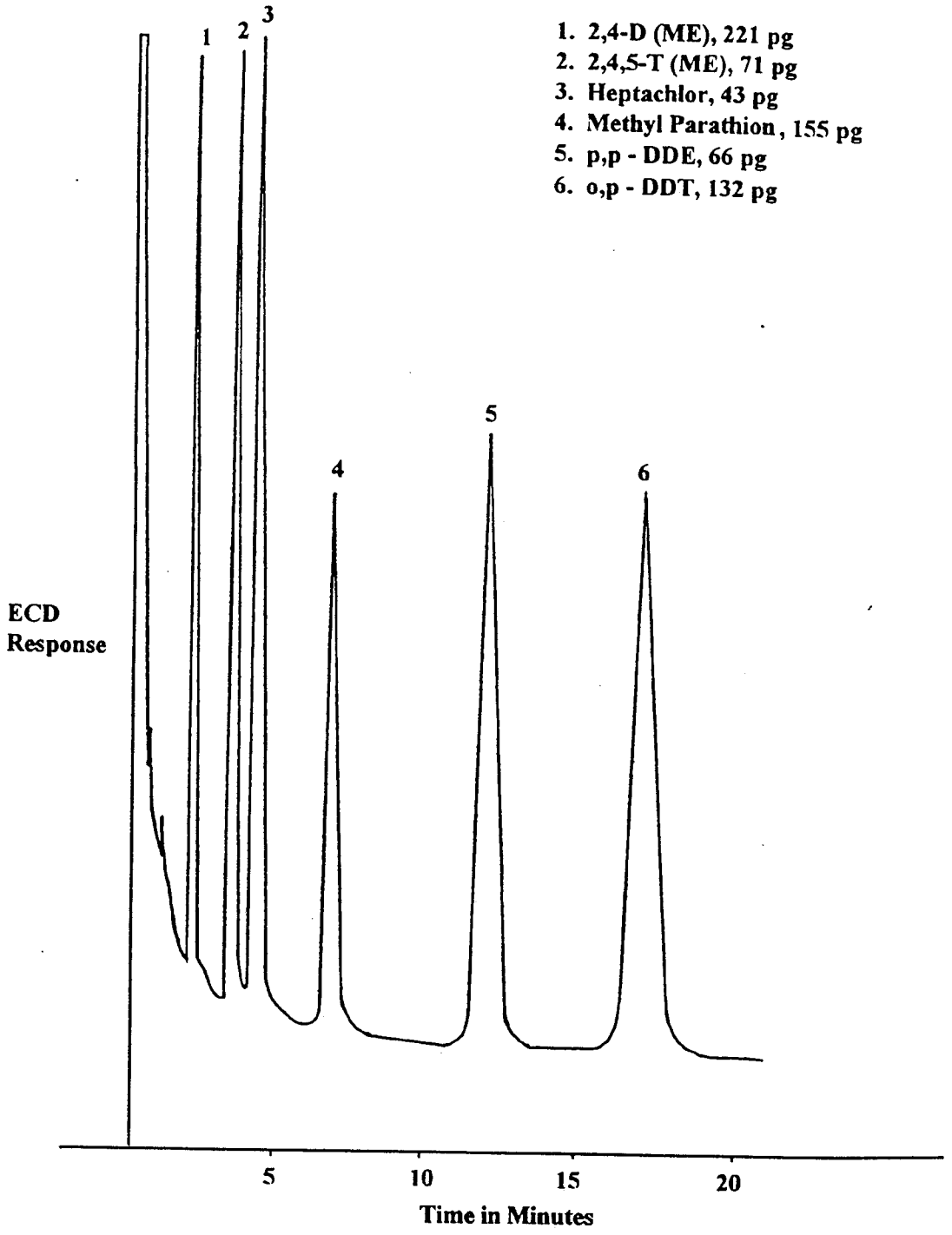
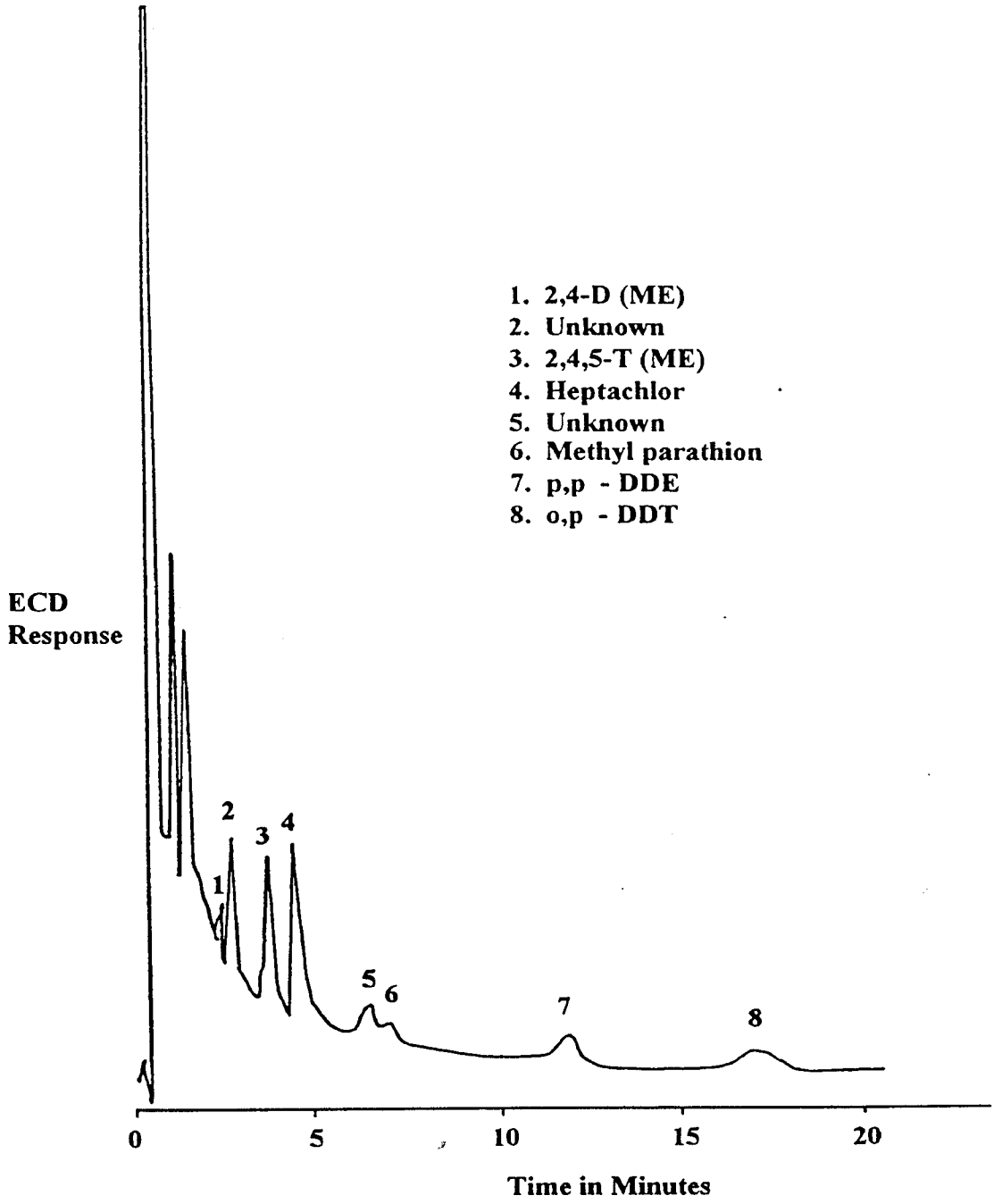


Figure 4. GC-ECD Chromatogram of an Ambient Air Sample



SULPHATION, TOTAL (PbO_2 CANDLE AND HUEY PLATE)

(Turbidimetric)

1. Introduction

1.1 Sulphur gases, such as sulphur dioxide, hydrogen sulphide and mercaptan, are common air pollutants. They originate mainly from the burning of sulphur-containing fuels, such as coal and gasoline, and from the sulphur-recovery process of sour gas plants. These gases are oxidized by lead dioxide to lead sulphate. This oxidation is known as total sulphation. The lead dioxide candle or plate (Huey plate) is commonly used for monitoring sulphur pollution of the atmosphere.

2. Principle

2.1 The lead dioxide candle or plate is exposed in the field for approximately four weeks. The exposed lead dioxide is removed from the support media and digested with sodium carbonate solution. The unreacted lead dioxide is removed by filtration. The filtrate is acidified to pH 2.5 and the sulphate is precipated as $BaSO_4$. The resulting turbidity of the $BaSO_4$ suspension is measured in a spectrophotometer at 420 nm.

3. Scope

3.1 The detection limit is 2 mg/L SO_4 in the test solution.

4. Interference

4.1 Colour interferes. Such interference is eliminated by using a sample blank.

5. Apparatus

5.1 Jars (20-cm circumference) and Huey plates.
5.2 Surgical gauze, Curity, or equivalent (60 cm length, 5 cm width).
5.3 Blender.
5.4 Spectrophotometer.
5.5 Nessler tube, matched 50 mL, 2.5 cm diameter.
5.6 Spoon, 0.5 g capacity.

6. Reagents

6.1 Lead dioxide (Anachemia, technical grade).

6.2 Methanol, 100%.

6.3 Gum tragacanth (2%): dissolve 20 g in 100 mL methanol and dilute to 1 litre with distilled water.

6.4 Sodium carbonate solution (2%): dissolve 20 g anhydrous sodium carbonate in distilled water and dilute to 1 litre.

6.5 Sodium carbonate solution (1%): dissolve 100 g anhydrous sodium carbonate in distilled water and dilute to 10 litres.

6.6 Dilute hydrochloric acid solution (1+2): dissolve 100 mL conc. HCl in 200 mL distilled water.

6.7 Sulphate reagent: Sulfaver IV (Hach Chemical Company, or equivalent).

6.8 Stock sulphate solution (1000 mg/L SO_4): dissolve 1.479 g of anhydrous sodium sulphate in 1% Na_2CO_3 solution and dilute to 1000 mL with 1% Na_2CO_3 solution.

6.9 Working standards - dilute each of the following aliquots of the stock to 900 mL with 1% Na_2CO_3 solution, adjust the pH to 2.5 by adding (1+1) HCl with constant stirring. Stir for 10 minutes to drive off the CO_2. Dilute to 1000 mL in a volumetric flask with distilled water:

mL stock/1000 mL	conc. mg/L SO_4
2.0	2.0
5.0	5.0
10.0	10.0
20.0	20.0
40.0	40.0
50.0	50.0

7. Procedure

7.1 Sampling

7.1.1 Preparation of the candle: wrap a tape of surgical gauze, 60 cm long and 5 cm wide around a jar of 20-cm circumference. Secure the gauze to the jar with cotton thread and paint it with a PbO_2 mixture prepared as follows:

Slowly add 300 mL of 2% gum solution to approximately 300 g of PbO_2, in portions, with continuous stirring until a smooth paste entirely free from lumps is obtained. Using a small brush, spread the lead dioxide paste evenly

on the surgical gauze around the jar. Each cylinder should contain approximately 8-10 g of PbO_2.

7.1.2 Preparation of Huey Plate: grind 8 g of Gelman paper in a grinding mill and transfer it to a blender containing 800 mL of water. Blend for one minute. Add 128 g of PbO_2 and 44 mL of 2% gum tragacanth solution to the blender and blend for another 4 minutes. Attach a circular glass fibre disc to the plate and allow it to evaporate at room temperature in a fume hood. Pipet 10 mL of the blended suspension onto the Huey plate and allow it to dry in an oven at 50-55°C.

7.1.3 Expose the cylinder and/or two plates in the field for approximately 4 weeks.

7.2 Analysis

7.2.1 Measure the exposed areas of the painted gauze on the candle and/or the Huey plates in cm^2.

7.2.2 Remove the tape from the jar and place it in a 400 mL beaker. Put the two Huey plates, along with the gauze, into a 250 mL beaker. Care must be taken with this step to ensure that no $PbSO_4$ is lost during the transfer. Set up sample blanks by using an unexposed candle and two Huey plates. Use 2% Na_2CO_3 solution for the reagent blank.

7.2.3 Add 100 mL 2% sodium carbonate solution to the beaker containing the candle tape, and 50 mL to the beaker containing the Huey plates.

7.2.4 Stir the mixtures and allow them to stand for at least three hours.

7.2.5 Heat the samples for 45 minutes at approximately 80°C, keeping the volume above 60 mL mark of the beaker with distilled water for the candle tape and 30 mL mark for the Huey plates.

7.2.6 Filter the hot samples, rinse the beakers and wash the contents of the filter several times with hot distilled water.

7.2.7 Cool the filtrates to room temperature and acidify with (1+1) HCl to a pH of approximately 2.5, with constant stirring. Stir for 10 minutes to drive off the CO_2.

7.2.8 Using distilled water, adjust the volume of the filtrate to 200 mL for the candle sample and to 100 mL for the Huey plate sample.

7.2.9 Pipet 50.0 mL of sample, sample blank, reagent blank and working standards into separate 50-mL Nessler tubes. Add approximately 0.5 g of Sulfaver IV to each tube and stir well. Wait for 10 minutes.

7.2.10 Use the reagent blank for setting the spectrophotometer to 100% transmittance at 420 nm and read the percent transmittance for all the samples, sample blanks and standards.

8. Calculation

8.1 Prepare a calibration curve by plotting nm/L SO_4 vs percent transmittance. Read the concentration for the exposed and unexposed samples from the graph in units of mg/L SO_4. Subtract the value for unexposed sample from the exposed one to get the actual value. Calculate mg $BaSO_4$ as follows:

$$mg\ BaSO_4 = \frac{mg/L\ SO_4 \times total\ sample\ volume\ in\ mL \times 2.43}{1000}$$

where

$$2.43 = \frac{mol.\ weight\ of\ BaSO_4}{mol.\ weight\ of\ SO_4}$$

8.2 The following equation is used to express the total sulphation in units of mg SO_3/day/100 cm^2:

$$mg\ SO_3/day/100\ cm^2 = \frac{mg\ BaSO_4 \times 0.343 \times 100}{d \times a}$$

where

d = no. of days exposed.

a = surface area of the tape or Huey plate in cm^2.

$$0.343 = \frac{mol.\ weight\ of\ SO_3}{mol.\ weight\ of\ BaSO_4}$$

100 = conversion to 100 cm^2.

9. References

9.1 1989 Annual Book of ASTM Standards, Vol.11.03, p. 62.

9.2 Methods of Air Sampling and Analysis. APHA Intersociety Committee. M. Katz, Editor; 2nd Ed.; p. 682.

SULPHATION, TOTAL (PbO_2 CANDLE AND HUEY PLATE)

(Ion Chromatography)

1. Introduction

1.1 Sulphur gases, such as sulphur dioxide, hydrogen sulphide and mercaptans, are common air pollutants. They originate mainly from the burning of sulphur-containing fuels, such as coal and gasoline, and from the sulphur-recovery process of the sour gas industry. These gases are oxidized by lead dioxide to lead sulphate. This oxidation is known as total sulphation. The lead dioxide candle or plate (Huey plate) is commonly used for the monitoring of sulphur pollution in the atmosphere.

2. Principle

2.1 The lead dioxide candle or Huey plate is exposed in the field for a one or three month period. The exposed lead dioxide is removed from the support media and digested with sodium carbonate solution to solubilize the sulphate. The unreacted lead dioxide is removed by filtration. The filtrate is analyzed by ion chromatography (I.C.), using a guard column, an anion separator column and a continuous suppression system. Detection is by means of a conductivity cell. The I.C. is calibrated by the method of external standards. The response is quantified by comparing the peak height of the sample to that of the calibration standard.

3. Scope

3.1 The detection limit can be varied by adjusting the injection volume and concentrating the solution, if necessary. For the procedure specified below, which has been found suitable for our stations, the detection limit is 0.08 mg/L SO_4 in the test solution.

4. Interferences

4.1 No interferences are currently known. It is recommended that brown lead dioxide be used, as the use of black lead dioxide results in higher blanks.

5. Apparatus

5.1 Jars (20-cm circumference) and Huey plates.

5.2 Surgical gauze, Curity, or equivalent (60 cm length, 5 cm width).

5.3 Heating plate or bath.

5.4 Blender.

5.5 Ion chromatograph, Dionex 16, or equivalent
Equipped with: AG4A guard column
ASA4 separator column
AMMS suppressor
6.7 µL sample loop (approx. 7µL)
Inlet filter, 35 & 5 micron fritted discs

5.6 Integrator, Spectra Physics 4100, or equivalent.

5.7 3 mL injection syringe (disposable)

6. Reagents

6.1 Lead dioxide (BDH general purpose reagent).

6.2 Methanol, 100%.

6.3 Gum tragacanth (2%): dissolve 20 g in 100 mL methanol and dilute to 1 litre with distilled water.

6.4 Sodium carbonate solution (2%): dissolve 80 g anhydrous sodium carbonate in distilled water and dilute to 4 litres.

6.5 Sodium carbonate solution (1%): dissolve 40 g anhydrous sodium carbonate in distilled water and dilute to 4 litres.

6.6 Stock sulphate solution (1000 mg/L SO_4): dissolve 1.479 g of anhydrous sodium sulphate in 1% Na_2CO_3 solution and dilute to 1000 mL with 1% Na_2CO_3 solution.

6.7 Stock sulphate solution (100 mg/L): dilute 100 mL of 1000 mg/L SO_4 to 1 litre with 1% Na_2CO_3 solution.

6.8 Working standards: Using 1% Na_2CO_3, dilute each of the following aliquots of the stock to 1000 mL in a volumetric flask.

mL stock/1000 mL	conc. mg/L SO_4
25.0 of 100 mg/L SO_4	2.5
50.0 of 100 mg/L SO_4	5.0
10.0 of 1000 mg/L SO_4	10.0
20.0 of 1000 mg/L SO_4	20.0
40.0 of 1000 mg/L SO_4	40.0
50.0 of 1000 mg/L SO_4	50.0

6.9 Quality-Control Stock - NIST standard reference material 3181.

7. Procedure

7.1 Preparation of the candle: wrap a tape of surgical gauze, 60 cm long and 5 cm wide around a jar of 20-cm circumference. Secure the gauze to the jar with cotton thread and paint it with a PbO_2 mixture prepared as follows:

Slowly add 300 mL of 2% gum tragacanth solution to 300 g of PbO_2 (extra PbO_2 can be added to achieve the desired viscosity, if necessary), in portions, with continuous stirring until a smooth paste entirely free from lumps is obtained. Using a small brush, spread the lead dioxide paste evenly on the surgical gauze around the jar. Each cylinder should contain approximately 8-10 g of PbO_2.

7.2 Preparation of Huey plate: grind 8 g of Gelman paper in a grinding mill and transfer it to a blender containing 800 mL of water. Blend for one minute. Add 128 g of PbO_2 and 50 mL of 2% gum tragacanth solution to the blender and blend for another 4 minutes. Transfer the solution to a 1000 mL beaker containing a stirring bar, and stir frequently to keep the lead in suspension. Using acetone, attach a circular glass fibre disc to the plate by pouring 1 mL acetone onto the plate and allowing it to evaporate at room temperature in a fume hood. Pipet 10 mL of the blended suspension into the Huey plate and allow it to dry in an oven at 50-55°C.

7.3 Expose the cylinder and/or two plates in the field for approximately 1 to 3 months.

8. Analysis

8.1 Measure the exposed areas of the painted gauze on the candle and or Huey plates in cm^2.

8.2 Remove the tape from the jar and place it in a 400 mL beaker. Put the two Huey plates or the gauze into a 400 mL beaker. Care must be taken with this step to ensure that no $PbSO_4$ is lost during the transfer. Set up sample blanks by using an unexposed candle and two Huey plates. Use 2% Na_2CO_3 solution for the reagent blank.

8.3 Add 100 mL 2% sodium carbonate solution to the beaker containing the candle tape, and 50 mL to the beaker containing the Huey plates.

8.4 Stir the mixtures and allow them to stand for at least three hours.

8.5 Heat the samples for 45 minutes at approximately 80°C. Using distilled water, keep the volume above 60 mL mark of the beaker for the candle tape, and 30 mL mark for the Huey plates.

8.6 Filter the hot samples, rinse the beakers and wash the contents of the filter several times with hot distilled water.

8.7 Cool the filtrates to room temperature.

8.8 Using distilled water, adjust the volume of the filtrate to 200 mL for a candle sample, and to 100 mL for the Huey plates sample.

8.9 Using a 3 mL syringe, inject the sample into the 6.7 µL sample loop of the I.C. Use at least 10 times the injection loop volume to rinse the loop before injecting the sample.

8.10 The I.C. is calibrated using four standards. The analysis of Huey Plates requires 2.5, 5, 10, and 20 mg/L SO_4 standards. The analysis of lead dioxide candles requires 10, 20, 40 and 50 mg/L SO_4 standards. QC standards are made up at 20% QCA and 80% QCB of the concentration range being analyzed. Quality-control standards, QCA and QCB, are each analyzed twice per analytical run or batch of samples, immediately after the instrument has been completely calibrated for that run or batch. Once per analytical run or batch of samples, a known addition and duplicate analysis is carried out.

8.11 Ion chromatograph settings:

Fullscale, 10 µ℧/cm

Flow rate, 2.0 mL/min

Eluent approximate, 0.0022 M Na_2CO_3 - 0.0015 M $NaHCO_3$ (adjusted to give optimum retention time and peak resolution)

Regenerant 0.020 N H_2SO_4

Regenerant flowrate, 3-4 mL/min (adjusted to give a stable baseline)

8.12 Integrator setting, attenuation 512

9. Calculation

9.1 Samples

The SP 4100 integrator is programmed to calculate the best fit line from the calibration standards. This is used to determine the response factor, and consequently, the sample concentration. The concentration of the unexposed sample blank is also determined. The actual value is determined by subtracting the unexposed sample response from the exposed sample response. Calculate the mg $BaSO_4$ as follows:

$$mg\ BaSO_4 = \frac{mg/L\ SO_4 \times total\ sample\ volume\ in\ mL \times 2.43}{1000}$$

where

$$2.43 = \frac{mol.\ weight\ of\ BaSO_4}{mol.\ weight\ of\ SO_4}$$

b) The following equation is used to express the total sulphation in units of SO_3/day/100 cm^2.

$$mg\ SO_3/day/100\ cm^2 = \frac{mg\ BaSO_4 \times 0.343 \times 100}{d \times a}$$

where
d = no. of days exposed
a = surface area of the tape or Huey plates in cm^2

$$0.343 = \frac{mol.\ weight\ of\ SO_3}{mol.\ weight\ of\ BaSO_4}$$

$$100 = conversion\ to\ 100\ cm^2$$

9.2 Quality Control

The two results, A and B, their sum (A+B) and their difference (A-B) are recorded and a sequential plot of these values is maintained over time. The standard deviation of accumulated (A-B) data from a previous set can be used to estimate and set control limits within which the individual points (A+B) and (A-B) are expected to fall. Thus,

$$\underline{\text{Warning}} \text{ limits are } \overline{(A+B)} \pm 2s_D \text{ and } \overline{(A-B)} \pm 2s_D$$

$$\underline{\text{Control}} \text{ limits are } \overline{(A+B)} \pm 3s_D \text{ and } \overline{(A-B)} \pm 3s_D$$

The duplicate analysis determines precision per analytical run or batch of samples. The known addition analysis verifies the absence of matrix effect per analytical run or batch of samples.

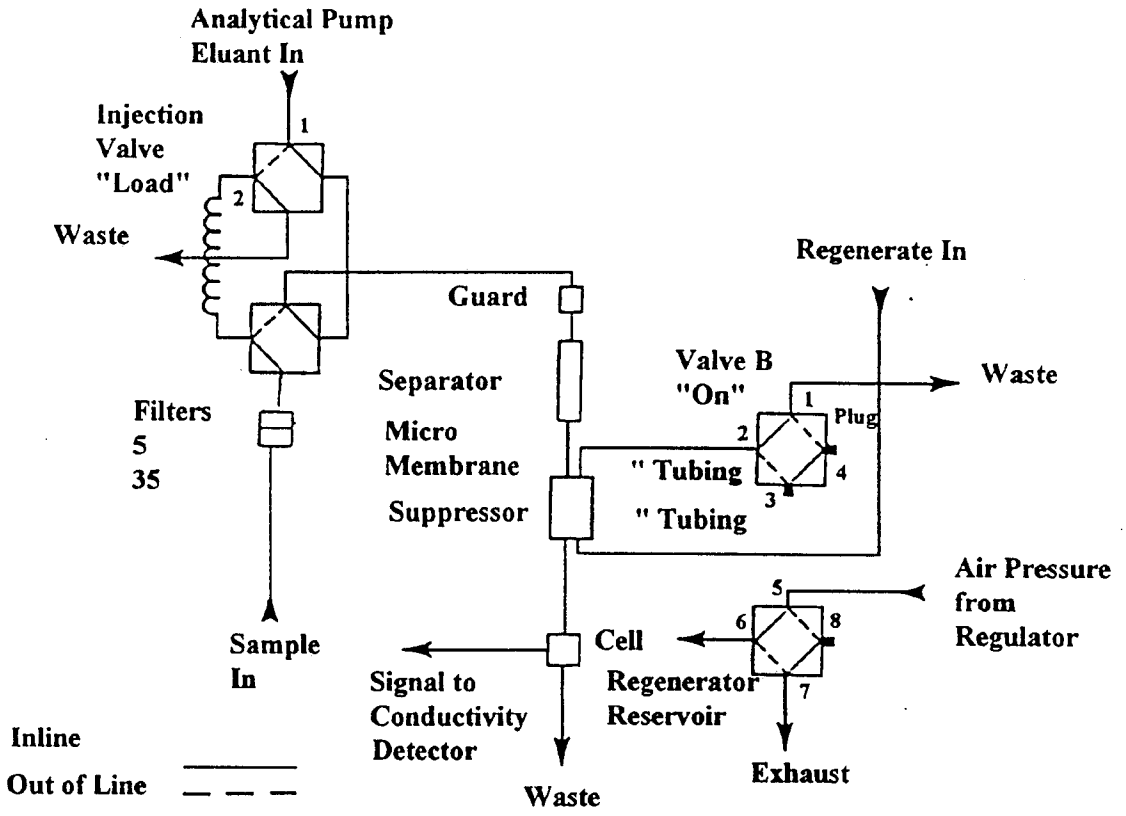
10. References

10.1 1989 Annual Book of ASTM Standards, Vol. 11.03., p. 62.

10.2 Methods of Air Sampling, 2nd Ed., p. 682.

10.3 Quality Control and Data Evaluation Procedures, Section I, Analytical Reproductibility, Ontario Ministry of the Environment, July, 1976.

Figure 1. Ion Chromatographic Flow Diagram for Candle and Huey Extract



August 1992 Method No. 14547

SULPHATION (K_2CO_3 PLATE)

(Ion Chromatography)

1. Introduction

1.1 The major anthropogenic source of sulphur dioxide is the incineration of waste gas streams at sour gas processing facilities, oil refineries and coal-burning power plants. Minor sources include fugitive emissions from oil fields, sour line heaters and wood-burning fireplaces. Sulphur dioxide is considered to be one of the major pollutants of concern because it plays a role in urban smog and acid rain.

The potassium carbonate plate is a passive sampling device, in that the sulphur dioxide is carried to the collection plate by air movement and diffusion. Because of its low cost, the potassium carbonate plate can be used for high-density networking to delineate spatial variability. In this way, it complements the high-cost, continuous monitors that are necessary to determine temporal variability.

2. Principle

2.1 The potassium carbonate plate is exposed in the field for a one to three month period. The exposed potassium carbonate in the support media is treated with hydrogen peroxide to oxidize any sulfite to sulphate. The extract is analyzed by ion chromatography (I.C.) using a guard column, an anion separator column and a continuous suppression system. Detection is by means of a conductivity cell. The I.C. is calibrated by the method of external standards. The response is quantified by comparing the peak height of the sample to that of the calibration standard.

3. Scope

3.1 The detection limit can be varied by adjusting the injection volume and concentrating the solution, if necessary. For the procedure specified below, which has been found suitable for our stations, the detection limit is 0.02 mg/L SO_4 in the test solution.

4. Interferences

4.1 No interferences are currently known.

5. Apparatus

5.1 Millipore 47-mm petri dishes

5.2 Whatman 540 4.7-cm filter paper

5.3 Ion chromatograph, Dionex 16, or equivalent
Equipped with: AG4A guard column
ASA4 separator column
AMMS suppressor
6.7 µL sample loop (approx. 7 µL)
Inlet filter, 35 & 5 micron fritted discs

5.4 Integrator, Spectra Physics 4100, or equivalent.

5.5 3 mL injection syringe (disposable)

6. Reagents

6.1 Potassium carbonate anhydrous (BDH Analytical Reagent)

6.2 Glycerol

6.3 Acetone

6.4 Hydrogen Peroxide (0.01%) (v/v): pipette 0.33 mL of 30% hydrogen peroxide and dilute to 1 litre with distilled water.

6.5 K_2CO_3 glycerol solution (25%/10%) (w/v): dissolve 125 g of potassium carbonate in 400 mL of distilled water. Add 50 mL of glycerol and dilute to 0.5 litre with distilled water. Stirring is required to make a well-mixed mixture.

6.6 Stock sulphate solution (1000 mg/L SO_4): dissolve 1.8145 g of anhydrous potassium sulphate in 0.01% H_2O_2 and dilute to 1 litre with 0.01% H_2O_2.
Stock sulphate solution (100 mg/L SO_4): dilute 100 mL of 1000 mg/L SO_4 to 1 litre with 0.01% H_2O_2.
Working standards - dilute each of the following aliquots of the stock to 1000 mL with 0.01% H_2O_2 solution in a volumetric flask.

mL Stock/1000 mL	conc. mg/L SO_4
25.0 of 100 mg/L SO_4	2.5
50.0 of 100 mg/L SO_4	5.0
10.0 of 1000 mg/L SO_4	10.0

6.7 Quality Control Stock - NIST Standard Reference Material 3181.

7. Procedure

7.1 Preparation of potassium carbonate plates: soak filter papers in distilled water overnight. Change water several times. Add one filter to each petri dish, invert covers and allow to dry overnight. Attach filter to petri dish with acetone by adding 2 drops of acetone near the centre. Using a weight, allow good contact between the filter and the petri dish while allowing acetone to evaporate at room temperature. To each plate add 250 µL of potassium carbonate solution. Invert covers and allow to dry overnight.

7.2 Expose two plates in the field for approximately 1 to 3 months.

8. Analysis

8.1 Pipette 5 mL of 0.01% hydrogen peroxide into the petri dish containing the exposed filter. Set up sample blanks by using an unexposed potassium carbonate plate. Cap and allow to soak for approximately 24 hrs.

8.2 Pipe a 1-mL aliquot into a disposable 16 x 100 mm disposable culture tube and make up to 10 mL with 0.01% hydrogen peroxide.

8.3 Inject the sample with a 3 mL syringe into the 6.7 µL sample loop of the I.C. Use at least 10 times the injection loop volume to rinse the loop before injecting the sample.

8.4 The I.C. is calibrated using four standards 0, 2.5, 5 and 10 mg/L SO_4. QC standards are made up at 20% QCA and 80% QCB of the concentration range being analyzed. Quality control standards, QCA and QCB, are each analyzed twice per analytical run or batch of samples, immediately after the instrument has been completely calibrated for that run or batch. Once per analytical run or batch of samples, a known addition and duplicate analysis is carried out.

8.5 Ion chromatograph settings:

- Fullscale, 3 μ℧/cm
- Flow rate, 2.0 mL/min
- Eluent approximate, 0.0022 M Na_2CO_3 - 0.0015 M $NaHCO_3$ (adjusted to give optimum retention time and peak solution)
- Regenerant 0.020 N H_2SO_4
- Regenerant flowrate, 3-4 mL/min (adjusted to give a stable baseline)

8.6 Integrator setting, attenuation 512.

9. Calculation

9.1 Samples

The SP 4100 integrator is programmed to calculate the best fit line from the calibration standards. This is used to determine the response factor and consequently, the sample concentration. The concentration of the unexposed sample blank is also determined. The actual value is determined by subtracting the unexposed sample response from the exposed sample response. Calculate the mg SO_4 per plate as follows:

$$mg\ SO_4/plate = mg/L\ SO_4 \times total\ sample\ volume\ in\ litres \times dilution\ factor$$

The following equation is used to express the total sulphation in units of mg SO_3/day/100 cm^2.

$$mg\ SO_3/day/100\ cm^2 = \frac{mg\ SO_4 \times 0.833 \times 100}{d \times a}$$

where

d = no. of days exposed

a = surface are of potassium carbonate plate in cm^2

$$0.833 = \frac{mol.\ weight\ of\ SO_3}{mol.\ weight\ of\ SO_4}$$

$$100 = conversion\ to\ 100\ cm^2$$

9.2 Quality Control

The two results, A and B, their sum (A+B) and their difference (A-B) are recorded and a sequential plot of these values is maintained over time. The standard deviation of accumulated (A-B) data from a previous set can be used to estimate and set control limits within which the individual points (A+B) and (A-B) are expected to fall. Thus,

$$\underline{\text{Warning}} \text{ limits are } \overline{(A + B)} \pm 2s_D \text{ and } \overline{(A - B)} \pm 2s_D$$

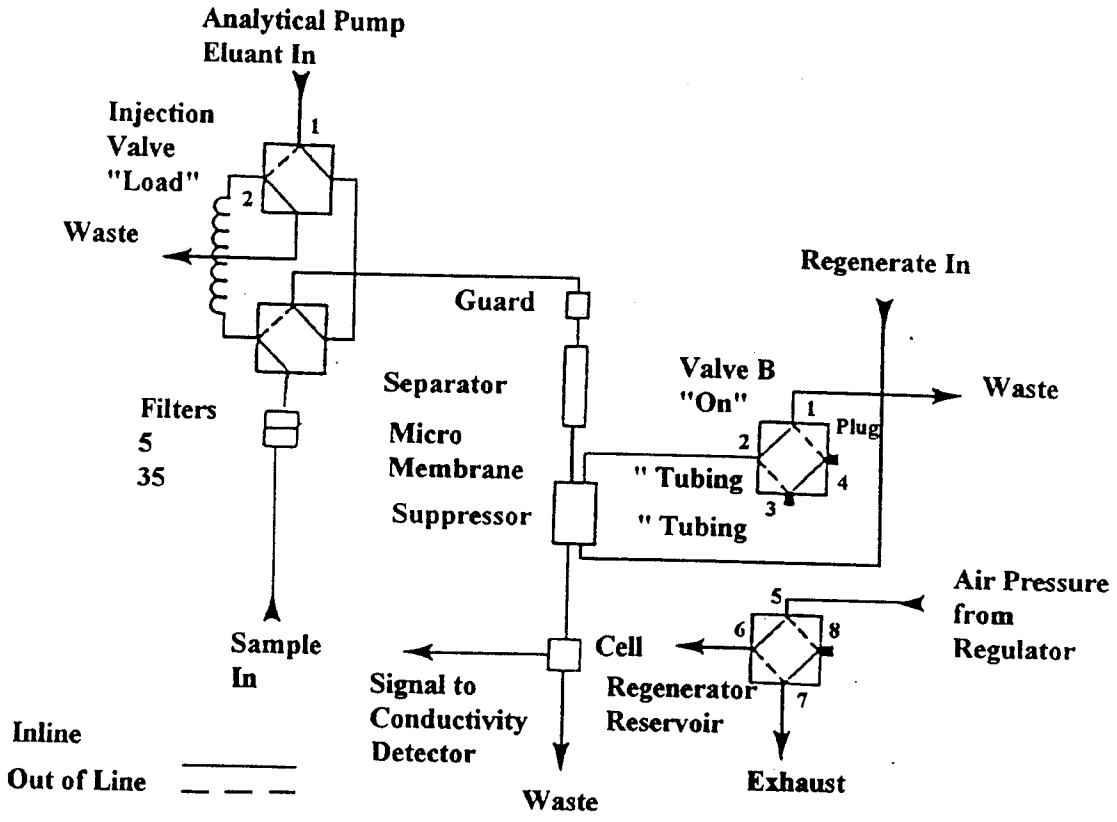
$$\underline{\text{Control}} \text{ limits are } \overline{(A + B)} \pm 3s_D \text{ and } \overline{(A - B)} \pm 3s_D$$

The duplicate analysis determines precision per analytical run or batch of samples. The known addition analysis verifies the absence of matrix effect per analytical run or batch of samples.

10. Reference

10.1 Quality Control and Data Evaluation Procedures, Section I, Analytical Reproducibility, Ontario Ministry of the Environment, July, 1976.

Figure 1. Ion Chromatographic Flow Diagram for Potassium Carbonate Plate



September 1992

Method No. 15050

SULPHUR DIOXIDE

(West-Gaeke, Colorimetric)

1. Introduction

1.1 Sulphur dioxide originates mainly from the burning of sulphur-containing fuels, such as coal and gasoline, and from the sulphur-recovery process of the sour gas plants. In addition, sulphur dioxide is an emission product of oil and gas refineries.

2. Principle

2.1 Sulphur dioxide is absorbed by aspirating ambient air through a solution of potassium tetrachloromercurate (TCM). The absorbed sulphur dioxide forms a coloured complex with formaldehyde and pararosaniline, which is measured at 575 nm.

3. Scope

3.1 The detection limit is 0.01 mg/L in the test solution.

4. Interference

4.1 Nitrogen oxides, ozone and heavy metals interfere. Oxides of nitrogen are eliminated by sulphamic acid, whereas ozone is eliminated by time delay and heavy metals are eliminated by EDTA.

5. Apparatus

5.1 Sampling train consisting of 4 impingers, a rotameter and a vacuum pump.

5.2 Spectrophotometer, 1-cm cells.

6. Reagents

6.1 Absorbing solution (0.04 M potassium tetrachloromercurate, TCM): dissolve 10.86 g of mercuric chloride, 5.96 g of potassium chloride and 0.066 g of EDTA disodium salt in 1 litre of distilled water. The pH of this reagent must not be less than 5.2.

6.2 Sulphamic Acid (0.6%): dissolve 0.6 g of sulphamic acid in 100 mL of distilled water. Prepare fresh immediately before use.

6.3 Buffer solution (pH 4.7): dissolve 13.61 g of sodium acetate trihydrate in distilled water in a 100 mL volumetric flask. Add 5.7 mL of glacial acetic acid and dilute to volume with distilled water.

6.4 Hydrochloric Acid (1 N): dilute 86 mL of conc. KCl to 1 litre with distilled water.

6.5 Phosphoric Acid (3 M): dilute 205 mL of conc. phosphoric acid to 1 litre with distilled water.

6.6 Purified pararosaniline stock solution (0.2%): weigh 200 mg of 99% pure dye and dissolve it by shaking with 100 mL of 1 N HCl in a 250 mL glass-stoppered Erlenmeyer flask.

6.7 Purification Procedure (required when 99% pure dye is not available): equilibrate 100 mL of 1-butanol and 100 mL of 1 N HCl in a 250 mL separatory funnel. Weigh 100 mg of pararosaniline hydrochloride in a beaker. Add 50 mL of the equilibrated acid and allow to stand for 10-15 minutes. Add 50 mL of the equilibrated 1-butanol to a 125 mL separatory funnel. Transfer the acid solution containing pararosaniline to the funnel and shake for 5 minutes. Allow the two phases to separate. Transfer the lower (aqueous) phase into another separatory funnel and add a 20 mL portion of equilibrated 1-butanol. Repeat the above operation until all the violet impurity is removed. Filter through glass wool in a 50 mL volumetric flask and dilute to volume with 1N HCl. Assay each lot of the dye as described in the reference.

6.8 Pararosaniline reagent: pipet 20 mL of stock pararosaniline reagent into a 250 mL volumetric flask. For each percent below one hundred percent add another 0.2 mL of the stock reagent. Add 200 mL of 3 M H_3PO_4 and dilute to volume with distilled water.

6.9 Formaldehyde (0.2%): dilute 5 mL of 36-38% formaldehyde to 1 litre with distilled water. Prepare fresh daily.

6.10 Starch solution: prepare a paste by adding 1 g of starch to 5 mL of distilled water. Add 200 mL of boiling water to the paste and stir until all starch dissolves.

6.11 Stock sodium thiosulphate solution (0.050 N): dissolve 12.5 g of sodium thiosulphate, $Na_2S_2O_3.5H_2O$, in 1000 mL of distilled water. Standardize the solution against potassium dichromate after at least two weeks storage. Use boiled distilled water and add 2 mL of chloroform to minimize bacterial decomposition of the thiosulphate solution.

6.12 Standard potassium dichromate solution (0.050 N): dissolve 2.452 g anhydrous potassium dichromate, $K_2Cr_2O_7$, in distilled water and dilute to 1000 mL.

6.13 Standardization of sodium thiosulphate: to 80 mL distilled water add, with stirring, 1 mL conc. H_2SO_4, 10.0 mL 0.05 N $K_2Cr_2O_7$ and 0.5 g potassium iodide. Allow the reaction mixture to stand 6 min. in the dark before titration with the 0.050 N $Na_2S_2O_3$ titrant, adding 0.5 mL of starch near the end point. At the end point, the colour changes from opaque blue to colorless.

$$Normality\ of\ Na_2S_2O_3 = \frac{10.0 \times 0.050}{mL\ of\ Na_2S_2O_3\ consumed}$$

6.14 Standard sodium thiosulphate solution (0.010 N): dilute 100.0 mL of stock 0.050 N sodium thiosulphate with distilled water to volume in a 500 mL volumetric flask. Prepare fresh daily.

6.15 Stock iodine solution (0.100 N): place 12.8 g of iodine in a 250 mL beaker, add 40 g of KI and 25 mL of water. Stir until all is dissolved and then dilute to 1000 mL with water.

6.16 Standard iodine solution (0.010 N): dilute 50.0 mL of the stock iodine solution to 500 mL with distilled water.

6.17 Stock sulphite solution: dissolve 0.40 g anhydrous sodium sulphite in 500 mL of boiled and cooled distilled water. One mL of this solution produces a colour equivalent to that of 0.3-0.4 mg of SO_2 in the test solution. Standardize this solution by adding 25 mL of distilled water and 50.0 mL of the 0.010 N iodine solution to a 500 mL Erlenmeyer flask. To a second Erlenmeyer flask, add 25.0 mL of the stock sulphite solution and 50.0 mL of the 0.010 N iodine solution. Stopper the flasks and allow to react for 5 minutes in the dark. Titrate each flask with 0.010 N thiosulphate to a pale yellow colour. Add 5 mL of starch solution and continue the titration to the end point. Calculate the concentration of SO_2 in the standard solution as follows:

$$mg/L\ SO_2 = \frac{(C - D) \times N \times 32.03 \times 1000}{mL\ sulphite\ solution}$$

where
- C = mL of thiosulphate solution for the blank.
- D = mL of thiosulphate solution for the sample.
- N = normality of the thiosulphate solution.
- 32.03 = equivalent weight of SO_2.
- 1000 = converts mg/mL SO_2 to mg/L SO_2.

6.18 Standard sulphite solution: immediately after standardization of the stock sulphite solution, pipet 2.0 mL into a 100 mL volumetric flask and dilute to volume with 0.04 M TCM. The solution should be stored at 5°C.

6.19 Working standards - prepare working standards by pipeting the following volumes of the standard solution into 25 mL volumetric flasks:

mL standard solution/25 mL	mg SO_2/25 mL
1.0	6 - 8
2.0	12 - 16
3.0	18 - 24
4.0	24 - 32
5.0	30 - 40 .

Dilute the contents of each flask to 10 mL by adding 0.4M TCM. Add the remaining reagents as described in procedure 7. (See steps 7.2.3 and 7.2.4).

Notes:

1. Absorbance of standards must be read within 30 minutes of preparation.
2. Actual concentrations depend on results obtained from the standardization of sulphite.

6.20 Silica gel.

7. Procedure

7.1 Sampling

7.1.1 In order, assemble 4 midget impingers, the rotameter and the pump. Place 10.0 mL of 0.04 M TCM absorbing solution in each of the first and second impingers, and silica gel in the fourth. Keep the third impinger empty.

7.1.2 Aspirate air at the rate of 0.5 to 2.5 litres/min for 30-60 minutes. Record the total air volume sampled. Measure and record air temperature and atmospheric pressure.

7.1.3 Preserve the sample in a dark place or at 5°C in a refrigerator.

7.2 Analysis

7.2.1 Transfer the sample quantitatively to a 25 mL volumetric flask. Rinse with distilled water and add the rinse to the flask.

7.2.2 Prepare a reagent blank by adding 10 mL of the unexposed absorbing reagent to a 25 mL volumetric flask.

7.2.3 Add 1 mL of 0.6% sulphamic acid to each flask and allow to react for 10 min. to destroy the oxides of nitrogen.

7.2.4 Add 2 mL of the 0.2% formaldehyde and 5 mL of pararosaniline reagent to each flask. Dilute to 25 mL with distilled water and allow to stand for 30 minutes.

7.2.5 Determine the absorbances of the sample and the blank at 575 nm against distilled water as reference.

7.2.6 Prepare working standards as described in 6.19 and follow steps 7.2.3-7.2.5.

8. Calculation

8.1 Prepare a calibration curve by plotting the absorbances vs µg SO_2. Read the concentration of sample from the graph in units of µg SO_2. The final result is expressed as

$$\mu g\ SO_2/m^3 = \frac{\mu g\ SO_2}{m^3\ of\ air\ at\ STP}$$

9. Reference

9.1 1989 Annual Book of ASTM Standards for Atmospheric Analysis, Vol. 11.03, p. 80.

September 1992

Method No. 16060

VINYL CHLORIDE

(Gas Chromatography)

1. Introduction

1.1 Vinyl chloride is a toxic gas. It has been linked with angiosarcoma of the liver, a rare form of cancer. It is present in the ambient air in the vicinity of vinyl chloride and polyvinyl chloride manufacturing plants.

2. Principle

2.1 Vinyl chloride is collected by passing ambient air through a spherocarb tube. The adsorbed vinyl chloride is desorbed by means of a flasher, using nitrogen as the eluent gas. An aliquot of the eluent gas is injected into a Porapak Q column, using a sample loop, and analyzed by a gas chromatograph equipped with a photo-ionization detector.

3. Scope

3.1 The detection limit is 0.5 ppb for an ambient air sample collected at 50 cc/min for 24 hours.

4. Interference

4.1 Certain volatile hydrocarbons and halogenated hydrocarbons, such as butadiene, have GC retention times similar to that of vinyl chloride. Therefore, they may interfere.

5. Apparatus

5.1 Air sampling train (Nutech, or equivalent) consists of two sampling cartridges, meter devices and a vacuum pump.
5.2 Flasher (Bendix, or equivalent).
5.3 Mechanical weather station.
5.4 Gas chromatograph equipped with a photo-ionization detector (HNU Corp.).
5.5 Porapak Q column (6' x ⅛").
5.6 Precolumn carbowax 20 M (1' x ⅛").
5.7 Gas dilution apparatus (Matheson, or equivalent).

5.8 Volumeter (Brooks Instrument Corp., or equivalent).

5.9 Spherocarb sample cartridges (400 mg of 60/80 mesh spherocarb per tube).

6. Reagents

6.1 Vinyl chloride 100 ppm standard.

6.2 Spherocarb, 60/80 mesh.

6.3 Purified air supply.

7. Procedure

7.1 Sampling

7.1.1 Set up weather station to determine wind direction.

7.1.2 Connect two cartridges in series and draw air through them at ≈50 cc/min for 24 hours. A higher flow rate may be used if the draw time is shorter.

7.1.3 After sampling is completed, store the cartridges under refrigeration until the analysis can be carried out.

7.2 Analysis

7.2.1 Using the gas dilution apparatus, prepare standards of vinyl chloride of 1.0, 2.5, and 5.0 ppm. Using a sample loop, inject 1 cc of each standard into the GC column.

7.2.2 Place the adsorption tube in the Bendix flasher and heat to 300°C for three minutes and elute the vinyl chloride into the volumeter, using N_2 as eluent gas (volume 200 cc).

7.2.3 Using a sample loop, inject a 1 cc sample into the GC column.

7.2.4 Condition for the gas chromatograph (Shimadzu GC 9A with HNU photo ionization detector).

7.2.4.1 Oven Temperature: 120°C.

7.2.4.2 Auxiliary Valve Zone Temperature: 100°C.

7.2.4.3 Detector Temperature: 190°C.

7.2.4.4 Nitrogen Carrier Gas: 15 cc/min.

7.2.4.5 Lamp Intensity: 90%.

7.2.5 Run blanks and standards in accordance with the quality-control program.

8. Calculation

$$\text{Concentration of Eluent Gas in ppm} = \frac{\text{Area Counts for the Sample}}{\text{Response factor}}$$

9. Precision

9.1 In a single laboratory (Alberta Environmental Centre), using standards of 1, 10 and 25 ppb, the coefficients of variation were 7.4%, 2.6% and 4.4%, respectively.

10. Recovery Efficiency

10.1 In a single laboratory (Alberta Environmental Centre), using 7 standards of 1.0 ppb, 25 standards at 5.0 ppb and 7 standards at 25 ppb, the recoveries were 87%, 84% and 92%, respectively. The standards were passed through a spherocarb tube at a flow rate of 50 cc/min for 18 hours and then thermally desorbed into the GC column. Using the recovery efficiency, a correction factor could be applied.

11. References

11.1 J.E. Purcell; AM. Lab., May 1975, p. 99.

11.2 "Determination of vinyl chloride in the atmosphere", Ontario Ministry of the Environment, January 2, 1975.

Figure 1. Schematic of Apparatus for VCM Analysis

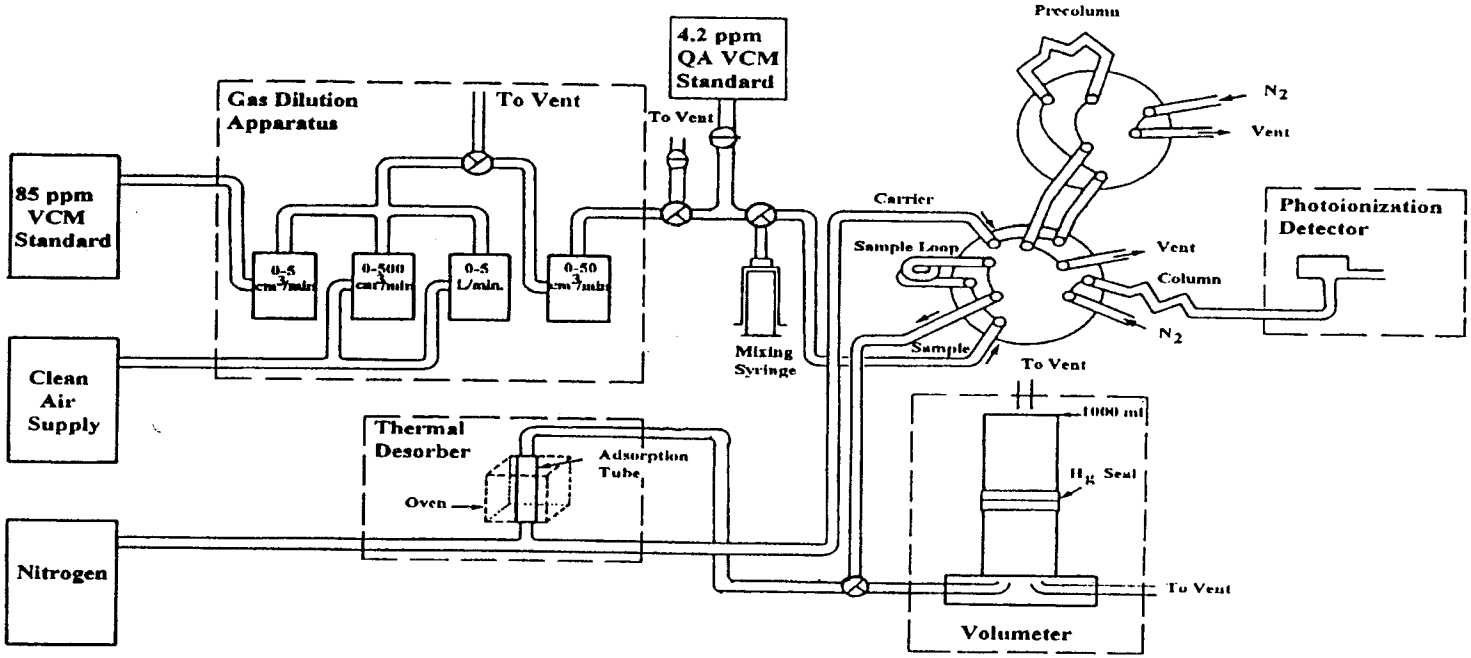
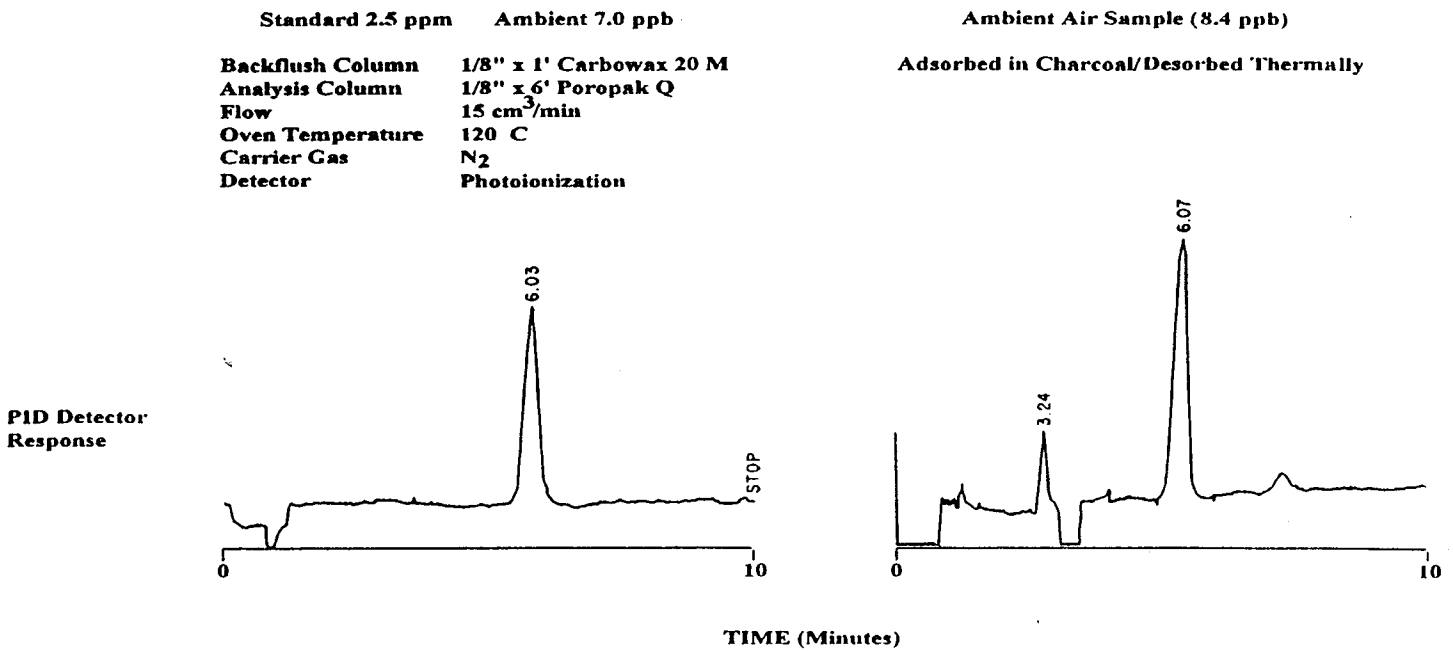


Figure 2. Chromatogram of VCM Analysis



September 1992 Method No. 17070

VOLATILE ORGANICS

(Gas Chromatography)

1. Introduction

1.1 Emissions of volatile organics from industrial activities can pose a health hazard owing to the biological activity of the compounds. Possible fugitive emissions in the vicinity of a chemical plant could include styrene, benzene, toluene, ethylbenzene, o -, m - & p - xylenes, trimethylbenzene, diethylbenzene, and diisopropylbenzene, etc. This method is designed to monitor the aforementioned compounds.

2. Principle

2.1 Volatile organics are collected from ambient air by absorbing them in Tenax-filled sorbent collection tubes or passive sampling devices. Air sampling rates as low as 25 cc/min are required to collect benzene quantitatively. The absorbed organics are extracted from the Tenax with n-pentane. The n-pentane solution is analyzed by gas chromatography using crosslinked methyl silicone stationary phase (OV-1) on a fused silica capillary column. A triple detector system involving flame ionization, photo-ionization and mass-selective detection is used to provide excellent reliability.

3. Detection limit

COMPOUND	*$\mu g/m^3$ of air
Benzene	10
Toluene	9
Ethylbenzene	10
m & p-Xylene	10
Styrene	9
o-Xylene	9
Trimethylbenzene	10
Diethylbenzene	7
Diisopropylbenzene	10

*Based on 25 cc/min sampling rate for 3 hours.

4. Interferences

4.1 Organic homologues having similar retention time would be expected to interfere. By using the triple-detector technique, most interferences can be eliminated.

5. Apparatus

5.1 Absorption tubes - SKC Inc. 5 mm x 50 mm tubes with two sections containing Tenax sorbent, 50 and 100 mg, and glass sealed at both ends. SKC catalogue number 226-35-03.

5.2 Passive Sampling pump - Manufactured by Scientific Instrumentation Specialists, Moscow Idaho, USA. These are filled in the lab using the Tenax from two of the SKC tubes.

5.3 Sampling pump - Dupont personal monitor pump 0-1 L/min, or equivalent low-flow pump.

5.3.1 GC

Varian, Model 6000, dualchannel, or equivalent.

Varian Vista 40/integrator, printer plotter, with double disk storage.

5.3.2 Gas Requirements

5.3.2.1 Helium, zero grade, hydrocarbons <0.5 ppm is used for carrier and detector make-up gas.

5.3.2.2 CO_2 with Hydro-syphon is used for cooling injector.

5.3.2.3 Hydrogen zero grade is used for FID flame.

5.3.2.4 Air zero grade is used for FID flame.

5.3.3 Injector

5.3.3.1 Varian 1095/11095 on-column capillary injector with cryogenics, temperature programmable, 5 µL fused-silica syringe.

Temperature program: Inject at 30°C.
Heat 100°C/min to final temperature of 210°C.
Hold at 210°C for 35 min, then cool down to 30°C for next injection.

5.3.4 Column

Hewlett-Packard fused-silica, crosslinked methyl silicone (OV-1), 0.52 µm film thickness, 0.31 mm internal diameter, 30 m length, H.P. catalogue number 19091A, option 115, ultra high-performance capillary column.

Temperature program:	Initial 35°C, hold for 3 min
	Heat to 50°C at 15°C/min and hold for 15 min
	Heat to 200°C at 15°C/min and hold for 10 min
Flow Rate:	3 mL/min Helium

5.3.5 Detectors

The column effluent is split using a Valco stainless steel cross fitting with 1/32" ports. One 0.32 mm capillary fused-silica tube leads from the cross to the FID detector, another 0.32 mm capillary fused-silica tube leads to the PID detector, and a 100 microm x 1 metre long fused-silica tube leads to a direct interface with the MSD. In this way, a 3 mL/min flow through the column is split, with approximately 1 mL/min flow to each of the three detectors.

5.3.5.1 FID Varian

Temperature: 325°C
Range: 10-12
Hydrogen Flow: 25 cc/min
Air Flow: 300 cc/min
Carrier Make-up Gas: Helium, 28 cc/min

5.3.5.2 PID - HNU model PI-52 with 10.2 ev lamp

Temperature: 200°C
Lamp Intensity: 4
Input Alternation: x1 or x 10
Detector Offset Course: 1 to 60
Helium Carrier Make-up Gas: 27 cc/min
The inlet to the PID requires some modification to accept the capillary column.

5.3.5.3 Mass Selective - Hewlett Packard 5970B

HP9133D Winchester disk drive
HP82906A Printer
HP9836 Computer
Capillary direct Interface
PFTBA calibration compound
NBS Revision E Library Data Base with subsets
Ion Source temperature 200°C
Interface temperature 250°C

Scan Aquisition

Resulting EM Voltage: 2200

Solvent Delay: 2.5 minutes

Scan Threshold: 35

Scans Per Second: 1.62

Low Mass: 35

High Mass: 300

Selective Ion Monitoring Acquisition

Resulting EM Voltage: 2000

Solvent Delay: 2.5 minutes

Set up the selective ion group table as follows:

Group	Start Time (min)	Ion Mass	Dwell	Cycles/second
1	2.8	78.10	100	6.3
2	4.8	91.10, 92.10	50	6.3
3	8.0	51.10, 78.10, 91.10, 104.10, 106.10	20	6.3
4	19.0	105.10, 120.10	50	6.3
5	21.0	105.10, 119.10, 134.10	30	6.7
6	23.0	147.20, 162.20	50	6.3

The compounds and their corresponding selected ions are as follows.

Compound	Mass Ions (m/z)
Benzene	78.10
Toluene	91.10, 92.10
Ethylbenzene	91.10, 106.10
Xylene	91.10, 106.10
Styrene	51.10, 78.10, 104.10
Trimethylbenzene	105.10, 120.10
Diethylbenzene	105.10, 119.10, 134.10
Diisopropylbenzene	147.20, 162.20

6. Procedure

6.1 Sampling

6.1.1 Set up a weather station to determine wind speed and direction.

6.1.2 Connect two Tenax absorbing tubes in series and draw air through them at 50 cc/min. If quantitative benzene & toluene collection is required, the flow rate should be lowered to 20 cc/min. The air should be sampled for 3 h.

6.1.3 Uncap the passive sampler and set out in a covered location for a period of 3 to 24 hours. Each of the organic compounds has its own passive sampling rate and calibration is required. An approximate passive rate of 50 cc/min, however, is being used for calculations.

6.1.4 After sampling is completed, cap the absorbing tube or passive sampler and store under refrigeration until the analysis can be carried out.

6.2 Preparation of Standards

6.2.1 99+% solvents from organic solvent kit So160A from North American Scientific are used.

6.2.2 Standard mixture (900 ppm):

Add 100 µL of each of the 99+% solvents to a 100 mL volumetric flask and make up to 100 mL with n-Pentane.

An average concentration of 900 ppm was used to represent the components of this mixture, but the actual concentration with respect to densities is: (to nearest 5 ppm)

Benzene	880
Toluene	865
Ethylbenzene	865
o-Xylene	880
m-Xylene	865
p-Xylene	860
Styrene	905
Trimethylbenzene	865
Diethylbenzene	870
Diisopropylbenzene	860

6.2.3 Intermediate standard mixture (9 ppm):

Add 100 µL of 900 ppm Organic Standard Mix to a 10 mL volumetric flask and make up to 10 mL with n-Pentane.

6.2.4 Working standard mixtures:

Dilute the 9 ppm standard to make up a series of standards:

Concentration	Volume of 9 ppm Std. Mix Used	Diluted to: (with n-Pentane)
22.5 ppb	25 µL	10 mL
45.0 ppb	50 µL	10 mL
67.5 ppb	75 µL	10 mL
90.0 ppb	100 µL	10 mL
180.0 ppb	200 µL	10 mL
360.0 ppb	400 µL	10 mL
450.0 ppb	500 µL	10 mL
900.0 ppb	1000 µL	10 mL

The ambient levels of these compounds are low so that the 90 ppb standard is usually used for calibration.

6.3 Sample extraction

6.3.1 Transfer the Tenax from the absorption tube to a 5 mL vial, add 2 mL of n-pentane, and cap the vial. Similarly, transfer the Tenax from the passive sampler to a 5 mL vial, but add 4 mL of n-pentane.

6.3.2 Shake the sample on a vortex mixer for 30 minutes. Filter the pentane extract through a 0.45 micron filter and transfer to an amber vial for refrigerated storage.

6.4 Analysis

6.4.1 Analyze the sample by injecting 2 µL of the n-pentane extract into the GC using the instrument conditions specified in section 5.

6.5 Calculations

$$\text{Response factor} = \frac{\text{Area counts for the standard}}{\text{Concentration of the standard (ppb)}}$$

$$\text{Conc. in the extract (ppb)} = \frac{\text{Response factor}}{\text{Area counts for the sample}}$$

$$\text{Conc. in Ambient Air } (\mu g/m^3) = \frac{\text{Conc. in the extract } \mu g/mL \times \text{volume of extract } mL}{\text{Vol. of air sampled in } m^3}$$

6.6 Precision and Accuracy

6.6.1 Recovery Efficiency

6.6.1.1 The sample collection efficiencies were determined by volatilizing a known quantity of organic compounds into a stream of air and adsorbing the vapour on Tenax tubes. The apparatus used is illustrated in Figure 3.

6.6.1.2 In a single laboratory (Alberta Environmental Centre), using standards of 900 ppb (0.9 ppm), the average recovery efficiencies for five samples using Tenax adsorption tubes were:

Compound	Recovery Efficiency	Coefficient of Variation
Benzene	90.7%	2.0%
Toluene	98.6%	2.6%
Ethylbenzene	94.7%	3.4%
m & p-Xylene	95.0%	2.4%
Styrene	87.5%	1.6%
o-Xylene	93.6%	2.6%
Trimethylbenzene	91.5%	2.6%
Diethylbenzene	88.3%	1.7%
Diisopropylbenzene	90.1%	2.9%

7. References

7.1 Bente M. Wotha, Atmospheric Environment, Vol. 17, #9, pp. 1713 - 1722, 1983.

7.2 J. Rudolph and C. Jebsen, Intern. J. Environ. Anal. Chem, Vol. 13, pp. 129 - 139, 1983.

7.3 E.D. Pellizzari, J.E. Buch, R.E. Berkley, and J. McRae, Analytical Letters, Vol. 9, #1, pp. 45 - 63, 1976.

Figure 1. Dynamic Sampling Device

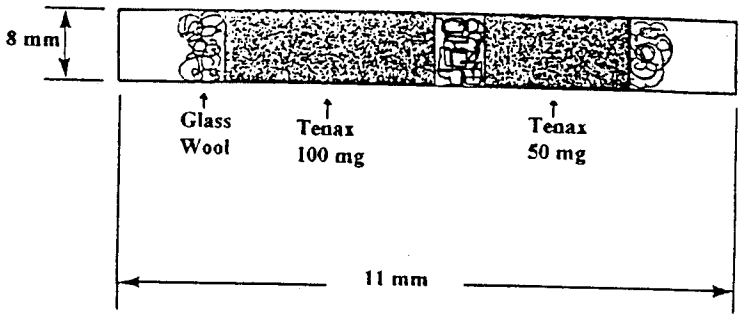


Figure 2. Passive Sampling Device

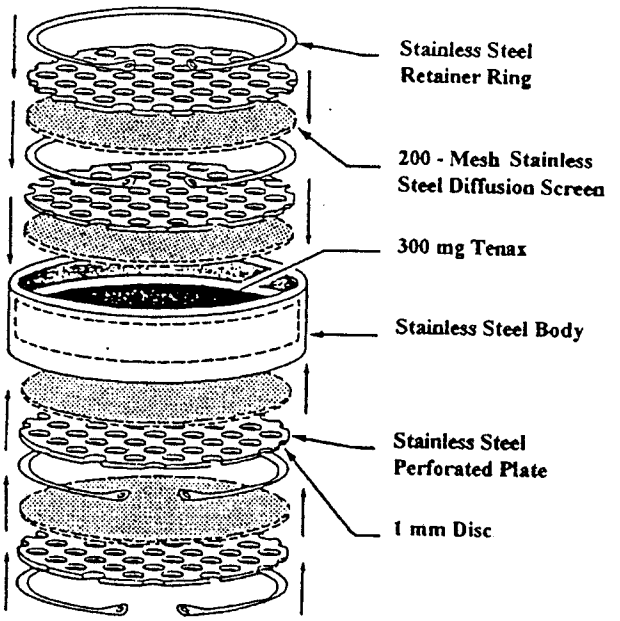


Figure 3. Calibration Apparatus for Collection Efficiency Studies

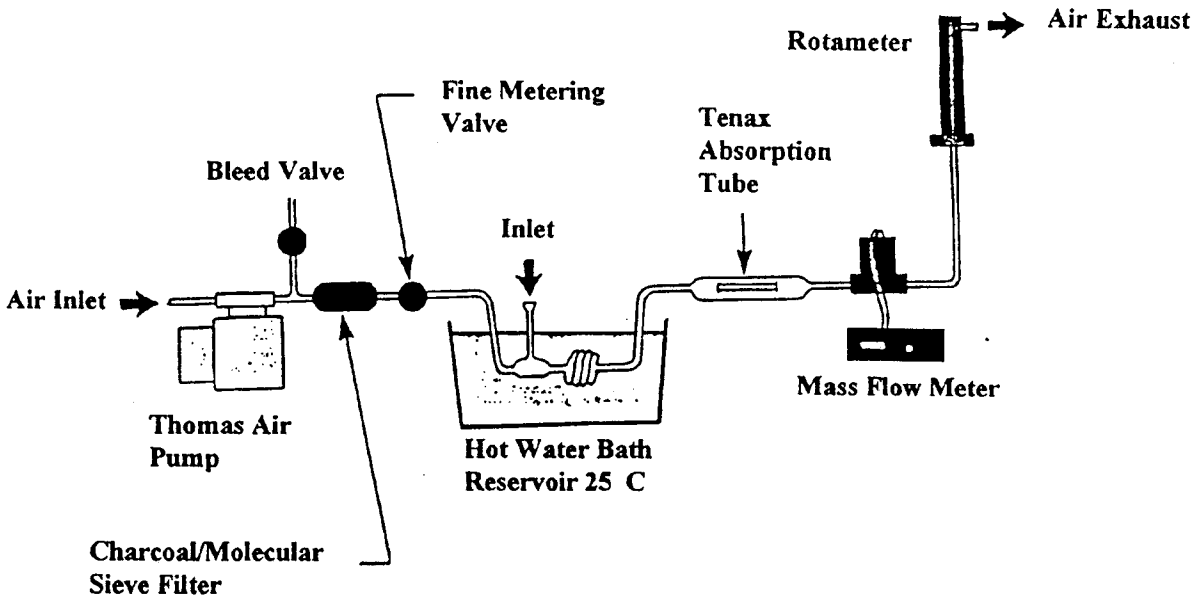


Figure 4. Schematic of Apparatus for Volatile Organics Analysis

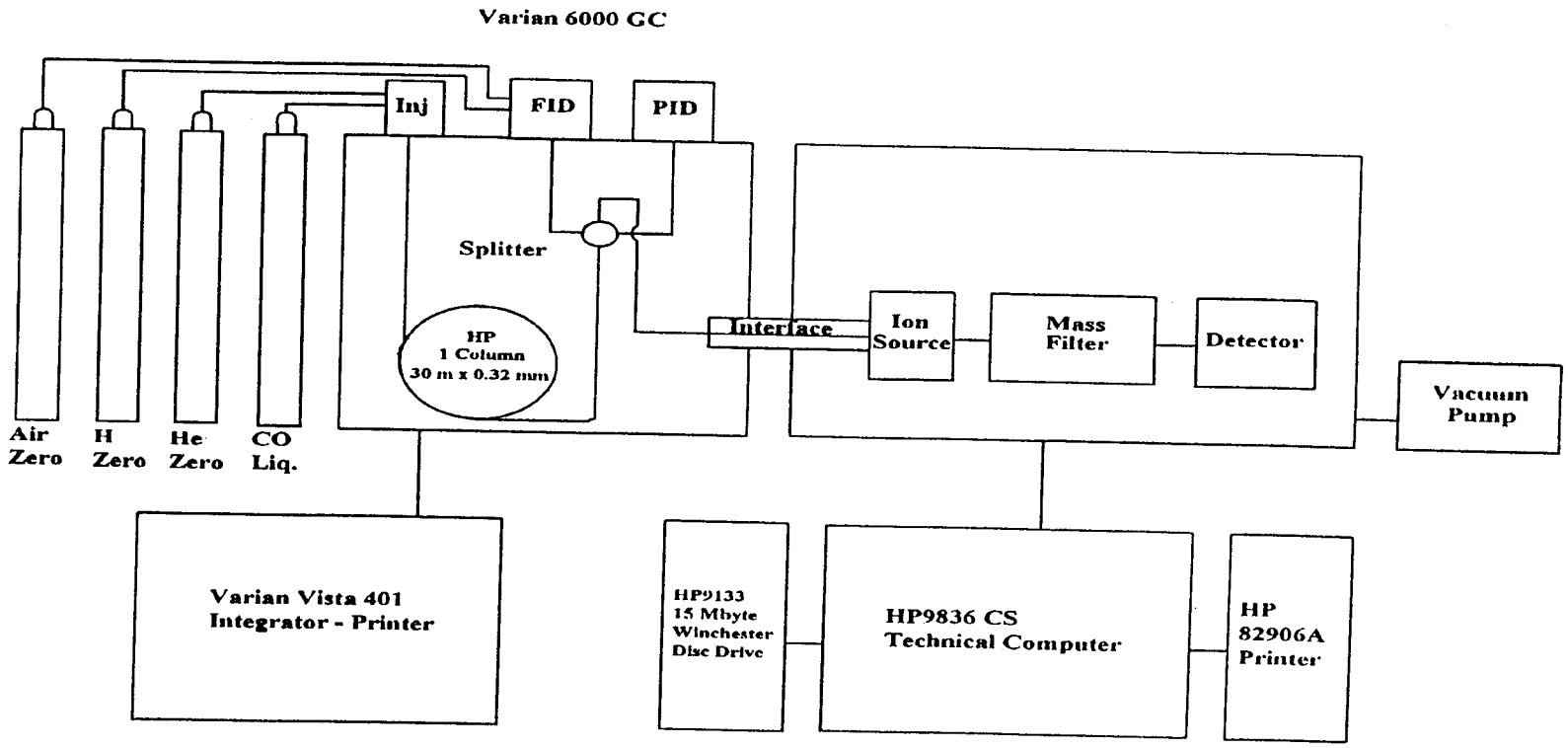
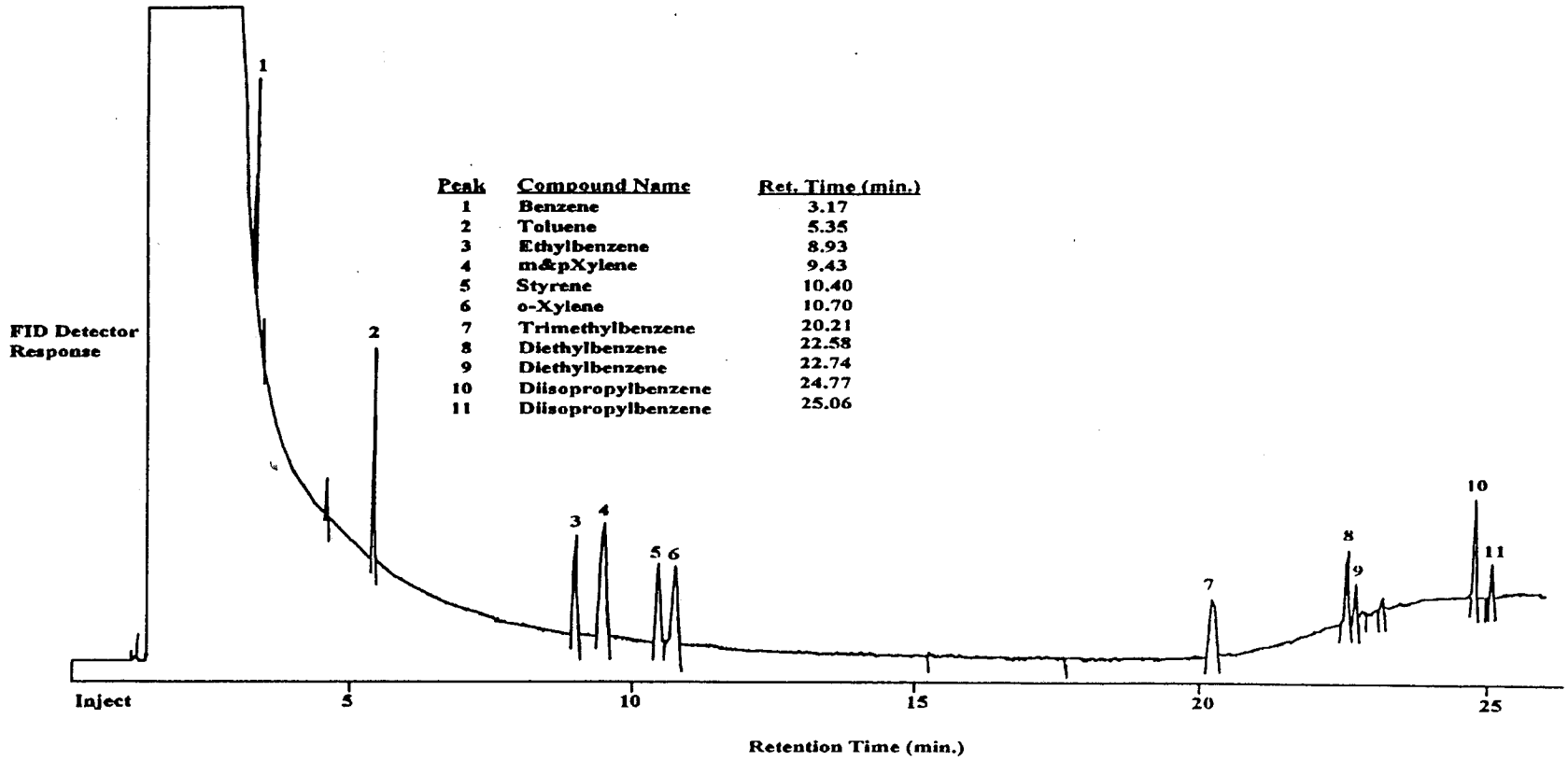
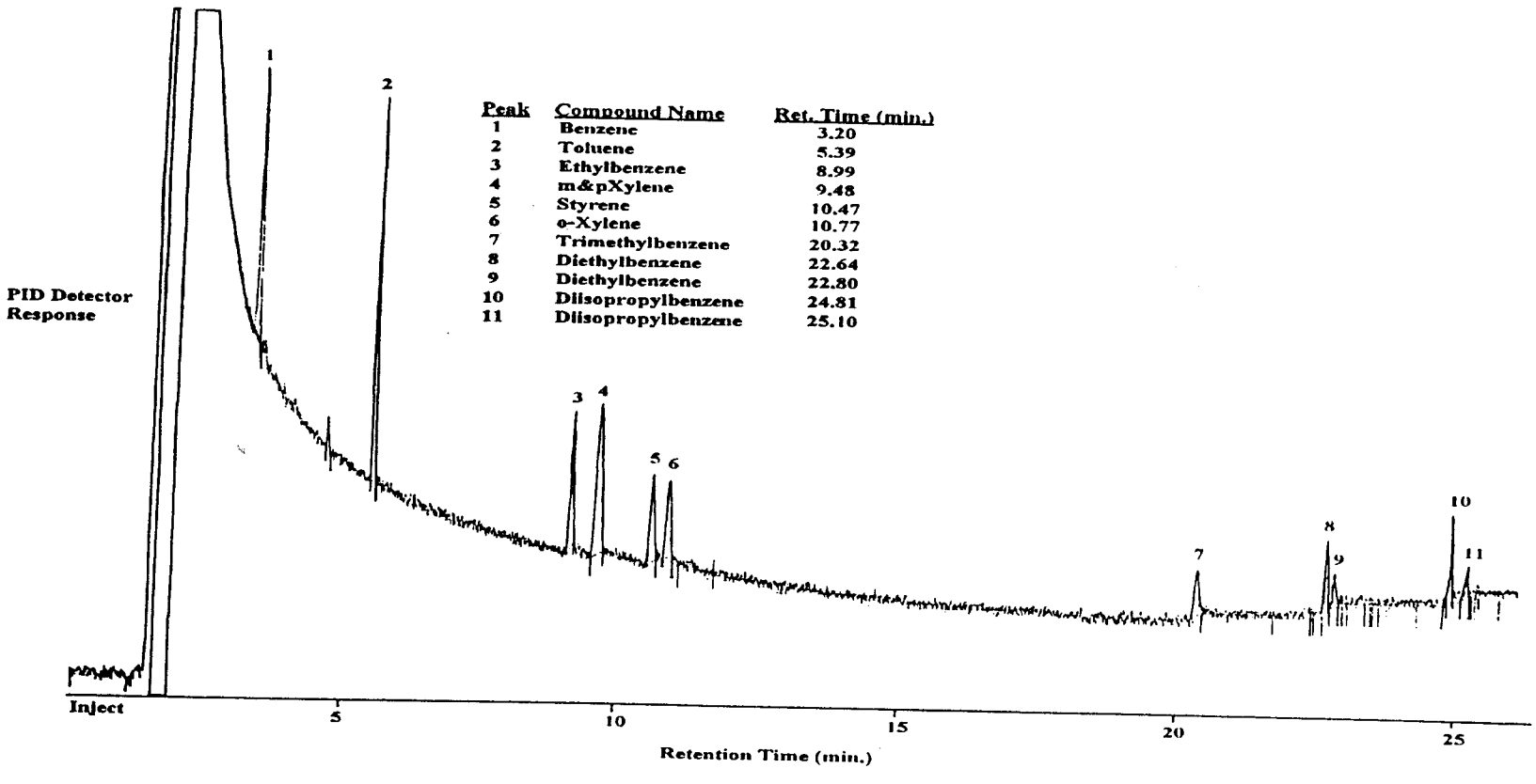


Figure 5. Chromatogram of a 180 ppb Standard by FID



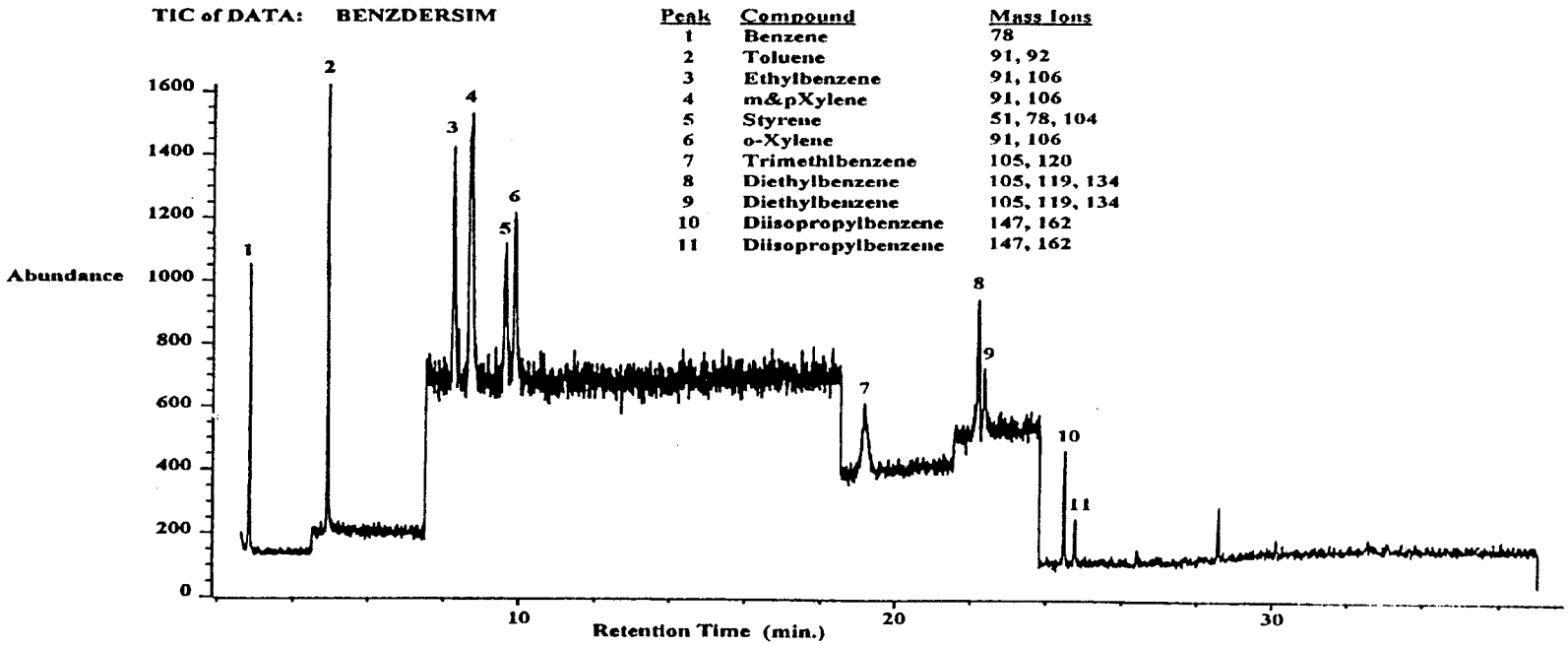
Peak	Compound Name	Ret. Time (min.)
1	Benzene	3.17
2	Toluene	5.35
3	Ethylbenzene	8.93
4	m&pXylene	9.43
5	Styrene	10.40
6	o-Xylene	10.70
7	Trimethylbenzene	20.21
8	Diethylbenzene	22.58
9	Diethylbenzene	22.74
10	Diisopropylbenzene	24.77
11	Diisopropylbenzene	25.06

Figure 6. Chromatogram of a 180 ppb Standard by PID



Peak	Compound Name	Ret. Time (min.)
1	Benzene	3.20
2	Toluene	5.39
3	Ethylbenzene	8.99
4	m&pXylene	9.48
5	Styrene	10.47
6	o-Xylene	10.77
7	Trimethylbenzene	20.32
8	Diethylbenzene	22.64
9	Diethylbenzene	22.80
10	Diisopropylbenzene	24.81
11	Diisopropylbenzene	25.10

Figure 7. Selective Ion Monitoring of a 22.5 ppb Organic Standard by MSD



Peak	Compound	Mass Ions
1	Benzene	78
2	Toluene	91, 92
3	Ethylbenzene	91, 106
4	m&pXylene	91, 106
5	Styrene	51, 78, 104
6	o-Xylene	91, 106
7	Trimethlbenzene	105, 120
8	Diethylbenzene	105, 119, 134
9	Diethylbenzene	105, 119, 134
10	Diisopropylbenzene	147, 162
11	Diisopropylbenzene	147, 162

September 1992 Method No. 18080

VOLATILE ORGANIC ACIDS (C_2 - C_5)

(Gas Chromatography)

1. Introduction

1.1 Volatile fatty acids (C_2-C_5) are commonly used in polymer formulations and other industrial applications. They are also produced from anaerobic digestion of sewage and other organic wastes. They are of environmental concern because humans are affected by their very strong odor and irritating nature.

2. Principle

2.1 The volatile acids (acetic, propionic, butyric, isobutyric, valeric, isovaleric) are adsorbed on silica gel tubes (1.0 g adsorbent) by drawing air through the tubes at a constant rate (200 mL/min). 5 mL micro impingers filled with 2 mL water and sampled at up to 200 mL/min, as well as passive sampling devices filled with 1.25 g silica gel can also be used. Using 4 mL deionized H_2O, the volatile acids are extracted and then acidified with formic acid. The extract is analyzed by gas chromatography, using a packed column (GP15%-SP-1220/1% H_3PO_4 on 100/120 Chromosorb WAW). A flame ionization detector is used, and the results are quantified by comparison to external standards.

3. Scope

3.1 The instrumental detection limits are:

Acetic acid	0.15 ppm
Propionic acid	0.12 ppm
Isobutyric acid	0.088 ppm
Butyric acid	0.093 ppm
Isovaleric acid	0.098 ppm
Valeric acid	0.095 ppm

The concentration range for the analysis is from the detection limit to 50 ppm for the extracted solutions.

4. Interferences

4.1 Very high humidity (>70%) would reduce the collection efficiency. Certain organic compounds with similar GC retention times would interfere with the identification and quantifying of the acids. Substances normally found in air have not been found to interfere. The FID detector responds very weakly to formic acid. This causes interference with the acetic acid determinations at very low concentrations (<1 ppm).

5. Apparatus

5.1 Air sampling train consisting of

5.1.1 Glass absorption tubes of 6 mm OD x 4 mm ID x 100 mm long, containing 1.0 g of silica gel preconditioned at 500°C for 30 min, and H_3PO_4 treated glass wool plugs, or 5 mL micro impingers containing 2 mL distilled and deionized water, or passive sampling devices filled with 1.25 g preconditioned silica gel.

5.2 Thomas diaphragm air pump calibrated at 200 mL/min.

5.3 Extraction equipment consisting of:

5.3.1 Screw-cap vials, 1 dram size (~5 mL), Supelco #2-3247

5.3.2 Teflon-coated silicone septa, Supelco #2-3273

5.3.3 1-mL syringe, Hamilton microliter &7101

5.3.4 Centrifuge, Clay Adams Dynac Model 0101

5.4 Analysis System:

5.4.1 Varian 6000 GC equipped with:

5.4.1.1 Vista 401 computing integrator

5.4.1.2 Flame ionization detector

5.4.1.3 6 mm OD x 2 mm ID x 3 m universal glass column packed with GP 15%SP-1220/1% H_3PO_4 on 100/120 Chromosorb WAW.

6. Reagents

6.1 Nitrogen zero carrier gas

6.2 Air zero gas for FID

6.3 Hydrogen zero gas for FID

6.4 Glass wool, Phosphoric acid treated Supelco #2-0383

6.5 Silica gel grade 12, 45/60 mesh Chromatographic Specialties #C23030

6.6 Formic acid, Aristar BDH Grade, 50 ppm acetic acid, maximum

6.7 Acetic acid, 99.8% Baker analyzed

6.8 Propionic acid, 99% BDH
6.9 Isobutyric acid, 99.5% BDH
6.10 Butyric acid, 99% BDH
6.11 Isovaleric acid, 99% BDH
6.12 Valeric acid, 98% BDH
6.13 Distilled and deionized water

7. Procedure

7.1 Sampling

7.1.1 Set up a weather station to determine wind direction.

7.1.2 Connect 2 adsorption cartridges in series and draw air through them at 200 mL/min for 3 h. The flow rate may be varied as long as the total volume sampled does not exceed 36 litres, i.e. if sampled at 100 mL/min the sampling time could be extended to 6 h. After sampling is completed, the tubes are sealed, kept cool and shipped to the laboratory for analysis.

7.2 Alternative Sampling Procedure

7.2.1 5-mL micro impingers containing 2 mL of water can also be used with sampling rates up to 200 mL/min. Passive sampling devices can be set out under appropriate cover for periods up to 24 h. A passive sampling rate of 50 cc/min is used for calculations at present until further testing is done to determine the actual rates for each compound.

7.3 Analysis

7.3.1 Preparation of standards:

7.3.1.1 1000 ppm v/v stock solution:

7.3.1.1.1 Add 100 µL of each acid (acetic, propionic, butyric, isobutyric, valeric, isovaleric) to a 100 mL volumetric flask and dilute to volume with distilled and deionized water.

7.3.1.1.2 Because the densities of these acids vary, on a wt/wt basis, these solutions would have the concentrations as tabulated below.

Component	1000 ppm v/v
Acetic acid	1050 ppm wt/wt (mg/L)
Propionic acid	994 ppm wt/wt (mg/L)
Butyric acid	958 ppm wt/wt (mg/L)
Isobutyric acid	947 ppm wt/wt (mg/L)
Valeric acid	940 ppm wt/wt (mg/L)
Isovaleric acid	928 ppm wt/wt (mg/L)

7.3.1.2 Working Standards

7.3.1.2.1 Prepare working standards by diluting 1000 ppm stock standards according to the table below.

Concentration	Vol. of 1000 ppm stock std	Vol of soln
1 ppm	100 µL	100 mL
5 ppm	500 µL	100 mL
10 ppm	1000 µL	100 mL
25 ppm	2500 µL	100 mL
50 ppm	5000 µL	100 mL

Again, the concentrations would have to be converted, if a wt/wt basis is required.

7.3.1.3 Extraction:

7.3.1.3.1 The silica gel from the exposed tube or the passive sampling device is transferred to a 5 mL vial. 4 mL of distilled and deionized water are added and the vial is capped. The sample vial is then shaken on a vortex mixer for 1 h and centrifuged for 10 min to settle the fine particles. The water extract is transferred with a plastic pasteur pipet to another 5 mL vial, and 25 microlitres of formic acid are added to acidify the sample. A 1 µL injection into the GC is used for analysis.

7.3.1.3.2 If impingers are used, the 2 mL impinger solution is transferred to a 5 mL vial and acidified with 12 microlitres of formic acid. A 1 µL injection into the GC is used for analysis.

7.3.1.4 GC Analysis Conditions:

Carrier Gas: N_2 zero gas, 35 mL/min

FID Gases: H_2 zero gas, 25 mL/min

Air zero gas, 300 mL/min

Column Oven: 110°C (± 5°C depending on the column packing density)

Injector Temp: 170°C

Detector Temp: 200°C; range 10-12; Attenuation 1

Injector Volume: 1 µL

(See figure 1 for a chromatogram of a sample.)

7.3.1.5 The GC is calibrated using 1, 5, 10 and 25 ppm standards. Samples, blanks and duplicates are run in accordance with the quality control program.

8. Calculations

8.1 The concentration of a particular acid in a sample is calculated by comparing its peak area with that of the standard.

$$Response\ Factor = \frac{Area\ counts\ for\ the\ standard}{Conc.\ of\ the\ standard\ in\ ppm}$$

$$Conc.\ in\ the\ extract = \frac{Area\ counts\ for\ the\ sample}{Response\ Factor}$$

$$Conc.\ in\ ambient\ air = \frac{Conc.\ in\ the\ extract\ (\mu g/mL) \times volume\ of\ extract\ (mL)}{Volume\ of\ air\ sampled\ in\ m^3}$$

9. Precision and Accuracy

9.1 The sample collection efficiencies were determined by volatilizing a quantity of organic acids in a stream of air and adsorbing the vapor on silica gel tubes or absorbing in water in midget impingers. The apparatus is illustrated in Figure 2.

9.1.1 In a single laboratory (Alberta Environmental Centre), using standards having a concentration of 1 ppm and 50 ppm, the mean, standard deviation and coefficient of variation for retention times and area count response for 5 samples were as follows:

Retention times (min)			Response (area counts)		
at 1 ppm					
mean	s.d.	C.V.	mean	s.d.	C.V.
1.598	0.004	0.25%	2687	251	9.3%*
to					
8.848	0.012	0.14%	5503	421	7.7%
at 50 ppm					
1.575	0.019	1.21%	135296	895	0.7%
to					
8.583	0.031	0.36%	323638	3570	1.1%

9.1.2 In a single laboratory (Alberta Environmental Centre), using a standard generated atmosphere of 5 ppm vapour and 50 ppm vapour and silica gel adsorption for 5 samples, the collection efficiency was as follows:

mean (%)	s.d. (%)	of 5 ppm vapour
98.6	3.3	
to	to	
97.6	9.2	
mean (%)	s.d.(%)	of 50 ppm vapour
99.8	2.1	
to	to	
96.6	2.9	

9.1.3 In a single laboratory (Alberta Environmental Centre), using a standard generated atmosphere of 5 ppm vapour, and midget impinger collection for 5 samples, the collection efficiency was as follows:

means (%)	s.d. (%)	of 5 ppm vapour
81.5	4.4	
to	to	
93.3	5.4	

NOTES The formic acid peak interferes slightly with the acetic acid peak at low concentrations.

Commercial silica gel tubes, Orbo-53 from Supelco, are currently available and preliminary tests have shown them to be effective.

10. References

10.1 A long-term sampling method for the collection of C1-C4 fatty acids; James C. Gilland, Gary T. Johnston, William A. McGee; Am. Ind. Hyg. Assoc. J.; (42) 8: 630-2, August, 1981.

10.2 Manual and Automated Gas Chromatography procedures for the Determination of Volatile Fatty Acids; Technical Report #TR76; Water Res. Cent.; Medmenham, England; 1978.

10.3 A Review of the Analysis of Free Fatty Acids [C2-C6]; G.C. Cochrane; Journal of Chromatographic Science; Vol. 13, Sept. 1975, 440-446.

Figure 1. FID Chromatogram of a 5ppm Volatile Fatty Acid Standard

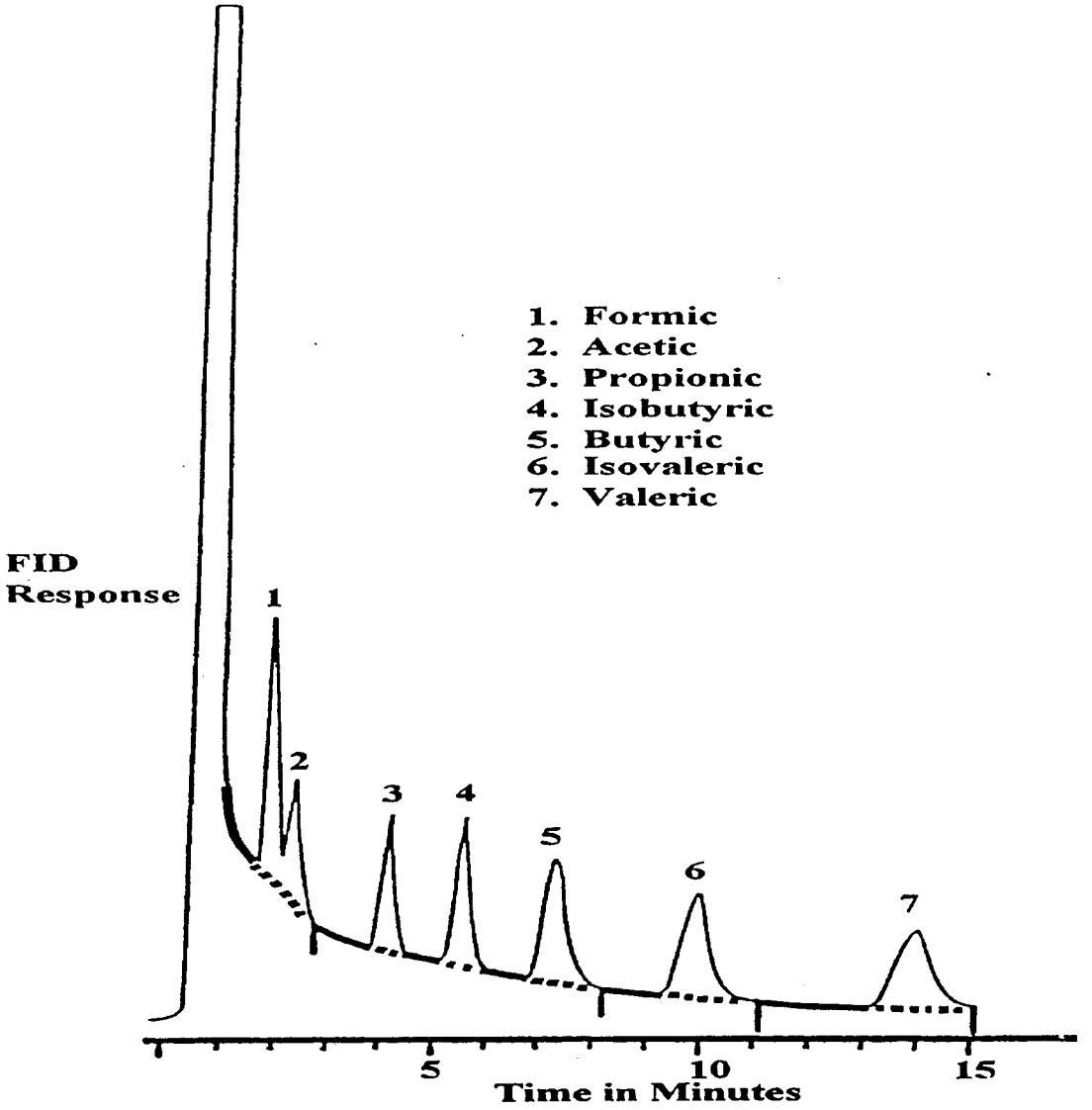


Figure 2. Calibration Apparatus for Collection Efficiency Studies

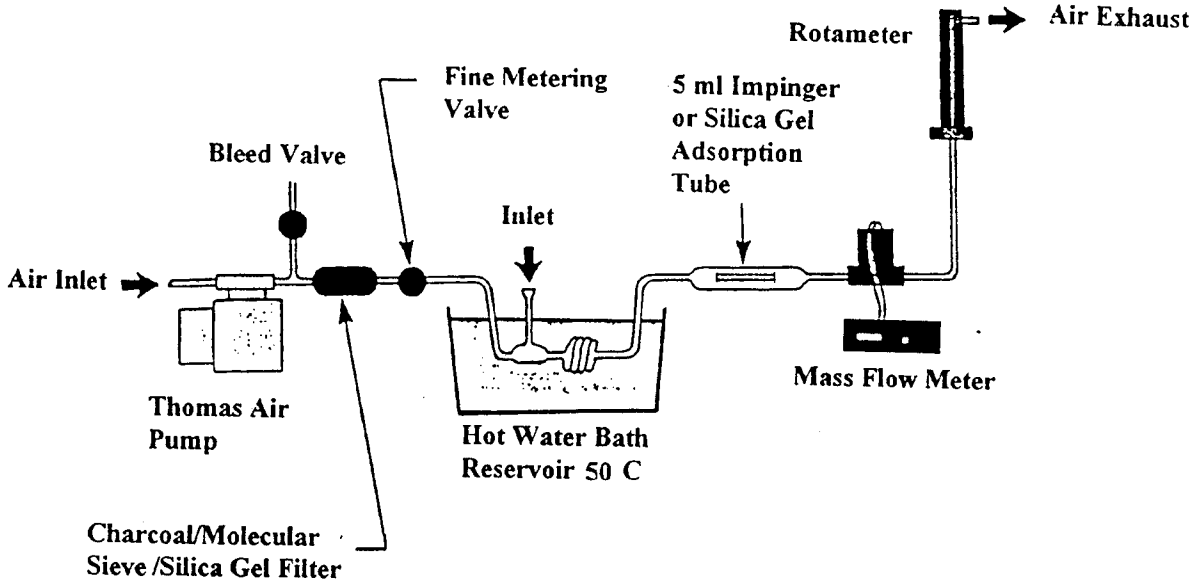


Figure 3. Dynamic Sampling Device

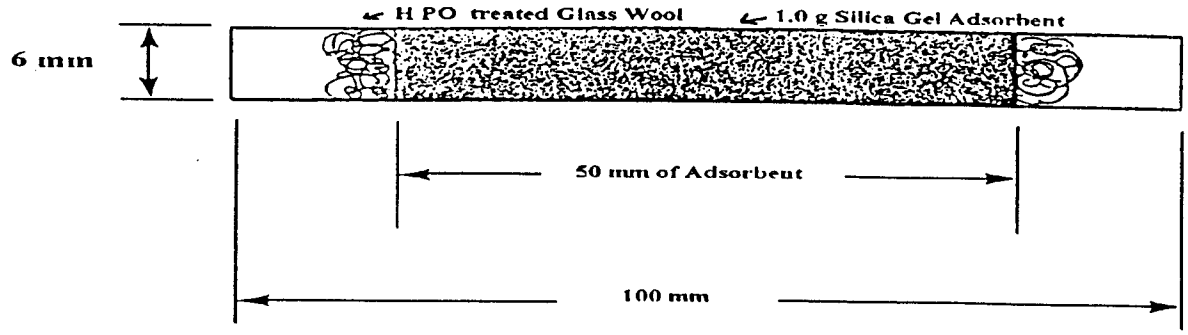
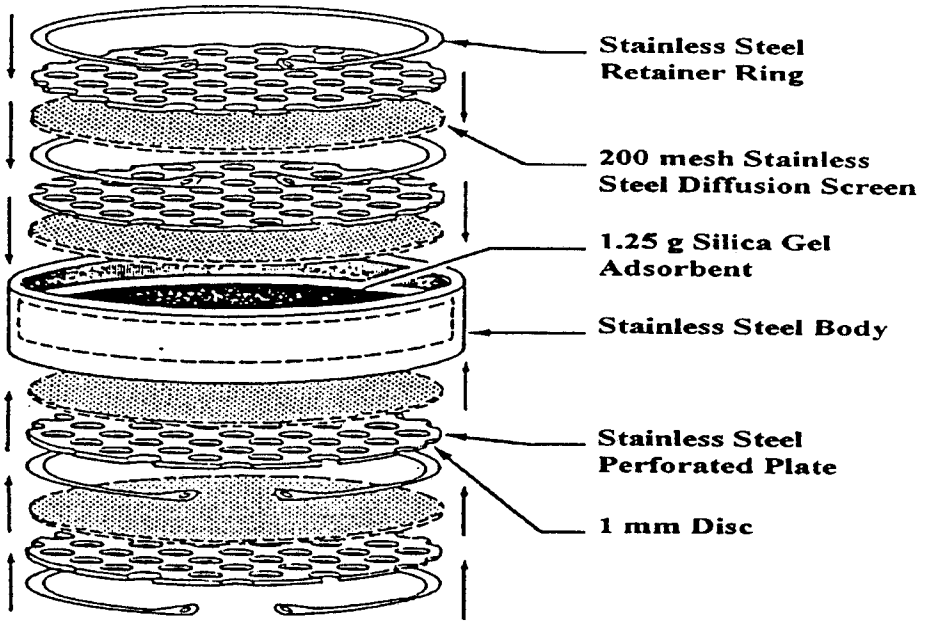


Figure 4. Passive Sampling Device



September 1992 Method No. 21516

BENZO (a) PYRENE

(HPLC/Fluorescence)

1. Introduction

1.1 Polycyclic aromatic hydrocarbons are present in airborne particulate matter. They mainly originate from car exhaust, and the burning of coal and refuse. Benzo (a) pyrene is the most carcinogenic of all the polycyclic hydrocarbons.

2. Principle

2.1 Airborne particulate matter is collected on a glass fibre filter using a high-volume sampler. The sample is extracted with cyclohexane in a Soxhlet extractor for six hours. The solvent is evaporated in a flash evaporator at 40°C. The residue is dissolved in exactly 1.5 ml of methanol. The resulting solution is analyzed by a high performance liquid chromatograph equipped with a fluorescence detector.

3. Scope

3.1 The detection limit for BaP is 0.01 µg/1000 m^3 of air.

4. Apparatus

4.1 High-volume sampler (Haskin Scientific Ltd., Montreal, or equivalent).
4.2 Flow chart paper and ink.
4.3 Teflon/glass fibre backed filter, 20 x 25 cm, Pallflex, or equivalent.
4.4 Analytical balance, sensitivity of 0.1 mg.
4.5 Circular metal punch, 46 mm diameter.
4.6 Soxhlet apparatus.
4.7 Stirrer, hotplate combination (Thermolyne type 1000, or equivalent).
4.8 Flash evaporator.
4.9 High performance chromatographic pump (Spectra Physics SP8700R) Liquid Chromatograph, or equivalent.
4.10 Reverse phase liquid chromatographic column (Whatman Partisil 10, ODS-2, 0.26 x 25 cm LC column, or equivalent).

4.11 Fluorescence spectrophotometer equipped with flow cell (Perkin-Elmer 204 A, or equivalent).

4.12 Recorder integrator (Hewlett Packard 3380 Integrator, or equivalent).

4.13 1000 µl Lambda pipet, 500 µl Lambda pipet.

4.14 Auto sampler (Perkin-Elmer LC 420, 42 sample tray, or equivalent).

4.15 Hand crimper.

4.16 Auto sampler vials, amber if possible.

5. Reagents

5.1 Cyclohexane: HPLC grade.

5.2 Methanol: HPLC grade.

5.3 Acetonitrile: HPLC grade.

5.4 Stock BaP solution (1 mg/mL): weigh 100 mg BaP and dissolve in 100 mL of acetonitrile.

5.5 Intermediate BaP solution (10 µg/mL): pipet 1.0 mL of stock BaP into a 100 mL volumetric flask and dilute to volume with acetonitrile.

5.6 Working standard BaP solution (100 ng/mL or 0.1 ng/µL): pipet 1.0 mL of intermediate BaP solution into a 100 mL volumetric flask and dilute to volume with acetonitrile.

5.7 Helium: zero grade.

6. Procedure

6.1 Sampling

6.1.1 Condition the filter overnight at room temperature and 40% humidity or dry it in a desiccator for 24 hours.

6.1.2 Weigh the filter and record the weight on a data sheet.

6.1.3 Place the filter on a high-volume sampler. Fix a flow chart for recording air flow and sampling time. Set the timer for 24 hours' sampling.

6.2 Analysis

6.2.1 Weigh the filter and record final weight in grams.

6.2.2 Cut 4 discs from the filter with metal punch (16% of the filter).

6.2.3 Extract for six hours in a Soxhlet apparatus using 110 mL of HPLC grade cyclohexane.

6.2.4 Allow flask to cool and remove solvent in a flash evaporator at 40°C. Evaporate any residual cyclohexane by blowing nitrogen or helium into the flask.

6.2.5 Rinse flask with 1500 µL of methanol. Transfer each aliquot with a pasteur pipet into a disposable syringe.

6.2.6 Filter the sample through the syringe tip filter (0.2 µm, Gelman 4450, or equivalent) into a glass vial.

6.2.7 Cap the vial with a metal cap fitted with a Teflon septum. Use a hand crimper for capping the vial.

6.2.8 Turn instrument on, following manufacturer's instructions, and allow 30 minutes to warm up.

6.2.9 Set instrumental conditions as described and allow degassed and filtered solvents to pump through the column for 1 hour.

6.2.10 Set up the sample tray in the following order:

Calibration Standard
MeOH blank
Standard
Standard
9 samples
duplicate or spike
standard
9 samples
duplicate or spike
standard

6.2.11 Inject 20 µL sample using a sample loop.

NOTE:

Routine quality control must be followed to ensure the precision and accuracy of the method. With every series of nine extractions, one sample should be analyzed in duplicate with its mate being spiked with 100 ng of BaP. This will allow the technician to detect any changes occurring within the total analysis. Also, standards should be run at a minimum of once every nine samples to ensure reproducibility of standard areas. If these practices are followed, the method should fall easily within the tolerances quoted for precision and accuracy.

7. Instrumental Conditions

7.1 High performance liquid chromatograph:

Solvent A:	Acetonitrile 90%
Solvent B:	H_2O 10%
Pressure:	max psi 2500
Total Flow:	1.00 mL/min

7.2 Fluorescence spectrophotometer:

PM Gain:	Normal
Sens. Range:	0.3
Sens. Fine:	FULL
Shutter:	OPEN
Ex. Slit:	11 nm
Em. Slit:	11 nm
Ex. λ:	384 nm
Em. λ:	406 nm
Response:	SLOW
Zero Suppression:	ON
Mode:	NORMAL
Scan:	STOP
Scan Speed:	OFF

7.3 Integrator:

Start Delay:	8 or OFF
Stop Time for Integrator:	15 min.
Auto Sampler Interval:	17 min.
Chart Speed:	0.5 cm/min.
Chart:	Auto
Slope Sensitivity:	0.3 mv/min.
Attenuation:	2
Area Reject:	OFF
Method:	ESTD (External Standard)
XF Factor:	9.375

8. Calculation

8.1 Calculate the amount of BaP in the extracted sample in micrograms.

$$BaP\ (\mu g) = \frac{A \times B \times 1500}{C \times D \times 1000}$$

where

A	=	area of sample peak.
B	=	amount of standard injected in nanograms. (Std. Conc. X loop volume)
C	=	volume of sample injected in microlitres.
D	=	area of standard peak.
1500 µL	=	final sample volume.
1000	=	to convert ng to µg

8.2 The concentration of sample is expressed as µg of BaP in a gram of particulate or as µg per 1000 m^3 of air. Since the extracted sample represents only 16% of the total, a factor of 6.25 is employed to express the total concentration.

$$\mu g\ BaP/gm\ particulate = \frac{BaP\ \mu g \times 6.25}{E}$$

where E = gm of particulate deposited on the filter

$$\mu g\ BaP/1000\ m^3\ of\ air = \frac{BaP\ \mu g \times 6.25 \times 1000}{Total\ m^3\ of\ air}$$

9. Precision and Accuracy (by manual injection)

9.1 In a single laboratory (Alberta Environmental Centre), using high-volume filters at concentrations of 10 ng, 112 ng and 338 ng, the coefficients of variation were 20.4%, 5.51% and 3.16%, respectively.

9.2 In a single laboratory (Alberta Environmental Centre), using high-volume filters at concentrations of 5 ng, 142 ng and 334 ng, the recoveries were 103%, 92% and 100%, respectively.

10. References

10.1 M.A. Fox and S.W. Stanley, Anal. Chem., Vol. 48, 1976, p. 992.

10.2 M. Dong, D. C. Locke and E. Ferrand, Anal. Chem., Vol. 48, 1976, p. 368.

Figure 1. Chromatogram of Standards

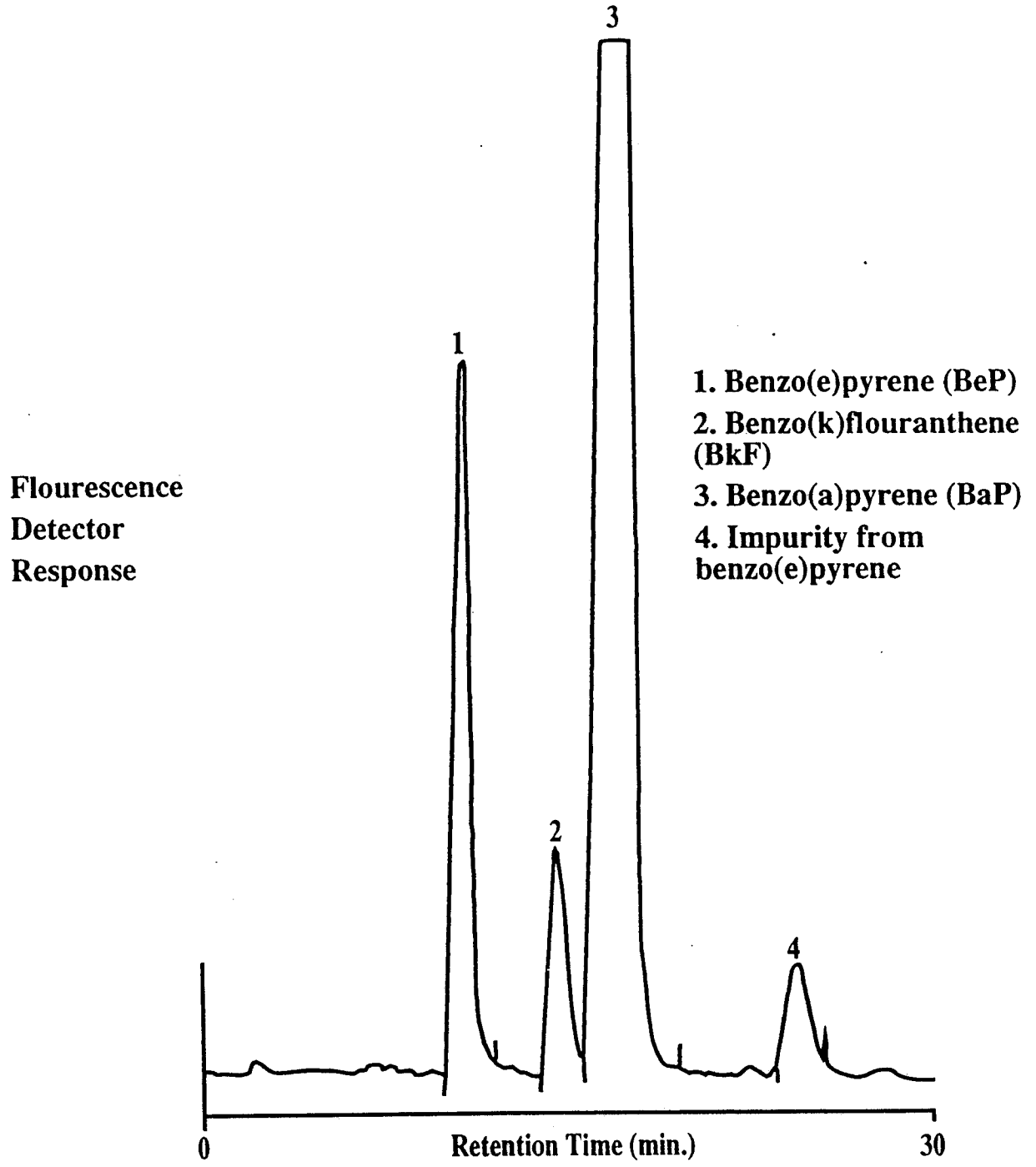
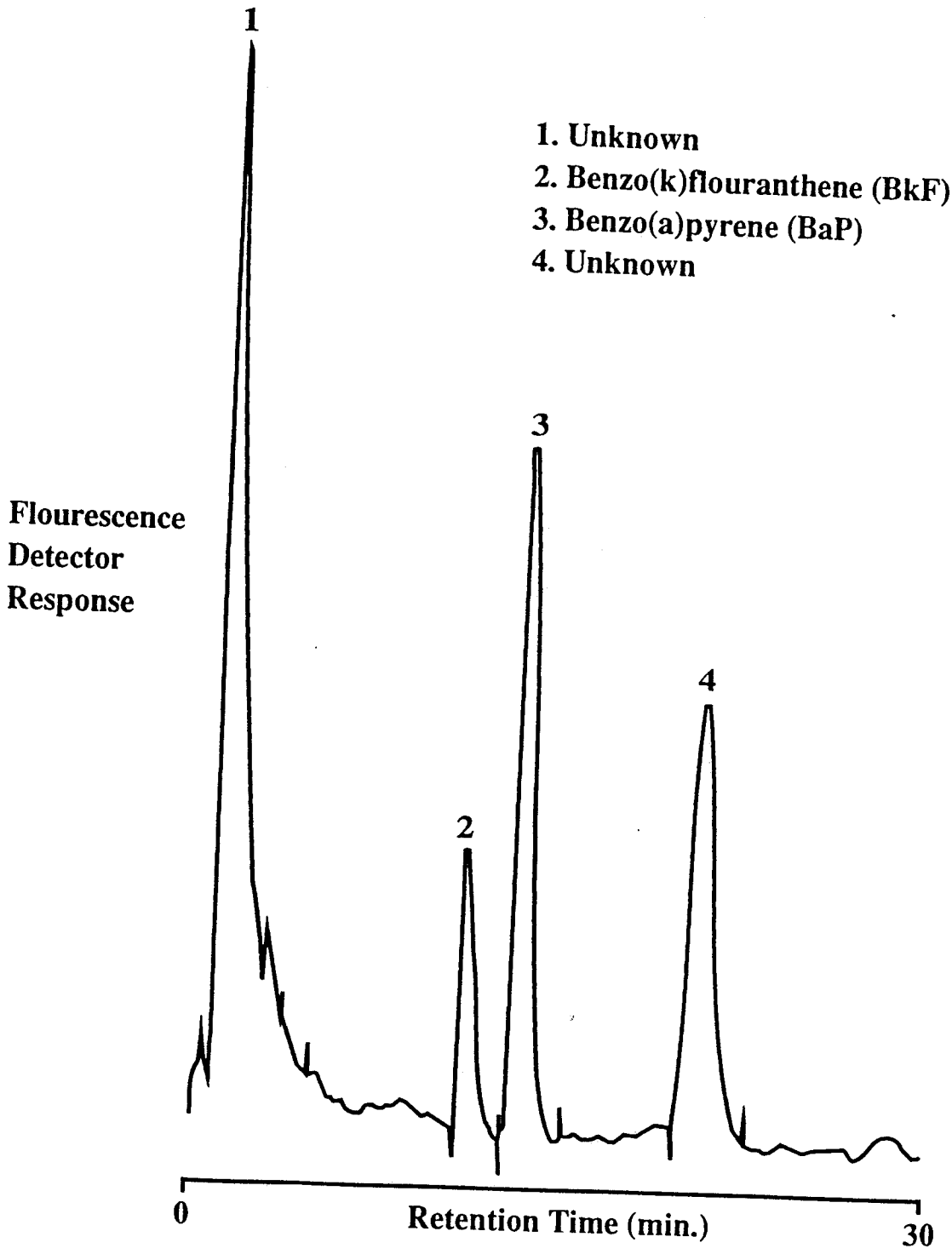


Figure 2. Chromatogram of a Sample



CARBON PARTICLES

(Gravimetric)

1. Introduction

1.1 The main sources of carbon particles in ambient air are lamp black-producing plants. Carbon also originates from the burning of natural gas and refuse.

2. Principle

2.1 Carbon particles are collected on a glass fibre filter, using a high-volume sampler. The sample is digested with hydrofluoric acid and then treated with ammonium hydroxide, nitric acid and hydrochloric acid to dissolve the filter and inorganics, and to decompose the organics. The free residual carbon is filtered, dried at 150°C and ignited at 700°C. The difference in weight before and after the ignition provides a measure of the carbon in the sample.

3. Scope

3.1 The detection limit is 1 $\mu g/m^3$ of air.

4. Apparatus

4.1 High volume sampler (Haskin Scientific Ltd., Montreal, or equivalent).
4.2 Flow-chart paper and ink.
4.3 Analytical balance, sensitivity of 0.1 mg.
4.4 Glass fibre filter, 20 x 25 cm (Gelman Type A, or equivalent).
4.5 Circular metal punch, 46 mm diameter.

5. Reagents

5.1 Hydrofluoric acid, conc.
5.2 Hydrochloric acid, conc.
5.3 Ammonium hydroxide, conc.
5.4 Nitric acid, conc.
5.5 Lamp black (Fisher Scientific, or equivalent).

6. Procedure

6.1 Sampling

6.1.1 Condition the filter overnight at room temperature and 40% humidity or dry it in a desiccator for 24 hours.

6.1.2 Weigh the filter and record the weight on a data sheet.

6.1.3 Place the filter on a high-volume sampler. Fix a flow chart for recording air flow and sampling time. Set the timing for 24 hours' sampling.

6.2 Analysis

6.2.1 Read the average flow rate and the time of sampling from the flow chart and record these data on the data sheet.

6.2.2 Dry the filter at room temperature and 40% humidity or dry it in a desiccator for 24 hours.

6.2.3 Weigh the filter and record the final weight in grams.

6.2.4 Cut 2 discs (8%) from the exposed and unexposed glass fibre filter. Place the discs separately into 100 mL Teflon beakers.

6.2.5 Place the beakers on a hot plate at 40°C and dissolve the filters by dropwise addition of hydrofluoric acid. Evaporate the acid slowly at 40°C.

6.2.6 With vigorous stirring, add 5 mL of distilled water and then 10 mL of concentrated ammonium hydroxide to each beaker.

6.2.7 Add 10 mL of concentrated nitric acid and a few glass beads to each beaker. Evaporate to 10 mL.

6.2.8 Dilute the mixtures to 25 mL with distilled water and add 5 mL of concentrated hydrochloric acid.

6.2.9 Bring the resulting mixture to boiling and filter the hot solution through a Gooch crucible and an asbestos mat of known tare weight. Wash the crucible and its contents with 50 mL of a warm 1% nitric acid solution.

6.2.10 Dry the crucible and its contents at 150°C to a constant weight (about 2 hours).

6.2.11 Heat the crucible to 700°C in a muffle furnace for 2 hours, cool and reweigh.

7. Calculation

7.1 Calculate the total volume of air in m^3 from the flow rate and the sampling time.

7.2 Determine the weight of total suspended particulate matter collected on the filter paper.

7.3 The concentration is expressed as

$$\mu g\ carbon/m^3 = \frac{[(W_1 - W_2) - (W_3 - W_4)] \times 12.5 \times 10^6}{V}$$

where

W_1 = weight of the crucible containing the sample, after drying at 105°C, in grams.

W_2 = weight of the crucible containing the sample, after heating at 700°C, in grams.

W_3 = weight of the blank, after drying at 150°C, in grams.

W_4 = weight of the blank, after heating at 700°C, in grams.

12.5 = conversion factor to change 8% of the filter to 100%.

10^6 = conversion factor to change grams to micrograms.

V = volume of air in m^3 = (F x T).

where

F = average flow rat in m^3/min.

T = sampling time in minutes.

(0.0283 = conversion factor to change ft^3 to m^3, if necessary).

8. Reference

8.1 V.P. Kukreja and J.L. Bove, Environ. Sc. & Technol., Vol. 10, 1976, p. 187.

COAL PARTICLES

(Gravimetric)

1. Introduction

1.1 Coal particles are present in ambient air as suspended particulate matter, mainly in the vicinity of coal mines.

2. Principle

2.1 The sample is collected on a glass fibre filter, using a high-volume sampler. The filter is dried at room temperature and weighed. A portion of the filter is heated at 500°C in a muffle furnace to a constant weight. The amount of coal particles is calculated from the difference of weights and expressed as micrograms per m^3 of air.

3. Scope

3.1 The detection limit is 1 $\mu g/m^3$ of air.

4. Interference

4.1 Organic compounds interfere. A correction factor is used to eliminate this interference.

5. Apparatus

5.1 High-volume sampler (Haskin Scientific Ltd., Montreal, or equivalent).
5.2 Flow-chart paper and ink.
5.3 Glass fibre filter, 20 x 25 cm (Gelman type A, or equivalent).
5.4 Circular metal punch, 46 mm diameter.
5.5 Analytical balance, sensitivity 0.1 mg.
5.6 Muffle furnace.
5.7 Platinum crucible.

6. Reagents

6.1 No reagents are required.

7. Procedure

7.1 Sampling

7.1.1 Condition the filter overnight at room temperature and 40% humidity, or dry it in a desiccator for 24 hours.

7.1.2 Weigh the filter and record the weight on a data sheet.

7.1.3 Place the filter on a high-volume sampler. Fix a flow chart for recording air flow and sampling time. Set the timer for 24 hours' sampling.

7.2 Analysis

7.2.1 Read the average flow rate and the time of sampling from the flow chart and record these data on the data sheet.

7.2.2 Dry the filter at room temperature and 40% humidity, or dry it in a desiccator for 24 hours.

7.2.3 Weigh the filter and record the weight in grams.

7.2.4 Cut 5 discs (20%) from the filter with the metallic punch and place them in a platinum crucible.

7.2.5 Weigh the platinum crucible with the discs.

7.2.6 Heat the platinum crucible with the filter at 500° ± 10°C to a constant weight.

8. Calculation

8.1 Calculate the total volume of air in m^3 from the flow rate and sampling time.

8.2 Determine the weight of total suspended particulate matter collected on the filter paper.

8.3 The concentration of coal particles is expressed as

$$\mu g/m^3 = \frac{5.5\ (W_1 - W_2) \times 10^6}{V}$$

where

10^6 = conversion factor to change gram to microgram.

V = volume of air in m^3 = (F x T).

where F = average flow rate in m^3/min.

T = sampling time in minutes.

(0.0283 = conversion factor to change ft^3 to m^3, if necessary).

W_1 = weight of 5 discs + platinum crucible in grams.

W_2 = weight of the residue left after heating at 500°C + platinum crucible in grams.

The factor 5.5 refers to

1. 100% of filter (20% taken for analysis).
2. 13% of the total combustible as inorganic ash; to be added.
3. 3% of the total combustible as organics; to be deducted.

Note:

A number of experiments at the Alberta Environmental Centre with different types of coal and high-volume air samples containing coal showed that, the average inorganic residue in coal is approximately 13% of the coal-combustible, and free atmospheric organics, not associated with coal, amount to approximately 3% of the total combustible materials on the filter.

9. References

9.1 D.W. Koppenaal and S.E. Monahan, Environ. Sc. & Technol., Vol. 10, 1976, p. 1104.

9.2 ASTM, Part 26, 1977, p. 373.

FLUORIDE, WATER SOLUBLE

(Specific-Ion Electrode)

1. Introduction

1.1 During the combustion of coal, as well as during the process of industrial operations to produce phosphate fertilizer, iron and steel, glass and ceramics, fluorine compounds are set free as gaseous and/or particulate fluoride.

2. Principle

2.1 Using a high-volume sampler, particulate matter is collected on a Teflon filter reinforced with glass fibre. Fluoride is extracted with 0.1N NaOH solution at 90°C and determined by a fluoride specific-ion electrode in conjunction with a standard calomel reference electrode. The potential developed by the presence of fluoride ions is measured by an expanded scale pH/mV meter.

3. Scope

3.1 The method is applicable only to water-soluble fluorides. The detection limit is 0.01 µg F/m^3 of air.

4. Interference

4.1 Polyvalent cations such as Si, Fe and Al interfere. A buffer is used to eliminate these interferences.

5. Apparatus

5.1 High-volume sampler (Haskin Scientific Ltd., Montreal, or equivalent).
5.2 Flow-chart paper and ink.
5.3 Analytical balance, sensitivity of 0.1 mg.
5.4 Teflon filter, 20 x 25 cm (Pallflex TM, or equivalent).
5.5 Circular metal punch, 46 mm diameter.
5.6 Fluoride electrode (Orion 94-09, or equivalent) and standard calomel reference electrode.
5.7 pH meter with expanded mV scale.

5.8 Magnetic stirrer and Teflon-coated stirring bar.

6. Reagents

6.1 Sodium hydroxide solution (0.1N): dissolve 8 g NaOH in 2 litres distilled water.

6.2 Sodium hydroxide solution (6N): dissolve 240 g NaOH in distilled water and dilute to 1 litre.

6.3 Total ionic strength adjustment buffer (TISAB): add 58 mL of glacial acetic acid and 12 g of sodium citrate dihydrate to 300 mL of distilled water. Stir to dissolve and cool to room temperature. Adjust the pH of the solution to 5.2 with 6N NaOH. Transfer the solution to a 1000 mL volumetric flask and dilute to volume with distilled water.

6.4 Stock fluoride solution (100 mg/L F): dissolve 0.221 g anhydrous sodium fluoride in distilled water and dilute to 1000 mL.

6.5 Working fluoride standards - prepare as follows:

mL stock/1000 mL	conc. mg/L F
2.5	0.25
5.0	0.50
10.0	1.00
15.0	1.50
20.0	2.00

7. Procedure

7.1 Sampling

7.1.1 Condition the filter overnight at room temperature and 40% humidity, or dry it in a desiccator for 24 hours.

7.1.2 Weigh the filter and record the weight on a data sheet.

7.1.3 Place the filter on a high-volume sampler. Fix a flow chart for recording air flow and sampling time. Set the timer for 24 hours' sampling.

7.2 Analysis

7.2.1 Read the average flow rate and the time of sampling from the flow chart and record these data on the data sheet.

7.2.2 Dry the filter at room temperature and 40% humidity, or dry it in a desiccator for 24 hours.

7.2.3 Weigh the filter and record the final weight in grams.

7.2.4 Cut 2 discs (8%) from the exposed and unexposed filter. Place the discs separately into 250 mL Erlenmeyer flasks containing 100 mL distilled water. Heat the sample and the blank on a hot plate at 90°C for 2 hours.

7.2.5 Cool the samples to room temperature and filter them separately into 100 mL volumetric flasks and dilute to volume with distilled water.

7.2.6 Pipet 10.0 mL sample, standards, and 10.0 mL distilled water as blank, into 200 mL beakers. Add 50 mL buffer to each beaker.

7.2.7 Place the electrodes in the solution. Stir the solution using a magnetic stirrer. Record the corresponding millivolt reading when the reading is stable.

8. Calculation

8.1 Using two-cycle semi-log graph paper, prepare a calibration curve by plotting mg/L F on the log scale vs millivolts on the linear scale. Read the fluoride concentration from the graph in units of mg/L F.

8.2 Calculate the total volume of air in m^3 from the flow rate and sampling time.

8.3 Determine the weight of total suspended particulate matter collected on the filter. Calculate the fluoride in the sample as follows:

$$mg\ F = \frac{mg/L\ F \times total\ sample\ volume\ in\ mL}{1000}$$

$$The\ final\ result\ is\ expressed\ as\ \mu g\ F/m^3 = \frac{W \times 12.5 \times 10^3}{V}$$

$$and/or\ as\ mg\ F/g\ in\ total\ suspended\ particulate\ matter = \frac{W \times 12.5}{W_1}$$

where

W = mg F in 8% of the filter.

W_1 = weight of the total particulate matter in grams.

12.5 = conversion factor to change 8% of the filter to 100%.

V = volume of air in m^3 (F x T).

where

F = average flow rate in m^3/minutes.

T = sampling time in minutes.

(0.0283 = conversion factor to change ft^3 to m^3, if necessary).

9. References

9.1 Orion Research Inc., Instruction Manual for Fluoride Electrode, Model 94-09, 1977.

9.2 Methods of Air Sampling and Analysis. APHA Intersociety Committee. M. Katz, Editor; 2nd Edition, p. 417.

September 1992 Method No. 23535

LEAD

(X-ray Fluorescence)

1. Introduction

1.1 The burning of leaded gasoline produces PbBrCl, one of the major components of smog. Certain industries, such as battery plants and refineries, also produce lead emissions.

2. Principle

2.1 Airborne particulates are collected on a Teflon filter (Pallflex, TM), using a high-volume air sampler. Two 47 mm discs are cut from the filter. The filters are analyzed using an energy dispersive X-ray fluorescence analyzer. The characteristic lead Lα(10.549 KeV) and Lβ(12.611 KeV) emissions are quantified against standards by means of a channel-by-channel linear XML program.

3. Scope

3.1 Lower quantifiable limit is 0.07 $\mu g/cm^2$ of the filter and 0.05 $\mu g/cm^2$ of air.

4. Interferences

4.1 Arsenic K∝ line interferes with the L∝ line of lead.

4.2 When using a silver X-ray tube, the Compton scatter region overlaps the lead Lβ line. This makes quantification of the Lβ line less reliable at lower levels.

5. Apparatus

5.1 High-volume sampler (Haskin Scientific Ltd.), chart paper, etc.

5.2 Teflon filter, 20 x 25 cm. (Pallflex TM).

5.3 Circular metal punch, 47 mm in diameter.

5.4 Energy-dispersive X-ray fluorescence spectrometer with 361 IBM computer, United Scientific Spectrace 440, equipped with a silver X-ray tube, a 47 mm 10-position sample tray, and a sample rotator.

5.5 X-ray standards: 0.0, 3.5, 4.9, 12.4 $\mu g/cm^2$ Pb.

6. Procedure

6.1 Sampling

6.1.1 Condition the filter overnight at room temperature and 40% humidity, or dry it in a desiccator for 24 hours.

6.1.2 Weigh the filter and record the weight on a data sheet.

6.1.3 Place the filter on a high-volume sampler. Fix a flow chart for recording air flow and sampling time. Set the timing for 24 hours' sampling.

6.2 Analysis

6.2.1 Read the average flow rate and the sample time of sampling from the flow chart and record these data.

6.2.2 Dry the filter at room temperature and 40% humidity, or dry it in a desiccator for 24 hours.

6.2.3 Weigh the filter and record the final weight in grams.

6.2.4 Fold the high-volume filter with the exposed (particulate loaded) sides together. While in this sandwiched form, cut two sets of 47 mm discs.

6.2.5 Cut two sets of discs from the blank filter paper of the same batch.

6.2.6 Analyze the discs by X-ray fluorescence, with every sixth sample being a duplicate. In order to remove inhomogeneity effects, rotate the samples while being analyzed.

X-ray Spectrometer settings:

1. Use the thin molybdenum filter 0.05 mm.
2. Anode current 0.10 amperes.
3. Anode voltage 34 KeV.
4. Range 0-20 KeV.
5. Sample rotator on.
6. Pulsed mode.

7. Calculation

7.1 Quantification is done by means of the XMIL program. This program uses channels (points on the output histogram) for each peak to determine the background and net counts. The net counts for the Lα lines are compared against those for the standards. In this way, the sample is quantified as a ratio of the standard. This ratio is used to calculate the absolute value in $\mu g/cm^2$. To calculate the result in $\mu g/m^3$ of air, multiply the result, $\mu g/cm^2$ of filter by the total area of the exposed filter and the total volume of air.

8. Precision and Accuracy

8.1 Two different Pb standards were run a total of ten times each. The 4.9 $\mu g/cm^2$ standard had a mean of 4.961 $\mu g/cm^2$ and a standard deviation of .106 $\mu g/cm^2$, and the 12.4 $\mu g/cm^2$ standard had a mean of 12.130 $\mu g/cm^2$ and a standard deviation of .425.

9. References

9.1 Tracor Northern Operators Manual "Tracor X-ray Spectrace 5000 Operators Manual".

9.2 Columbia Scientific "Spectrace Operating Manual".

9.3 Dzubay, T.G., "X-ray Fluorescence Analysis of Environmental Samples" Ann Arbor Science, 1978.

MULTI ELEMENTS

(X-ray Fluorescence)

1. Introduction

1.1 X-ray fluorescence (XRF) can be used to analyze sodium and elements having a higher atomic number. The elements that occur on particulate filters at measurable concentration are Al, Si, Ca, Zn, S, Pb, Cl, Cu, Fe, Br and K. A second group of elements, which are toxic to the environment, such as Ni, Co, Mn, Cr, Mo, Ti, Se, As, Br, Sb, V, Cd, and Pb, can be measured when they are present in sufficient concentration. XRF is a technique that lends itself to the environmental concerns of monitoring particulate deposition in response to such questions as acidic deposition or toxic element distribution in the environment.

2. Principle

2.1 X-rays refer to that band of radiation between visible light and gamma rays. In X-ray fluorescence, the X-rays are generated by means of electrons impinging on a metal target. This process generates several different types of X-ray radiation. The more important are ejection of inner shell electrons and the generation of X-rays characteristic of that element, and bremstrahlung radiation produced by the deceleration of an electron (bending of its path) as it passes close to the electromagnetic field of electrons and nuclei of the target. In XRF, this fluorescent radiation is then collimated onto the sample, in turn generating X-ray photons. The photons from the sample are then quantified by means of a multi-channel analyzer that uses a lithium-drifted silicon detector held at liquid nitrogen temperature.

2.2 The characteristic radiation emitted by the sample is caused by the exciting radiation removing inner-shell electrons. These inner-shell vacancies are then filled by the outer-shell electrons, which collapse causing the emission of an X-ray photon characteristic of the transition. These photons are unique to that element and can be used to identify it. Because of the inner-shell nature of the transition, no information regarding the valence state or types of compounds that the element is bound in is available.

2.3 The spectra produced is a histogram of intensity (# of counts in each channel) versus the energy of each channel. With the 1012 channel in the multi-channel analyzer, the resolution of a 0 to 20 KeV spectrum is 20 eV per channel. The elemental concentrations are determined by a comparative procedure in which pure element standards are analyzed

and the number of counts produced within a region of interest for the standard are ratioed to those produced for the sample. The process is complicated by the spectral background and instrument noise produced during the analysis. The calculations are carried out on a computer program (XML) which uses digital filtering to remove instrument noise and background continuum and a least-squares minimization to assume the best-fit ratios. The elemental concentration is then converted from micrograms per square centimetre of filter to micrograms per cubic metre of air by dividing the total micrograms per filter by the total volume of air sampled.

3. Apparatus

3.1 High-volume air sampler (Haskin Scientific Ltd.), chart paper, etc.

3.2 Cellulose filter paper, 20 x 25 cm (Whatman 41, or equivalent).

3.3 Circular metal punch, 47 mm diameter.

3.4 Energy-dispersive X-ray fluorescent spectrometer equipped with a silver X-ray tube and an ASI 386 IBM computer linked to a United Scientific Spectra 440.

3.5 X-ray standards: thin-film standards are on cellulose or nucleopore filters supplied by Columbia Scientific Ltd., and Micromatter Inc.

4. Procedure

4.1 Sampling

4.1.1 Dry the sample in a desiccator for 24 hours.

4.1.2 Weigh the filter and record the weight on a data sheet.

4.1.3 Place the filter on a high-volume sampler. Fix a flow chart for recording air flow and sampling time. Set the timer for 24 hours' sampling.

4.2 Analysis

4.2.1 Read the average flow rate and record the time of sampling from the flow chart and record the data on the data sheet.

4.2.2 Dry the filter in a desiccator for 24 hours.

4.2.3 Weigh the filter and record the final weight in grams.

4.2.4 Fold the filter so that the exposed sides are together, cut two sets of 47 mm diameter discs.

4.2.5 Cut two sets of discs from the blank filter paper of the same batch.

4.2.6 Analyze the discs by XRF using appropriate duplicates and standards in accordance with the quality control program.

NOTE: The precision and accuracy of the method depends on the type of samples. When it is decided to look only at a single element, an excitation voltage a few KeV above the element line is the most efficient. The minimum detection within a 95% confidence level corresponds to the concentration equal to three times the standard deviation of the background noise.
Good quantitative analysis depends on good sample preparation; the requirement being flat uniform size and reproducible placement in the sample chamber.

5. Calculations

5.1 Standards are run and stored as reference peaks in the computer program XML (super multiple least squares). These reference standards are then ratioed, by means of XML, to the peaks present in the samples. This ratio is called the K ratio.

$$\text{conc. in the sample} = K \times \text{conc. of the standard}$$

5.2 As the reference standards are expressed in $\mu g/cm^2$, the determined sample concentration is in $\mu g/cm^2$.

5.3 To convert this to µg/sample multiply by the area of the filter (area of the filter: 433 cm^2). To determine the ambient concentration in $\mu g/m^3$ of air, divide µg/sample by the total volume of air. To determine the variance of a given analysis, the formula is;

$$\sigma\% = \frac{N_a + N_b \times 100}{N_p}$$

where $\sigma\%$ = the variance
N_a = the total number of counts (gross)
N_b = background counts
N_p = no. of counts in the peak

The detection limit (which is an arbitrary defined term) is 2 times the background noise, in this case (95% confidence level).

M.D.L. (minimum detection limit) = 3 times std. dev.

* For more detailed understanding of the calculations, see NBS Special Publication No. 604, page 273, "Least-Squares Fit With Digital Filter" by Jan J. McCarthy and Frederick H. Schamber; and page 193, "Curve Fitting Techniques and Their Applications to the Analysis of Energy Dispersive Spectra" by Frederick H. Schamber.

6. References

6.1 United Scientific - Spectra Operating Manual.

6.2 Tracor Northern Operators Manual "Tracor X-ray Spectrace 5000 Operators Manual".

6.3 Jenkins, Ron A; "Introduction to X-ray Spectrometry", Heydon and Sons Ltd. 1976.

6.4 Price, James H., et al; "Cost Effective Measurement of Elemental Concentrations of Aerosols in Texas by X-ray Fluorescence Analysis", 75th Annual Meeting of the Air Pollution Control Association, June 1982.

NITRATE

(Ion Chromatography)

1. Introduction

1.1 Nitrate in airborne suspended particulate matter is present mainly as nitric acid aerosol, or as ammonium nitrate originating from nitric acid and fertilizer plants and from the application of fertilizer. In addition, nitrate is formed by the oxidation of atmospheric nitric oxides which are emitted from automobiles, power plants and various chemical plants.

2. Principle

2.1 Using a high-volume sampler, particulate matter is collected on a Teflon filter reinforced with glass fibre. A portion of the filter is extracted with hot water ultrasonically and the nitrate is determined by ion chromatography.

3. Scope

3.1 The detection limit is 0.01 µg NO_3/m^3 of air, using a 55 µL loop.

4. Interference

4.1 High levels of bromide and sulphate and some organic acids may interfere.

5. Apparatus

5.1 High-volume sampler (Haskin Scientific Ltd., Montreal, or equivalent).
5.2 Flow-chart paper and ink.
5.3 Analytical balance, sensitivity of 0.1 mg.
5.4 Teflon filter reinforced with glass fibre, 20 x 25 cm (Pallflex TM, or equivalent).
5.5 Circular metal punch, 46 mm diameter.
5.6 Dionex model 16 ion chromatograph equipped with:
5.6.1 Spectraphysics 4100 computing integrator
5.6.2 55 µL sample loop
5.6.3 AG3-Anion guard #30986

5.6.4 AS3-Anion Separator #30985

5.6.5 AFS-Anion Fibre Suppressor #35350

6. Reagents

6.1 Regeneration solution (0.025N H_2SO_4): dilute 2.8 mL of conc. H_2SO_4 to 4 litres with distilled water.

6.2 Stock nitrate solution (1000 mg/L NO_3): dissolve 1.3707 g of $NaNO_3$, dried at 105°C for 2 hours, in distilled water and dilute to 1000 mL.

6.3 Working standards - prepare as follows:

mL stock/1000 mL	conc. mg/L NO_3
0.5	0.5
1.0	1.0
2.0	2.0
10.0	10.0
20.0	20.0

6.4 Standard anion eluent (0.003M $NaHCO_3$, 0.0024M Na_2CO_3): dissolve 1.0080g $NaHCO_3$ and 1.0176g Na_2CO_3 in 4 litres of distilled water.

6.5 High-purity distilled water.

7. Procedure

7.1 Sampling

7.1.1 Condition the filter overnight at room temperature and 40% humidity, or dry it in a desiccator for 24 hours.

7.1.2 Weigh the filter and record the weight on a data sheet.

7.1.3 Place the filter on a high-volume sampler. Fix a flow chart for recording air flow and sampling time. Set the timer for 24 hours' sampling.

7.2 Analysis

7.2.1 Read the average flow rate and the time of sampling from the flow chart and record these data on the data sheet.

7.2.2 Dry the filter at room temperature and 40% humidity, or dry it in a desiccator for 24 hours.

7.2.3 Weigh the filter and record the final weight in grams

7.2.4 Cut 2 discs (8%) from the exposed and unexposed filter. Place the discs into a 120 mL screw cap vial containing 50 mL distilled water. Extract the sample

and the blank ultrasonically on a hot plate at 50°C for 10 minutes. Cool to room temperature.

7.2.5 Inject the sample, using a 55 µL loop.

7.2.6 Run duplicates and spiked samples in accordance with the quality control program.

7.2.7 IC Conditions:

Eluent:	0.003M $NaHCO_3$/0.0024M Na_2CO_3
Flow Rate:	152 mL/hr
Conductivity Meter Setting:	10 µMHO full scale
Injection Volume:	55 µL
Recorder Speed:	30 cm/hr

8. Calculation

8.1 Quantitative results are obtained by the method of external standards, using peak heights. The results are read directly from the SP4100 computing integrator in terms of mg/L NO_3.

8.2 Calculate the total volume of air in m^3 from the flow rate and sampling time.

8.3 Determine the weight of total suspended particulate matter collected on the Teflon filter. Calculate the nitrate as:

$$mg\ NO_3 = \frac{mg/L\ NO_3 \times total\ sample\ volume\ in\ mL}{1000}$$

The final result is expressed as

$$\mu g\ NO_3/m^3 = \frac{W \times 12.5 \times 10^3}{V}$$

and/or as

$$mg/g\ NO_3\ in\ total\ suspended\ particulate\ matter = \frac{W \times 12.5}{W_1}$$

where

W	=	mg NO_3 in 8% of the filter.
W_1	=	weight of the total particulate matter in grams.
(12.5	=	conversion factor to change 8% of the filter to 100%.)
V	=	volume of air in m^3 (F x T).

where

F = average flow rate in m^3/min.

T = sampling time in minutes.

(0.0283 = conversion factor to change ft^3 to m^3, if necessary).

9. Precision and Accuracy

9.1 In a single laboratory (Alberta Environmental Centre), using high-volume air samples, the coefficients of variation were 2-4% for samples in the concentration range of 0.18 to 5.34 mg/L NO_3.

9.2 In a single laboratory (Alberta Environmental Centre), using high-volume air samples, the recoveries were 96-105% for samples in the concentration range of 0.74 to 8.30 mg/L NO_3.

10. Reference

10.1 "Analysis of Nitrate and Sulphate Collected on Air Filters" by Dionex Corporation; Application Note 2 (Revised 5/78).

ORGANICS, CYCLOHEXANE SOLUBLE

(Extraction/Gravimetric)

1. Introduction

1.1 Organics in ambient air originate mainly from automobile exhaust, the burning of coal and oil, and from petrochemical plants. A nonpolar solvent like benzene or cyclohexane is required to extract and separate organic compounds from the inorganic ones in the suspended particulate matter. Cyclohexane is preferred to benzene because it is less toxic.

2. Principle

2.1 A high-volume air sampler is used to collect airborne particulate matter on a glass fibre filter. A portion of the exposed filter is extracted with cyclohexane in a Soxhlet apparatus for six hours. The extract is filtered through a sintered crucible into a preweighed evaporating flask and the solvent is removed in a flash evaporator at 40°C. The flask is reweighed. The difference in weight is due to cyclohexane soluble organics.

3. Scope

3.1 The method is capable of measuring a part of the total airborne organics, those that are soluble in cyclohexane. The detection limit is 1 $\mu g/m^3$ of air.

4. Interference

4.1 No known interferences.

5. Apparatus

5.1 High-volume sampler (Haskin Scientific Ltd., Montreal, or equivalent).
5.2 Flow-chart paper and ink.
5.3 Glass fibre filter, 20 x 25 cm (Gelman Type A, or equivalent).
5.4 Analytical balance, sensitivity of 0.1 mg.
5.5 Circular metal punch, 46 mm diameter.
5.6 Soxhlet apparatus.
5.7 Flash evaporator.

6. Reagents

6.1 Activated charcoal.

6.2 Cyclohexane: spectrograde or a good technical grade. Technical-grade cyclohexane must be purified by passing it through a column of activated charcoal (column length 45 cm and diameter 5 cm) at the rate of 1 litre per hour.

7. Procedure

7.1 Sampling

7.1.1 Condition the filter overnight at room temperature and 40% humidity, or dry it in a desiccator for 24 hours.

7.1.2 Weigh the filter and record the weight on a data sheet.

7.1.3 Place the filter on a high-volume sampler. Fix a flow chart for recording air flow and sampling time. Set the timing for 24 hours' sampling.

7.2 Analysis

7.2.1 Read the average flow rate and the time of sampling from the flow chart and record these data on the data sheet.

7.2.2 Dry the filter at room temperature and 40% humidity, or dry it in a desiccator for 24 hours.

7.2.3 Weigh the filter and record the final weight in grams.

7.2.4 Cut 5 discs (20%) from the filter with a metal punch.

7.2.5 Extract for six hours in a Soxhlet apparatus, using 75-80 mL of pure cyclohexane.

7.2.6 Allow the flask to cool for 15 minutes and filter the extract while warm by vacuum through a sintered glass funnel (avoid using a rubber stopper). Rinse the flask and the funnel with 5-10 mL ether.

7.2.7 Transfer the extract to a preweighed clean flask and remove the solvent in a flash evaporator at 40°C.

7.2.8 After the complete evaporation of the solvent, weigh the flask to obtain the weight of the cyclohexane-soluble organics.

8. Calculation

8.1 Calculate the total volume of air in m^3 from the flow rate and sampling time.

8.2 Determine the weight of total suspended particulate matter in grams collected on the glass fibre filter.

8.3 Calculate the cyclohexane soluble organics as

$$\mu g/m^3 = \frac{W \times 5 \times 10^3}{V}$$

$$\text{and/or as } mg/gm \text{ of total suspended particulate matter} = \frac{W \times 5}{W_1}$$

where

W = weight of cyclohexane soluble organic in 20% of the filter in milligrams.

W_1 = weight of the total particulate matter in grams.

5 = conversion factor to change 20% of the filter to 100%.

V = volume of air in m^3 = (F x T).

where

F = average flow rate in m^3/min.

T = sampling time in minutes.

(0.0283 = conversion factor to change ft^3 to m^3, if necessary).

9. Reference

9.1 J.L. Monkman, et al., International J. of Environ. Anal. Chem., Vol. 2, 1972, p. 63.

PARTICULATE MATTER, TOTAL SUSPENDED

(Gravimetric)

1. Introduction

1.1 Suspended particulate matter consists of inorganic and organic compounds that range in size from 0.01 μ to about 100 μ. They originate from car exhaust, the burning of coal and refuse and from various industrial activities.

2. Principle

2.1 Measured volumes of air are drawn through a previously dried and weighed Teflon filter. A high-volume sampler is used for this purpose. The filter is a 20 x 25 cm Teflon sheet reinforced with glass fibre which is supported on a metallic screen in the sampler. The flow rate is generally between 1.1 - 1.7 m^3/min (40-60 cfm). After the sampling period of 24 hours, the filter is dried at room temperature and weighed. The weight of suspended particulate matter is expressed as micrograms per m^3 of air.

3. Scope

3.1 The method is applicable for the measurement of solid and liquid particulates. The detection limit is 1 μg/m^3 of air.

4. Interference

4.1 No known interferences.

5. Apparatus

5.1 High-volume sampler (Haskin Scientific Ltd., Montreal, or equivalent).
5.2 Flow-chart paper and ink.
5.3 Analytical balance, sensitivity of 0.1 mg.
5.4 Teflon filter reinforced with glass fibre 20 x 25 cm (Pallflex, TM).

6. Reagents

6.1 No reagents are required.

7. Procedure

7.1 Sampling

7.1.1 Condition the filter overnight at room temperature and 40% humidity, or dry it in a desiccator for 24 hours.

7.1.2 Weigh the filter and record the weight on a data sheet.

7.1.3 Place the filter on a high-volume sampler. Fix a flow chart for recording air flow and sampling time. Set the timer for 24 hours' sampling.

7.2 Analysis

7.2.1 Read the average flow rate and the time of sampling from the flow chart and record these data on the data sheet.

7.2.2 Dry the filter at room temperature and 40% humidity, or dry it in a desiccator for 24 hours.

7.2.3 Weigh the filter and record the final weight in grams.

8. Calculation

8.1 Calculate the total volume of air in m^3 from the flow rate and the sampling time.

8.2 Determine the weight of total suspended particulate matter in grams collected on the filter.

8.3 Calculate the concentration of suspended particulate matter as

$$\mu g/m^3 = \frac{(W_2 - W_1) \times 10^6}{V}$$

where

W_2 = final weight of the filter in grams.

W_1 = initial weight of the filter in grams.

(10^6 = conversion factor to change grams to micrograms.)

V = volume of air sample in m^3 = (F x T).

where

F = average flow rate in m^3/min.

T = sampling time in minutes.

(0.0283 = conversion factor to change ft^3 to m^3, if necessary).

9. References

9.1 J.L. Monkman, et al., International J. of Environ. Anal. Chem., Vol. 2, 1972, p. 63.

9.2 Methods of Air Sampling and Analysis. APHA Intersociety Committee. M. Katz, Editor; 2nd Edition, p. 578.

POLYCYCLIC AROMATIC HYDROCARBONS
(HPLC)

1. Introduction

1.1 Polycyclic Aromatic Hydrocarbons (PAHs) are found in oil and coal-based products, and are produced by incomplete combustion and pyrolysis of fossil fuels and organic material.

2. Principle

2.1 Air particulates are collected on a Pallflex filter using a high-volume sampler. PAHs are extracted in a Soxhlet apparatus using cyclohexane. The cyclohexane is removed under vacuum and the sample is made up in methanol. The PAHs are separated on a reverse-phase column and monitored by fluorescence detection.

3. Scope

3.1 The scope of this method at present is qualitative.

4. Apparatus

4.1 High-volume sampler (Haskin Scientific Ltd., Montreal, or equivalent).
4.2 Flow-chart paper and ink.
4.3 Teflon filter reinforced with glass fibre, 20 x 25 cm (Pallflex TM, or equivalent).
4.4 Analytical balance, sensitivity of 0.1 mg.
4.5 Circular metal punch, 46 mm diameter.
4.6 Soxhlet apparatus.
4.7 Stirrer, hotplate combination (Thermolyne type 1000, or equivalent).
4.8 Flash evaporator.
4.9 High performance liquid chromatographic pump (Spectra Physics SP 8700, or equivalent).
4.10 Reverse phase liquid chromatograph column (Supelco LC PAH, 5 micron, 25cm x 4.6mm 1.0 and Whatman precolumn, or equivalent).
4.11 Fluorescence spectrophotometer equipped with flow cell (Perkin-Elmer 650-10S, or equivalent).
4.12 Recorder integrator (Hewlett Packard 3380, or equivalent).
4.13 Auto sampler (Perkin-Elmer LC420, 42 sample tray, or equivalent).

4.14 Lambda pipets, 100 ml to 1000 µL.

4.15 Hand crimper.

4.16 Auto sampler vials, amber.

4.17 Syringe filters, 0.45 µm, Millipore SJHV004NS, or equivalent.

5. Reagents

5.1 Cyclohexane, HPLC grade

5.2 Methanol, HPLC grade

5.3 Acetonitrile, HPLC grade

5.4 Helium, zero grade

5.5 PAH stock standards (200 µg/mL), purchased.

5.6 PAH standard solution (4 µg/mL), made by diluting 1 mL of 200 µg/mL stock standard in a 50 mL volumetric flask with methanol.

5.7 PAH working standard solution (0.7 ppm), made by diluting 0.35 mL of 4 µg/mL standard solution in a 2 mL volumetric flask with methanol.

6. Procedure

6.1 Sampling

6.1.1 Condition the filter overnight at room temperature and 40% humidity, or dry it in a desiccator for 24 hours.

6.1.2 Weigh the filter and record the weight on a data sheet.

6.1.3 Place the filter on a calibrated high volume sampler. Fix a flow chart for recording air flow and sampling time. Set the timer for 24 hours' sampling.

6.2 Analysis

6.2.1 Condition the filter before weighing.

6.2.2 Cut four discs (16%) from the filter with the 46 mm metal punch.

6.2.3 Extract for six hours in a Soxhlet apparatus using 110 mL of HPLC grade cyclohexane.

6.2.4 Allow flask to cool and remove solvent in a flash evaporator at 35°C. Do not take to dryness.

6.2.5 Evaporate any residual cyclohexane by blowing zero-grade helium into the flask.

6.2.6 Rinse flask with 1500 µL of methanol.

6.2.7 Transfer the clear sample with a disposable pasteur pipet into a disposable 3 mL syringe equipped with a filter. Cap the vial with a metal cap fitted with a Teflon septum. Use a hand crimper for capping the vial.

6.2.8 Turn the instrument on, following manufacturer's instructions, and allow 30 minutes to warm up.

6.2.9 Set instrument conditions as described and allow helium degassed solvents to pump through the column for one hour.

6.2.10 Set up the sample tray in the following repeating order set:

Calibration Standard
Blank
Standard 1
Standard 2
9 Samples
Duplicate or Spike

6.2.11 Inject sample using an automatic injector with a 10 µL loop.

NOTE: Routine quality control must be followed to ensure the precision and accuracy of the method. With every series of ten extractions, one sample should be analyzed in duplicate or be spiked with 150µg of BaP. This will enable the technician to detect any changes occurring within the total analysis. A blank and two standards should be run at a minimal interval of nine samples to ensure reproducibility of standard areas. If these practices are followed, the method should fall easily within the tolerances quoted for accuracy and precision.

7. Instrumental Conditions

7.1 For the analysis of Indeno (1,2,3-cd) pyrene (Diagram 1)

7.1.1 High performance liquid chromatograph

Column temperature: 32.5°C.
Solvent A: Acetonitrile, 1 mL/min.

7.1.2 Fluorescence Spectrophotometer

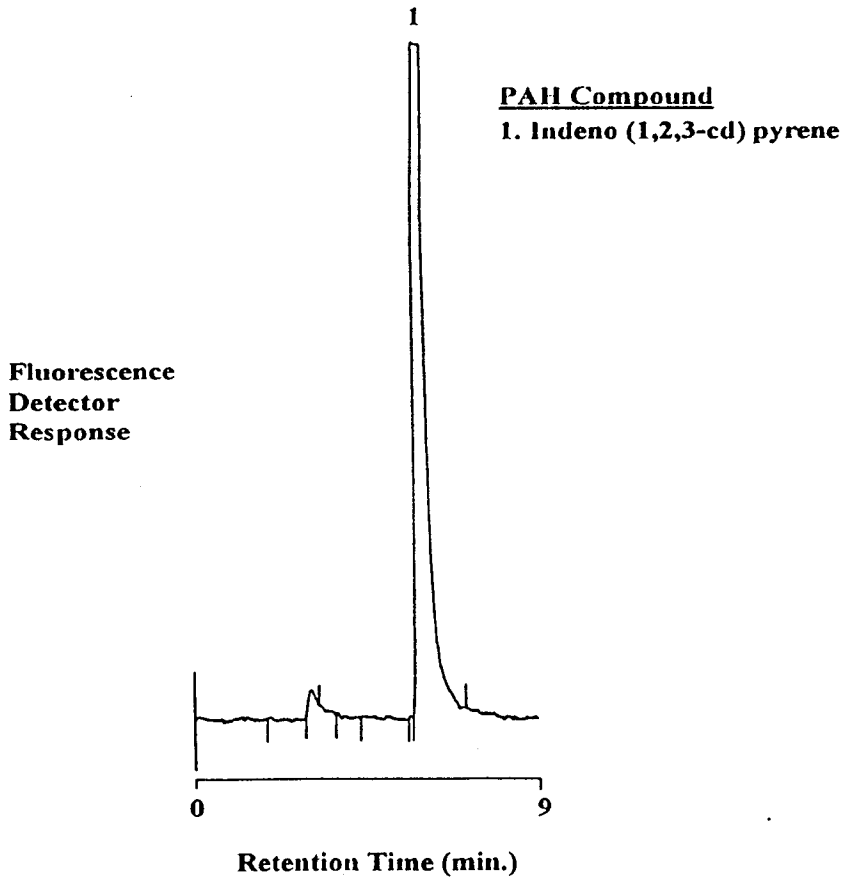
PM Gain:	Normal
Sensitivity Range:	0.3
Sensitivity Fine:	Full
Shutter:	Open
Excitation Slit:	11nm
Emission Slit:	11nm

Excitation λ:	305
Emission λ:	500
Response:	Slow
Zero Suppression:	OFF
Mode:	Normal

7.1.3 Integrator

Start Delay:	OFF
Stop Time for Integrator:	15 min
Auto Sampler Interval:	18 min
Chart Speed:	0.5 cc/min
Chart:	Auto
Slope Sensitivity:	0.1 mV/min
Attenuation:	1
Area Reject:	OFF

Figure 1. HPLC Chromatogram of a PAH Standard



7.2 For the analysis of:

- Anthracene
- Fluoranthene
- Benz (a) anthracene
- Chrysene
- Benzo (b) fluoranthene
- Benzo (k) fluoranthene
- Benzo (a) pyrene
- Dibenz (a,h) anthracene
- Benz (ghi) perylene

7.2.1 High performance liquid chromatograph

Column Temperature:	32.5°C
Solvent A:	Acetonitrile
Solvent B:	H_2O

Gradient run

Time (min)	%CH_3CN
0	76
10	76
15	100
25	100
30	76

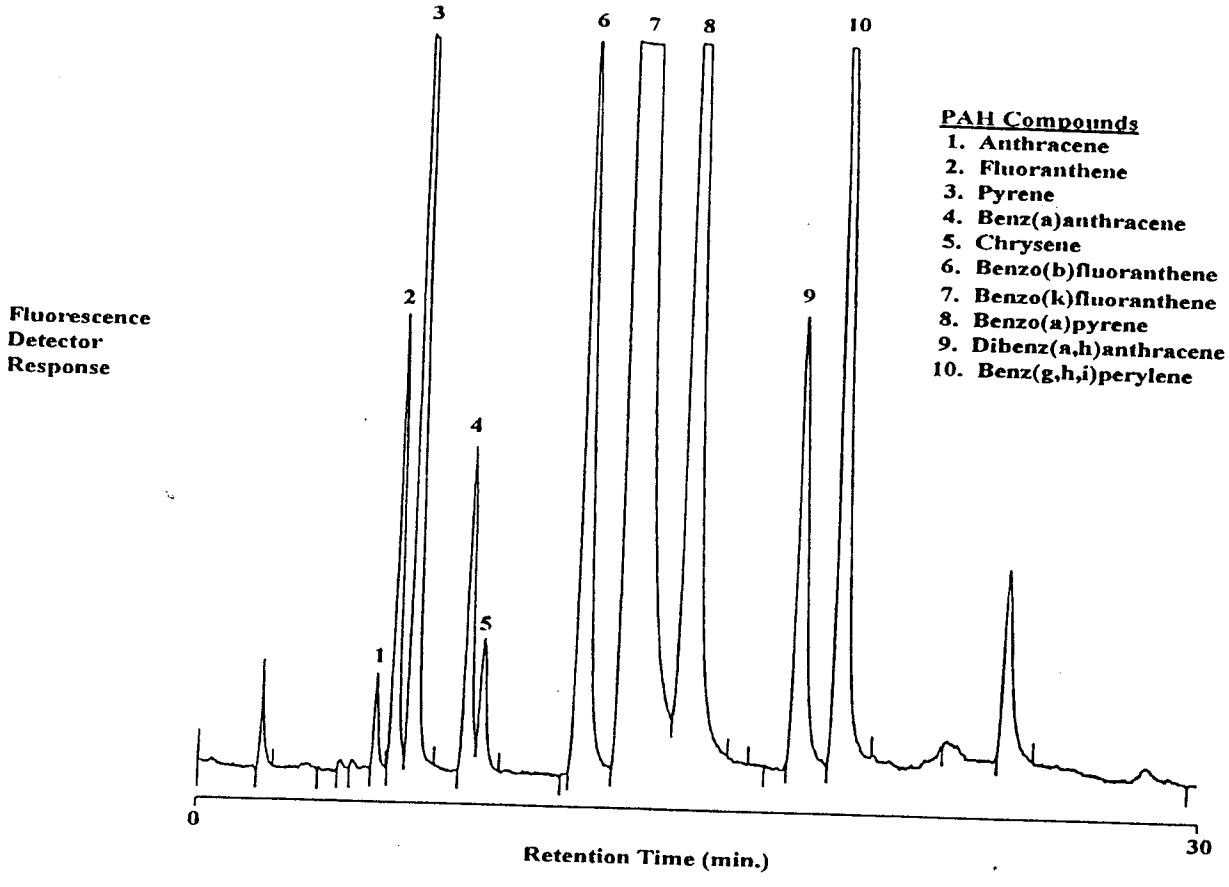
7.2.2 Fluorescence Spectrophotometer

PM Gain:	Normal
Sensitivity Range:	0.3
Sensitivity Fine:	Full
Shutter:	Open
Excitation Slit:	11nm
Emission Slit:	11nm
Excitation λ:	305
Emission λ:	430
Response:	Slow
Zero Suppression:	OFF
Mode:	Normal

7.2.3 Integrator

Start Delay:	OFF
Stop Time for Integrator:	30 min
Auto Sampler Interval:	33 min
Chart Speed:	0.5 cm/min
Chart:	Auto
Slope Sensitivity:	0.1 mV/min
Attenuation:	1
Area Reject:	OFF

Figure 2. HPLC Chromatogram of a PAH Standard



7.3 For the analysis of: Napthalene (Diagram 3)
Acenapthene/Acenapthylene
Fluorene
Phenanthrene

7.3.1 High Performance Liquid Chromatograph

Column Temperature:	32.5°C	
Solvent A:	Acetonitrile	45%
Solvent B:	H_2O	55%

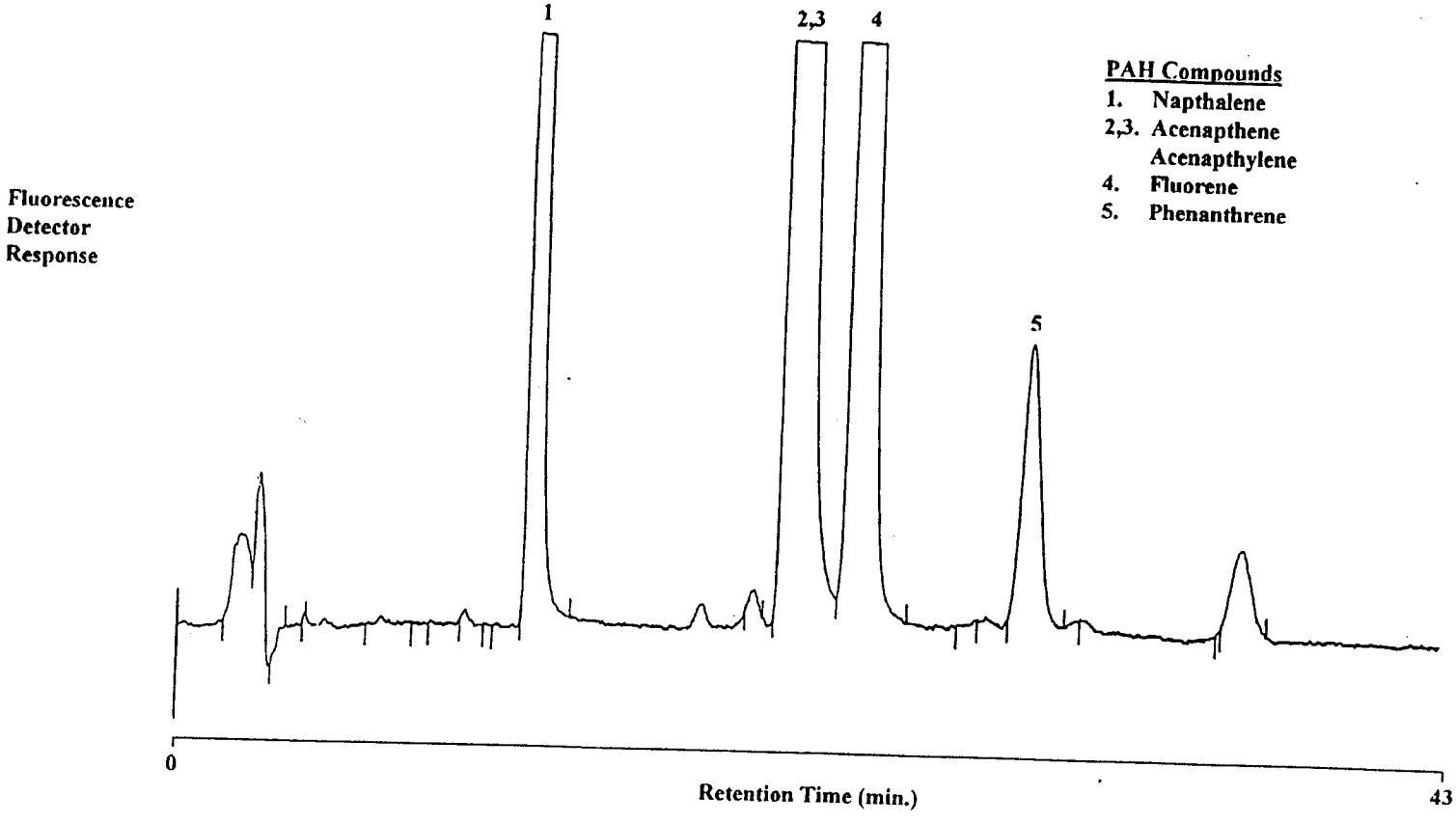
7.3.2 Fluorescence Spectrophotometer

PM Gain:	Normal
Sensitivity Range:	0.3
Sensitivity Fine:	Full
Shutter:	Open
Excitation Slit:	11nm
Emission Slit:	11nm
Excitation λ:	280
Emission λ:	340
Response:	Slow
Zero Suppression:	OFF
Mode:	Normal

7.3.3 Integrator

Start Delay:	OFF
Stop Time for Integrator:	40 min
Auto Sampler Internal:	43 min
Chart Speed:	0.5 cm/min
Chart:	Auto
Slope Sensitivity:	0.1 mV/min
Attenuation:	1
Area Reject:	OFF

Figure 3. HPLC Chromatogram of a PAH Standard



8. Calculation

8.1 Calculate the amount of each PAH in the extracted sample in nanograms

$$PAH(ng) = \frac{A \times B \times 1500}{C \times D}$$

where A = area of sample peak
B = amount of standard injected in nanograms
C = volume of sample injected in microlitres
D = area of standard peak
1500µL = sample volume

The concentration of sample is expressed as µg of PAH in a gram of particulate, or as µg per 1000 m^3 of air. Since the extracted sample represents only 16% of the total, a factor of 6.25 is employed to express the total concentration.

$$\mu g\ PAH/gm\ of\ particulate = \frac{PAH\ ng \times 6.25}{E \times 1000}$$

$$\mu g\ PAH/1000\ m^3\ of\ air = \frac{PAH\ ng \times 6.25 \times 1000}{Total\ m^3\ of\ air \times 1000}$$

where E = gm of particulate deposited on the filter
(1000 = to convert ng to µg)

9. References

9.1 May, W.E. and Wise, S.A., Anal. Chem., 56, 225 (1984).
9.2 Kline, W.F., Wise, S.A., and May, W.E., J. Liq. Chrom., 8, 222 (1985).
9.3 Ogan, K., Katz, E., and Slavin, W., Anal. Chem., 51, 1315 (1979).

September 1992 Method No. 26060

SULPHATE

(Ion Chromatography)

1. Introduction

1.1 The sources of sulphate in suspended particulate matter are numerous. It is formed mainly by the oxidation of atmospheric sulphur dioxide and hydrogen sulphide, which in turn originate from the burning of sulphur-containing fuels, such as coal and gasoline, and from the sulphur-recovery process of sour gas plants. Another major source of sulphates is the emissions from cement and fertilizer plants.

2. Principle

2.1 Using a high-volume sampler, particulate matter is collected on a Teflon filter reinforced with glass fibre. A portion of the filter is extracted with hot water ultrasonically and the sulphate is determined by ion chromatography.

3. Scope

3.1 The range is 0.05 µg SO_4/m^3 of air, using a 55 µL loop.

4. Interference

4.1 Bisulphate will interfere, if it is present in the sample.

5. Apparatus

5.1 High-volume sampler (Haskin Scientific Ltd., Montreal, or equivalent).
5.2 Flow-chart paper and ink.
5.3 Analytical balance, sensitivity of 0.1 mg.
5.4 Teflon filter reinforced with glass fibre, 20 x 25 cm (Pallflex TM, or equivalent).
5.5 Circular metal punch, 46 mm diameter.
5.6 Dionex model 16 ion chromatograph equipped with:
  5.6.1 Spectraphysics 4100 computing integrator.
  5.6.2 55 µL sample loop.
  5.6.3 AG3-Anion Guard #30986.

5.6.4 AS3-Anion Separator #30985.

5.6.5 AFS-Anion Fibre Suppressor #35350.

6. Reagents

6.1 Standard anion eluent (0.003M $NaHCO_3$, 0.0024M Na_2CO_3): dissolve 1.0080g $NaHCO_3$ and 1.0176g Na_2CO_3 in 4 litres of distilled water.

6.2 Stock sulphate solution (1000 mg/L SO_4): dissolve 1.8142g of anhydrous potassium sulphate with distilled water in a 1000 mL volumetric flask and dilute to volume.

6.3 Working standards - prepare as follows:

mL stock/1000 mL	conc. mg/L SO_4
1.0	1.0
5.0	5.0
10.0	10.0
20.0	20.0

7. Procedure

7.1 Sampling

7.1.1 Condition the filter overnight at room temperature and 40% humidity, or dry it in a desiccator for 24 hours.

7.1.2 Weigh the filter and record the weight on a data sheet.

7.1.3 Place the filter on a high-volume sampler. Fix a flow chart for recording air flow and sampling time. Set the timer for 24 hours' sampling.

7.2 Analysis

7.2.1 Read the average flow rate and the time of sampling from the flow chart and record these data on the data sheet.

7.2.2 Dry the filter at room temperature and 40% humidity, or dry it in a desiccator for 24 hours.

7.2.3 Weigh the filter and record the final weight in grams.

7.2.4 Cut two discs (8%) from the exposed and unexposed filter. Place them into 120 mL screw cap containers containing 50 mL distilled water. Extract the sample and the blank ultrasonically on a hot plate at 50°C for 10 minutes. Cool to room temperature.

7.2.5 Inject the sample, using a 55 µL loop.

7.2.6 Run duplicates and spiked samples in accordance with the quality control program.

7.2.7 IC Condition:

Eluent:	0.003M $NaHCO_3$/0.0024M Na_2CO_3
Flow Rate:	152 mL/hr
Conductivity meter setting:	10 µ MHO full scale
Injection volume:	55 µL
Recorder speed:	30 cm/hr

8. Calculation

8.1 Quantification is done by the method of external standards using peak heights. The results are read directly from the SP4100 integrator in terms of mg/L SO_4.

8.2 Calculate the total volume of air in m^3 from the flow rate and sampling time.

8.3 Determine the weight of total suspended particulate matter collected on the filter. Calculate the sulphate as

$$mg\ SO_4 = \frac{mg/L\ SO_4 \times total\ sample\ volume\ in\ mL}{1000}$$

The final result is expressed as

$$\mu g\ SO_4/m^3 = \frac{W \times 12.5 \times 10^3}{V}$$

and/or as

$$mg/g\ SO_4\ in\ total\ suspended\ particulate\ matter = \frac{W \times 12.5}{W_1}$$

where

W	=	mg SO_4 in 8% of the filter.
W_1	=	weight of the total particulates in grams.
(12.5	=	conversion factor to change 8% of the filter to 100%.)

V = volume of air in m^3 = (F x T).

where

F = average flow rate in m^3/min.

T = sampling time in minutes.

(0.0283 = conversion factor to change ft^3 to m^3, if necessary).

9. Precision and Accuracy

9.1 In a single laboratory (Alberta Environmental Centre), using high-volume filter samples, the coefficients of variation were 2 - 4% for samples in the concentration range of 1.56 to 27.59 mg/L SO_4.

9.2 In a single laboratory (Alberta Environmental Centre), using high-volume air samples, the recoveries were 98 - 110% for samples in the concentration range of 1.26 to 8.80 mg/L SO_4.

10. Reference

10.1 "Analysis of Nitrate and Sulphate Collected on Air Filters" by Dionex Corporation; Application Note 2 (Revised 5/78).

CALCIUM, TOTAL AND WATER SOLUBLE

(DCP)

1. Introduction

1.1 Dustfall contains a significant amount of calcium compounds, such as limestone ($CaCO_3$) and gypsum ($CaSO_4$).

2. Principle

2.1 The dust sample is digested with 5% HNO_3/15% HCl, and is determined by DCP.

3. Scope

3.1 The detection limit for calcium by this procedure is 0.01 mg/L as $CaCO_3$ in the test solution.

4. Interference

4.1 Most polyvalent cations interfere to some degree. In normal dustfall, however, they are present in insignificant concentrations in comparison to calcium. Thus, they do not affect the test.

5. Apparatus

5.1 Plastic dustfall collector, 20 cm high and 10 cm in diameter (equivalent to 1.5L Frig-O-Seal juice server).
5.2 Sieve, 20 mesh size.
5.3 Lindberg hotplate, 12" x 30".
5.4 Magnetic stir plate and Teflon-coated stir bar.
5.5 Beckman Spectraspan V DCP.

6. Reagents

6.1 Algicide - $CuSO_4$.
6.2 Isopropanol

6.3 5%HNO_3/15% HCl: Add 50 mL of concentrated HNO_3 and 150 mL of concentrated HCl to 500 mL of distilled water and make up to 1 litre with distilled water.

6.4 Stock calcium standard solution (1000 mg/L Ca): add 2.4973 g $CaCO_3$, oven dried at 105°C overnight, to approximately 100 mL of distilled water and then add 50 mL of concentrated HNO_3 to dissolve. Then add 150 mL concentrated HCl, cool to room temperature and dilute to 1 litre with distilled water.

6.5 Working calcium standards: dilute the following aliquots of stock calcium standard to 500 mL with 5% HNO_3/15% HCl solution.

mL Stock/500 mL	Conc mg/L Ca
25 mL of 1000 mg/L Ca	100.0
5 mL of 1000 mg/L Ca	20.0
50 mL of 100 mg/L Ca	10.0

6.6 Quality control stock calcium solution (1000 mg/L Ca): using $CaCO_3$, obtained from a supplier other than that used to prepare the stock calcium solution, dissolve 2.4973 g $CaCO_3$, oven dried at 105°C overnight, in 100 mL of distilled water and then add 50 mL concentrated HNO_3 to dissolve. Add 150 mL concentrated HCl, cool to room temperature, and dilute to 1 litre with distilled water.

6.7 Working Quality Control Standards: dilute the following aliquots of stock quality control standard to 250 mL with 5% HNO_3/15% HCl solution.

mL Stock/250 mL	Concentration mg/L Ca
25 mL of 1000 mg/L Ca	100.0
50 mL of 100 mg/L Ca	10.0
10 mL of 10 mg/L Ca	0.25

6.8 Blank (<0.05 mg/L Ca) - 5% HNO_3/15% HCl solution.

7. Procedure

7.1 Sampling

7.1.1 Pour 500 mL of distilled water and 5 mg of $CuSO_4$ into the dustfall collector in summer to prevent growth of algae and bacteria. Use 500 mL of 50% isopropanol in winter, usually starting about September, to prevent freezing. Expose the collector in the field for approximately 4 weeks.

7.2 Analysis

7.2.1 Acid wash all glassware used.

7.2.2 Filter the contents of the collector through a 20 mesh sieve into a 600 mL beaker. Rinse the container with distilled and deionized water using a rubber policeman and add the rinse to the filtrate.

7.2.3 Adjust the volume of the filtrate to 300 mL, or record the volume if above 300 mL.

7.2.4 Thoroughly mix the dustfall sample by using a magnetic stirrer.

7.2.5 Pipet 50 mL of the well-stirred sample, and 50 mL of distilled and deionized water as a blank into separate 250 mL beakers.

7.2.6 Add 15 mL concentrated HCl and 5 mL concentrated HNO_3 to the beakers.

7.2.7 Place beakers on a hotplate in a fumehood and set to a slow boil for 90 minutes.

7.2.8 Filter the hot sample into a 100 mL volumetric flask through a Whatman 2V filter and dilute to volume when cooled to room temperature.

7.2.9 Analyze the filtrate by DCP using the instrument conditions specified below:

Wavelength:	317.933 nm
Order:	71
State:	Ion
Plasma Position:	0
Entrance Slits:	50 x 300µm
Exit Slits:	100 x 300µm
Detection Limit (DL):	0.009 mg/L
Linear Dynamic Range (LDR):	0.09 to 100 mg/L
Background Equivalent Concentration (BEC):	0.3 mg/L
Precision:	RSD at 10 x BEC 0.9%
Mode:	Internal at 10 seconds and 3 counts
Photomultiplier Tube (PMT):	1

8. Calculations

8.1 The calcium concentration is expressed as $CaCO_3$

$$mg\ CaCO_3 = \frac{(a-b) \times c \times d \times e}{f \times 1000}$$

where a = conc. of Ca in sample (mg/L)
b = conc. of Ca in blank (mg/L)

c = Final dilution-volume after digestion (Step 8)
d = 2.5 conversion factor (Ca to $CaCO_3$)
e = Total volume of sample in mL (Step 3)
f = Aliquot of sample used in digestion (Step 5)

If the total volume is 300 mL, then the simple formula of (a-b) x 1.5 can be used. The final result is expressed as

$$mg\ CaCO_3/cm^2/day = \frac{mg\ CaCO_3 \times 30}{a \times d}$$

where a = area of the dustfall collector opening in cm^2
d = no. of days exposed

9. Precision and Accuracy

9.1 In a single laboratory (Alberta Environmental Centre) using, a 10 mg/L calcium standard over a period of twelve months, the coefficient of variation was 4.8%.

10. References

10.1 Std. Meth., 17th Ed., p. 3-85.
10.2 Handbook of Spectral Line Characteristics for the DC Plasma Echelle Systems, Spectra Metrics, Inc.

DUSTFALL, TOTAL AND FIXED

(Gravimetric)

1. Introduction

1.1 Dustfall is the settleable fraction of the total particulate matter in air. It is collected in an open jar of a specified size containing water as the collecting medium.

1.2 Total Dustfall is defined as the amount of material left after evaporation of a sample of dustfall and its subsequent drying. Total Fixed Dustfall is the residue that is left after ignition of the Total Dustfall sample. The Total Dustfall includes both suspended and dissolved matter. The loss in weight after ignition is mainly the result of organic matter combustion.

2. Principle

2.1 A well-mixed sample is evaporated in a pre-weighed platinum crucible on a water bath and then dried in an oven at 105°C for one hour. The residue is the total dustfall. The total dustfall is then ignited at 550°C for 30 minutes in order to determine the total fixed dustfall.

3. Scope

3.1 The method covers a procedure for the field collection of settleable particulate matter in ambient air and its determination. The detection limit is 10 mg/L total and/or fixed dustfall in the test solution.

4. Interference

4.1 A-20 mesh sieve is used to eliminate deposits, such as insects and bird droppings.

5. Apparatus

5.1 Dustfall collector: the dustfall collector is an open-topped plastic container with flat bottom, 10 cm in diameter and 20 cm high. A holder is to be provided to secure safe positioning of the collector in the field.

5.2 Sieve: 20-mesh size.

5.3 Nickel crucibles of 50 mL capacity.

5.4 Laboratory oven.

5.5 Muffle furnace.

5.6 Desiccator.

5.7 Analytical balance of 200 g capacity and a sensitivity of 0.1 mg.

6. Reagents

6.1 $CuSO_4$.

6.2 Isopropanol.

7. Procedure

7.1 Sampling

7.1.1 Pour 500 mL distilled water and 5 mg $CuSO_4$ in the collector in the summer. Use 500 mL of (1+1) distilled water-isopropanol in winter. Expose the collector in the field for approximately 4 weeks.

7.2 Analysis

7.2.1 Filter the contents of the collector through a 20 mesh sieve into a 600 mL beaker. Rinse the container with distilled water using a rubber policeman, and add the rinse to the filtrate.

7.2.2 Adjust the volume of the filtrate to 300 mL.

7.2.3 Ignite the nickel crucibles in a muffle furnace at 550°C for 30 minutes. If greater that 300 mL record that volume, cool in a desiccator and weigh.

7.2.4 Thoroughly mix the sample with a magnetic stirrer, and pipet 50 mL into a preweighed nickel crucible.

7.2.5 Evaporate the sample to dryness in an oven set at 105°C ± 2°C.

7.2.6 Cool in a desiccator, weigh and record the weight.

7.2.7 Ignite the crucible with the residue for 30 minutes at 550°C, cool in a desiccator, weigh and record the weight.

8. Calculation

$$\text{Total dustfall, mg} = \frac{(B - A) \times 300}{\text{vol. of sample used for evaporation}}$$

$$\text{Total fixed dustfall, mg} = \frac{(C - A) \times 300}{\text{vol. of sample used for evaporation}}$$

A = initial weight of empty nickel crucible in mg.
B = weight of nickel crucible in mg after evaporation.
C = weight of nickel crucible in mg after ignition.

$$\text{The results are expressed as mg/100 cm}^2\text{/30 days} = \frac{mg \times 100 \times 30}{a \times d}$$

where
a = area of the dustfall collector opening in cm^2.
d = no. of days exposed.

9. References

9.1 1989 Annual Book of ASTM Standards, Vol. 11.3, p. 45.
9.2 Methods of Air Sampling and Analysis. APHA Intersociety Committee. M. Katz, Editor; 2nd Edition, p. 585.

FLUORIDE, WATER SOLUBLE

(Specific-Ion Electrode)

1. Introduction

1.1 During the combustion of coal and phosphate rocks, fluorine compounds, such as hydrofluoric acid and silicon tetrafluoride are released.

1.2 In the process of industrial operations to produce phosphate fertilizer, iron and steel, glass and ceramics, fluorine compounds are set free as gaseous and/or particulate fluoride.

2. Principle

2.1 Fluoride is determined using a fluoride specific-ion electrode in conjunction with a standard calomel reference electrode. The potential developed by the presence of fluoride ions is measured by an expanded-scale pH/mV meter.

3. Scope

3.1 The range is 0.05 mg/L to 2 mg/L fluoride in the test solution.

4. Interference

4.1 Polyvalent cations such as Si, Fe and Al interfere. A buffer prevents these interferences.

5. Apparatus

5.1 Plastic dustfall collector, 20 cm high and 10 cm in diameter.

5.2 Sieve, 20 mesh size.

5.3 pH meter with expanded mV scale.

5.4 Fluoride electrode (Orion 94-09, or equivalent).

5.5 Magnetic stirrer and Teflon-coated stirring bar.

6. Reagents

6.1 Total ionic strength adjustment buffer (TISAB): add 57 mL of glacial acetic acid, 58 g of sodium chloride, and 2 g CDTA (1,2-diamino-cyclohexane-tetra acetic acid) to

approximately 500 mL of distilled water. Stir to dissolve and cool to room temperature. Adjust the pH of the solution to between 5.0 and 5.5 with 5N NaOH. Transfer the solution to a 1000 mL volumetric flask and dilute to volume with distilled water.

6.2 Stock fluoride solution (100 mg/L F): dissolve 0.221 g anhydrous sodium fluoride in distilled water and dilute to 1000 mL.

6.3 Working standards - prepare as follows.

mL stock/1000 mL	conc. mg/L F
1.0	0.10
2.5	0.25
5.0	0.50
10.0	1.00
15.0	1.50
20.0	2.00

6.4 Algicide - $CuSO_4$.

6.5 Isopropanol.

7. Procedure

7.1 Sampling

7.1.1 Pour 500 mL distilled water and 5 mg $CuSO_4$ in the dustfall collector in the summer. Use 500 mL of (1+1) water-isopropanol in the winter. Expose the collector in the field for approximately 4 weeks.

7.2 Analysis

7.2.1 Filter the contents of the collector through a 20 mesh sieve into a 600 mL beaker. Rinse the container with distilled water, using a rubber policeman, and add the rinse to the filtrate.

7.2.2 Adjust the volume of the filtrate to 300 mL.

7.2.3 To a 25 mL sample in a 100 mL beaker, add 25 mL of buffer solution, stir three minutes and record the potential when the reading is stable.

8. Calculation

8.1 Using two-cycle semi-log graph paper, prepare a calibration curve by plotting mg/L on the log scale vs the mv readings on the linear scale. A straight line should be obtained. Read the fluoride concentration from the graph in units of mg/L F.

$$mg\ F = \frac{mg/L\ F \times total\ sample\ volume\ in\ mL}{1000}$$

$$The\ final\ result\ is\ expressed\ as\ mg\ F/cm^2/30\ days = \frac{mg\ F \times 30}{a \times d}$$

where

a = area of the dustfall collector opening in cm^2.

d = no. of days exposed.

9. References

9.1 Std. Meth., 17th Ed., p. 4-87.

9.2 Methods of Air Sampling and Analysis. APHA Intersociety Committee. M. Katz, Editor; 2nd Edition, p. 417.

METALS

(Atomic Absorption)

1. Introduction

1.1 In recent years, increasing emphasis has been placed on the characterization of heavy metals in the atmosphere. The major sources of heavy metals are smelting, refining and similar industries. Automobile exhaust, coal and fuel oil burning also release some heavy metals into the atmosphere.

2. Principle

2.1 The dust sample is digested with conc. HNO_3, and is determined by atomic absorption spectrometry.

3. Scope

3.1 The detection limit for each metal is reported in the individual method description.

4. Interference

4.1 Chemical: this type of interference occurs when samples are aspirated directly into the flame and when the element is in a molecular combination.

4.2 Non-atomic absorbance: light scattering can occur in samples that have high concentrations of dissolved solids.

4.3 Ionization interference: if the flame is too hot, the neutral atoms become ionized. This interference can be controlled by the addition of an easily ionized element.

4.4 Spectral interference: if the wavelength of another element present in the sample lies close to the wavelength of interest, then the absorbances of both elements will be detected, leading to erroneously high readings.

5. Apparatus

5.1 Plastic dustfall collector, 20 cm high and 10 cm in diameter.

5.2 Sieve, 20 mesh size.

5.3 Atomic absorption spectrophotometer.

6. Glassware Handling

6.1 Soak all glassware overnight in dilute HNO_3 to prevent metal contamination.
6.2 Rinse all glassware with distilled water before using.

7. Reagents

7.1 Algicide: do not use $CuSO_4$, or any metallic salts.
7.2 Isopropanol.
7.3 Standard metal solutions: see individual method description.
7.4 Working standards: see individual method description.
7.5 Conc. HNO_3.

8. Procedure

8.1 Sampling

8.1.1 Pour 500 mL distilled water in the dustfall collector in the summer. Use 500 mL of (1+1) water-isopropanol in the winter. Expose the collector in the field for approximately 4 weeks.

8.2 Analysis

8.2.1 Transfer the contents of the collector into a 600 mL beaker. Rinse the container with distilled water, using a rubber policeman, and add the rinse to the filtrate.
8.2.2 Dilute the volume of the filtrate to 300 mL.
8.2.3 Pipet a 250 mL sample into a 400 mL beaker.
8.2.4 Add 20 mL conc. HNO_3 and evaporate to approximately 5 mL at 80°C.
8.2.5 Cool, filter through 0.45 µm membrane filter and dilute to 50 mL with deionized water in a volumetric flask.
8.2.6 Analyze by atomic absorption without any further delay. Adjust atomic absorption spectrophotometer according to setting prescribed for each individual metal.

9. Calculation

9.1 Prepare calibration curves by plotting peak height readings of the standards vs mg/L metal. Read the concentration of each metal from the respective curve in units of mg/L.

$$mg\ metal = \frac{mg/L\ metal \times total\ sample\ volume\ in\ mL}{1000 \times 5}$$

$$The\ final\ result\ is\ expressed\ as\ mg/cm^2/30\ days = \frac{mg \times 30}{a \times d}$$

where

a = area of the dustfall collector opening in cm^2.

d = no. of days exposed.

10. Reference

10.1 Std. Meth., for Water & Wastewater, 17th Ed., p 3-13.

COPPER

(Atomic Absorption)

Analytical Range:	0.10 - 2.00 mg/L
Sensitivity:	0.10 mg/L
Detection Limit:	0.05 mg/L

1. Preparation of Standard Solution

1.1 Stock copper solution (1000 mg/L Cu): weigh 1.000 g of copper metal. Dissolve in 10 mL conc. HNO_3 and dilute to 1000 mL

1.2 Standard copper solution (100 mg/L Cu): carefully pipet 100.0 mL of the stock solution into a 1000 mL volumetric flask and dilute to volume.

1.3 Working Standards - prepare as follows:

mL std. sol/1000 mL	conc. mg/L Cu*
1.0	0.10
2.5	0.25
5.0	0.50
10.0	1.00
15.0	1.50
20.0	2.00

*Working standards are stored no longer than 5 days.

2. Instrument Parameters

Wavelength:	324.7 nm
Fuel and Oxidant:	Acetylene-Air
Flame Stoichiometry:	Oxidizing

LEAD

(Atomic Absorption)

Analytical Range:	0.10 - 5.00 mg/L
Sensitivity:	0.10 mg/L
Detection limit:	0.05 mg/L

1. Preparation of Standard Solution

1.1 Stock lead solution (1000 mg/L Pb): weigh 1.599 g of lead nitrate and dissolve in distilled water. Add 10 mL conc. HNO_3 and dilute to 1000 mL.

1.2 Standard lead solution (100 mg/L Pb): pipet 100.0 mL of the stock solution into a 1000 mL volumetric flask and dilute to volume.

1.3 Working standards - prepare as follows:

mL std. sol/1000 mL	conc. mg/L Pb*
1.0	0.10
2.5	0.25
5.0	0.50
10.0	1.0
25.0	2.50
50.0	5.00

*Store working standards no longer than 5 days.

2. Instrumental Parameters

Wavelength:	217.0 nm
Fuel and Oxidant:	Acetylene-Air
Flame Stoichiometry:	Oxidizing

ZINC

(Atomic Absorption)

Analytical Range:	0.10 - 5.00 mg/L
Sensitivity:	0.10 mg/L
Detection Limit:	0.05 mg/L

1. Standards

1.1 Stock zinc solution (1000 mg/L Zn): weigh 1.000 g zinc metal and dissolve in 10 mL conc. HNO_3. Make up to 1000 mL with distilled water.

1.2 Standard zinc solution (100 mg/L Zn): pipet 100.0 mL of the stock solution into a 1000 mL volumetric flask and dilute to volume.

1.3 Working standards - prepare as follows:

mL std. sol/1000 mL	conc. mg/L Zn*
1.0	0.10
2.5	0.25
5.0	0.50
10.0	1.00
25.0	2.50
50.0	5.00

*Working standards are stored no longer than 5 days.

2. Instrumental Parameters

Wavelength:	213.9 nm
Fuel and Oxidant:	Acetylene-Air
Flame Stoichiometry:	Oxidizing

ORTHOPHOSPHATE, WATER SOLUBLE

(Ascorbic Acid, Colorimetric)

1. Introduction

1.1 Orthophosphates are present in dustfall, mainly as ammonium phosphates originating from phosphate fertilizer plants and from the application of fertilizer.

2. Principle

2.1 Orthophosphate reacts with ammonium molybdate to form heteropolymolybdophosphoric acid. The molybdophosphoric acid is reduced by ascorbic acid to a blue-coloured complex. The intensity of the blue colour is proportional to the total phosphorus content of the sample, and it is determined at 660 nm.

3. Scope

3.1 The detection limit is 0.5 mg/L PO_4 in the test solution.

4. Interference

4.1 Arsenic and mercury interfere.

5. Apparatus

5.1 Plastic dustfall collector, 20 cm high and 10 cm in diameter.
5.2 Sieve, 20 mesh size.
5.3 Acid-washed glassware: wash with hot (1+1) HCl and rinse with distilled water. Reserve glassware for phosphorus determinations only.
5.4 Spectrophotometer, 1-cm cells.

6. Reagents

6.1 Algicide - $CuSO_4$.
6.2 Isopropanol.
6.3 Sulphuric acid (5N): dilute 140 mL conc. H_2SO_4 to one litre with distilled water.

6.4 Ammonium molybdate: dissolve 40 g of $(NH_4)_6Mo_7O_{24}.4H_2O$ in distilled water and dilute to one litre. Store in a plastic bottle at 4°C.

6.5 Ascorbic acid (0.1M): dissolve 1.76 g of ascorbic acid in 100 mL distilled water. Prepare fresh.

6.6 Potassium antimonyl tartrate: dissolve 0.30 g of potassium antimonyl tartrate in distilled water and dilute to 100 mL.

6.7 Mixed reagent: mix thoroughly 125 mL of 5N H_2SO_4 and 37.5 mL of ammonium molybdate solution. Add 75 mL of ascorbic acid solution and 12.5 mL of tartrate solution. Keep this solution in a refrigerator. It is stable for a period of two weeks.

6.8 Sodium hydroxide solution (1N): dissolve 40 g NaOH in 1 litre distilled water.

6.9 Stock phosphate solution (1000 mg/L PO_4): dissolve 1.433 g KH_2PO_4 in distilled water in a 1000 mL volumetric flask and dilute to volume.

6.10 Standard phosphate solution (100 mg/L PO_4): pipet 100.0 mL stock solution and dilute to 1000 mL with distilled water in a volumetric flask.

6.11 Working Standards - prepare as follows:

mL standard/1000 mL	conc. mg/L PO_4
5.0	0.5
10.0	1.0
25.0	2.5
50.0	5.0
100.0	10.0

7. Procedure

7.1 Sampling

7.1.1 Pour 500 mL distilled water and 5 mg $CuSO_4$ into the dustfall collector in the summer. Use 500 mL of (1+1) water-isopropanol in the winter. Expose the collector in the field for approximately 4 weeks.

7.2 Analysis

7.2.1 Filter the contents of the collector through a 20 mesh sieve into a 600 mL beaker. Rinse the container with distilled water using a rubber policeman, and add the rinse to the filtrate.

7.2.2 Dilute the volume of the filtrate to 300 mL.

7.2.3 Transfer 50.0 mL sample, blank and standards to separate 250 mL Erlenmeyer flasks.

7.2.4 Add two drops phenolphthalein and 1N NaOH solution dropwise until a light pink colour develops. Add 5N H_2SO_4 solution dropwise until the pink colour just disappears. Add 10 mL mixed reagent, mix well and allow 10 minutes for colour development.

7.2.5 Set the spectrophotometer to zero absorbance with the blank at 660 nm and read the absorbance.

8. Calculation

8.1 Prepare a calibration curve by plotting absorbances vs mg/L PO_4. Read the phosphate concentration of the sample from the graph in units of mg/L PO_4.

$$mg\ PO_4 = \frac{mg/L\ PO_4 \times total\ sample\ volume\ in\ mL}{1000}$$

$$The\ final\ result\ is\ expressed\ as\ mg\ PO_4/cm^2/30\ days = \frac{mg\ PO_4 \times 30}{a \times d}$$

where

a = area of the dustfall collector opening in cm^2.

d = no. of days exposed.

9. Reference

9.1 Std. Meth., 17th Ed, p. 4-177.

September 1992

Method No. 34545

PHOSPHORUS, TOTAL

(Ascorbic Acid - Colorimetric)

1. Introduction

1.1 Phosphorus compounds are present in dustfall, mainly as inorganic phosphates originating from phosphate fertilizer plants and from the application of fertilizers. Total phosphorus includes all soluble orthophosphates, insoluble polyphosphates and organic phosphates.

2. Principle

2.1 The sample is digested with sulphuric acid and potassium persulphate to convert organic phosphates and polyphosphates to soluble orthophosphate. The orthophosphate reacts with ammonium molybdate to form heteropolymolybdophosphoric acid. The molybdophosphoric acid is reduced to a blue-coloured complex by ascorbic acid. This blue colour is proportional to the total phosphorus content of the sample, and it is determined colorimetrically at 660 nm.

3. Scope

3.1 The detection limit in the test solution is 0.5 mg/L as PO_4.

4. Interference

4.1 Arsenic and mercury interfere.

5. Apparatus

5.1 Plastic dustfall collector, 20 cm high and 10 cm in diameter.
5.2 Sieve, 20 mesh size.
5.3 Acid-washed glassware: wash with hot (1+1) HCl and rinse with distilled water. Reserve glassware for phosphorus determinations only.
5.4 Spectrophotometer, 1-cm cells.

6. Reagents

6.1 Algicide: $CuSO_4$.

6.2 Isopropanol.

6.3 Strong acid solution: slowly add 300 mL conc. H_2SO_4 to about 600 mL distilled water. Cool, add 4 mL conc. HNO_3 and dilute to one litre.

6.4 Sulphuric acid (5N): dilute 140 mL conc. H_2SO_4 to one litre with distilled water.

6.5 Ammonium molybdate: dissolve 40 g of $(NH_4)_6Mo_7O_{24}.4H_2O$ in distilled water and dilute to one litre. Store in a plastic bottle at 4°C.

6.6 Ascorbic acid (0.1M): dissolve 1.76 g of ascorbic acid in 100 mL distilled water. Prepare fresh.

6.7 Potassium antimonyltartrate: dissolve 0.30 g of potassium antimonyl tartrate in distilled water and dilute to 100 mL

6.8 Mixed reagent: mix thoroughly 125 mL of 5N H_2SO_4 and 37.5 mL of ammonium molybdate solution. Add 75 mL of ascorbic acid solution and 12.5 mL of tartrate solution. This solution is kept in the refrigerator. It is stable for a period of two weeks.

6.9 Sodium hydroxide solution (1N): dissolve 40 g NaOH in 1 litre distilled water.

6.10 Stock phosphate solution (1000 mg/L PO_4: dissolve 1.4330 g KH_2PO_4, dried at 105°C for 2 hours in distilled water in a 1000 mL volumetric flask and make up to volume.

6.11 Standard solution (100 mg/L PO_4): pipet 100.0 mL of the stock solution and dilute to 1000 mL with distilled water in a volumetric flask.

6.12 Working standards - prepare working standards as follows:

mL std. sol/1000 mL	conc. mg/L PO_4
5.0	0.5
10.0	1.0
25.0	2.5
50.0	5.0
100.0	10.0

7. Procedure

7.1 Sampling

7.1.1 Pour 500 mL distilled water and 5 mg $CuSO_4$ in the dustfall collector in the summer. Use 500 mL of (1+1) water-isopropanol in the winter. Expose the collector in the field for approximately 4 weeks.

7.2 Analysis

7.2.1 Filter the contents of the collector through a 20 mesh sieve into a 600 mL beaker. Rinse the container with distilled water using a rubber policeman, and add the rinse to the filtrate.

7.2.2 Dilute the volume of the filtrate to 300 mL.

7.2.3 Transfer 50 mL of the thoroughly mixed sample, the blank and the standards to separate 250 mL Erlenmeyer flasks.

7.2.4 Add 1 mL of strong acid solution and 1 g potassium persulphate.

7.2.5 Boil gently for at least 90 minutes. Keep the volume above 25 mL.

7.2.6 While hot, filter into 50 mL volumetric flasks.

7.2.7 Add one drop phenolphthalein and 1N NaOH dropwise until a light pink colour develops. Add 10% H_2SO_4 dropwise until the pink colour just disappears. Add 10 mL mixed reagent and mix well.

7.2.8 Dilute to 50 mL with distilled water. Read the absorbance at 660 nm in a spectrophotometer using a 1-cm cell.

8. Calculation

Prepare a calibration curve by plotting absorbances vs mg/L PO_4. Read the phosphorus concentration of the sample from the graph in units of mg/L PO_4.

$$mg\ PO_4 = \frac{mg/L\ PO_4 \times total\ sample\ volume\ in\ mL}{1000}$$

The final result is expressed as

$$mg\ PO_4/cm^2/30\ days = \frac{mg\ PO_4 \times 30}{a \times d}$$

where

a = area of the dustfall collector opening in cm^2.

d = no. of days exposed.

9. Reference

9.1 Std. Meth., 17th Ed., p. 4-177.

SULPHATE, WATER SOLUBLE

(Turbidimetric)

1. Introduction

1.1 Gaseous and particulate sulphur compounds are common pollutants in the atmosphere. In the particulate fraction, some are present as suspended particulate matter and some settle on dust particles. A major constituent of dust particles is gypsum. Sulphuric acid, ammonium and sodium sulphates are also present in dustfall.

2. Principle

2.1 Sulphate is determined by the turbidimetric method. The pH of the sample is adjusted to 2.5 and the sulphate is precipitated as $BaSO_4$. The resulting turbidity of the $BaSO_4$ suspension is measured in a spectrophotometer at 420 nm.

3. Scope

3.1 The detection limit in the test solution is 2 mg/L SO_4.

4. Interference

4.1 Colour and suspended matter interfere. Suspended matter is removed by filtration. Sample blank is used for coloured samples.

5. Apparatus

5.1 Plastic dustfall collector, 20 cm high and 10 cm in diameter.
5.2 Sieve, 20-mesh size.
5.3 Spectrophotometer.
5.4 Nessler tube, matched 50 mL, 2.5 cm diameter.

6. Reagents

6.1 Algicide - do not use $CuSO_4$.
6.2 Isopropanol.

6.3 Dilute hydrochloric acid (1+2): dissolve 100 mL conc. HCl in 200 mL distilled water.

6.4 Sulphate reagent: Sulfaver IV (Hach Chemical Company), or equivalent.

6.5 Stock sulphate solution (1000 mg/L): dissolve 1.479 g anhydrous sodium sulphate in distilled water and dilute to 1000 mL.

6.6 Working sulphate standards - prepare as follows:

mL stock/1000 mL	conc. mg/L SO_4
2.0	2.0
5.0	5.0
10.0	10.0
20.0	20.0
40.0	40.0
50.0	50.0

7. Procedure

7.1 Sampling

7.1.1 Pour 500 mL distilled water in the dustfall collector in the summer. Use 500 mL of (1+1) water-isopropanol in the winter. Expose the collector in the field for approximately 4 weeks.

7.2 Analysis

7.2.1 Filter the contents of the collector through a 20-mesh sieve into a 600 mL beaker. Rinse the container with distilled water using a rubber policeman, and add the rinse to the filtrate.

7.2.2 Dilute the volume of the filtrate to 300 mL.

7.2.3 Transfer 50.0 mL sample, standards and blank to separate 100 mL beakers and adjust the pH to 2.5 by slowly adding hydrochloric acid with constant stirring. Stir 10 minutes to drive off the CO_2.

7.2.4 Transfer to Nessler tubes. Add approximately 0.5 g Sulfaver IV, stir and wait for 10 minutes.

7.2.5 Use the reagent blank for setting the spectrophotometer to 100 percent transmittance at 420 nm.

7.2.6 Read the percent transmittance for all the samples and the standards.

8. Calculation

8.1 Prepare a calibration curve by plotting mg/L SO_4 vs percent transmittance.

8.2 Read the sulphate concentration of the sample from the graph in units of mg/L SO_4.

$$mg\ SO_4 = \frac{mg/L\ SO_4 \times total\ sample\ volume\ in\ mL}{1000}$$

$$The\ result\ is\ expressed\ as\ mg\ SO_4/cm^2/30\ days = \frac{mg\ SO_4 \times 30}{a \times d}$$

where

a = area of the dustfall collector opening in cm^2.

d = no. of days exposed.

9. Reference

9.1 Std. Meth., 17th Ed., p. 4-207.

SULPHUR, TOTAL

(Leco Induction Furnace/Sulphur Titrator)

1. Introduction

1.1 A substantial amount of elemental sulphur and sulphurous compounds is emitted to the atmosphere from the burning of sulphur-containing oil, gas and coal, and from the sulphur-recovery process of sour gas plants. Most of the particulate sulphur and sulphur compounds settle on dust particles. To assess the level of sulphur pollution in the vicinity of sour gas plants, it is necessary to determine the sulphur content in dust particles adjacent to the plants.

2. Principle

2.1 Samples containing sulphur or sulphur compounds are oxidized in oxygen to SO_2 in a Leco furnace. The SO_2 is allowed to react with iodine, which is liberated from the reaction of KIO_3 and KI with HCl.

The analysis proceeds according to the following equation:

$$KIO_3 + 5KI + 6HCL \longrightarrow 6KCL + 3I_2 + 3H_2O$$

$$SO_2 + I_2 + 2H_2O \longrightarrow H_2SO_4 + 2HI$$

2.2 Dilute HCl is poured into a titration vessel and KI and starch solutions are added. A small amount of standard KIO_3 solution is added. The release of free I_2 is indicated when the starch turns blue. An automatic buret containing the KIO_3 is then refilled to the zero or starting point. The sample under test is combusted in oxygen and the resulting SO_2 from the burning sample is directed to the titration vessel where it reacts with free iodine, and the starch turns colourless. More KIO_3 is added to form more free iodine and to bring the solution back to its original colour. This is repeated in a continuous manner until all the sulphur has been oxidized to SO_2 and titrated. The total millilitres of KIO_3 needed for the titration are equivalent to the total micrograms of sulphur in the sample.

3. Scope

3.1 The detection limit is 10 µg/gm of dust.

4. Apparatus

4.1 Plastic dustfall collector, 20-cm high and 10 cm in diameter.
4.2 Sieve, 20-mesh size.
4.3 Leco Induction Furnace.
4.4 Leco Sulphur Titrator.
4.5 Leco Crucibles.
4.6 Scoop.
4.7 Water aspirator (vacuum), Gooch crucible and glass fibre filter.
4.8 10 µg and 100 µg syringes.

5. Reagents

5.1 Algicide: do not use $CuSO_4$.
5.2 Isopropanol.
5.3 Accelerators: granular tin, iron chip and copper rings.
5.4 Potassium iodide solution (3%): dissolve 6 g potassium iodide in 200 mL distilled water.
5.5 Starch solution (0.25%): to 800 mL boiling distilled water, slowly add a suspension of 2.5 g starch in 200 mL distilled water. Cool and add 200 mL KI solution.
5.6 Potassium iodate solution (0.0444%): dissolve 0.4440 g potassium iodate in distilled water in a 1000 mL volumetric flask and dilute to the mark with distilled water.
5.7 Dilute HCl solution: dilute 15 mL conc. HCl to 1 litre with distilled water in a volumetric flask.
5.8 Standard sulphur solution (10 mg/mL S): dissolve 1.000 g pure sublimed sulphur in 100 mL spectra-grade benzene.
5.9 Working sulphur standard - use the following volumes of the standard solution to prepare the calibration curve.

µl S standard	mg S
10.0	0.1
20.0	0.2
40.0	0.4
80.0	0.8
100.0	1.0

6. Procedure

6.1 Sampling

6.1.1 Pour 500 mL distilled water in the dustfall collector in the summer. Use 500 mL of (1+1) distilled water-isopropanol in the winter. Expose the collector in the field for approximately 4 weeks.

6.2 Analysis

6.2.1 Filter the total dustfall sample and/or aliquot through a Gooch crucible, using a glass fibre filter.

6.2.2 Fill a series of Leco crucibles in the following order:

6.2.2.1 One scoop tin.

6.2.2.2 Blank and standard for calibration curve; the filter containing the dustfall sample.

6.2.2.3 Two scoops iron.

6.2.2.4 One copper ring.

6.2.3 Fill ⅓ of the titration cell with dilute HCl solution and add 5 mL starch solution.

6.2.4 Slowly add KIO_3 solution until the meter needle reaches the middle of the scale.

6.2.5 Place the crucible into the Leco furnace. Set "Grid Tap" switch to "High" and put igniter on. Apply a continuous stream of oxygen during the total time of titration at a flow rate of approximately 1 litre/minute through the pipe provided on the sample holder of the furnace.

6.2.6 Titrate with the KIO_3 solution by using both coarse and fine push buttons to bring the solution colour from blue to colorless.

6.2.7 Titration is ended when the meter needle returns to its original setting. Record volume of KIO_3 used for the titration.

7. Calculation

7.1 Prepare a calibration curve by plotting volume of KIO_3 solution used vs mg sulphur. Read the sulphur concentration from the graph in units of mg S.

$$\textit{The result is expressed as } mg/cm^2/30 \textit{ days} = \frac{mg\ S \times 30}{a \times d}$$

where

a = area of the dustfall collector opening in cm^2.

d = no. of days exposed.

8. Reference

8.1 Instruction Manual for Operation of Leco Sulphur Determinators, Models 517, 518 and 532, Laboratory Equipment Corporation, Saint Joseph, Michigan, U.S.A.

UREA

(Diacetylmonoxime, Colorimetric)

1. Introduction

1.1 Urea is present in dustfall as fine particles originating from urea fertilizer plants and from its application.

2. Principle

2.1 Urea forms a yellow-coloured complex with diacetylmonoxime. The intensity is measured spectrophotometrically at 478 nm.

3. Scope

3.1 The range is 5 mg/L to 25 mg/L urea in the test solution.

4. Interference

4.1 No known interference.

5. Apparatus

5.1 Plastic dustfall collector, 20 cm high and 10 cm in diameter.
5.2 Spectrophotometer, 1-cm cells.
5.3 Teflon screw-capped culture tube, 16 x 100 mm.

6. Reagents

6.1 Diacetylmonoxime: dissolve 3.0 g in 100 mL distilled water.
6.2 Ferric chloride (0.1M): dissolve 2.7 g $FeCl_3.6H_2O$ in 100 mL distilled water.
6.3 Acid mixture: mix 300 mL 85% phosphoric acid, 100 mL conc. H_2SO_4, 1.8 mL of 0.1M $FeCl_3$ and a solution of 0.237 g $MnSO_4$ in 400 mL distilled water.
6.4 Urea stock solution (500 mg/L urea): dissolve 0.500 g urea in distilled water and dilute to 1000 mL with distilled water in a volumetric flask.

6.5 Working standards - prepare as follows:

mL stock/1000 mL	conc. mg/L urea
10.0	5.0
20.0	10.0
30.0	15.0
40.0	20.0
50.0	25.0

Prepare working standards weekly.

7. Procedure

7.1 Sampling

7.1.1 Expose the empty collector in the field for approximately 4 weeks.

7.2 Analysis

7.2.1 Dissolve the collected urea and filter the sample into a 100 mL volumetric flask. Dilute to volume with distilled water.

7.2.2 Pipet 1.0 mL sample, standards and blank into separate culture tubes.

7.2.3 Add 2.5 mL acid mixture and 0.25 mL diacetylmonoxime solution. Cap tightly.

7.2.4 Shake the mixture well and heat the test tubes in a boiling water bath for 30 minutes in the dark (wrap the test tubes with aluminum foil).

7.2.5 Allow to cool to room temperature and read the absorbance at 478 nm in a 1-cm cell against the blank.

8. Calculation

8.1 Prepare a calibration curve by plotting mg/L urea vs absorbance. Read the concentration of the sample in units of mg/L urea.

$$mg\ urea = \frac{mg/L\ urea \times total\ sample\ volume\ in\ mL}{1000}$$

$$The\ final\ result\ is\ expressed\ as\ mg\ urea/cm^2/30\ days = \frac{mg\ urea \times 30}{a \times d}$$

where

a = area of the dustfall collector opening in cm^2.

d = no. of days exposed.

9. Reference

9.1 R.B. Moore and N.J. Kauffman, Anal. Biochem., Vol. 33, 1970, p. 263.

8.3 Calculate the cyclohexane soluble organics as

$$\mu g/m^3 = \frac{W \times 5 \times 10^3}{V}$$

$$\text{and/or as } mg/gm \text{ of total suspended particulate matter} = \frac{W \times 5}{W_1}$$

where

W = weight of cyclohexane soluble organic in 20% of the filter in milligrams.

W_1 = weight of the total particulate matter in grams.

5 = conversion factor to change 20% of the filter to 100%.

V = volume of air in m^3 = (F x T).

where

F = average flow rate in m^3/min.

T = sampling time in minutes.

(0.0283 = conversion factor to change ft^3 to m^3, if necessary).

9. Reference

9.1 J.L. Monkman, et al., International J. of Environ. Anal. Chem., Vol. 2, 1972, p. 63.

ALDEHYDES

(Iodometric Titration)

1. Introduction

1.1 Aldehydes, especially formaldehyde and acetaldehyde, are present as air pollutants along with other volatile organics. The main sources of aldehydes are various chemical plants, such as those manufacturing fibreglass, acetic acid, and formaldehyde resin.

2. Principle

2.1 Aldehydes are collected in 1% sodium bisulphite solution to form addition compounds. The excess bisulphite is destroyed with iodine solution. By adjusting the pH of the solution, the addition compounds are decomposed, freeing bisulphite ion equivalent to the aldehydes present in the sample. The liberated bisulphite ion is titrated with a standard iodine solution.

3. Scope

3.1 The detection limit, using a 2-litre gas sample, is 1 mg. The method cannot distinguish formaldehyde from other aldehydes and the total is reported as formaldehyde.

4. Interference

4.1 Acetone interferes.

5. Apparatus

5.1 Sampling train consisting of a probe, gas-collecting flask, barometer, manometer and vacuum pump.

6. Reagents

6.1 Starch solution (1%): prepare a paste by adding 1 g of starch to 5 mL of distilled water. Add 45 mL of boiling water to the paste and stir until all starch dissolves.

6.2 Sodium bisulphite solution (1%): dissolve 1 g of sodium bisulphite in 100 mL of distilled water.

6.3 Standard sodium thiosulphate solution (0.050 N): dissolve 12.41 g of sodium thiosulphate, $Na_2S_2O_3.5H_2O$, in 1000 mL of distilled water. Standardize the solution against potassium dichromate after at least two weeks' storage. Use boiled distilled water and add 2 mL of chloroform to minimize bacterial decomposition of the thiosulphate solution.

6.4 Standard potassium dichromate solution (0.050N): dissolve 2.452 g anhydrous potassium dichromate, $K_2Cr_2O_7$, in distilled water and dilute to 1000 mL.

6.5 Standardization of sodium thiosulphate solution: to 80 mL distilled water add while stirring, 1 mL conc. H_2SO_4, 10.0 mL 0.050N $K_2Cr_2O_7$ and 0.5 g potassium iodide. Allow the reaction mixture to stand 6 minutes in the dark before titration with the 0.050N $Na_2S_2O_3$ titrant, adding 0.5 mL of starch near the end point. At the end point, the colour changes from opaque blue to colorless.

$$Normality\ of\ Na_2S_2O_3 = \frac{10.0 \times 0.050}{mL\ of\ Na_2S_2O_3\ consumed}$$

6.6 Stock iodine solution (0.10N): place 12.8 g or iodine in a 250 mL beaker, add 40 g of KI and 25 mL of water. Stir until all is dissolved and then dilute to 1000 mL with distilled water.

6.7 Standard iodine solution (0.010N): dilute 100.0 mL of 0.10N iodine solution to 1000 mL with distilled water. Standardize this solution against 0.050N sodium thiosulphate solution as follows:

Pipet 50.0 mL standard iodine solution and 50 mL distilled water into 125 mL Erlenmeyer flasks.

Add 50 mL distilled water, 5 mL (1+5) HCl and 1 mL starch solution to both the flasks. Titrate with 0.050N sodium thiosulphate until the blue colour disappears.

$$Normality\ of\ iodine\ solution = \frac{(a - b) \times N}{50.0}$$

where

N = normality of $Na_2S_2O_3$ solution.

a = mL of $Na_2S_2O_3$ solution consumed by the iodine standard.

b = mL of $Na_2S_2O_3$ solution consumed by the blank.

6.8 Buffer solution: dissolve 80 g of anhydrous sodium carbonate in 500 mL of distilled water. Using a pH meter, adjust the pH of this solution to 9.6 ± 0.1 with glacial acetic acid. Dilute to 1 litre with distilled water.

6.9 Silica gel.

7. Procedure

7.1 Sampling

7.1.1 For instructions on setting up the sampling train see Ref. No. 1.

7.1.2 Transfer 25 mL of 1% sodium bisulphite solution into the 2-litre round bottom flask and evacuate it to approximately 75 mm of mercury. Collect the sample and transfer it to a polyethylene bottle.

7.2 Analysis

7.2.1 Measure the sample volume.

7.2.2 Pipet 10.0 mL of sample and 10.0 mL of absorbing solution as blank into separate 125 mL Erlenmeyer flasks. Add 2 mL of 1% starch solution and then start adding 0.10N iodine solution dropwise until a dark blue colour is produced.

7.2.3 Bubble air through both solutions for several minutes in order to remove sulphur dioxide resulting from the decomposition of bisulphite.

7.2.4 Add 0.050N sodium thiosulphate dropwise to decolourize the solutions, then add a few drops of 0.010N iodine solution to give a faint blue colour.

7.2.5 Cool the solution in an ice bath and add 50 mL of chilled buffer. Keep the flasks in the ice bath for 10-15 minutes.

7.2.6 Titrate the liberated bisulphite with 0.010N iodine solution to the same faint blue colour.

8. Calculation

8.1 The weight of the aldehyde is expressed as

$$mg\ formaldehyde = \frac{0.010 \times (V_s - V_b) \times 0.15 \times sample\ volume\ in\ mL}{N \times ml\ of\ sample\ used\ for\ titration}$$

where

0.010 = exact normality of the 0.010N iodine solution used for titrating the sample aliquot.

V_s	=	volume of the 0.010N iodine solution used for titrating the sample.
V_b	=	volume of the titrant for blank.
0.15	=	1 mL of 0.010N iodine solution is equivalent to 0.15 mg of formaldehyde.

The final result is expressed as

$$mg\ formaldehyde/m^3 = \frac{mg\ formaldehyde}{m^3\ of\ collected\ gas\ at\ STP}$$

9. References

9.1 Source Sampling Code, Method 6, Alberta Environment.

9.2 Wilson, K.W., Anal. Chem., Vol. 30, 1958, p. 1127.

AMMONIA-NITROGEN

(Direct Nesslerization)

1. Introduction

1.1 Ammonia is present as free ammonia gas or as ammonium phosphate, nitrate and sulphate in the stack emissions of fertilizer plants.

2. Principle

2.1 Ammonia forms a coloured complex with Nessler reagent, the intensity of which is measured at 410 nm.

3. Scope

3.1 The detection limit is 0.2 mg/L NH_3-N in the test solution. The range is 0.2 to 2.5 mg/L NH_3-N, at 410 nm. The range could be extended to 10 mg/L NH_3-N by using a small-sized cell at 525 nm.

4. Interference

4.1 Some volatile organic compounds may yield a yellowish or greenish colour, and often cause a turbidity following addition of the Nessler reagent. No specific procedure can be recommended for eliminating them.

4.2 Sulphide, formaldehyde, calcium, magnesium and iron may interfere by causing turbidity following addition of the Nessler reagent. This can be avoided by pretreatment of the sample with zinc sulphate and alkali.

5. Apparatus

5.1 Sampling train consisting of a pitot assembly, impinger train, umbilical cord, vacuum pump and metering devices.

5.2 Spectrophotometer.

5.3 Nessler tubes, matched, 50 mL, short form.

5.4 pH meter.

6. Reagents

6.1 Ammonia-free water: slowly pass distilled water through a 2.5-cm column of glass tubing (1.2 to 2.5 cm diameter) which has been charged with 2 parts by volume of a strongly basic anion-exchange resin and 1 part by volume of a strongly acidic cation-exchange resin.

6.2 Silica gel.

6.3 Zinc sulphate solution: dissolve 100 g $ZnSO_4.7H_2O$ in ammonia-free distilled water and dilute to 1 litre.

6.4 Sodium hydroxide solution (1N): dissolve 40 g NaOH in 500 mL ammonia-free distilled water and dilute to 1 litre.

6.5 Hydrochloric acid solution (1N): dilute 86 mL of conc. HCl to 1 litre with distilled water.

6.6 Rochelle salt solution: dissolve 50 g potassium sodium tartrate tetrahydrate, $KNaC_4H_4O_6.4H_2O$ in 100 mL ammonia-free distilled water. Boil the solution and allow to evaporate to approximately 70 mL. Cool to room temperature and dilute to 100 mL with ammonia-free distilled water.

6.7 Nessler Reagent: dissolve 100 g anhydrous mercuric iodide and 70 g anhydrous potassium iodide. In a small quantity of water, slowly add this solution while stirring to a cool solution of 160 g NaOH in 500 mL water. Dilute to 1 litre with ammonia-free distilled water.

6.8 Stock ammonia solution (1000 mg/L NH_3-N): dissolve 3.819 g anhydrous NH_4Cl, dried at 100°C for 2 hours, in ammonia-free distilled water in a 1000 mL volumetric flask and dilute to volume.

6.9 Standard ammonia solution (10 mg/L NH_3-N): dilute 10.0 mL stock ammonia solution to 1000 mL with ammonia-free distilled water.

6.10 Working standards - prepare as follows:

mL std. sol/1000 mL	conc. mg/L NH_3-N
20.0	0.2
40.0	0.4
60.0	0.6
100.0	1.0
200.0	2.0

7. Procedure

7.1 Sampling

7.1.1 For instructions on setting up the sampling train see Ref. No. 1.

7.1.2 Collect the sample in two impingers, each containing 100 mL of 1N HCl solution.

7.1.3 Transfer the sample from the two impingers into a polyethylene bottle. Rinse the nozzle and probe with distilled water and add this rinse to the same bottle. Add 0.8 mL conc. H_2SO_4/L and store the sample at 4°C.

7.2 Analysis

7.2.1 Rinse all glassware with ammonia-free distilled water.

7.2.2 Filter the sample if it contains suspended matter. Adjust the pH to 6-7 by adding 10N NaOH dropwise. Measure the sample volume.

7.2.3 If the sample is turbid, add 1 mL $ZnSO_4$ solution to 100 mL of the sample and mix thoroughly. Adjust the pH to 10.5, adding 1N NaOH solution dropwise. Allow the treated sample to stand to form a heavy white precipitate. Filter the precipitate. Use ammonia-free filter paper.

7.2.4 Transfer 50.0 mL sample, blank and working standards to separate 50 mL Nessler tubes.

7.2.5 Add 2 drops of Rochelle salt and mix well.

7.2.6 Add 1 mL Nessler reagent and mix well. Allow to stand for 10 minutes. If NH_3-N concentration is very low, use 30 minutes contact time for sample, blank, and standards.

7.2.7 Set the spectrophotometer to 100 percent transmittance with the blank at 410 nm and read the percent transmittance.

7.2.8 For higher concentrations read % transmittance at 525 nm, using smaller size cell.

8. Calculation

8.1 Prepare a calibration curve by plotting percent transmittance vs mg/L NH_3-N. Read the sample concentration from the graph in units of mg/L NH_3-N.

$$mg\ NH_3\text{-}N = \frac{mg/L\ NH_3\text{-}N \times total\ sample\ volume\ in\ mL}{1000}$$

The final result is expressed as

$$mg\ NH_3\text{-}N/m^3 = \frac{mg\ NH_3\text{-}N}{m^3\ of\ collected\ gas\ at\ STP}$$

9. Precision and Accuracy

9.1 In a single laboratory (Alberta Environmental Centre), using stack emission samples from a fertilizer plant at concentrations of 0.3 and 2.3 mg/L NH_3-N, the coefficients of variation were 3.4 and 6.7%, respectively.

9.2 In a single laboratory (Alberta Environmental Centre), using stack emission samples from a fertilizer plant at concentrations of 0.5 and 1.5 mg/L NH_3-N, the recoveries were 98% and 99%, respectively.

10. References

10.1 Source Sampling Code, Method 5, Alberta Environment.

10.2 Std. Meth., 17th Ed., p. 4-117.

10.3 Text Book of Qualitative Inorganic Analysis by "Vogel", 4th Ed., 1981; p. 731.

CHLORIDE

(Colorimetric)

1. Introduction

1.1 Chloride is present as chloride salts and as hydrochloric acid in stack emissions of fertilizer, paper and pulp, and metal-extracting plants.

2. Principle

2.1 The chloride ion displaces the thiocyanate ion from mercuric thiocyanate. The displaced thiocyanate ion reacts with the ferric ion to form red-coloured ferric thiocyanate. The concentration is proportional to the original chloride concentration and is measured at 480 nm.

3. Scope

3.1 The detection limit is 0.2 mg/L chloride in the test solution. The method is applicable to water-soluble chlorides only and it cannot distinguish between hydrochloric acid and chloride salts. The total is determined as chloride.

4. Interference

4.1 Bromides, iodides, cyanides, thiosulphates and nitrites interfere.

5. Apparatus

5.1 Sampling train consisting of a pitot assembly, impinger train, umbilical cord, vacuum pump and metering devices.

5.2 Spectrophotometer, 1-cm cells.

6. Reagents

6.1 Ferric nitrate solution: dissolve 202 g of $Fe(NO_3)_3.9H_20$ in 500 mL distilled water. Add 22 mL conc. nitric acid. Dilute to one litre with distilled water.

6.2 Mercuric thiocyanate solution: dissolve 4.17 g of $Hg(SCN)_2$ in 1 L methanol. Stir the solution using a magnetic stirrer for 30 minutes. Allow the solution to stand for 24 hours before use. Store the reagent in an amber bottle.

6.3 Stock chloride solution (1000 mg/L Cl): dissolve 1.648 g of sodium chloride, dried at 140°C for 2 hours in distilled water. Dilute to 1000 mL with distilled water.

6.4 Standard chloride solution (100 mg/L Cl): dilute 100.0 mL of the stock chloride solution to 1000 mL with distilled water.

6.5 Working standards - prepare as follows:

mL std. sol./1000 mL	conc. mg/L Cl
5.0	0.5
10.0	1.0
20.0	2.0
40.0	4.0
60.0	6.0

6.6 Silica gel.

7. Procedure

7.1 Sampling

7.1.1 For instructions on setting up the sampling train, see Ref. No. 1.

7.1.2 Collect the sample in two impingers, each containing 100 mL of distilled water.

7.1.3 Transfer the sample from the two impingers into a polyethylene bottle. Rinse the probe with distilled water and add this rinse to the sample bottle. Store the sample at 5°C.

7.2 Analysis

7.2.1 Rinse all glassware in dilute nitric acid for several hours before use.

7.2.2 Measure the sample volume.

7.2.3 Transfer 25.0 mL sample, blank and standards to separate glass-stoppered 125 mL Erlenmeyer flasks. Add 5 mL of ferric nitrate solution and 2.5 mL of mercuric thiocyanate solution to each flask. Mix thoroughly and allow to stand for 10 minutes.

7.2.4 Measure the absorbance of the colour at 480 nm.

8. Calculation

8.1 Prepare a calibration curve by plotting absorbance vs concentration. Read the sample concentration from the graph in units of mg/L Cl.

$$mg\ chloride = \frac{mg/L\ Cl \times total\ sample\ volume\ in\ mL}{1000}$$

The final result is expressed as

$$mg\ chloride/m^3 = \frac{mg\ chloride}{m^3\ of\ collected\ gas\ at\ STP}$$

9. References

9.1 Source Sampling Code, Method 5, Alberta Environment.
9.2 Std. Meth., 17th Ed., p. 4-69.

CHLORINE AND HYDROCHLORIC ACID GAS

(Titrimetric)

1. Introduction

1.1 Chlorine and hydrochloric acid gas are present in the stack emissions of pulp and paper plants.

2. Principle

2.1 Chlorine liberates equivalent amounts of free iodine from potassium iodide solution at pH 3-4. The liberated iodine is titrated with a standard solution of sodium thiosulphate, using starch as an indicator. Hydrochloric acid is determined by titrating against a standard sodium hydroxide solution.

3. Scope

3.1 The detection limit for chlorine is 0.04 mg/L, and for hydrochloric acid it is 0.1 mg/L in the test solution.

4. Interference

4.1 Sulphur dioxide interferes.

5. Apparatus

5.1 Sampling train consisting of a pitot assembly, impinger train, umbilical cord, vacuum pump and metering devices.

6. Reagents

6.1 Acetic acid, glacial.
6.2 Potassium iodide.

6.3 Standard sodium thiosulphate solution (0.025N): dissolve 12.41 g $Na_2S_2O_3.5H_2O$ in 2 litres of freshly boiled distilled water and standardize the solution against potassium dichromate after at least two weeks' storage. Use boiled distilled water and add 2 mL of chloroform to minimize bacterial decomposition of the thiosulphate solution.

6.4 Potassium dichromate solution (0.100N): dissolve 4.904 g of potassium dichromate, dried at 103°C for 2 hours in distilled water and dilute to 1000 mL.

6.5 Starch solution: prepare a paste by adding 1 g of starch to 5 mL of distilled water. Add 200 mL of boiling water to the paste and stir until all starch dissolves.

6.6 Standardization of sodium thiosulphate: pipet 10.0 mL of 0.100N potassium dichromate solution into a 400 mL beaker containing 25 mL of water, 2 g KI and 5 mL of (1+5) HCl. Allow the reaction to proceed in the dark for 5 minutes. Dilute to approximately 200 mL and titrate with 0.025N $Na_2S_2O_3$, adding 0.5 mL of starch near the end point. At the end point, the colour changes from opaque blue to colorless.

$$Normality\ of\ Na_2S_2O_3 = \frac{10 \times 0.100}{mL\ Na_2S_2O_3\ consumed}$$

6.7 Potassium biphthalate solution (0.050N): dry 10-15 g of powdered $KHC_8H_4O_4$ at 120 °C for 2 hours. Cool in a desiccator. Weigh 10.000 g and transfer it to a 1000 mL volumetric flask. Dissolve with distilled water and dilute to volume.

6.8 Standard sodium hydroxide solution (0.100N): dissolve 11.0 g of NaOH in 10 mL distilled water, cool, and filter through a Gooch crucible. Dilute 5.45 mL of the filtrate to 1000 mL with distilled water in a 1000 mL volumetric flask. Standardize this solution by titrating it against 0.050N potassium biphthalate solution. Use a 25 mL buret for the sodium hydroxide solution. Titrate to pH 8.7. Calculate the normality of the NaOH solution as follows:

$$Normality = \frac{N \times V_1}{V_2}$$

where

N	=	normality of potassium biphthalate.
V_1	=	mL of potassium biphthalate solution taken for titration.
V_2	=	mL of NaOH solution used for titration.

6.9 Silica gel.

6.10 Methyl red indicating solution: add 0.02 g methyl red (not salt form) to 60 mL ethanol and make up to 100 mL with distilled water.

7. Procedure

7.1 Sampling

7.1.1 For instructions on setting up the sampling train, see Ref. No. 1.

7.1.2 Collect the sample in 2 impingers, each containing 100 mL of distilled water, followed by another 2 impingers, each containing 100 mL of 5% sodium hydroxide solution. The first two impingers are held in a water bath at ambient temperature, and the third and forth impingers are placed in an ice bath.

7.1.3 Transfer the contents of the first and second impinger into a polyethylene bottle (sample A) and the contents of the third and fourth impingers into another polyethylene bottle (sample B). Store both samples at 5°C.

7.2 Analysis

7.2.1 Chlorine

7.2.1.1 Measure the volumes of samples A and B.

7.2.1.2 Transfer 50.0 mL of each sample and 50 mL distilled water as blank to separate 250 mL Erlenmeyer flasks.

7.2.1.3 Check the pH of each solution and adjust to pH 3-4 with acetic acid.

7.2.1.4 Add approximately 1 g potassium iodide and mix with a stirring rod. Allow the reaction to proceed in the dark for 5 minutes.

7.2.1.5 Titrate by adding 0.025N thiosulphate solution until the yellow colour of the liberated iodine is almost discharged. Add 1 mL starch solution and titrate until the blue colour is discharged. Avoid direct sunlight during titration.

7.2.2 Hydrochloric Acid

7.2.2.1 Transfer 50.0 mL of sample A and 50 mL of distilled water as blank into separate 250 mL Erlenmeyer flasks.

7.2.2.2 Titrate with standard 0.100N sodium hydroxide solution to the methyl red endpoint.

8. Calculation

8.1 The amount of chlorine in samples A and B is expressed as

$$mg\ Cl = \frac{[(X_1-Y) + (X_2-Y)] \times N \times 35.45 \times \textit{total volume of sample (A + B) in mL}}{\textit{mL of samples (A + B) used for titration}}$$

where

X_1 = mL of thiosulphate required for the titration of the aliquot taken from sample A.

X_2 = mL of thiosulphate required for the titration of the aliquot taken from sample B.

Y = mL of thiosulphate required for the titration of the blank.

N = normality of thiosulphate.

The final result is expressed as

$$mg\ Cl/m^3 = \frac{mg\ Cl}{m^3\ of\ collected\ gas\ at\ STP}$$

The amount of HCl in sample A is expressed as

$$mg\ HCl = \frac{(C-D) \times N \times 36.5 \times volume\ of\ sample\ A\ in\ mL}{mL\ of\ sample\ A\ used\ for\ titration}$$

where

C = mL of NaOH required for the titration of the aliquot taken from sample A.

D = mL of NaOH required for the titration of the blank.

N = normality of NaOH solution.

9. Precision and Accuracy

9.1 In a single laboratory (Alberta Environmental Centre), using stack emission samples at concentrations of 1.7 and 9.0 mg/L Cl, the coefficients of variation were 0.7% and 1%, respectively.

9.2 In a single laboratory (Alberta Environmental Centre), using stack emission samples at concentrations of 5.0 and 10.0 mg/L Cl, the recoveries were 97% and 98%, respectively.

10. References

10.1 Source Sampling Code, Method 5, Alberta Environment.

10.2 Std. Meth., 17th Ed., p. 4-48.

CHLORINE AND HYDROCHLORIC ACID GAS

(Ion Chromatography)

1. Introduction

1.1 Chlorine and hydrochloric acid gas are present in the stack emissions of pulp and paper plants.

2. Principle

2.1 See method for anions by ion chromatography.

3. Scope

3.1 The range is 0.01 to 5.0 mg/L, using a 500 µL loop.

4. Interference

4.1 Carbonate and sulphide in high concentrations, and organic acids will interfere.

5. Apparatus

5.1 Sampling train consisting of a pitot assembly, impinger train, umbilical cord, vacuum pump and metering devices.

5.2 Dionex model 2020i-ion chromatograph equipped with:

- 5.2.1 Spectra Physics SP4270 computing integrator.
- 5.2.2 500 µL sample loop.
- 5.2.3 Precolumn.
- 5.2.4 Separator.
- 5.2.5 Suppressor.
- 5.2.6 Conductivity detector.

6. Reagents

6.1 Stock chloride solution (1000 mg/L): dissolve 1.648 g of sodium chloride (dried at 140°C for two hours) in distilled water and dilute to one litre.

6.2 Standard chloride solution (100 mg/L): dilute 100 mL of the stock solution to 1000 mL with distilled water.

6.3 Working standards: prepare solutions of 0.075, 0.120, 0.375, and 0.60 mg/L concentration by appropriate dilution of the standard solution.

6.4 Silica gel.

6.5 Stock hypochlorite solution (1000 mg/L: dilute 28.94 mL of 5% hypochlorite solution to 1000 mL with distilled water.

6.6 Stock chlorate solution (1000 mg/L): dissolve 1.2765 g of $NaClO_3$ in distilled water and dilute to one litre.

6.7 Potassium biphthalate solution (0.050N): dry 10-15 g of powdered $KHC_8H_4O_4$ at 120 °C for 2 hours. Cool in a desiccator. Weigh 10 g and transfer to a 1000 mL volumetric flask. Dissolve with distilled water and dilute to volume.

6.8 Standard sodium hydroxide solution (0.100N): dissolve 11 g of NaOH in 10 mL distilled water, cool, and filter through a Gooch crucible. Dilute 5.45 mL of the filtrate to 1000 mL with distilled water in a 1000 mL volumetric flask. Standardize this solution by titrating it against 0.050N potassium biphthalate solution. Use a 25 mL buret for the sodium hydroxide solution. Titrate to the inflection point, which should be close to pH 8.7. Calculate the normality of the NaOH solution as follows:

$$Normality = \frac{N \times V_1}{V_2}$$

where

N = normality of potassium biphthalate.

V_1 = mL of potassium biphthalate solution taken for titration.

V_2 = mL of NaOH solution used for titration.

7. Procedure

7.1 Sampling

7.1.1 For instructions on setting up the sampling train, see Ref. No. 1.

7.1.2 Collect the sample in 2 impingers, each containing 100 mL of distilled water, followed by another 2 impingers, each containing 100 mL of 5% sodium hydroxide solution. The first two impingers are held in a water bath at ambient temperature, and the third and fourth impingers are placed in an ice bath.

7.1.3 Transfer the contents of the first and second impingers into a polyethylene bottle (sample A) and the contents of the third and fourth impingers into another

polyethylene bottle (sample B). Store both samples at 5°C. Record the volumes of samples A and B.

7.2 Analysis

7.2.1 Chlorine

7.2.1.1 Sample A is in water and can be injected directly into the ion chromatograph. Sample B is in NaOH and must first be passed through an onguard H cartridge to neutralize the NaOH.

7.2.1.2 Inject the samples by means of a 500 µL loop.

7.2.1.3 Run duplicates and spiked samples in accordance with the quality control program.

7.2.1.4 Set the computing integrator at low attenuations to check for low concentrations (128 mV full scale).

7.2.2 Hydrochloric Acid

7.2.2.1 Transfer 50.0 mL of sample A and 50 mL of distilled water as a blank into separate 250 mL Erlenmeyer flasks.

7.2.2.2 Titrate with standard 0.100N sodium hydroxide solution to the methyl red end point.

8. Calculation

8.1 The amount of chlorine in sample A and sample B is expressed as

$$mg\ Cl = \frac{mg\ Cl}{1000\ mL} \times volume\ of\ sample\ in\ mL$$

The final result is expressed as

$$mg\ Cl/m^3 = \frac{mg\ Cl}{m^3\ of\ collected\ gas\ at\ STP}$$

The amount of HCl in sample A is expressed as

$$mg\ HCl = \frac{(C-D) \times N \times 36.5 \times volume\ of\ sample\ A\ in\ mL}{mL\ of\ sample\ A\ used\ for\ titration}$$

where

C = mL of NaOH required for the titration of the aliquot taken from sample A.

D = mL of NaOH required for the titration of the blank.

N = normality of NaOH solution.

9. Precision and Accuracy

9.1 In a single laboratory (Alberta Environmental Centre), using stack emission samples at concentrations of 1.7 and 9.0 mg/L Cl, the coefficients of variation were 0.7% and 1%, respectively.

9.2 In a single laboratory (Alberta Environmental Centre), using stack emission samples at concentrations of 5.0 and 10.0 mg/L Cl, the recoveries were 97% and 98%, respectively.

10. References

10.1 Source Sampling Code, Method 5, Alberta Environment.

10.2 Std. Meth., 17th Ed., p. 4-75.

10.3 Ion Chromatography Manual, Dionex Corporation.

FLUORIDE, WATER SOLUBLE

(Specific-Ion Electrode)

1. Introduction

1.1 During the combustion of coal and phosphate rocks, fluorine compounds, such as hydrofluoric acid and silicon tetrafluoride, are released to the atmosphere.

1.2 In the process of industrial operations to produce phosphate fertilizer, iron and steel, glass and ceramics, fluorine compounds are set free as gaseous and/or particulate fluoride.

2. Principle

2.1 Fluoride is determined using a fluoride specific-ion electrode in conjunction with a standard calomel reference electrode. The potential developed by the presence of fluoride ions is measured by an expanded scale pH/mV meter.

3. Scope

3.1 The method is applicable to the determination of water soluble fluorides. The detection limit is 0.1 mg/L fluoride in the test solution.

4. Interference

4.1 A buffer is used to prevent interferences from extreme pH and certain polyvalent cations, such as Si, Fe and Al.

5. Apparatus

5.1 Sampling train consisting of a pitot assembly, impinger train, umbilical cord, vacuum pump and metering devices.

5.2 pH meter with expanded mV scale.

5.3 Fluoride electrode (Orion 94-09, or equivalent).

5.4 Standard calomel reference electrode.

5.5 Magnetic stirrer and Teflon-coated stirring bar.

5.6 Teflon beakers, 200 mL capacity.

6. Reagents

6.1 Sodium hydroxide solution (5N): dissolve 200 g NaOH of distilled water and dilute to 1 litre.

6.2 Total ionic strength adjustment buffer (TISAB): add 57 mL of glacial acetic acid, 58 g of sodium chloride and 2 g CDTA (1,2-cyclohexylene diamine tetraacetic acid) to approximately 500 mL of distilled water. Stir to dissolve and cool to room temperature. Adjust the pH of the solution to 5 - 5.5 with 5N NaOH. Transfer the solution to a 1000 mL volumetric flask, add 1 mL of the 100 mg/L stock fluoride standard and dilute to the mark with distilled water.

6.3 Acetic acid (6M): dilute 343 mL of glacial acetic acid to 1 litre with distilled water.

6.4 Sodium acetate-acetic acid buffer solution (4M): dilute 667 mL 6M acetic acid with distilled water to 1 litre. Slowly add 5N NaOH solution to the acetic acid, with constant stirring until a pH of 5 is reached.

6.5 Sodium acetate (15%): dissolve 150 g sodium acetate in distilled water and dilute to 1 litre.

6.6 Silica gel.

6.7 Stock fluoride solution (100 mg/L F): dissolve 0.2210 g anhydrous sodium fluoride in distilled water and dilute to 1000 mL

6.8 Working standards - prepare as follows:

mL stock/1000 mL	conc. mg/L F
2.5	0.25
5.0	0.5
10.0	1.0
20.0	2.0
25.0	2.5
50.0	5.0
100.0	10.0
200.0	20.0
250.0	25.0

7. Procedure

7.1 Sampling

7.1.1 For instructions on setting up the sampling train see Ref. No.1.

7.1.2 Collect the sample in two impingers, each containing 100 mL of distilled water. Transfer both impinger solutions into a polyethylene bottle. Do not use glass bottles for storage. Rinse the nozzle and probe with distilled water and add this rinse to the same bottle. Preserve the sample at 5°C.

7.2 Analysis

7.2.1 Measure the sample volume and check the pH.

7.2.1.1 Determination of fluoride in neutral solutions.

7.2.1.1.1 If the sample pH is between 5 and 9.5, proceed as follows:

7.2.1.1.1.1 Transfer 50.0 mL sample, blank and standards (0.25 to 2.5 mg/L) into separate 200 mL Teflon beakers. Add 50 mL TISAB solution to each beaker.

7.2.1.1.1.2 Insert the electrodes and stir solution using a magnetic stirrer for 3 minutes.

7.2.1.1.1.3 Record the potential when the reading is stable.

7.2.1.2 Determination of fluoride in acid solutions.

7.2.1.2.1 If the sample pH is less than 5, proceed as follows:

7.2.1.2.1.1 Pipet 10.0 mL of sample, blank and standards (2.5 - 25.0 mg/L) into separate 100 mL volumetric flasks.

7.2.1.2.1.2 Dilute the contents of each flask to volume with 15% sodium acetate solution.

7.2.1.2.1.3 Transfer 50 mL of the diluted sample, blank and standards into separate 200 mL Teflon beakers. Add 50 mL of TISAB solution to each beaker.

7.2.1.2.1.4 Stir the solution for 3 minutes and record the potential when the reading is stable.

7.2.1.3 Determination of fluoride in alkaline solutions.

7.2.1.3.1 If the sample pH is greater than 9.5, proceed as follows:

7.2.1.3.1.1 Pipet 10.0 mL of sample, blank and standards (2.5 - 25.0 mg/L) into separate 100 mL volumetric flasks.

7.2.1.3.1.2 Dilute the contents of each flask to volume with 4M sodium acetate-acetic acid buffer solution

7.2.1.3.1.3 Transfer 50 mL of the diluted sample, blank and standards into separate 200 mL Teflon beakers. Add 50 mL of TISAB solution to each beaker.

7.2.1.3.1.4 Stir the solution for 3 minutes and record the potential when the reading is stable.

8. Calculations

8.1 Using 2 cycle semi-log graph paper, prepare two curves by plotting concentrations (0.25 - 2.5 mg/L & 2.5 - 25 mg/L) on the log scale vs the mV readings on the linear scale. Read the sample concentration from the appropriate graph in units of mg/L F.

$$mg\ fluoride = \frac{mg/L\ F \times total\ sample\ volume\ in\ mL}{1000}$$

The final result is expressed as

$$mg\ fluoride/m^3 = \frac{mg\ fluoride}{m^3\ of\ collected\ gas\ at\ STP}$$

9. Precision and Accuracy

9.1 In a single laboratory (Alberta Environmental Centre), using stack emission samples from a fertilizer plant at concentrations of 2.0 and 9.0 mg/L F, the coefficients of variation were 0.2% and 0.8%, respectively.

9.2 In a single laboratory (Alberta Environmental Centre), using stack emission samples from a fertilizer plant at concentrations of 1.2 and 4.8 mg/L F, the recoveries were 98% and 100%, respectively.

10. References

10.1 Source Sampling Code, Method 5, Alberta Environment.

10.2 Std. Meth., 17th Ed., p. 4-87.

10.3 Orion Instruction Manual for Fluoride Electrode Model 94-09, 1976.

HYDROGEN SULPHIDE

(Colorimetric)

1. Introduction

1.1 Hydrogen sulphide is a toxic and malodorous air pollutant. It is present in stack emission of pulp and paper plants, and oil and gas refineries.

2. Principle

2.1 Hydrogen sulphide is absorbed in zinc acetate solution and is precipitated as zinc sulphide. The precipitate is treated with acid to liberate the H_2S, which is allowed to react with p-aminodimethylaniline sulphate in the presence of ferric chloride. The colour intensity of the resulting methylene blue is measured at 600 nm.

3. Scope

3.1 The detection limit is 0.1 mg/L sulphide in the test solution.

4. Interference

4.1 Mercaptans and alkyl sulphides provide positive interference.

5. Apparatus

5.1 Sampling train consisting of a pitot assembly, impinger train, umbilical cord, vacuum pump and metering devices.

5.2 Spectrophotometer, 1-cm cells.

6. Reagents

6.1 Zinc acetate solution (1%): dissolve 10 g of zinc acetate in distilled water and dilute to 1 litre.

6.2 Silica gel.

6.3 Amine-sulphuric acid stock solution: dissolve 27.2 g N,N-dimethyl-p-phenylenediamine sulphate, $NH_2C_6H_4N(CH_3)_2.H_2SO_4$, (also called p-aminodimethylaniline sulphate) in a cold mixture of 50 mL conc. sulphuric acid and 20 mL distilled water. Cool and dilute to 100 mL with distilled water. Store in a dark glass bottle in a refrigerator.

6.4 Amine-sulphuric acid solution: dilute 5 mL amine-sulphuric acid stock solution to 200 mL in a volumetric flask with (1+1) sulphuric acid.

6.5 Ferric chloride solution: dissolve 100 g ferric chloride ($FeCl_3.6H_2O$) in 40 mL distilled water.

6.6 Diammonium hydrogen phosphate solution: dissolve 40 g $(NH_4)_2HPO_4$ in distilled water and dilute to 100 mL.

6.7 Standard iodine solution (0.025N): dissolve 10 g KI in 800 mL distilled water in a 1000 mL volumetric flask. Add 3.2 g of iodine and dilute to volume with distilled water. Prepare the standard daily.

6.8 Standard sodium thiosulphate (0.025N): weigh 12.41 g of $Na_2S_2O_3.5H_2O$ into a 2000 mL volumetric flask and dilute to volume with distilled water.

6.9 Potassium dichromate (0.100N): dissolve 4.904 g of potassium dichromate dried for 2 hours at 103°C, in distilled water and dilute to 1000 mL.

6.10 Starch solution: prepare a paste by adding 10 g of starch to 20 mL of distilled water. Add 2 litres of boiling water to the paste and stir until all starch dissolves. Add a small amount of salicylic acid to prevent mold formation.

6.11 Standardization of sodium thiosulphate: pipet 10.0 mL of 0.100N potassium dichromate solution into a 400 mL beaker containing 25 mL or water, 2 g KI and 5 mL of (1+5) HCl. Allow the reaction to proceed in the dark for 5 minutes, dilute to approximately 200 mL and titrate with 0.025N $Na_2S_2O_3$, adding 0.5 mL of starch near the end point. At the end point, the colour changes from opaque blue to colorless.

$$\textit{Normality of } Na_2S_2O_3 = \frac{10.0 \times 0.100}{\textit{mL of } Na_2S_2O_3 \textit{ consumed}}$$

6.12 Standardize the 0.025N iodine solution against the above standard $Na_2S_2O_3$ as follows:

6.12.1 Pipet 50.0 mL standard iodine solution and 50 mL distilled water into separate 125 mL Erlenmeyer flasks.

6.12.2 Add 50 mL distilled water, 5 mL (1+5) HCl and 1 mL starch solution to both flasks. Titrate with 0.025N sodium thiosulphate until the blue colour disappears.

$$Normality\ of\ iodine\ solution = \frac{(a - b) \times N}{50.0}$$

where

N = normality of $Na_2S_2O_3$ solution.
a = mL of $Na_2S_2O_3$ solution consumed by the iodine standard.
b = mL of $Na_2S_2O_3$ solution consumed by the blank.

6.13 Stock sulphide solution (1000 mg/L S): dissolve 3.75 g $Na_2S.9H_2O$ in boiled and cooled distilled water in a 500 mL volumetric flask and dilute to volume. Prepare daily.

6.14 Standard sulphide solution (10 mg/L S): dilute 10.0 mL stock sulphide solution to 1000 mL with boiled and cooled distilled water. Standardize in duplicate immediately before use as follows:

6.14.1 Pipet 100.0 mL sulphide solution into an Erlenmeyer flask, add 10.0 mL standard 0.025N iodine solution and a few drops of conc. HCl, and titrate with 0.025N $Na_2S_2O_3$ to the starch end point. Run a blank on the reagents.

$$mg/L\ S = \frac{(A - B) \times 0.4 \times 1000 \times 0.025}{100 \times N}$$

where

0.4 = 1 mL of 0.025N iodine solution is equivalent to 0.4 mg of sulphide.
A = mL of $Na_2S_2O_3$ used for the blank.
B = mL of $Na_2S_2O_3$ used for the standard.
N = exact normality of thiosulphate.

6.15 Working standard solutions: pipet the following volumes into 50 mL volumetric flasks containing 10 mL of 1% zinc acetate solution. Do not make up to volume at this time (see analysis part, step 3).

mL standard sulphide/50 mL	conc. mg/L S *
0.50	0.10
1.25	0.25
2.50	0.50
3.50	0.70
5.00	1.00

*Note: Exact concentration depends on the actual concentration of standard sulphide solution.

7. Procedure

7.1 Sampling

7.1.1 For instruction on setting up the sampling train see Ref. No.1.

7.1.2 Collect the sample in two impingers, each containing 100 mL of 1% zinc acetate solution. Transfer the sample into a polyethylene bottle.

7.2 Analysis

7.2.1 Measure the sample volume.

7.2.2 Shake the sample well and transfer 10.0 mL of the sample and 1% zinc acetate as blank into 50 mL volumetric flasks.

7.2.3 Add 1 mL amine-sulphuric acid reagent and 2 drops of $FeCl_3$ solution into the flasks containing standards, sample and blank. Shake well and wait one minute for colour development.

7.2.4 Add 1 mL $(NH_4)_2HPO_4$ solution, stir and wait for 1 minute.

7.2.5 Dilute the contents of each flask to volume with distilled water.

7.2.6 Set the spectrophotometer to 100 percent transmittance with the blank at 600 nm.

7.2.7 Measure the percent transmittance.

8. Calculation

8.1 Prepare a calibration curve of concentration vs percent transmittance. Read the sample concentration from the graph in units of mg/L S.

$$mg\ sulphide = \frac{mg/L\ S \times total\ sample\ volume\ in\ mL}{1000}$$

The final result is expressed as

$$mg\ sulphide/m^3 = \frac{mg\ sulphide}{m^3\ of\ collected\ gas\ at\ STP}$$

LEAD

(Direct Current Plasma)

1. Introduction

1.1 Lead emissions from stationary sources are collected using a sampling train equipped with filters and impingers.

2. Principle

2.1 Particulate matter in various sections of the sampling train is first weighed and then digested. The extracted lead is measured by Direct Current Plasma Spectroscopy.

3. Scope

3.1 For a total sampling volume of 2.8 cubic metres, the detection limit for lead collected on glass fibre filters is approximately 50 µg per cubic metre.

4. Interference

4.1 See method No. 61010.

5. Apparatus

5.1 Analytical balance, sensitivity 0.1 mg.
5.2 DCP (direct current plasma) spectrometer.
5.3 Hot plate with thermostat control.
5.4 Class A volumetric pipets and flasks.

6. Glassware Handling

6.1 See method No. 61010.

7. Reagents

7.1 HNO_3, conc.

7.2 HCl, conc.

7.3 HF, conc.

7.4 H_2SO_4, conc.

7.5 Aqua regia: prepare by mixing one part HNO_3 conc. with three parts HCl conc., both reagent grade. This formulation should include one part of water if the aqua regia is to be stored for any length of time. Without water, objectionable quantities of chlorine and other gases are evolved. Preferably, prepare enough to use for the amount of samples on hand.

7.6 Stock lead solution (1000 mg/L Pb): weigh 1.599 g of lead nitrate and dissolve in 300 mL of distilled water. Add 20 mL of concentrated HNO_3 and dilute to 1000 mL.

7.7 Standard lead solution (100 mg/L Pb): pipet 100 mL of the stock solution into a 1000 mL volumetric flask and dilute to volume with distilled water.

7.8 Working standards: using 100 mg/L standard, prepare as follows:

mL std. sol/1000 mL	conc. mg/L Pb
1.0	0.1
2.0	0.2
10.0	1.0
20.0	2.0
50.0 (or 5.0*)	5.0
10.0*	10.0
20.0*	20.0

*prepare using stock solution of 1000 mg/L Pb.

7.9 Quality control standards: prepare using SRM NBS 3128 (10,000 mg/L Pb). Make intermediate solution and prepare at least three different concentrations i.e., 0.1, 1, 4, 16 mg/L.

7.10 QC intermediate: pipet 20.0 mL of NBS 3128 into a 2000 mL volumetric flask, add 40.0 mL of conc. HNO_3 and dilute to volume with distilled water.

7.11 QC solutions - prepare as follows:

mL 100 mg/L Pb Std/1000 mL	conc. mg/L Pb
1.0	0.1
10.0	1.0
mL 100 mg/L Pb std/100 mL	
4.0	4.0
16.0	16.0

Note: Standards and QC solution must be in the same matrix used to dissolve the samples. If the samples were dissolved in aqua regia, use 2 mL of it to acidify your standards and QC samples.

8. Procedure

8.1 Sampling

8.1.1 For instructions on setting up the sampling train, see Ref. No.1.

8.1.2 Collect the sample in 2 impingers, each containing 100 mL of 5% aqua regia, followed by another 2 impingers, one of which contains 100 mL of distilled water while the other contains approximately 200 g of preweighed silica gel. Crushed ice is placed around the five impingers to keep the temperature of the gases leaving the impingers around 21°C.

8.1.3 Adjust the filter heating system to provide a temperature of 107°C at the filter holder.

8.1.4 Remove the filter from its holder, transfer to its container, and seal.

8.1.5 Transfer the contents of the first two impingers to a container and label No.1.

8.1.6 Transfer the contents of the third impinger and label it No.2.

8.1.7 Using a rubber policeman if necessary, transfer the silica gel from the fifth impinger to a container, and seal.

8.2 Analysis

Solutions

8.2.1 Pipet 50 mL of sample (aqua regia impingers) to a 150 mL beaker.

8.2.2 Add 5 mL of aqua regia and slowly boil to a 20 mL volume.

8.2.3 Add 5 mL of aqua regia, cover with watch glass and reflux for about 2 hours. Add more aqua regia if required.

8.2.4 Let cool and wash watch glass and beaker walls.

8.2.5 Filter (if necessary) into a 100 mL volumetric flask and make up to volume with deionized distilled water.

Adjust the DCP as follows:

Order:	61
Wavelength:	363.348
Entrance Slit:	50 x 300
Exit Slit:	100 x 300
Plasma Position:	Zero
Detection Limit:	0.01 mg/L

Linear dynamic range LDR 0.1 to 600 mg/L
Background equivalent concentration BEC 0.4 mg/L
Precision (RSD) at 20 x BEC 0.8%
Mode internal at 10 seconds and 3 counts
Photomultiplier tube PMT

Filters

8.2.6 Fold filter and tie with thread.

8.2.7 Using a tweezer, place filter in Teflon beaker.

8.2.8 Put 2 mL of distilled water on top, just to make it wet, so that the reaction with HF does not become violent.

8.2.9 Add HF drop by drop until the filter dissolves (about 4 mL). Do not add the acid too fast or at one time; the reaction may become violent with possible loss of lead.

8.2.10 Keep the temperature of the hot plate at 40°C, evaporate the HF almost completely at that temperature. Do not leave any HF unevaporated, also do not bone-dry the sample. Occasionally swirl the beaker during evaporation.

8.2.11 Add 4 mL of conc. HNO_3 dropwise, shake the beaker by hand and evaporate the acid to about 1 mL.

8.2.12 Add 20 mL of water, dissolve the residue in it and heat for 30 minutes at 60° to 80°C.

8.2.13 Filter the sample into a 100 mL volumetric flask. Wet the filter with dilute HNO_3 before filtering.

8.2.14 Make up to volume with deionized distilled water.

8.2.15 Analyze, using the same DCP settings as in 8.2.5.

8.2.16 Do not digest more than 10-12 samples at a time. Run duplicate blanks.

9. Calculation: Solutions

$$mg\ Pb = mg/L \times total\ sample\ volume\ in\ mL \times final\ volume\ in\ litres/aliquot\ in\ mL$$

Filters

$$mg\ Pb = mg/L \times final\ volume\ in\ litres$$

10. Precision and Accuracy

10.1 In a single laboratory (Alberta Environmental Centre), using samples with concentrations of 5, 11 and 200 mg/L, the recoveries were from 99 to 102.6%.

11. References

11.1 Environment Canada, Standard Reference Methods for Source Testing, 1979.
11.2 S.N. Linzon, et al., J. Air Poll. Control Assoc., Vol. 26, 1976, p. 650.
11.3 Spectraspan V, Spectrametrics Inc.

NITROGEN OXIDES

(Phenol-Disulphonic Acid, Colorimetric)

1. Introduction

1.1 Nitrogen oxides are present in stack emissions of nitric acid, fertilizer, and coal and gas-fired power plants.

2. Principle

2.1 A gas sample is collected in an evacuated flask containing a solution of hydrogen peroxide in dilute sulphuric acid. Oxides of nitrogen are oxidized to nitric acid by the hydrogen peroxide solution. The resulting nitrate ion is reacted with phenol-disulphonic acid to produce a yellow-coloured complex, the intensity of which is measured at 410 nm.

3. Scope

3.1 The method determines total oxides of nitrogen and is reported as NO_2. The detection limit is 0.2 mg/L NO_2 in the test solution.

4. Interference

4.1 Inorganic nitrates, nitrites, and sulphur dioxide interfere.

5. Apparatus

5.1 Sampling train consisting of a probe, gas-collecting flask, barometer, manometer and vacuum pump.
5.2 Spectrophotometer, 1-cm cells.
5.3 Evaporating dishes, 200 mL capacity.

6. Reagents

6.1 Sulphuric acid (0.3%): dilute 3 mL of conc. H_2SO_4 to 1 litre with distilled water.
6.2 Absorbing solution: add 10 mL of 30% hydrogen peroxide to 1 litre of 0.3% sulphuric acid solution.

6.3 Ammonium hydroxide, conc.

6.4 Phenol-disulphonic acid solution (25%, W/V): commercially available.

6.5 Potassium nitrate stock solution (1 mL = 1 mg NO_2): dry potassium nitrate, KNO_3, in an oven at 105°C for 2 hours. Dissolve 2.198 g of the salt in distilled water and dilute to 1000 mL in a volumetric flask.

6.6 Potassium nitrate standard solution (1 mL = 100 µg NO_2): dilute 50.0 mL of KNO_3 stock solution to 500 mL with distilled water in a volumetric flask.

6.7 Sodium hydroxide solution (1N): dissolve 40 g sodium hydroxide in distilled water and dilute to 1 litre.

6.8 Silica gel.

7. Procedure

7.1 Sampling

7.1.1 For instruction on setting up the sampling train and collecting the gas sample see Ref. No.1.

7.1.2 Transfer 25 mL of absorbing solution into a sampling flask and evacuate it to approximately 75 mm of mercury. Collect the sample.

7.1.3 After sampling, allow the gas to remain in contact with the absorbing solution overnight. Better absorption is achieved if the sample is shaken occasionally. Transfer the sample to a polyethylene bottle, rinse the flask with distilled water and transfer it to the bottle. Add 1N NaOH dropwise until the sample is alkaline.

7.2 Analysis

7.2.1 Transfer the sample to a 50 mL volumetric flask and make up to volume with absorbing solution.

7.2.2 Pipet 25.0 mL sample and absorbing solution as blank into separate 200 mL evaporating dishes.

7.2.3 Pipet 1.0, 2.0, 3.0, and 4.0 mL of standard solution (1 mL = 100 µg NO_2) into separate 25 mL volumetric flasks and dilute to volume with absorbing solution. Transfer all 25 mL solutions into separate 200 mL evaporating dishes.

7.2.4 Add 10 mL distilled water and add 1N NaOH solution dropwise (about 55 drops) to each solution until the pH is between 9-12.

7.2.5 Evaporate each to dryness on a water bath (or in a drying oven at no more than 70°C) and allow to cool (do not use hot plate for evaporation).

7.2.6 Add 2 mL of phenol-disulphonic acid solution to each residue and mix thoroughly with a polyethylene rod.

7.2.7 Add 1 mL of water and 4 drops of conc. H_2SO_4 to each dish and heat on a water bath for 3 min. with occasional stirring. Allow the mixture to cool, add 10 mL of distilled water to each and mix well by stirring.

7.2.8 Add enough concentrated NH_4OH dropwise (about 3-5 mL) to each dish with constant stirring to raise the pH to 10.

7.2.9 Centrifuge the solutions if they contain solids and transfer them into 100 mL volumetric flasks. Wash the evaporating dishes three times with 4 to 5 mL of water. Make up t0 volume with distilled water.

7.2.10 Set the spectrophotometer to 410 nm and use the blank to set zero absorbance.

7.2.11 Measure the absorbance of each sample. If the absorbance is out of the calibration scale, dilute the remaining half of the sample and repeat steps 2 - 10.

8. Calculation

8.1 Determine the calibration factor K as follows:

$$K = 100\frac{A_1 + 2A_2 + 3A_3 + 4A_4}{A_1^2 + A_2^2 + A_3^2 + A_4^2}$$

where

A_1 = Absorbance of the 100 µg NO_2 standard.
A_2 = Absorbance of the 200 µg NO_2 standard.
A_3 = Absorbance of the 300 µg NO_2 standard.
A_4 = Absorbance of the 400 µg NO_2 standard.

Total µg NO_2 = 2 x K x A x F

where

K = Calibration factor.
A = Absorbance of the sample.
2 = $\frac{sample\ volume}{aliquot}$, eg:, $\frac{50\ mL}{25\ mL}$
F = Dilution factor (required only if sample dilution is needed to reduce the absorbance so it is in the range of calibration).

The final result is expressed as

$$mg\ NO_2/m^3 = \frac{\mu g\ NO_2 \times 10^{-3}}{m^3\ of\ collected\ gas\ at\ STP}$$

9. Precision and Accuracy

9.1 In a single laboratory (Alberta Environmental Centre), using stack emission samples at concentrations of 10.5 and 150 mg/L NO_2, the coefficients of variation were 2.8% and 1.8%, respectively.

9.2 In a single laboratory (Alberta Environmental Centre), using stack emission samples at concentrations of 9.5 and 50 mg/L NO_2, the recoveries were 98% and 102%, respectively.

10. References

10.1 Source Sampling Code, Method 6, Alberta Environment.

10.2 1989 Book of ASTM Standards, Vol. 11.03, p. 33.

NITROGEN OXIDES

(Ion Chromatography)

1. Introduction

1.1 Nitrogen oxides are present in stack emissions of nitric acid, fertilizer, and coal and gas-fired power plants.

2. Principle

2.1 A gas sample is collected in an evacuated flask containing a solution of hydrogen peroxide in dilute sulphuric acid. Oxides of nitrogen are oxidized to nitric acid by the hydrogen peroxide solution. The nitrate ion is then measured by ion chromatography.

3. Scope

3.1 The method determines total nitrate and is reported as NO_2. The range is 0.01 to 20 mg NO_2/L in test solution.

4. Interferences

4.1 High levels of bromine, sulphate, chloride, and some organic acids may interfere with nitrate determination.

4.2 Sulphite interferences can be distinguished by adding hydrogen peroxide and noting the decrease in the nitrate and increase in sulphate level (sulphite is normally not present).

4.3 A suppressor interaction causes nitrate peaks to tail, but the method still provides sufficient precision and accuracy.

5. Apparatus

5.1 Sampling train consisting of a probe, gas-collecting flask, barometer, manometer, and vacuum pump.

5.2 Dionex model 2020i ion chromatograph equipped with

5.2.1 Spectra Physics SP4270 computing integrator.

5.2.2 Precolumn.

5.2.3 Separator.

5.2.4 Suppressor.

5.2.5 Conductivity detector.

6. Reagents

6.1 Stock nitrate solution (1000 mg NO_3/L): dissolve 1.3707 g of oven-dried sodium nitrate in deionized and distilled water and dilute to one litre.

6.2 Standard nitrate solution (100 mg NO_3/L): dilute 100 mL of the stock solution to 1000 mL with deionized and distilled water.

6.3 Working standards (0-20 mg NO_3/L): prepare solutions by appropriate dilution of the standard solution, using deionized and distilled water and absorbing solution. It is important that the matrix of the working standard approximate the sample matrix after dilution.

6.4 Sulphuric acid (0.3%): dilute 3 mL of concentrated H_2SO_4 to 1 litre with deionized and distilled water.

6.5 Absorbing solution: add 10 mL of 30% hydrogen peroxide to 1 litre of 0.3% sulphuric acid solution.

6.6 Sodium hydroxide solution (IN): dissolve 40 g sodium hydroxide in deionized and distilled water and dilute to 1 litre.

6.7 Silica gel.

7. Procedure

7.1 Sampling

7.1.1 For instruction on setting up the sampling train and collecting gas samples see Ref. No.1.

7.1.2 Transfer 25 mL of absorbing solution into a sampling flask and evacuate it to approximately 75mm of mercury. Collect the sample.

7.1.3 After sampling, allow the gas to remain in contact with the absorbing solution overnight. Better absorbtion is achieved if the sample is shaken occasionally. Transfer the sample to a polyethylene bottle, rinse the flask with deionized and distilled water and transfer it to the bottle. Add 1N NaOH dropwise until the sample is alkaline.

7.2 Analysis

7.2.1 Dilute a 5 mL sample to volume in a 100 or 200 mL volumetric with distilled and deionized water.

7.2.2 Inject the diluted sample into the ion chromatograph using the following instrument conditions:

7.2.2.1 No sample loop.

7.2.2.2 Eluent is 3.6 mM $NaHCO_3$ at 2.5 cc/min flow rate.

7.2.2.3 Output range is 3 µS.

7.2.3 The nitrate peak is integrated electronically at approximately eleven minutes. Allow sufficient time for the sulphate peak to elute before injecting the next sample.

7.2.4 Run duplicates and spiked samples in accordance with the quality control program.

8. Calculation

mg NO_2 = mg/L NO_3 x sample volume in litres x dilution x 0.7419

where, 0.7419 = conversion factor from NO_3 to NO_2

$$mg\ NO_2/m^3 = \frac{mg\ NO_2}{m^3\ of\ collected\ gas\ at\ STP}$$

9. Precision and Accuracy

9.1 In a single laboratory (Alberta Environmental Centre), using 15 EPA interlab NO_x samples over a period of 4 years, and a concentration range of 91 µg to 650 µg, the percent recovery ranged from 91.4 to 111.1% with a coefficient of variation of 5.5%.

10. References

10.1 Source Sampling Code, Method 6, Alberta Environment.

10.2 ASTM, Part 26, 1977, p. 498.

10.3 Ion Chromatography Manual, Dionex Corporation.

ORTHOPHOSPHATE, WATER SOLUBLE

(Ascorbic acid, Colorimetric)

1. Introduction

1.1 Orthophosphates are present in the stack emissions of fertilizer plants.

2. Principle

2.1 Orthophosphate is reacted with ammonium molybdate to form a heteropoly acid, molybdophosphoric acid. The molybdophosphoric acid is reduced to a blue-coloured complex by ascorbic acid. The blue colour, which is proportional to the orthophosphate content of the sample, is measured at 650 or 880 nm.

3. Scope

3.1 The detection limit is 0.10 mg/L P_2O_5 in the test solution. The range is 0.10 to 5.0 mg/L P_2O_5.

4. Interference

4.1 Arsenic interferes by forming a blue colour with ammonium molybdate.

5. Apparatus

5.1 Sampling train consisting of a pitot assembly, impinger train, umbilical cord, vacuum pump and metering devices.

5.2 Spectrophotometer, 1-cm cells.

6. Reagents

6.1 Sulphuric acid (5N): dilute 140 mL conc. H_2SO_4 to one litre with distilled water.

6.2 Ammonium molybdate: dissolve 40 g of $(NH_4)_6Mo_7O_{24}.4H_2O$ in distilled water and dilute to one litre. Store in a plastic bottle at 4°C.

6.3 Ascorbic acid (0.1M): dissolve 1.76 g of ascorbic acid in 100 mL distilled water. Prepare the solution on the day to be used.

6.4 Potassium antimonyl tartrate: dissolve 0.30 g of potassium antimonyl tartrate in distilled water and dilute to 100 mL.

6.5 Mixed reagent: thoroughly mix 125 mL of 5N H_2SO_4 and 37.5 mL of ammonium molybdate solution. Add 75 mL of ascorbic acid solution and 12.5 mL of tartrate solution. This solution is kept in the refrigerator. It is stable for a period of two weeks.

6.6 Sodium hydroxide (1N): dissolve 40 g NaOH in one litre of distilled water.

6.7 Stock phosphate solution (1000 mg/L P_2O_5): dry KH_2PO_4 for 2 hours at 105°C. Weigh 1.917 g KH_2PO_4, dissolve in distilled water and dilute to 1000 mL

6.8 Standard phosphate solution (100 mg/L P_2O_5): dilute 100.0 mL of the stock phosphate solution to 1000 mL with distilled water.

6.9 Working standards - prepare as follows:

mL std. sol./1000 mL	conc. mg/L P_2O_5
2.0	0.2
5.0	0.5
10.0	1.0
25.0	2.5
50.0	5.0

7. Procedure

7.1 Sampling

7.1.1 For instructions on setting up the sampling train see Ref. No.1.

7.1.2 Collect the sample in two impingers, each containing 100 mL of distilled water.

7.1.3 Transfer the sample from the two impingers into a polyethylene bottle. Rinse the probe with distilled water and add this rinse to the sample bottle.

7.2 Analysis

7.2.1 Measure the sample volume. Filter it through 0.45 µ membrane filter.

7.2.2 Pipet 50.0 mL of sample, blank and standards into separate 250 mL Erlenmeyer flasks.

7.2.3 Add two drops phenolphthalein and 1N NaOH solution dropwise to each flask until a light pink colour develops. Add 5 N H_2SO_4 until the pink colour just disappears.

7.2.4 Add 10 mL mixed reagent, mix well and allow 10 minutes for colour development.

7.2.5 Set the spectrophotometer to zero absorbance with the blank at 650 or 880 nm and read the absorbance.

8. Calculation

8.1 Prepare a calibration curve by plotting absorbance vs concentration. Read the sample concentration from the graph in units of mg/L P_2O_5.

$$mg\ P_2O_5 = \frac{mg/L\ P_2O_5 \times total\ sample\ in\ mL}{1000}$$

The final result is expressed as

$$mg\ P_2O_5/m^3 = \frac{mg\ P_2O_5}{m^3\ of\ collected\ gas}$$

9. Precision and Accuracy

9.1 In a single laboratory (Alberta Environmental Centre), using stack emission samples from a fertilizer plant at concentrations of 0.3 and 4.0 mg/L P_2O_5, the coefficients of variation were 1.5% and 0.0%, respectively.

9.2 In a single laboratory (Alberta Environmental Centre), using stack emission samples from a fertilizer plant at concentrations of 0.4 and 5.0 mg/L P_2O_5, the recoveries were 98% and 101%, respectively.

10. References

10.1 Source Sampling Code, Method 5, Alberta Environment.

10.2 Std. Meth., 17th Ed., p. 4-177.

ORTHOPHOSPHATE, WATER SOLUBLE

(Vanadomolybdophosphoric acid, Colorimetric)

1. Introduction

1.1 Orthophosphates are present in the stack emissions of fertilizer plants.

2. Principle

2.1 Orthophosphate reacts with ammonium molybdate under acidic conditions to form a heteropoly acid, molybdophosphoric acid. The acid forms a yellow colour in the presence of vanadium. The intensity of the yellow colour, which is proportional to the phosphate concentration, is measured at 420 nm.

3. Scope

3.1 The detection limit is 2 mg/L P_2O_5 in the test solution. The range is 2.0 to 60 mg/L P_2O_5.

4. Interference

4.1 Arsenic and sulphide interfere.

5. Apparatus

5.1 Sampling train consisting of a pitot assembly, impinger train, umbilical cord, vacuum pump and metering devices.
5.2 Spectrophotometer, 1-cm cells.
5.3 pH meter.

6. Reagents

6.1 Ammonium molybdate solution: dissolve 40 g ammonium molybdate, $(NH_4)_6Mo_7O_{24}.4H_2O$, in 400 mL boiling distilled water. Cool and bring volume back to 400 mL.

6.2 Ammonium metavanadate solution: dissolve 2.0 g ammonium metavanadate, NH_4VO_3, by heating to boiling in 250 mL distilled water. Cool and bring volume back to 250 mL. Add 350 mL conc. HCl.

6.3 Vanadate-molybdate reagent: cool the solution of ammonium metavanadate to room temperature and add the ammonium molybdate solution. Mix well.

6.4 Stock phosphate solution (1000 mg/L P_2O_5): dry KH_2PO_4 for two hours at 105°C. Weigh 1.917 g KH_2PO_4, dissolve in distilled water in a 1000 mL volumetric flask and dilute to volume.

6.5 Working standards - prepare as follows:

mL stock solution/1000 mL	conc. mg/L P_2O_5
5.0	5.0
10.0	10.0
20.0	20.0
40.0	40.0
60.0	60.0

6.6 Silica gel.

7. Procedure

7.1 Sampling

7.1.1 For instructions on setting up the sampling train see Ref. No.1.

7.1.2 Collect the sample in two impingers, each containing 100 mL distilled water. Transfer the sample into a polyethylene bottle. Rinse the probe with distilled water and add this rinse to the sample bottle.

7.2 Analysis

7.2.1 Measure the sample volume. Filter it through a 0.45 µ membrane filter and use a pH meter to check that the pH of the sample is between 4 and 10. If the pH is less than 4, adjust by adding a NaOH solution. If the pH is greater than 10, adjust by adding conc. HCl. Dilute the sample to 250 mL in a volumetric flask.

7.2.2 Pipet 50.0 mL sample, standards and blank into separate 100 mL volumetric flasks.

7.2.3 Add 25 mL vanadate-molybdate reagent to each flask and dilute to volume with distilled water. Allow 10 minutes for colour development.

7.2.4 Set the spectrophotometer to zero absorbance with the blank at 420 nm.

7.2.5 Read the absorbance for the sample and standards.

8. Calculation

8.1 Prepare a calibration curve by plotting concentration vs absorbance. Read the sample concentration from the graph in units of mg/L P_2O_5.

$$mg\ P_2O_5 = \frac{mg/L\ P_2O_5 \times total\ sample\ volume\ in\ mL}{1000}$$

The final result is expressed as

$$mg\ P_2O_5/m_3 = \frac{mg\ P_2O_5}{m^3\ of\ collected\ gas\ at\ STP}$$

9. Precision and Accuracy

9.1 In a single laboratory (Alberta Environmental Centre), using stack emission samples from a fertilizer plant at concentrations of 4.0 and 38.5 mg/L P_2O_5, the coefficients of variation were 2.5% and 0.4%, respectively.

9.2 In a single laboratory (Alberta Environmental Centre), using stack emission samples from a fertilizer plant at concentrations of 5.0 and 58.5 mg/L P_2O_5, the recoveries were 101% and 98%, respectively.

10. References

10.1 Source Sampling Code, Method 5, Alberta Environment.

10.2 Std. Meth., 17th Ed., p. 4-173.

PARTICULATE MATTER

(Gravimetric)

1. Introduction

1.1 Particulate matter is present in the stack emissions of all industrial plants.

2. Principle

2.1 Particulate matter is collected on a preweighed glass fibre or paper filter and/or in impingers containing distilled water. The impinger sample is evaporated in a pre-weighed platinum crucible on a water bath and then dried in an oven. The particulate matter collected on a pre-weighed filter paper is allowed to dry in a desiccator for 24 hours. The particulate matter in the filter paper and in the impingers is reported separately.

3. Scope

3.1 The detection limit is 10 mg particulate matter/L in the test solution and 1 mg on the filter.

4. Apparatus

4.1 Sampling train consisting of a pitot assembly, filter holder and cyclone, impinger train, umbilical cord, vacuum pump and metering devices.
4.2 Glass fibre filter, or equivalent.
4.3 Petri dishes.
4.4 Desiccator.
4.5 Analytical balance of 200 g capacity and a sensitivity of 0.1 mg.

5. Reagents

5.1 Silica gel.
5.2 Acetone.

6. Procedure

6.1 Sampling

6.1.1 For instructions on setting up the sampling train and collecting the sample see Ref. No.1.

6.1.2 Collect the sample on a pre-weighed filter and/or in two impingers, each containing 100 mL distilled water. The use of a cyclone is optional.

6.1.3 Remove the filter from the filter holder and store in a petri dish.

6.1.4 Transfer the samples from the two impingers into a polyethylene bottle.

6.1.5 Rinse the nozzle, probe and cyclone with 1+1 water-acetone mixture and transfer it to a separate bottle.

6.2 Analysis

6.2.1 Impinger Solution

6.2.1.1 Measure the volume of the sample.

6.2.1.2 Ignite the platinum crucibles in a muffle furnace at 550°C for 30 minutes, cool them in a desiccator and weigh.

6.2.1.3 Pipet 50 mL of a well-stirred aqueous sample into a pre-weighed platinum crucible.

6.2.1.4 Evaporate the sample to dryness by heating on a water bath.

6.2.1.5 Samples containing ammonium salts must be evaporated to dryness in an oven set at 50 ± 1°C.

6.2.1.6 Dry the sample evaporated on the water bath for 1 hour in an oven at 105 ± 1°C, cool in a desiccator, weigh and record the weight.

6.2.2 Filter Paper

6.2.2.1 Place the filter paper in a desiccator and dry to a constant weight. Record the weight.

6.2.3 Probe and Cyclone Washing

6.2.3.1 Measure the volume of the washing.

6.2.3.2 Pipet 50 mL of the well-stirred sample into a preweighed platinum crucible.

6.2.3.3 Evaporate the sample to dryness by heating on a water bath. Dry the sample for 1 hour in an oven at 105°C ± 1°C. Samples containing ammonium salts must be evaporated first at room temperature in a fume hood and then in an oven at 50°C. Weigh and record the weight.

7. Calculation

7.1 Particulate matter in the impinger solution:

$$mg = \frac{(B - A) \times \text{impinger sample volume in mL}}{\text{mL sample used for evaporation}}$$

where

A = initial weight of the empty platinum in mg.

B = weight of the platinum in mg after evaporation.

7.2 Particulate matter on the filter paper:

$$mg = (W_2 - W_1)$$

where

W_1 = initial weight of the unused filter paper in mg.

W_2 = final weight of the used filter paper after drying in mg.

7.3 Particulate matter in the probe and cyclone washing:

$$mg = \frac{(X - Y) \times \text{volume of the probe and cyclone washing in mL}}{\text{mL sample used for evaporation}}$$

where

Y = initial weight of the empty platinum in mg.

X = weight of the platinum in mg after evaporation.

The final result for (a), (b) and (c) is expressed as

$$\text{mg particulate matter/m}^3 = \frac{\text{mg particulate matter}}{\text{m}^3 \text{ of collected gas at STP}}$$

8. Precision and Accuracy (Particulate matter at 50°C):

8.1 In a single laboratory (Alberta Environmental Centre), using fertilizer stack samples at concentrations of 570, 459 and 302 mg/L, the coefficients of variation were 2.1%, 2.2% and 4.6%, respectively.

8.2 In a single laboratory (Alberta Environmental Centre), using fertilizer stack samples at concentrations of 501 and 4088 mg/L, the recoveries were 99% and 98%, respectively.

9. References

9.1 Source Sampling Code, Method 4, Alberta Environment.

9.2 EPA Federal Register, Vol. 42, No. 160, August, 1977, p. 41776, Method 5.

9.3 D.R. Kendall, J.Air. Pollu. Control Assoc., Vol. 26, 1976, p. 871.

PHENOLS

(Colorimetric)

1. Introduction

1.1 Phenols are defined as hydroxy derivatives of benzene. They occur in stack emissions of oil refineries, fibreglass plants and petrochemical plants.

2. Principle

2.1 The phenols are distilled and then allowed to react with 4-aminoantipyrine at a pH of 10.0 ± 0.2 in the presence of potassium ferricyanide to form a coloured antipyrine dye. This dye is either extracted from aqueous solution with chloroform and the absorbance is measured at 460 nm, or kept in an aqueous solution and the absorbance is measured at 510 nm.

3. Scope

3.1 The chloroform extraction method is capable of detecting 0.002 mg phenol/L in the test solution. The minimum detectable quantity by aqueous extraction method is 0.1 mg/L. The method cannot distinguish between polyhydroxy benzenes and monohydroxy benzene. The total is measured as monohydroxy benzene.

4. Interference

4.1 Phenol-decomposing bacteria: the decomposition can be inhibited by adding $CuSO_4$ at the time of sampling.

4.2 Oxidizing substances (such as chlorine) are removed by adding an excess of ferrous sulphate or sodium arsenite.

4.3 Reducing sulphur compounds are removed by acidifying the sample to a pH of less than 4 with H_3PO_4, using a pH meter and aerating briefly by stirring before the $CuSO_4$ is added.

5. Apparatus

5.1 Sampling train consisting of a pitot assembly, impinger train, umbilical cord, vacuum pump and metering devices.
5.2 Distillation apparatus, all glass.
5.3 pH meter.
5.4 Spectrophotometer, 10-cm cells.
5.5 Separatory funnel, 1 litre capacity.

6. Reagents

6.1 Stock phenol solution (1000 mg/L): dissolve 1.00 g reagent-grade phenol in distilled water and dilute to 1000 mL with distilled water. If extreme accuracy is required, standardize as described in Std. Meth., 16th Ed., p. 560.
6.2 Standard phenol solution A (10mg/L): dilute 10.0 mL stock phenol solution to 1000 mL in distilled water.
6.3 Standard phenol solution B (1 mg/L): dilute 100.0 mL of standard phenol solution A to 1000 mL with distilled water.
6.4 Working phenol standards A - prepare as follows:

mL std. sol.A/1000 mL	conc. mg/L
10.0	0.100
20.0	0.200
30.0	0.300
40.0	0.400
50.0	0.500

6.5 Working phenol standards B - prepare as follows:

mL std. sol.B/1000 mL	conc. mg/L
2.0	0.002
10.0	0.010
25.0	0.025
50.0	0.050
75.0	0.075
100.0	0.100

6.6 Copper sulphate solution: dissolve 100 g $CuSO_4.5H_2O$ in distilled water and dilute to 1 litre.

6.7 Phosphoric acid solution (8.5%): dilute 10 mL 85% H_3PO_4 to 100 mL with distilled water.

6.8 Aminoantipyrine solution: dissolve 2.0 g 4-aminoantipyrine in distilled water and dilute to 100 mL. Prepare fresh each day.

6.9 Potassium ferricyanide - dissolve 8.0 g $K_3Fe(CN)_6$ in distilled water and dilute to 100 mL. Filter if necessary. Prepare fresh each week.

6.10 Ammonium chloride solution - dissolve 50 g NH_4Cl in distilled water and dilute to 1 litre.

6.11 Sodium hydroxide solution (1%) - dissolve 20 g NaOH in 2 litres of distilled water.

7. Procedure

7.1 Sampling

7.1.1 For instructions on setting up the sampling train see Ref. No.1.

7.1.2 Collect the sample in 2 impingers, each containing 500 mL of 1% NaOH.

7.1.3 Transfer the samples to a polyethylene bottle. Rinse nozzle and probe with water. Add this rinse to the sample bottle. Acidify the sample to pH 3-4 with 8.5% H_3PO_4 and preserve by adding 5 mL copper sulphate solution.

7.2 Analysis

7.2.1 Chloroform Extraction Method:

7.2.1.1 Measure the sample volume.

7.2.1.2 Transfer 500 mL of the sample into a distillation flask and distill until about 450 mL have been collected.

7.2.1.3 Allow the sample to cool slightly and add an additional 50 mL distilled water.

7.2.1.4 Continue distillation until exactly 500 mL have been collected.

7.2.1.5 Pipet 500 mL of each working standard B into 600 mL beakers. Also, prepare a reagent blank of 500 mL distilled water.

7.2.1.6 Add 10 mL ammonium chloride solution to sample, standards and blank, and adjust the pH to 10.0 ± 0.2 with concentrated ammonium hydroxide. Transfer to 1-litre separatory funnels.

7.2.1.7 To each separatory funnel, add 3.0 mL 4-aminoantipyrine solution and shake well.

7.2.1.8 To each separatory funnel, add 3.0 mL potassium ferricyanide solution and shake well.

7.2.1.9 Allow 3 minutes for colour development.

7.2.1.10 Add exactly 40 mL of chloroform and shake for 4 minutes.

7.2.1.11 Allow the layers to separate and swirl to break loose all chloroform.

7.2.1.12 Draw off chloroform layer from separatory funnels into 50 mL beakers containing 3 - 4 grams of sodium sulphate.

7.2.1.13 Measure the percent transmittance of the solutions at 460 nm using the reagent blank as reference. Use 10-cm cells and take the readings as soon as possible.

7.2.2 Direct Photometric Method:

7.2.2.1 Measure the sample volume.

7.2.2.2 Distill 250 - 300 mL of the sample until approximately 10 mL is left.

7.2.2.3 Cool the distillate and transfer 50 mL to a 100 mL beaker.

7.2.2.4 Pipet 50 mL distilled water and 50 mL of each working standard A into 100 mL beakers.

7.2.2.5 Add 1 mL of ammonium chloride solution to sample, standards and blank and adjust the pH to 10.0 ± 0.2 with concentrated ammonium hydroxide.

7.2.2.6 Add 1 mL aminoantipyrine. Mix well.

7.2.2.7 Add 1 mL potassium ferricyanide. Mix well.

7.2.2.8 Read percent transmittance at 510 nm using the reagent blank as reference.

8. Calculation

8.1 Prepare two calibration curves by plotting the corresponding mg/L vs percent transmittance, using working standards A & B. Read the concentration in units of mg/L phenols from the appropriate curve.

$$mg\ phenols = \frac{mg/L\ phenol \times total\ sample\ volume\ in\ mL}{1000}$$

The final result is expressed as

$$mg\ phenols/m^3 = \frac{mg\ phenols}{m^3\ of\ collected\ gas\ at\ STP}$$

9. References

9.1 Source Sampling Code, Method 4, Alberta Environment.

9.2 Std. Meth., 16th Ed., p. 560.

SULPHATE

(Turbidimetric)

1. Introduction

1.1 Sulphate is present mainly in stack emissions of sulphuric acid and fertilizer plants. It is present either as sulphuric acid or as ammonium sulphate.

2. Principle

2.1 Sulphate is determined by the turbidimetric method. The pH of the sample is adjusted to 2.5 and the sulphate is precipitated as $BaSO_4$. The resulting turbidity of the $BaSO_4$ is measured in a spectrophotometer at 420 nm.

3. Scope

3.1 The detection limit is 5 mg/L SO_4 in the test solution. The method does not distinguish between sulphuric acid and other sulphates. The total is reported as sulphate.

4. Interference

4.1 Colour and suspended matter interfere. Orthophosphates above concentrations of 400 mg/L P_2O_5 interfere.

5. Apparatus

5.1 Sampling train consisting of a pitot assembly, impinger train, umbilical cord, vacuum pump and metering devices.
5.2 Spectrophotometer.
5.3 Nessler tubes, matched 50 mL, 2.5-cm diameter.
5.4 Spoon, 0.5 g capacity.

6. Reagents

6.1 Dilute hydrochloric acid (1+1).
6.2 Sulphate reagent: Sulfaver IV (Hach Chemical Company), or equivalent.

6.3 Stock sulphate solution (1000 mg/L): dissolve 1.479 g anhydrous sodium sulphate in distilled water and dilute to 1000 mL.

6.4 Working sulphate standards - prepare as follows:

mL stock/1000 mL	conc. mg/L SO_4
5.0	5.0
10.0	10.0
20.0	20.0
40.0	40.0
50.0	50.0

6.5 Silica gel.

7. Procedure

7.1 Sampling

7.1.1 For instruction on setting up the sampling train see Ref. No.1.

7.1.2 Collect the sample in two impingers, each containing 100 mL distilled water.

7.1.3 Transfer both impinger solutions to a polyethylene bottle. Rinse the probe with distilled water and add this rinse to the sample bottle.

7.2 Analysis

7.2.1 Measure the sample volume.

7.2.2 Transfer 50.0 mL sample, standards and blank to 100 mL beakers and adjust the pH to 2.5 by slowly adding (1+1) hydrochloric acid.

7.2.3 Transfer the solutions to Nessler tubes.

7.2.4 Add approximately 0.5 g of Sulfaver IV to each tube, stir and wait 10 minutes.

7.2.5 Use the blank for setting the spectrophotometer to 100 percent transmittance at 420 nm and read the percent transmittance for the sample, standards and blank.

8. Calculation

8.1 Prepare a calibration curve by plotting the concentration vs percent transmittance. Read the sulphate concentration in units of mg/L SO_4.

$$mg\ SO_4 = \frac{mg/L\ SO_4 \times total\ sample\ volume\ in\ mL}{1000}$$

The final result is expressed as

$$mg\ SO_4/m^3 = \frac{mg\ SO_4}{m^3\ of\ collected\ gas\ at\ STP}$$

9. Precision and Accuracy

9.1 In a single laboratory (Alberta Environmental Centre), using stack emission samples from a fertilizer plant at concentrations of 10.0 and 51.7 mg/L SO_4, the coefficients of variation were 0.1% and 2.2%, respectively.

9.2 In a single laboratory (Alberta Environmental Centre), using stack emission samples from a fertilizer plant at concentrations of 18.5 and 28.5 mg/L SO_4, the recoveries were 83% and 90%, respectively.

10. References

10.1 Source Sampling Code, Method 5, Alberta Environment.

10.2 Std. Meth., 17th Ed., p. 4-207.

SULPHUR DIOXIDE AND SULPHURIC ACID MIST

(Barium perchlorate, Titrimetric)

1. Introduction

1.1 Sulphur dioxide originates mainly from the burning of sulphur-containing fuels, such as coal and gasoline, and from the sulphur-recovery process of sour gas plants. In addition, sulphur dioxide is an emission product of oil and gas refineries. Sulphur dioxide in the atmosphere is slowly oxidized to SO_3 which, in turn, reacts with atmospheric moisture to form sulphuric acid mist.

2. Principle

2.1 Stack emission is passed through an impinger containing isopropanol and then through second and third impingers containing 3% H_2O_2 solution. Sulphuric acid mist and sulphur trioxide are absorbed in the isopropanol impinger and SO_2 is oxidized to H_2SO_4 by hydrogen peroxide in the second and third impingers. Both fractions are titrated separately against barium perchlorate.

3. Scope

3.1 This method is applicable for the separate determination of sulphuric acid mist and sulphur dioxide in source emission and both are reported as H_2SO_4. The detection limit is 0.1 mg/L H_2SO_4 in the test solution.

4. Interference

4.1 Cations and certain anions such as sulphite and phosphate interfere. Cation interference can be avoided by treating the sample with EDTA prior to titration.

5. Apparatus

5.1 Gas sampling train consisting of a pitot assembly, filter holder, impinger train, umbilical cord, vacuum pump and metering devices.

5.2 pH meter.

6. Reagents

6.1 Silica gel.

6.2 Isopropanol (85%): mix 850 mL of isopropanol with 150 mL of deionized distilled water. A portion of this solution to be used in the first impinger is acidified with acetic acid to pH 3.5.

6.3 Mixed thorin indicator: dissolve 0.2 g thorin and 0.32 g of indigo carmine with distilled water and transfer to a 100 mL volumetric flask. Mix well before using.

6.4 Barium perchlorate (0.010N): dissolve 1.950 g of barium perchlorate, $Ba(ClO_4)_2.3H_2O$, in 200 mL deionized distilled water and dilute to 950 mL with 85% isopropanol. Adjust the pH to 3.5 with acetic acid and make up the volume to 1000 mL with 85% isopropanol. Standardize the barium perchlorate solution against 15 mL of 0.010N sulphuric acid containing 85 mL of isopropanol. Use mixed thorin as indicator.

6.5 Sulphuric acid standard (0.010N): purchase, or standardize against .010N NaOH which has been previously standardized against potassium bi-phthalate (see method for chlorine and hydrochloric acid).

6.6 Acetic acid.

6.7 EDTA (5%): dissolve 5 g disodium ethylenediamine tetra-acetate dihydrate in 100 mL of deionized distilled water.

6.8 Hydrogen peroxide (3%): dilute 100 mL of 30% H_2O_2 to 1 litre with deionized distilled water.

7. Procedure

7.1 Sampling

7.1.1 For instructions on setting up the sampling train and collecting gas sample see Ref. No.1.

7.1.2 Place .50 mL of 85% isopropanol (pH 3.5) in the first impinger and 150 mL of 3% hydrogen peroxide in each of the second and third impingers. Collect the sample.

7.1.3 Measure the contents of the first impinger and transfer it (including pyrex wool and filter paper from the filter holder) to a polyethylene bottle. Rinse the probe and the first impinger with 85% isopropanol, and add this rinse to the bottle.

7.1.4 Transfer the solutions from the second and third impingers to another polyethylene bottle. Rinse with distilled water and add the rinse to the same bottle.

7.2 Analysis

7.2.1 Sulphuric Acid

7.2.1.1 Shake the container holding isopropanol and filter. If the filter breaks up, allow fragments to settle. If it remains unbroken, decant the sample to another bottle and rinse the bottle with 85% isopropanol.

7.2.1.2 Measure the volume of the sample.

7.2.1.3 Pipet 25.0 mL of the sample and 25.0 mL of the 85% isopropanol absorbing solution as blank into separate 250 mL Erlenmeyer flasks.

7.2.1.4 Using a pH meter, adjust the pH to 3.5, if necessary, by adding acetic acid.

7.2.1.5 Add 2-4 drops of mixed thorin indicator.

7.2.1.6 Titrate to the violet end point, using 0.010N barium perchlorate, and record the volume.

7.2.2 Sulphur Dioxide

7.2.2.1 Measure the combined volume of the sample collected in the second and third impingers.

7.2.2.2 Pipet 15.0 mL of the sample and 15.0 mL of the 3% hydrogen peroxide absorbing solution as blank into separate 250 mL Erlenmeyer flasks.

7.2.2.3 Dilute to 100 mL with 100% isopropanol and adjust the pH to 3.5 with dilute acetic acid. Use a pH meter.

7.2.2.4 Add 2-4 drops of mixed thorin indicator.

7.2.2.5 Titrate to the violet end point, using 0.010N barium perchlorate, and record the volume.

8. Calculation

8.1 The amount of sulphuric acid in the first impinger is expressed as:

$$mg\ H_2SO_4 = \frac{N \times 49 \times (V_s - V_b) \times V_t}{V_a}$$

The amount of SO_2 as sulphuric acid in the second and third impingers is also given by the same expression as above,

where

N	=	normality of barium perchlorate.
V_s	=	volume of titrant for the sample.
V_b	=	volume of titrant for the blank.
V_t	=	total volume of the sample.
V_a	=	volume of the sample used for titration
49	=	equivalent weight of H_2SO_4.

The final result is expressed as:

$$mg\ H_2SO_4/m^3 = \frac{total\ mg\ H_2SO_4}{m^3\ of\ collected\ gas\ at\ STP}$$

9. Precision and Accuracy

9.1 In a single laboratory (Alberta Environmental Centre), using stack samples at concentrations of 4.3 and 13.8 mg/L H_2SO_4, the coefficients of variation were 0.82% and 0.15%, respectively.

9.2 In a single laboratory (Alberta Environmental Centre), using stack samples at concentrations of 1.8 and 13.4 mg/L H_2SO_4, the recoveries were 97% and 100 %, respectively.

10. References

10.1 Source Sampling Code, Method 5, Alberta Environment.

10.2 Methods of Air Sampling and Analysis. APHA Intersociety Committee. M. Katz, Editor; 2nd Edition, p. 855.

SULPHUR DIOXIDE AND SULPHURIC ACID MIST

(Ion Chromatography)

1. Introduction

1.1 Sulphur dioxide originates mainly from the burning of sulphur-containing fuels, such as coal and gasoline, and from the sulphur-recovery process of sour gas plants. In addition, sulphur dioxide in the atmosphere is slowly oxidized to SO_3 which, in turn, reacts with atmospheric moisture to form sulphuric acid mist.

2. Principle

2.1 Stack emission is passed through an impinger containing isopropanol and then through second and a third impingers containing 3% H_2O_2 solution. Sulphuric acid mist and sulphur trioxide are absorbed in the isopropanol impinger and SO_2 is oxidized to H_2SO_4 by hydrogen peroxide in the second and third impingers. The sulphate ion is then measured by ion chromatography. See the method for anions by ion chromatography

3. Scope

3.1 The method determines sulphate and is reported as H_2SO_4. The range is 0.1 to 190 mg/L in test solution.

4. Interferences

4.1 Bisulphate will interfere with sulphate analysis. If the column deteriorates in efficiency, it will not completely separate oxalate (usually not present).

5. Apparatus

5.1 Gas sampling train consisting of a pitot assembly, filter holder, impinger train, umbilical cord, vacuum pump, and metering devices.

5.2 pH meter.

5.3 Dionex model 2020i ion chromatograph equipped with:

5.3.1 Spectra Physics SP4270 computing integrator.

5.3.2 Precolumn.

5.3.3 Separator.

5.3.4 Suppressor.

5.3.5 Conductivity detector.

6. Reagents

6.1 Silica gel.

6.2 Isopropanol (85%): mix 850 ml of isopropanol with 150 ml of deionized and distilled water. A portion of this solution to be used in the first impinger is acidified with acetic acid to pH 3.5.

6.3 Stock sulphate solution (1000 mg/L): dissolve 1.8142 g of oven-dried K_2SO_4 in deionized and distilled water and dilute to one litre.

6.4 Working standards (0-190 mg/L): prepare solutions by appropriate dilutions of the stock solution using deionized and distilled water and/or isopropanol. It is important that the matrix of the working standards approximate the sample matrix after dilutions.

6.5 Acetic acid.

6.6 EDTA (5%): dissolve 5 g disodium ethylenediamine tetra-acetate dihydrate in 100 ml of deionized and distilled water.

6.7 Hydrogen peroxide (3%): dilute 100 ml of 30% H_2O_2 to 1 litre with deionized and distilled water.

7. Procedure

7.1 Sampling

7.1.1 For instructions on setting up the sampling train and collecting gas sample see Ref. No.1.

7.1.2 Place 150 mL of 85% isopropanol (pH 3.5) in the first impinger and 150 ml of 3% hydrogen peroxide in each of the second and third impingers. Collect the sample.

7.1.3 Measure the contents of the first impinger and transfer it (including pyrex wool and filter paper from the filter holder) to a polyethylene bottle. Rinse the probe and the first impinger with 85% isopropanol, and add this rinse to the bottle.

7.1.4 Transfer the solution from the second and third impingers to another polyethylene bottle. Rinse with distilled water and add the rinse to the same bottle.

7.2 Analysis

7.2.1 Shake the container holding isopropanol and filter. If the filter breaks up, allow fragments to settle. If it remains unbroken, decant the sample to another bottle and rinse the bottle with 85% isopropanol.

7.2.2 Measure the volume of the sample.

7.2.3 Measure the combined volume of the sample collected in the second and third impingers.

7.2.4 Dilute 5 mL of each sample to 100 mL or in separate volumetric flasks.

7.2.5 Inject the sample directly into the ion chromatograph, using the following instrument conditions:

7.2.5.1 No sample loop.

7.2.5.2 Eluent is 2.8 mM $NaHCO_3$ and 2.2 mM Na_2CO_3.

7.2.5.3 Flow rate is 2.0 cc/min.

7.2.5.4 Output range is 30 µS.

7.2.6 The sulphate peak is integrated electronically at approximately eleven minutes run time.

8. Calculation

8.1 The amount of sulphuric acid in the first impinger is expressed as:

$$mg\ H_2SO_4 = mg/L\ SO_4 \times sample\ volume\ (L) \times dilution \times 1.021$$

$$where,\ 1.021 = conversion\ factor\ SO_4\ to\ H_2SO_4$$

8.2 The amount of SO_2 as sulphuric acid in the second and third impinger is also given by the expression as above.

8.3 The final result is expressed as:

$$mg\ H_2SO_4/m^3 = \frac{total\ mg\ H_2SO_4}{m^3\ of\ collected\ gas\ at\ STP}$$

9. Precision and Accuracy

9.1 In a single laboratory (Alberta Environmental Centre), using 14 EPA interlab SO_2 samples over a period of 4 years, and a concentration range of 200 µg to 1,296 µg, the percent recovery ranged from 96.4% to 103.6%, with a coefficient of variation of 2.1%.

10. References

10.1 Source Sampling Code, Method 5, Alberta Environment.

10.2 Ion Chromatography Manual, Dionex Corporation.

TOLUENEDIISOCYANATE (TDI)

(Colorimetric)

1. Introduction

1.1 The main sources of 2,4 TDI are emissions from plants that manufacture wood products.

2. Principle

2.1 TDI is hydrolysed by a HCl-acetic acid solution to the corresponding toluene-diamine derivative. The diamine is diazotized by the sodium nitrite-sodium bromide solution. The addition of N-(Naphthyl)-ethylenediamine forms a coloured complex, which is measured at 550nm.

3. Scope

3.1 The detection limit is 1.0 µg TDI/mL in the test solution.

4. Interference

4.1 Any free aromatic amine may be a positive interference. Methylene-di-(4-phenylisocyanate) will form a coloured complex. However, its colour development time is about 1 to 2 hours, compared with 5 minutes for TDI. Therefore, MDI will generate no interference.

4.2 The method is not specific for TDI.

5. Apparatus

5.1 Sampling equipment consisting of:

5.1.1 All-glass, calibrated, midget impinger containing the absorbing solution.

5.1.2 Battery-operated personal sampling pump, MSA Model G, or equivalent. The sampling pump is protected from splashover or water condensation by an absorption tube loosely packed with a plug of glass wool and inserted between the exit arm of the impinger and the pump.

5.1.3 Wet test meter.

5.1.4 Thermometer.

5.1.5 Manometer.

5.1.6 Stopwatch.

5.1.7 Spectrophotometer.

5.1.8 Cells, 1- and 5-cm matched cells.

5.1.9 Volumetric flasks of 50, 100 and 1000 mL capacity.

5.1.10 Analytical balance, sensitivity 0.1 mg.

5.1.11 Pipets, 0.5, 1 and 15 mL.

5.1.12 Graduate cylinders, 25-50 mL.

6. Reagents

6.1 Purity of reagents - All reagents must be made using ACS reagents, or better.

6.1.1 Deionized distilled water.

6.1.2 2,4 Toluenediamine.

6.1.3 Hydrochloric Acid, conc.

6.1.4 Glacial Acetic Acid, conc.

6.1.5 Sodium Nitrite.

6.1.6 Sodium Bromide.

6.1.7 Sodium Nitrite solution: dissolve 3.0 g of sodium nitrite and 5.0 g of sodium bromide in about 80 mL of deionized distilled water. Make up to volume in a 100 mL volumetric flask with deionized distilled water. This solution is stable for one week if refrigerated.

6.1.8 Sulfamic Acid.

6.1.9 Sulfamic Acid solution, 10% w/v: dissolve 10g of sulfamic acid in 100 mL water.

6.1.10 N-(1-Naphthyl)-Ethylene Diamine Dihydrochloride solution: dissolve 50 mg in about 25 mL of water. Add 1 mL of conc. HCl and dilute to 50 mL in a 50 mL volumetric flask. Solution should be clear and colourless; colouring caused from contamination by free amines. If solution is coloured, make up a new solution. The solution is stable for 4 days.

6.1.11 Absorbing solution: add 35 mL conc. HCl and 22 mL glacial acetic acid to approximately 600 mL water. Dilute the solution with 1 litre distilled water. 15 mL is used in each impinger.

6.1.12 Standard solution A: weigh 140 mg of 2,4 toluenediamine (equivalent to 200 mg of 2,4 toluenediisocyanate). Dissolve in 660 mL of glacial acetic acid, transfer to a 1-L volumetric flask and make up to volume with distilled water.

6.1.13 Standard solution B: transfer 10 mL of solution A to a 1 litre volumetric flask. Add 27.8 mL of glacial acetic acid so that when solution B is diluted to 1 litre with distilled water, it will be 0.6 N with respect to acetic acid. This solution contains an equivalent of 2 µgTDI/mL.

6.1.14 Calibration and standard solutions:

6.1.14.1 To each of a series of eight graduate cylinders add 5 mL of 1.2 N hydrochloric acid.

6.1.14.2 To these cylinders add the following amounts of 0.6 N acetic acid:10.0, 9.5, 9.0, 8.0, 7.0, 6.0, 5.0 and 0.0 mL, respectively.

6.1.14.3 To the cylinders add standard solution B in the same order as the acetic acid was added: 0.0, 0.5, 1.0, 2.0, 3.0, 4.0, 5.0 and 10 mL, so that the final volume is 15 mL (i.e., 0.0 mL of the standard is added to the 10 mL acetic acid; 0.5 mL of the standard is added to the 9.5 mL acid etc.). The cylinders now contain the equivalent of 0.0,1.0, 2.0, 4.0, 6.0, 8.0, 10.0 and 20.0 µg TDI, respectively. The standard containing 0.0 mL standard solution is a blank.

6.1.14.4 Add 0.5 mL of the 3.0% sodium nitrite reagent to each cylinder. Mix. Let stand for 2 min.

6.1.14.5 Add 1 mL of the 10% sulfamic acid solution. Mix. Allow to stand for 2 min.

6.1.14.6 Make up to 20 mL with water.

6.1.14.7 A standard curve is constructed by plotting the absorbance against micrograms (µg) TDI.

6.1.15 Cleaning of apparatus: All apparatus should be cleaned in a hot detergent solution to remove any oil.

7. Analysis

7.1 Determine sample volume.

7.2 Pipet a 5 mL aliquot of the sample and the blank into separate graduate cylinders.

7.3 Add 1 mL of 10% sulfamic solution to each cylinder, agitate for 30 seconds and allow solution to stand 2 min. to destroy all the excess nitrous acid present.

7.4 Add 1 mL of 0.1% N-(1-Naphthyl) - ethylenediamine solution to each cylinder. Agitate and allow colour to develop. Colour will be developed in 5 min. A reddish blue or pink colour indicates the presence of TDI.

7.5 Add 13 mL of water to bring the final volume to 20 mL.

N.B. If your aliquot is different, adjust the volume of water so that the final volume will be 20 mL.

7.6 Using the blank, adjust the spectrophotometer to '0' absorbance at 550 nm.

7.7 Determine the absorbance of each solution, using 1-cm cell at 550 nm.

8. Calculations

8.1 Subtract the blank absorbance, if any, from the sample absorbance.

8.2 From the calibration curve, read the micrograms TDI corresponding to the absorbance of the sample.

8.3 Calculate the concentration of TDI by multiplying the concentration (from calibration curve) by the total sample volume in litres.

$$mgTDI = mg/L \times Volume\ (in\ litres)$$

9. Reference

9.1 Methods of Air Sampling and Analysis, APHA Intersociety Committee, 2nd Ed., p. 915.

UREA

(Diacetylmonoxime, Colorimetric)

1. Introduction

1.1 Urea is present as fine particulates in stack emissions of urea fertilizer plants.

2. Principle

2.1 Urea forms a yellow-coloured complex with diacetylmonoxime, the intensity of which is measured spectrophotometrically at 478 nm.

3. Scope

3.1 This method is suitable for the determination of urea in stack emissions containing urea in the range of 5 to 25 mg/L in the test solution.

4. Interference

4.1 No known interference.

5. Apparatus

5.1 Sampling train consisting of a pitot assembly, filter holder, impinger train, umbilical cord, vacuum pump and metering devices.
5.2 Spectrophotometer, 1-cm cells.
5.3 Teflon screw-capped culture tube, 16 x 100 mm.

6. Reagents

6.1 Diacetylmonoxime: dissolve 3.0 g in 100 mL distilled water.
6.2 Ferric chloride (0.1M): dissolve 2.7 g $FeCl_3.6H_2O$ in 100 mL distilled water.
6.3 Acid mixture: mix 300 mL 85% phosphoric acid, 100 mL conc. H_2SO_4, 1.8 mL of 0.1M $FeCl_3$ and a solution of 0.237 g $MnSO_4$ in 400 mL distilled water.
6.4 Silica gel.

6.5 Urea stock solution (500 mg/L urea): dissolve 0.250 g urea in distilled water and dilute to 500 mL with distilled water in a volumetric flask.

6.6 Working standards - prepare as follows:

mL stock/200 mL	conc. mg/L urea
2.0	5.0
4.0	10.0
6.0	15.0
8.0	20.0
10.0	25.0

Prepare working standards weekly.

7. Procedure

7.1 Sampling

7.1.1 For instruction on setting up the sampling train, see Ref. No.1.

7.1.2 Collect the sample either in two impingers, each containing 100 mL of distilled water, or on a particulate filter.

7.1.3 Transfer the impinger solution to a polyethylene bottle. Rinse the probe with distilled water and add this rinse to the bottle. Fold the filter with the particulate and place it in a petri dish. Store the aqueous sample at 5°C.

7.2 Analysis

7.2.1 Stir well and transfer the aqueous sample to a 250 mL volumetric flask and dilute to volume. Dissolve the solid sample in distilled water in a 100 mL volumetric flask and dilute to volume.

7.2.2 Pipet 1.0 mL of the sample, standards and blank into separate culture tubes. Add 2.5 mL acid mixture and 0.25 mL of diacetylmonoxime solution. Cap tightly.

7.2.3 Shake the mixture well and heat the culture tubes in a boiling water bath for 30 minutes in the dark (wrap the culture tubes with aluminum foil).

7.2.4 Allow to cool to room temperature and read the absorbance at 478 nm in a 1-cm cell against a reagent blank.

8. Calculation

8.1 Prepare a calibration curve by plotting mg/L urea vs absorbance. Read the concentration of samples in units of mg/L urea.

$$mg\ urea = \frac{mg/L\ urea \times total\ sample\ volume\ in\ mL}{1000}$$

The final result is expressed as

$$mg\ urea/m^3 = \frac{mg\ urea}{m^3\ of\ collected\ gas\ at\ STP}$$

9. References

9.1 Source Sampling Code, Method 5, Alberta Environment.

9.2 R.B. Moore and N.J. Kauffman, Anal. Biochem., Vol. 33, 1970, p. 263.

ACIDITY

(Titration)

1. Introduction

1.1 The acidity of water is the capacity of the water to donate protons. The acidity in atmospheric precipitation gases from the dissolution of acidic gases, such as sulphur dioxide and nitric oxides.

2. Principle

2.1 The sample is titrated electrometrically with a standard sodium hydroxide solution to a pH of 5.6. The acidity is expressed as positive H^+ microequivalent/L ($+H^+$ µ eq/L).

3. Scope

3.1 The detection limit is +40 H^+ µeq/L.

4. Interference

4.1 No known interference.

5. Apparatus

5.1 pH meter.

6. Reagents

6.1 Standard sodium carbonate solution (0.020N): dissolve 1.060 g anhydrous Na_2CO_3, dried at 140°C for 2 hours, in CO_2-free distilled water and dilute to 1000 mL.

6.2 Stock sulphuric acid solution (0.1N): dilute 2.8 mL conc. H_2SO_4 to 1000 mL with distilled water.

6.3 Standard sulphuric acid (0.020N): dilute 200 mL of the 0.1N stock sulphuric acid solution to 1000 mL with CO_2-free distilled water. Standardize with 0.020N Na_2CO_3 solution as follows: dilute 10.0 mL 0.020N Na_2CO_3 solution to 100 mL with CO_2-free

distilled water and titrate with 0.020N sulphuric acid using methyl orange as indicator. The required normality is given by:

$$N = \frac{0.020 \times 10}{mL\ acid\ used}$$

6.4 pH 4.0 and 7.0 buffers.

6.5 Stock sodium hydroxide solution (1N): dissolve 40.0 g NaOH pellets in CO_2-free distilled water and dilute to 1000 mL.

6.6 Standard sodium hydroxide solution (0.020N): dilute 20.0 mL 1N NaOH in distilled water and dilute to 1000 mL. Standardize with 0.020N sulphuric acid using methyl red as indicator and store in a polyethylene bottle.

7. Procedure

7.1 Standardize the pH meter using the two buffers.

7.2 Pipet 50.0 mL of the sample into a 250 mL beaker.

7.3 If the pH of the sample is above 4.0, add 0.020N standard sulphuric acid dropwise to lower the pH to 4.0. Purge the sample with nitrogen to remove CO_2 formed from carbonate and bicarbonate. If the initial sample has a pH less than 4.0, the addition of sulphuric acid is not required.

7.4 Titrate the sample to pH 5.6 using 0.020N standard sodium hydroxide solution.

8. Calculation

$$Acidity\ (as\ H^+\ \mu eq/L) = \frac{[(V_1 \times N_1) - (V_2 \times N_2)] \times 10^6}{mL\ sample\ used\ for\ titration}$$

where

V_1 = vol. in mL of standard NaOH solution used in titration.

N_1 = normality of standard NaOH solution.

V_2 = vol. in mL of standard H_2SO_4 solution used to reduce pH to 4.

N_2 = normality of standard H_2SO_4 solution.

9. References

9.1 Methods for Chemical Analysis of Water and Wastes, U.S.; E.P.A. - 625-/6-74-003.

9.2 Std. Meth. for Water and Wastewater, 17th Ed., p. 2-30.

9.3 The Canadian Network for Sampling Precipitation (CANSAP), by R.L. Berry; Internal Report ARQA 45-77, Downswiew, Ontario.

September 1992 Method No. 51515

ALKALINITY

(Titration)

1. Introduction

1.1 The alkalinity of water is defined as the capacity of the water to accept protons. Soluble bicarbonates, carbonates and hydroxides are responsible for the alkalinity of precipitation.

2. Principle

2.1 The alkalinity is determined by titrating the sample with strong acid to pH 4.0, then purging the sample with nitrogen to remove CO_2 formed from carbonate and bicarbonate. Finally, the sample is backtitrated with strong alkali to pH 5.6. The alkalinity is expressed as negative H^+ microequivalent/L (-H^+ µeq/L).

3. Scope

3.1 The detection limit is -40 H^+ µeq/L.

4. Interference

4.1 No known interference.

5. Apparatus

5.1 pH meter.

6. Reagents

6.1 Standard sodium carbonate solution (0.020N): dissolve 1.060 g anhydrous Na_2CO_3, dried at 140°C for 2 hours, in CO_2-free distilled water and dilute to 1000 mL.

6.2 Stock sulphuric acid solution (0.1N): dilute 2.8 mL conc. H_2SO_4 to 1000 mL with distilled water.

6.3 Standard sulphuric acid (0.020N): dilute 200 mL of the 0.1N stock sulphuric acid solution to 1000 mL with CO_2-free distilled water. Standardize with 0.020N Na_2CO_3 solution as follows: dilute 10.0 mL 0.020N Na_2CO_3 solution to 100 mL with CO_2-free distilled water and titrate with 0.020N sulphuric acid using methyl orange as indicator. The required normality is given by:

$$N = \frac{0.020 \times 10}{mL\ acid\ used}$$

6.4 pH 4.0, 7.0 and 10.0 buffers.

7. Procedure

7.1 Standardize the pH meter using three buffers.

7.2 Titrate 50.0 mL sample with 0.020N H_2SO_4 to pH 4.0. Purge the sample with nitrogen to remove CO_2 formed from carbonate and bicarbonate.

7.3 Backtitrate the sample to pH 5.6 using 0.020N sodium hydroxide solution.

8. Calculation

$$Alkalinity\ (as\ -H^+\ \mu eq/L) = \frac{[(V_1 \times N_1) - (V_2 \times N_2)] \times 10^{-6}}{mL\ sample\ used\ for\ titration}$$

where

V_1 = vol. in mL of standard NaOH solution used for backtitrating the sample from pH 4.0 to pH 5.6.

N_1 = normality of standard NaOH solution.

V_2 = vol. in mL of standard H_2SO_4 solution used for titrating the sample to pH 4.0.

N_2 = normality of standard H_2SO_4 solution.

9. References

9.1 Methods for Chemical Analysis of Water and Wastes, U.S.; E.P.A. - 625-16-74-003.

9.2 Std. Meth. for Water and Wastewater, 17th Ed., p. 2-35.

9.3 The Canadian Network for Sampling Precipitation (CANSAP), by R.L. Berry; Internal Report ARQA 45-77, Downsview, Ontario.

September 1992

Method No. 52020

AMMONIA-NITROGEN

(Automated Colorimetric)

1. Introduction

1.1 Ammonia present in atmospheric precipitation arises from fertilizers and industrial activity. Also, alkaline soil releases ammonia under warm climatic conditions.

2. Principle

2.1 Ammonia is measured by the Berthelot reaction in which a blue-coloured compound related to indophenol is formed with phenol and NaOCl in alkaline solution. Sodium nitroprusside is added to increase the sensitivity of the reaction.

3. Scope

3.1 The range is 0.002 to 0.100 mg/L NH_3-N.

4. Interference

4.1 Colour and turbidity may interfere.

5. Apparatus

5.1 Automated system consisting of:
- 5.1.1 Sampler.
- 5.1.2 Proportioning pump.
- 5.1.3 Manifold with 50°C heating bath.
- 5.1.4 Colorimeter with 630 nm filters and 50-mm flow cell.
- 5.1.5 Recorder.

6. Reagents

6.1 Ammonia-free distilled water: prepare all reagents with ammonia-free deionized water.

6.2 Hypochlorite solution: dilute 200 mL of 5.25% NaOCl solution (or commercial bleach) to one litre with distilled water.

6.3 Nitroprusside solution: dissolve 0.5 g sodium nitroprusside in distilled water and dilute to one litre.

6.4 Alkaline phenol: dissolve 83 g of phenol in 250 mL distilled water in a 1000 mL volumetric flask. Cautiously, in small increments, add 180 mL of 20% NaOH. Dilute to one litre with distilled water.

6.5 Complexing reagent: dissolve 33 g of potassium sodium tartrate and 24 g of sodium citrate in 950 mL of distilled water. Adjust the pH of this solution to 5.0 with sulphuric acid and dilute to one litre with distilled water. Add 0.5 mL Brij 35.

6.6 Stock ammonia solution (1000 mg/L NH_3-N): dissolve 4.701 g $(NH_4)_2SO_4$, dried at 105°C for 2 hours, in 1000 mL distilled water.

6.7 Standard ammonia solution (10 mg/L NH_3-N): dilute 10.0 mL of the stock solution to 1000 mL with distilled water.

6.8 Working standards - prepare as follows:

mL std./1000 mL	conc. mg/L NH_3-N
0.5	0.005
2.0	0.020
4.0	0.040
6.0	0.060
8.0	0.080
10.0	0.100

7. Procedure

7.1 Measure the sample volume.

7.2 Filter through a 0.45 µ membrane filter.

7.3 Set up manifold as in diagram.

7.4 Load sampler and run duplicate and spiked sample in accordance with quality control program.

Note:

Ammonia can be very common in a laboratory environment. To avoid this contamination, wash all glassware first with dilute HCl and then with ammonia-free water.

8. Calculation

8.1 Prepare a calibration curve by plotting peak heights vs mg/L NH_3-N. Read the concentration of the sample from the graph in units of mg/L NH_3-N.

$$mg\ NH_3\text{-}N = \frac{mg/L\ NH_3\text{-}N \times sample\ volume\ in\ mL}{1000}$$

9. Precision and Accuracy

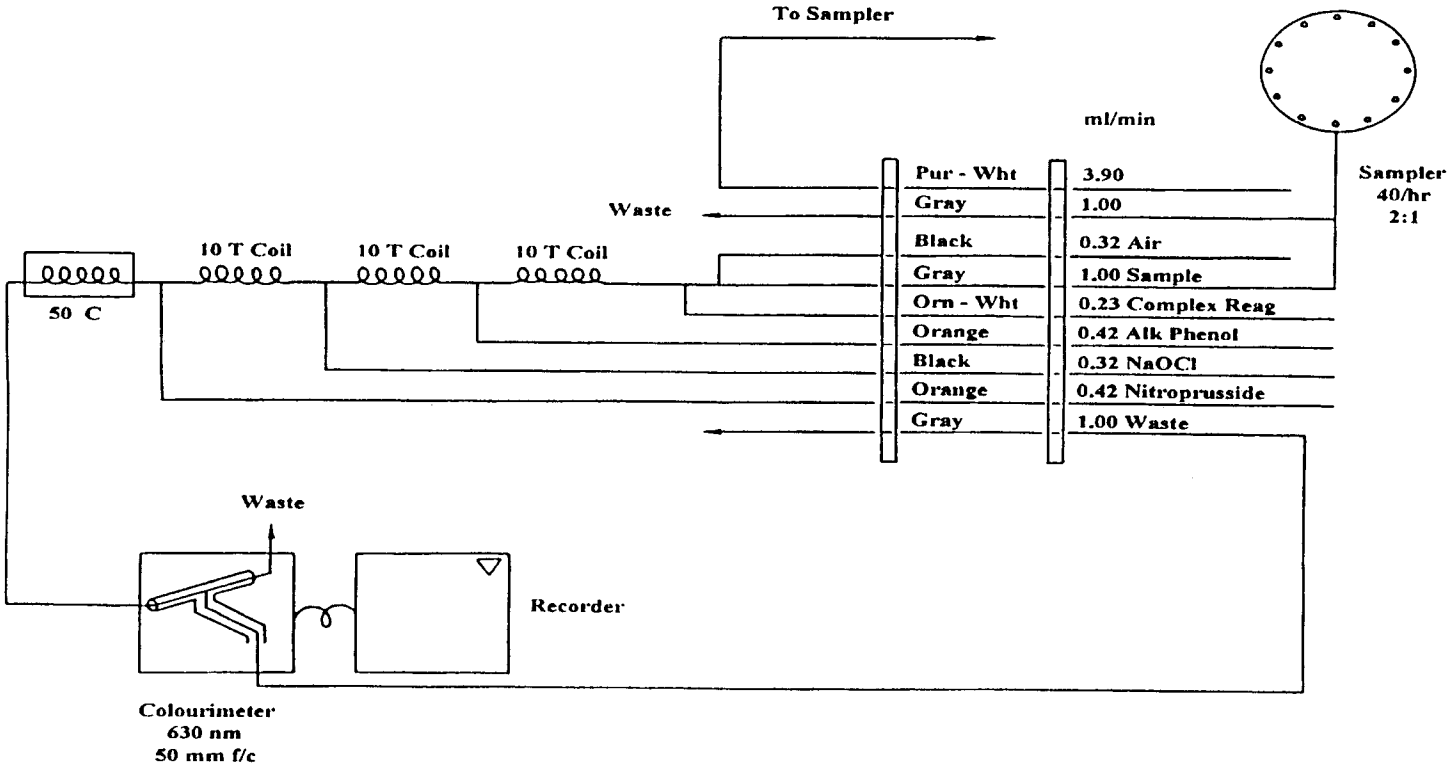
9.1 In a single laboratory (Alberta Environmental Centre), using surface water at concentrations of 0.029, 0.060 and 0.093 mg/L NH_3-N, the coefficients of variation were 4.7%, 2.0% and 1.1%, respectively.

9.2 In a single laboratory (Alberta Environmental Centre), using surface water at concentrations of 0.008, 0.015 and 0.039 mg/L NH_3-N, the recoveries were 104%, 97% and 105%, respectively.

10. Reference

10.1 "Ammonia in Water and Seawater", Technicon Industrial Method No. 154-71W.

Figure 1. Flow Diagram for Automated Colorimetric System for Ammonia



March 1993 Method No. 52121

ANIONS, DISSOLVED

(Ion Chromatography)

1. Introduction

1.1 Ion chromatography is particularly well suited for the analysis of anions in precipitation samples. In particular, sulphate is detectable at lower concentrations than by other methods. The anions Cl, NO_2, NO_3, PO_4, and SO_4 are analyzed simultaneously in an eight- minute run.

2. Principle

2.1 Like other chromatographic techniques, ion chromatography consists of a stationary phase (the ion exchange resin) and a mobile phase (the eluent). The equilibrium of the ion between the two phases governs the amount of time that the ion is retained in the column. Those ions with the least affinity for the exchange site are carried through first by the eluent stream.

2.2 The technique consists of injecting the sample by means of a sample loop into the eluent stream. The eluent carries it sequentially through the separator column, the micro membrane suppressor and the conductivity detector. The eluent for anions is dilute carbonate-bicarbonate solution (0.0020 M Na_2CO_3/0.0025 M $NaHCO_3$). The separator is a pellicular anion-exchange resin and has affinity for anions in the following order: $F < CO_3\text{-}HCO_3 < Cl < NO_2 < Br < NO_3 < PO_4 < SO_4$. When the eluent carries the sample through the separator, the ions with greater affinity are retained longer in the column. They leave the separator as their sodium salts and then enter the micro membrane suppressor.

2.3 The suppressor removes the background conductivity arising from the eluent. It does this by exchanging all the cations for hydrogen ion. This converts the highly conducting $NaHCO_3\text{-}Na_2CO_3$ to H_2CO_3, which has a very low conductivity. It also converts all the anions of interest to their acid form (i.e. HF, H_2SO_4, etc.) The ions leave the suppressor and enter the detector, a conductivity meter. As they are now in their acid form, they give a strong linear response.

3. Scope

3.1 The detection limit is reported in the individual method.

4. Interferences

4.1 Interferences are discussed in the individual method.

5. Apparatus

5.1 Dionex model 2020i ion chromatograph equipped with:

5.1.1 Spectraphysics 4270 computing integrator.

5.1.2 130 µL sample loop.

5.1.3 Guard column, 4mm x 50mm, 37042 AG4A.

5.1.4 Separator column, 4mm x 250 mm, 37041 AS4A.

5.1.5 Micro membrane suppressor, 38019, or electrolytic suppressor.

6. Reagents

6.1 High-purity, distilled and deionized water.

6.2 Standard eluent (0.0025 M $NaHCO_3$, 0.002M Na_2CO_3): dissolve 0.84 g $NaHCO_3$ and 0.848 g Na_2CO_3 and make up to four litres with distilled water.

6.3 Regeneration solution (25mN H_2SO_4): dissolve 2.775 ml of conc. H_2SO_4 and make up in 4 litres of water.

6.4 Stock standards: see individual anion methods.

7. Procedure

8. Precision and Accuracy

9. Calculations

All the above are discussed in the individual anion methods.

10. References

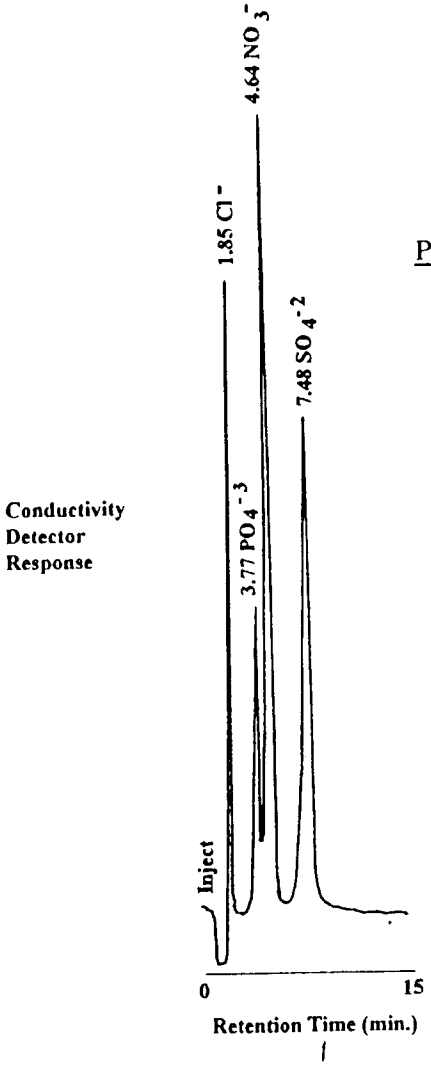
10.1 Ion Chromatographic Analysis of Environmental Pollutants, Vol. I & II, by E. Sawicki and J.D. Mulik, Ann Arbor Science.

10.2 Ion Chromatography Manual, Dionex Corporation.

Figure 1. Chromatogram of Standard Anions

Instrument Conditions

Eluent	0.0025N $NaHCO_3$/0.002 N Na_2CO_3
Flow Rate	2 mL/min
Guard Column	3 x 25 mm
Separator Column	3 x 250 mm
Suppressor	Micromembrane
Injection Volume	124 mL
Meter Full Scale	3 μ MHO



Peak	Anion	Conc.(ppm)	RT.(min.)
1	Cl-	0.259	1.85
2	PO^{-3}_4	0.819	3.77
3	NO_{-3}	1.36	4.64
4	SO^{-2}_4	1.189	7.48

September 1992

Method No. 52121A

CHLORIDE, DISSOLVED

(Ion Chromatography)

1. Introduction

1.1 Chloride present in atmospheric precipitation arises from natural sources, such as soil, dust and seawater, and from industrial activity.

2. Principle

2.1 See method for anions by ion chromatography.

3. Scope

3.1 The range is 0.01 to 5.0 mg/L Cl, using a 124 µL loop.

4. Interferences

4.1 Hypochlorite, carbonate and sulphide in high concentrations and organic acids will interfere.

5. Apparatus

5.1 See the method for anions by chromatography.

6. Reagents

6.1 Stock chloride solution (1000 mg/L Cl): dissolve 1.648 g of sodium chloride (dried at 140°C for two hours) in distilled water and dilute to one litre.

6.2 Standard chloride solution (100 mg/L Cl): dilute 100.0 mL of the stock solution to 1000 mL with distilled water.

6.3 Working standards: prepare solutions of concentrations 0, 0.3, and 0.5 mg/L Cl by appropriate dilution of the standard solution.

7. Procedure

7.1 Inject the sample by means of a 124 µL loop.

7.2 Run duplicates and spiked samples in accordance with the quality-control program.

8. Precision and Accuracy

8.1 In a single laboratory (Alberta Environmental Centre), using precipitation samples collected at various locations across Alberta, with concentrations of 0.19, 0.32 and 0.43 mg/L Cl, the coefficients of variation were 0%, 2.00% and 1.95%, respectively.

8.2 In a single laboratory (Alberta Environmental Centre), using precipitation samples collected at various locations across Alberta, with concentrations of 0.098, 0.091 and 0.96 mg/L, the recoveries were 100.2%, 103.1% and 101.0%, respectively.

NITRATE, DISSOLVED

(Ion Chromatography)

1. Introduction

1.1 Nitrate is usually present in atmospheric precipitation as nitric acid or ammonium nitrate. Nitrate is formed by the oxidation of nitrogen oxides, which are emitted from combustion processes, automobiles, power plants, compressors and various chemical plants, such as nitric acid and fertilizer plants.

2. Principle

2.1 See method for anions by ion chromatography.

3. Scope

3.1 The range is 0.01 to 10.0 mg/L NO_3 using a 124 µL loop.

4. Interferences

4.1 High levels of bromide and sulphate, chloride and some organic acids may interfere with nitrate determinations.

5. Apparatus

5.1 See method for anions by ion chromatography.

6. Reagents

6.1 Stock nitrate solution (1000 mg/L NO_3): dissolve 1.3707 g of oven-dried sodium nitrate in distilled water and dilute to one litre.

6.2 Standard nitrate solution (100 mg/L NO_3): dilute 100.0 mL of the stock solution to 1000 mL with distilled water.

6.3 Working Standards: prepare solutions of concentrations 0.0, 1.4, 2.7 mg/L NO_3 by appropriate dilution of the standard solution.

7. Procedure

7.1 Inject the sample by means of a 124 µL loop.

7.2 Run duplicates and spiked samples in accordance with the quality-control program.

8. Precision and Accuracy

8.1 In a single laboratory (Alberta Environmental Centre), using precipitation samples collected at various locations across Alberta, with concentrations of 1.04, 1.13, 1.47 and 2.32 mg/L, the coefficients of variation were, 1.99%, 3.18%, 1.41% and 3.18%, respectively.

8.2 In a single laboratory (Alberta Environmental Centre), using precipitation samples collected at various locations across Alberta, with concentrations of 0.84, 0.86 and 1.04 mg/L, the recoveries were 98.9%, 102% and 101.0%, respectively.

Notes:

1. Analyze the samples as soon as possible.
2. Sulphite interferences can be distinguished by adding hydrogen peroxide and noting the decrease in the nitrate and increase in sulphate level (sulphite normally is not present).
3. Suppressor interaction causes nitrate peaks to tail, but they still give sufficient precision and accuracy.

ORTHO-PHOSPHATE, DISSOLVED

(Ion Chromatography)

1. Introduction

1.1 Phosphorous compounds present in atmospheric precipitation originate mainly from industrial activities, such as phosphate fertilizer and cement industries. Orthophosphate determination by ion chromatography does not include insoluble polyphosphates and organic phosphates.

2. Principle

2.1 See method for anions by ion chromatography.

3. Scope

3.1 The range is 0.01 to 10.0 mg/L PO_4 using a 124 µL loop.

4. Interferences

4.1 High levels of bromide and nitrate will interfere. Organic acids, such as succinic and glutaric, may interfere.

5. Reagents

5.1 Stock phosphate solution (1000 mg/L PO_4): dissolve 1.437 g of KH_2PO_4 in distilled water and dilute to one litre.

5.2 Standard phosphate solution (100 mg/L PO_4): dilute 100.0 mL of the stock solution to 1000 mL with distilled water.

5.3 Working standards: prepare solution of concentrations 0.0, 0.8 and 1.6 mg/L PO_4 by appropriate dilution of the standard solution.

6. Procedure

6.1 Inject the sample by using a 124 µL loop.

6.2 Run duplicates and spiked samples in accordance with the quality-control program.

7. Precision and Accuracy

7.1 In a single laboratory (Alberta Environmental Centre), using precipitation samples collected at various locations across Alberta, with concentrations of 0.88, 0.79 and 0.59 mg/L, the coefficients of variation were 1.45%, 1.41% and 1.51%, respectively.

7.2 In a single laboratory (Alberta Environmental Centre), using precipitation samples collected from across Alberta, with concentrations of 0.34, 0.35 and 0.45 mg/L, the recoveries were 91.2%, 93.0% and 94.1%, respectively.

Notes:

1. Separate glassware washed with (1+1) HCl and rinsed with distilled water should be used.
2. Commercial detergents should not be used.

SULPHATE, DISSOLVED

(Ion Chromatography)

1. Introduction

1.1 Sulphate in atmospheric precipitation is formed by the oxidation of sulphur gases, such as sulphur dioxide, hydrogen sulphide and mercaptans. These sulphur gases originate from the burning of fossil fuels, gas processing plants, refineries and other industrial plants. The sulphate is usually present as sulphuric acid and ammonium sulphate.

2. Principle

2.1 See the method for anions by ion chromatography.

3. Scope

3.1 The range is 0.1 to 20.0 mg/L SO_4, using a 124 µL loop.

4. Interferences

4.1 Bisulphate will interfere with sulphate analysis. If the column deteriorates in efficiency, it will not completely separate oxalate (usually not present).

5. Apparatus

5.1 See the method for anions by ion chromatography.

6. Reagents

6.1 Stock sulphate solution (1000 mg/L SO_4): dissolve 1.8142 g of oven-dried K_2SO_4 in distilled water and dilute to one litre.

6.2 Standard sulphate solution (100 mg/L SO_4): dilute 100.0 mL of the stock solution to 1000 mL with distilled water.

6.3 Working standards: prepare solutions of concentrations 0.0, 1.2 and 2.3 mg/L SO_4 by appropriate dilution of the standard solution.

7. Procedure

7.1 Inject the sample, using 124 µL loop.

7.2 Run duplicates and spiked samples in accordance with the quality-control program.

8. Precision and Accuracy

8.1 In a single laboratory (Alberta Environmental Centre), using precipitation samples collected at various locations across Alberta, with concentrations of 1.02, 1.13, 1.69 and 2.52 mg/L, the coefficients of variation were 1.65%, 1.84%, 1.89% and 1.86%, respectively.

8.2 In a single laboratory (Alberta Environmental Centre), using precipitation samples collected at various locations across Alberta, with concentrations of 3.02, 1.79 and 1.25 mg/L, the recoveries were 99.8%, 99.7% and 100.3%, respectively.

CALCIUM, DISSOLVED

(Flame Emission)

1. Introduction

1.1 Calcium present in atmospheric precipitation arises from natural sources, such as soil and dust, or from man-made sources, such as the industrial activity associated with gypsum and cement manufacturing.

2. Principle

2.1 The sample is mixed with a solution of cesium and aspirated into a nitrous oxide-acetylene flame. The light energy emitted by the calcium is directly proportional to its concentration.

3. Scope

3.1 The range is 0.01 to 1.00 mg/L Ca. The detection limit can be extended to 0.002 mg/L Ca, if necessary.

4. Interference

4.1 Cesium is used to prevent the ionization of calcium. Up to 10 mg/L of sodium and potassium were found to have no significant effect on calcium concentrations. Use of a nitrous oxide-acetylene flame overcomes many of the inter-element interferences common to the air-acetylene flame.

5. Apparatus

5.1 Atomic absorption spectrophotometer (operated in the flame emission mode).
5.2 Gas cylinders, nitrous oxide and acetylene.
5.3 Automatic pipet.

6. Reagents

6.1 Distilled water: high purity deionized water.

6.2 Cesium chloride solution (10,000 mg/L Cs): dissolve 12.7 g CsCl in distilled water and dilute to one litre.

6.3 Stock calcium solution (1000 mg/L Ca): weigh 2.697 g anhydrous calcium carbonate, $CaCO_3$, powder (oven dried at 105°C overnight). Slowly add (1+1) HCl to dissolve the $CaCo_3$. Add 200 mL distilled water and boil for a few minutes to expel the CO_2. Cool, add a few drops methyl red solution and adjust to an intermediate orange colour by adding 3 N NH_4OH, or (1+1) HCl. Dilute to 1000 mL with distilled water.

6.4 Standard calcium solution (100 mg/L Ca): dilute 100.0 mL calcium stock solution to 1000 mL with distilled water.

6.5 Working standards - prepare as follows:

mL std./1000 mL	conc. mg/L Ca
0.5	0.05
1.0	0.10
2.5	0.25
5.0	0.50
7.5	0.75
10.0	1.0

7. Procedure

7.1 Measure the sample volume.

7.2 Turn instrument on and allow 30 minutes for instrument to warm up.

7.3 Follow manufacturer's instructions for making proper instrument settings. Pay particular attention to lighting the nitrous oxide-acetylene flame.

7.4 Add 2 mL CsCl solution to 100 mL of each sample, standard and blank to be run.

7.5 Run duplicate and spiked sample in accordance with quality-control program.

8. Instrument Parameters

8.1 Flame emission mode.

8.2 Wavelength: 422.7 nm.

8.3 Fuel: acetylene.

8.4 Oxidant: nitrous oxide.

9. Calculation

9.1 Prepare a calibration curve by plotting peak heights vs mg/L Ca. Read the concentration of the sample from the graph in units of mg/L Ca.

$$mg\ Ca = \frac{mg/L\ Ca \times sample\ volume\ in\ mL}{1000}$$

10. Precision and Accuracy

10.1 In a single laboratory (Alberta Environmental Centre), using snow samples collected in the Edmonton and the surrounding area at concentrations of 0.11, 0.42 and 0.66 mg/L Ca, coefficients of variation were 1.6%, 0.9% and 0.4%, respectively.

10.2 In a single laboratory (Alberta Environmental Centre), using snow samples collected in the Edmonton and the surrounding area at concentrations of 0.13, 0.38 and 0.64 mg/L Ca, recoveries were 103%, 95% and 99%, respectively.

11. References

11.1 Analytical Methods for Flame Spectroscopy, Varian Techtron Pty. Ltd.

11.2 Std. Meth. for Water and Wastewater, 17th Ed., p. 3-25.

CALCIUM, DISSOLVED

(Direct Current Plasma)

1. Introduction

1.1 Calcium present in atmospheric precipitation arises from natural sources, such as soil and dust, or from man-made sources, such as the industrial activity associated with gypsum and cement manufacturing.

2. Principle

2.1 The sample is aspirated into a high-energy dc argon plasma flame. The light energy emitted by the calcium ions is directly proportional to its concentration.

3. Scope

3.1 The range is 0.01 - 10 mg/L Ca in solution.

4. Interference

4.1 High concentrations of other metals can lead to chemical and ionization interference.

5. Apparatus

5.1 Beckman Spectraspan V DCP.
5.2 Ultrapure argon gas.

6. Reagents

6.1 Distilled water: high purity deionized water.
6.2 Stock calcium solution (1000 mg/L Ca): weigh 2.697 g anhydrous calcium carbonate, $CaCO_3$, powder (oven-dried at 105°C overnight). Slowly add 50% HCl to dissolve the $CaCO_3$. Add 200 mL distilled water and boil for a few minutes to expel the CO_2. Cool, add a few drops methyl red solution and adjust to an intermediate orange colour by adding 3N NH_4OH, or 50% HCl. Dilute to 1000 mL with distilled water.

6.3 Standard calcium solution (1000 mg/L Ca): dilute 100 mL calcium stock solution to 1000 mL with distilled water.

6.4 Working standards - prepare as follows:

mL std/1000 mL	conc. mg/L Ca
2.5	0.25
5.0	0.50
20.0	2.0
50.0	5.0

7. Procedure

7.1 Measure the sample volume.

7.2 Turn instrument on and allow 30 minutes to warm up.

7.3 Analyze the sample by direct aspiration using the instrument conditions specified below:

Wavelength	393.366
Order	57
State	Ion
Plasma Position	0
Entrance Slits	50 x 300µm
Exit Slits	100 x 300µm
Detection Limit (DL)	0.01 mg/L
Linear Dynamic Range (LDR)	0.007 to 10 mg/L
Background Equivalent Concentration (BEC)	0.007 mg/L
Precision	RSD at 14 x BEC 0.5%
Mode	internal at 10 seconds and 3 counts
Photomultiplier Tube (PMT)	1

8. Calculation

8.1 Prepare a calibration curve by plotting peak heights vs mg/L Ca. Read the concentration of the sample from the graph in units of mg/L Ca.

$$mg\ Ca = \frac{mg/L\ Ca \times sample\ volume\ in\ mL}{1000}$$

9. Precision and Accuracy

9.1 In a single laboratory (Alberta Environmental Centre), using a standard of 5 ppm, the coefficient of variation over a 12 month period was 1.2%.

9.2 In a single laboratory (Alberta Environmental Centre), using spiked samples in the range of 0.24 ppm to 4.2 ppm, the recoveries were 96% to 104.5% over a period of 12 months, with a coefficient of variation of 2.0%.

10. References

10.1 Std. Meth. Water and Wastewater, 17th Ed., p. 3-85.

10.2 Handbook of Spectral Line Characteristics for the DC Plasma Echelle Systems, Spectra Metrics, Inc.

March 1993 Method No. 52626

CATIONS, DISSOLVED

(Ion Chromatography)

1. Introduction

1.1 Ion chromatography is capable of measuring very low concentrations, which makes it particularly well suited for precipitation analysis. Sodium, ammonium, potassium, calcium, and magnesium cations can be analyzed in a single 15-minute run.

2. Principle

2.1 Like other chromatographic techniques, ion chromatography consists of a stationary phase and mobile phase. The equilibrium of each ion between the two phases governs the amount of time that the ion is retained in the column. Those ions with the least affinity for the exchange site are carried through first by the eluent stream.

2.2 The technique consists of injecting the sample by means of a sample loop into the mobile phase. The eluent carries it sequentially through a separator column, a suppressor column and a conductivity detector.

2.3 The eluent for cations is dilute acid (30 mM HCl). The separator is a pellicular cation exchange resin which has an affinity for cations in the following order $H^+ < Na^+ < NH_4^+ < K^+ < Mg^{++} < Ca^{++}$. When the eluent carries the sample through the separator, the ions with greater affinity are retained longer in the column, thus effecting a separation. They leave the separator as chloride salts and then enter the suppressor. The suppressor, which contains a micromembrane, has the function of removing background conductivity caused by the eluent. It accomplishes this by exchanging the chloride ions for hydroxyl ions. This converts the highly conducting H^+Cl^- to H_2O, which has a low conductivity. It also converts all the ions of interest (Na^+, NH_4^+, K^+, < Mg^{++}, Ca^{++}) to their hydroxide form. They leave the suppressor and enter the detector, a conductivity meter. Because they are now in the hydroxide form, the response is very sensitive, with excellent linearity.

3. Scope

3.1 The detection limit for each cation is reported in the individual method.

4. Interferences

4.1 Interferences are discussed in the individual method.

5. Apparatus

5.1 Dionex model 2020i or Dx-300 ion chromatograph equipped with:
- 5.1.1 200 µL sample loop.
- 5.1.2 Guard column, 4mm x 50mm, 44002, CG12.
- 5.1.3 Separator, 4mm x 250mm, 44001, CG12.
- 5.1.4 Micromembrane suppressor, 37076.

6. Reagents

6.1 High-purity distilled and deionized water.

6.2 Stock HCl (0.6N): add 25 mL conc. HCl and make up to 500 mL with water.

6.3 Standard cation eluent (0.020N): add 66.7 mL of conc. HCl to water and dilute to 2 litres.

6.4 Regeneration solution (0.02N) KOH: add 1.122 g of KOH and make up to 1 litre with water.

6.5 Regeneration solution: when auto-regeneration cartridge 39563 is used (0.10M tetrabutyl ammonium hydroxide), add 65.53 mL of 40% tetrabutylammonium hydroxide and make up to 1 litre with water. (Prepare 0.1M tetrabutylammonium hydroxide can be purchased from Dionex.

6.6 Standard stock solutions are discussed in the individual method descriptions.

7. Procedure
Precision and Accuracy
Calculations

7.1 All the above are discussed in the individual cation methods.

8. References

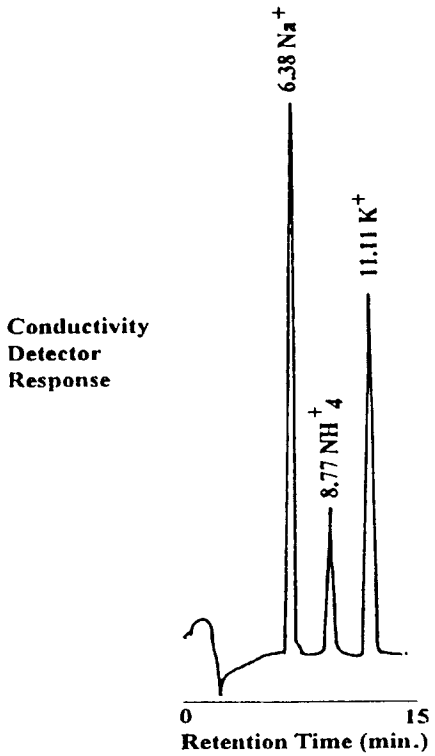
8.1 Ion Chromatographic Analysis of Environmental Pollutants. Vol. I & II, by E. Sawicki and J.D. Mulik, Ann Arbor Science.

8.2 Ion Chromatographic Manual, Dionex Corporation.

Figure 1. Chromatogram of Standard Cations

Instrument Conditions

Eluent	30 mN HCl
Flow Rate	1 mL/min
Guard Column	3 x 25 mm
Separator Column	3 x 150 mm
Suppressor	Micromembrane
Injection Volume	300 mL
Meter Full Scale	10 µ MHO



Peak	Cation	Conc.(ppm)	RT.(min.)
1	Na+	0.017	6.38
2	$NH+_4$	0.636	8.77
3	K+	0.688	11.11

AMMONIUM (NH^+_4)

(Ion Chromatography)

1. Introduction

1.1 Ammonia in atmospheric precipitation originates from fertilizer industries, combustion and industrial processes. Also, alkaline soils release ammonia under warm climatic conditions largely resulting from the decomposition of organic matter.

2. Scope

2.1 The range is 0.1 to 5.0 mg/L NH_4, using a 300 µL sample loop.

3. Interferences

3.1 All alkyl amines and high sodium levels will obscure low levels of NH_4.

4. Reagents

4.1 Stock NH_4 solution (1000 mg/L NH_4) - dissolve 2.9654 g of ammonium chloride (oven dried at 105°C for 2 hours) in 1000 mL of distilled water.

4.2 Standard solution (100 mg/L NH_4) - dilute 100.0 mL of stock solution to 1 litre with distilled water.

4.3 Working standards - prepare solutions of concentrations 0.02, 0.3 and 0.6 mg/L NH_4 by diluting the standard solution.

5. Procedure

5.1 Inject the sample, using a 300 µL loop.

5.2 Run standards, duplicates and spiked samples according to the quality-control program.

Note:

1. Ammonia can be very common in a laboratory and care must be taken to avoid contamination.
2. The ammonia calibration curve begins to deviate from linearity at a higher concentration (>10 mg/L).

6. Precision and Accuracy

6.1 In a single laboratory (Alberta Environmental Centre), using precipitation samples collected at various locations across Alberta, with concentrations of 5.69, 4.60 and 1.18 mg/L NH_4, the coefficients of variation were 1.71%, 1.24% and 2.19%, respectively.

6.2 In a single laboratory (Alberta Environmental Centre), using precipitation samples collected at various locations across Alberta with concentrations of 5.33, 4.51 and 5.50 mg/L NH_4, the recoveries were 101.5%, 100.8% and 103.9%, respectively.

POTASSIUM

(Ion Chromatography)

1. Introduction

1.1 Potassium present in atmospheric precipitation arises from natural sources, such as soil and dust, as well as industrial sources.

2. Scope

2.1 The range is 0.01 to 15 mg/L K using a 300 µL sample loop.

3. Interferences

3.1 Methyl amine interferes.

4. Reagents

4.1 Stock potassium solution (1000 mg/L K): dissolve 1.9067 g of dried potassium chloride in distilled water and dilute to 1 litre.

4.2 Standard solution (100 mg/L K): dilute 100.0 mL of stock solution to 1 litre with distilled water.

4.3 Working standards: prepare solutions of concentrations 0.02, 0.3 and 0.7 mg/L K by diluting the standard solution.

5. Procedure

5.1 Inject the sample using a 300 µL sample loop.

5.2 Run standards, duplicates and spiked samples according to the quality-control program.

6. Precision and Accuracy

6.1 In a single laboratory (Alberta Environmental Centre), using precipitation samples collected from various locations across Alberta, with concentrations of 1.94, 1.09 and 0.65 mg/L K, the coefficients of variations were 2.59%, 2.05% and 3.09%, respectively.

6.2 In a single laboratory (Alberta Environmental Centre), using precipitation samples collected from various locations across Alberta, with concentrations of 2.79, 2.30 and 3.02 mg/L K, the recoveries were 105.7%, 97.0% and 100.8%, respectively.

SODIUM

(Ion Chromatography)

1. Introduction

1.1 Sodium present in atmospheric precipitation arises from natural sources, such as soil and dust, as well as from industrial sources, such as caustic plants.

2. Scope

2.1 The range is 0.01 to 50 mg/L Na using a 300 µL sample loop.

3. Reagents

3.1 Stock sodium solution (1000 mg/L Na): dissolve 2.5420 g of oven-dried sodium chloride in four litres of distilled water.

3.2 Standard solution (100 mg/L Na): dilute 100.0 mL standard solution to 1 litre with distilled water.

3.3 Working standards: prepare solutions of concentrations 0.01, 0.2 and 0.4 mg/L Na by diluting the standard solution.

4. Procedure

4.1 Inject the sample using a 300 µL sample loop.

4.2 Run standards, duplicates and spiked samples according to the quality-control program.

Note: Care must be taken to avoid contaminating the sample by glassware, fingers, etc.

5. Precision and Accuracy

5.1 In a single laboratory (Alberta Environmental Centre), using precipitation samples collected at various locations across Alberta, with concentrations of 2.69, 1.21 and 0.74 mg/L Na, the coefficients of variation were 1.23%, 2.01% and 2.67%, respectively.

5.2 In a single laboratory (Alberta Environmental Centre), using precipitation samples collected at various locations across Alberta, with concentrations of 2.25, 1.90 and 2.84 mg/L Na, the recoveries were 107.5%, 102.8% and 101.1%, respectively.

MAGNESIUM, DISSOLVED

(Atomic Absorption)

1. Introduction

1.1 Magnesium present in atmospheric precipitation arises from natural sources, such as soil and dust, or from industrial activity.

2. Principle

2.1 The sample is mixed with a solution of cesium and aspirated into a nitrous oxide-acetylene flame. A light beam, furnished by the hollow-cathode lamp, is passed through the flame and directed onto a detector. Any free metallic atoms present in the flame absorb the incident light energy. The absorbed light energy is directly proportional to the concentration of magnesium present.

3. Scope

3.1 The range is 0.01 to 0.50 mg/L Mg. The detection limit can be extended to 0.005 mg/L Mg, if necessary.

4. Interference

4.1 Cesium is used to prevent ionization of magnesium. Up to 10 mg/L of sodium and potassium were found to have no significant effect on magnesium concentrations. Use of a nitrous oxide-acetylene flame overcomes many of the inter-element interferences common to the air-acetylene flame.

5. Apparatus

5.1 Atomic absorption spectrophotometer.
5.2 Gas cylinders, nitrous oxide and acetylene.
5.3 Automatic pipet.

6. Reagents

6.1 Distilled water: high purity deionized water.

6.2 Cesium chloride solution (10,000 mg/L Cs): dissolve 12.7 g CsCl in distilled water and dilute to one litre.

6.3 Stock magnesium solution (1000 mg/L Mg): dissolve 10.014 g of magnesium sulphate heptahydrate, $MgSO_4.7H_2O$, in 200 mL distilled water, add 1.5 mL conc. HNO_3, and make up to 1000 mL with distilled water.

6.4 Standard magnesium solution (100 mg/L Mg): dilute 100.0 mL magnesium stock solution to 1000 mL with distilled water.

6.5 Working standards - prepare as follows:

mL std./1000 mL	conc. mg/L Mg
0.5	0.05
1.0	0.10
2.0	0.20
3.0	0.30
4.0	0.40
5.0	0.50

7. Procedure

7.1 Measure the sample volume.

7.2 Turn instrument on and allow 30 minutes for instrument to warm up.

7.3 Select a magnesium hollow-cathode lamp and follow manufacturer's instructions for making proper instrument settings. Pay particular attention to lighting the nitrous oxide-acetylene flame.

7.4 Add 2 mL CsCl solution to 100 mL of each sample, standard and blank to be run.

7.5 Run duplicate and spiked sample in accordance with the quality-control program.

8. Instrument Parameters

8.1 Use Mg hollow-cathode lamp.

8.2 Wavelength: 285.2 nm.

8.3 Fuel: acetylene.

8.4 Oxidant: nitrous oxide.

9. Calculation

9.1 Prepare a calibration curve by plotting peak heights vs mg/L Mg. Read the concentration of the sample from the graph in units of mg/L Mg.

$$mg\ Mg = \frac{mg/L\ Mg \times sample\ volume\ in\ mL}{1000}$$

10. Precision and Accuracy

10.1 In a single laboratory (Alberta Environmental Centre), using snow samples collected in Edmonton and the surrounding area at concentrations of 0.02, 0.14 and 0.62 mg/L the coefficients of variation were 4.9%, 1.0% and 1.0%, respectively.

10.2 In a single laboratory (Alberta Environmental Centre), using snow samples collected in the Edmonton area at concentrations of 0.04, 0.10 and 0.29 mg/L the recoveries were 100%, 98% and 103%, respectively.

11. References

11.1 Analytical Methods for Flame Spectroscopy, Varian Techtron Pty. Ltd.

11.2 Std. Meth. for Water and Wastewater, 17th Ed., p. 3-112.

MAGNESIUM, DISSOLVED

(Direct Current Plasma)

1. Introduction

1.1 Magnesium present in atmospheric precipitation arises from natural sources, such as soil and dust, or from industrial activity.

2. Principle

2.1 The sample is aspirated into a high-energy dc argon plasma flame. The light energy emitted by the magnesium ion is directly proportional to its concentration.

3. Scope

3.1 The range is 0.01 to 60 mg/L Mg.

4. Interference

4.1 High concentrations of other metals can lead to chemical and ionization interferences.

5. Apparatus

5.1 Beckman Spectraspan V DCP.
5.2 Ultra high pure argon gas.

6. Reagents

6.1 Distilled water: high-purity deionized water.
6.2 Stock magnesium solution (1000 mg/L Mg): dissolve 10.014g of magnesium sulphate heptahydrate, $MgSO_4.7H_2O$, in 200 mL distilled water, add 1.5 mL conc. HNO_3, and make up to 1000 mL with distilled and deionized water.
6.3 Standard magnesium solution (100 mg/L Mg): dilute 100 mL magnesium stock solution to 1000 mL with distilled and deionized water.

6.4 Working standards - prepare as follows:

mL std/1000 ml	conc. mg/L Mg.
2.5	0.25
5.0	0.50
20.0	2.0
50.0	5.0

7. Procedure

7.1 Measure the sample volume.

7.2 Turn the instrument on and allow 30 minutes to warm up.

7.3 Analyze the sample by direct aspiration using the instrument conditions specified below:

Wavelength:	279.553 nm
Order:	80
State:	Ion
Plasma Position:	0
Entrance Slits:	50 x 300 µm
Exit Slits:	100 x 300 µm
Detection Limit (DL):	0.01 mg/L
Linear Dynamic Range (LDR):	0.002 to 60 mg/L
Background Equivalent Concentration (BEC):	0.006 mg/L
Precision:	RSD 2 x BEC 0.8%
Mode:	Internal at 10 seconds and 3 counts
Photomultiplier tube (PMT):	1

7.4 Run duplicate and spiked sample in accordance with the quality-control program.

8. Calculation

8.1 Prepare a calibration curve by plotting peak heights vs mg/L Mg. Read the concentration of the sample from the graph in units of mg/L Mg.

$$mg\ Mg = \frac{mg/L\ Mg \times sample\ volume\ in\ mL}{1000}$$

9. Precision and Accuracy

9.1 In a single laboratory (Alberta Environmental Centre), using a standard of 5 ppm, the coefficient of variation over a 12-month period was 1.6%.

9.2 In a single laboratory (Alberta Environmental Centre), using spiked samples in the range of 0.24ppm to 2.6ppm, the recoveries were 94.1% to 104.4% over a period of 12 months, with a coefficient of variation of 2.6%.

10. References

10.1 Std. Meth. for Water and Wastewater, 17th Ed, p. 3-110.

10.2 Handbook of Spectral Line Characteristics for the DC Plasma Echelle Systems, Spectra Metrics, Inc.

pH

(Electrometric)

1. Introduction

1.1 pH is the logarithm of the reciprocal of the hydrogen ion concentration, or more precisely, of the hydrogen ion activity in moles per litre. The pH of atmospheric precipitation samples is usually between 5 and 7.

2. Principle

2.1 A glass electrode in combination with a reference electrode, generally a saturated calomel electrode, is used for pH measurement. The glass electrode has a glass membrane, which forms a partition between the liquid sample and an internal solution of constant pH. The potential developed by the glass electrode with reference to the saturated calomel electrode is measured by an electrometer.

3. Interference

3.1 The glass electrode is relatively immune to almost all types of interfering materials. High sodium concentrations at a pH above 10 interfere. Approximate corrections for the sodium error may be made by consulting a chart supplied by the manufacturer of the electrode.

4. Apparatus

4.1 pH meter.
4.2 Glass electrode.
4.3 Reference electrode (saturated calomel).
4.4 Magnetic stirrer and stirring bar.

5. Reagents

5.1 Standard pH buffer solutions of pH 7.0 and pH 10.0 (available commercially).

6. Procedure

6.1 Set the temperature compensator of the pH meter to room temperature.

6.2 Set slope control to 100%.

6.3 Place the pH 7.0 buffer solution in a beaker and insert the electrodes into the solution. Start stirring gently and wait until the meter needle stabilizes.

6.4 Set the standardize control to the correct value of the buffer.

6.5 Repeat Step 6.3, with the pH 10.0 buffer.

6.6 Adjust slope control.

6.7 Place the electrodes in a beaker containing 50 mL of the sample and take the reading.

Notes:

1. Use the plastic protector for glass electrodes.
2. A calomel reference electrode that requires saturated KCl filling solution should contain a few KCl crystals. The level of KCl solution should be checked daily.
3. Leave electrodes in the buffer solution when not in use.

7. Calculations

7.1 The pH meter reads directly in pH units.

8. Precision and Accuracy

8.1 Forty-four analysts in 20 laboratories analyzed six synthetic water samples containing exact increments of hydrogen-hydroxyl ions, with the following results:

Increment as pH Units	Precision as Standard Deviation pH Units	Accuracy as Bias, %	Accuracy as Bias, pH Units
3.5	0.10	-0.29	-0.01
3.5	0.11	-0.00	
7.1	0.20	+1.01	+0.07
7.2	0.18	-0.03	-0.002
8.0	0.13	-0.12	-0.01
8.0	0.12	+0.16	+0.01

(FWPCA Method Study 1, Mineral and Physical Analyses)

9. References

9.1 Std. Meth. for Water and Wastewater, 17th Ed., p. 4-95.

9.2 Methods Manual for Chemical Analysis of Water and Wastes, U.S., E.P.A. - 625/6-74-003.

pH AND ACIDITY

(Electrometric and Gran's Plot Titration)

1. Introduction

1.1 There are two types of acidic solutions: those that are stongly acidic owing to free hydrogen ions and those that are weakly acidic as the result of acid salts that act as buffering agents and prevent the pH from rising above a certain level. Both types of acidity in acid rain affect lakes, soils and forests.

2. Principle

2.1 pH is measured with a digital pH/mV meter equipped with a glass electrode in combination with a reference electrode. The acidity is measured by titrating the sample against a standard NaOH solution. The amount of NaOH added to the sample is plotted against the Gran's function, which is calculated from the mV readings during the titration. End points are obtained from an extrapolation of the straight lines to the x-axis. For details of the principle, see the reference[1].

3. Range

3.1 pH: 3.00 - 8.00 pH units.

3.2 Acidity: Minimum detectable concentration 15 μeq H^+/L.

4. Interference

4.1 There are no known interferences.

5. Apparatus

5.1 pH meter (Radiometer) with millivolt scale.

5.2 Glass electrode with a separate reference electrode is preferred, or a combination electrode "Orion rugged low resistance".

5.3 Magnetic stirrer.

5.4 Eppendorf microliter pipet 10 & 20 mL.

5.5 Analytical balance.

6. Reagents

6.1 Commercial buffer solutions, pH 4.0 and 7.0.

6.2 Distilled water, conductivity <5 µmho.

6.3 Potassium biphthalate solution (0.05 N): dry 15 to 20 g of primary standard $KHC_8H_4O_4$ at 120°C. Cool in a desiccator. Weigh 10g ± 0.05g. to the nearest mg, transfer to a 1 L flask, and dilute to volume with distilled water.

6.4 Sodium hydroxide (0.1 N): dissolve 4 g of NaOH in 10 mL of distilled water, cool and filter. Dilute the filtrate to 1 L with distilled water and store in a refrigerator. Standardize this sodium hydroxide solution using 40 mL $KHC_8H_4O_4$ solution to the inflection point, which should be close to pH 8.7.

$$Normality\ of\ NaOH = \frac{A \times 40}{204.2 \times B}$$

where

A	=	weight of $KHC_8H_4O_4$ in 1 L
B	=	mL of NaOH used.
(204.2	=	mol.wt. of $KHC_8H_4O_4$)

6.5 Dilute sodium hydroxide (0.01 N): repeat the above standardization using a 1:10 dilution of $KHC_8H_4O_4$ and 0.01 N NaOH solution.

6.6 pH 4.0 standard H_2SO_4: dilute an ampule of conc. H_2SO_4 to 10^{-4} N with distilled water. Standardize this acid with 0.01 N NaOH, using the Gran's titration procedure below.

7. Procedure

7.1 Analysis should be carried out as soon as possible after the sample container has been opened.

7.1.1 Allow the samples and buffers to reach laboratory temperature before analysis.

7.1.2 pH Measurement

7.1.2.1 Calibrate the pH meter by setting the calibration control with pH 7 buffer and the slope control with pH 4 buffer. Rinse the electrode with distilled water between readings.

7.1.3

7.1.3.1 Pipet a 40 mL aliquot of sample in a plastic (Nalgene) beaker.

7.1.3.2 Place a clean magnetic bar into the beaker and place the beaker on a magnetic stirrer. Insert the electrode(s) into the sample.

7.1.3.3 Stir the sample slowly for 30 seconds.

7.1.3.4 Turn the stirrer off, allow the pH reading to stabilize (1 to 2 min) and record the reading.

7.1.4 Acidity Measurement

7.1.4.1 Set the meter to read in mV and start to stir the sample slowly. Record the initial mV reading using the expanded scale (0.0 mL NaOH).

7.1.4.2 Based on the initial pH reading, add increments of 0.01 N NaOH, allow 15 seconds for the reading to stabilize, and record the mV readings and the total volume added. Determine the increment size as follows:

Initial pH	Increment
5 to 7	10 µL
4 to 5	20 µL
<4	50 µL

Take four to six readings on the acidic (-mV) side of the inflection point and then add sufficient NaOH to shift the readings past the unstable area near the inflection point. Take 4-6 readings on the basic (+mV) side.

7.1.5 The electrode should be left in distilled water after analyses are completed.

8. Calculations

8.1 Calculate the Gran's function as follows:

$$\varphi = (V_x + V_b)\ 10^{E/g}$$

where

V_x = sample volume

V_b = titrant volume

E = absolute value of the mV reading

g = 59.157 mV at 25°C.

8.2 Plot Gran's function vs volume of NaOH added (mL). Extrapolate data points representing strong and weak acidity components to the volume axis. Note that a minimum of 4 points on a straight line is necessary to confirm the presence of strong acidity. Also note that the scale of the Gran's function axis (Y-axis) does not have to be the same on both sides of the inflection point.

8.3 Calculate the strong and total acidity components as follows:

$$Acidity\ (\mu\ eqL) = \frac{V \times N \times 10^3}{0.04L}$$

where

V = volume axis intercept in (mL)

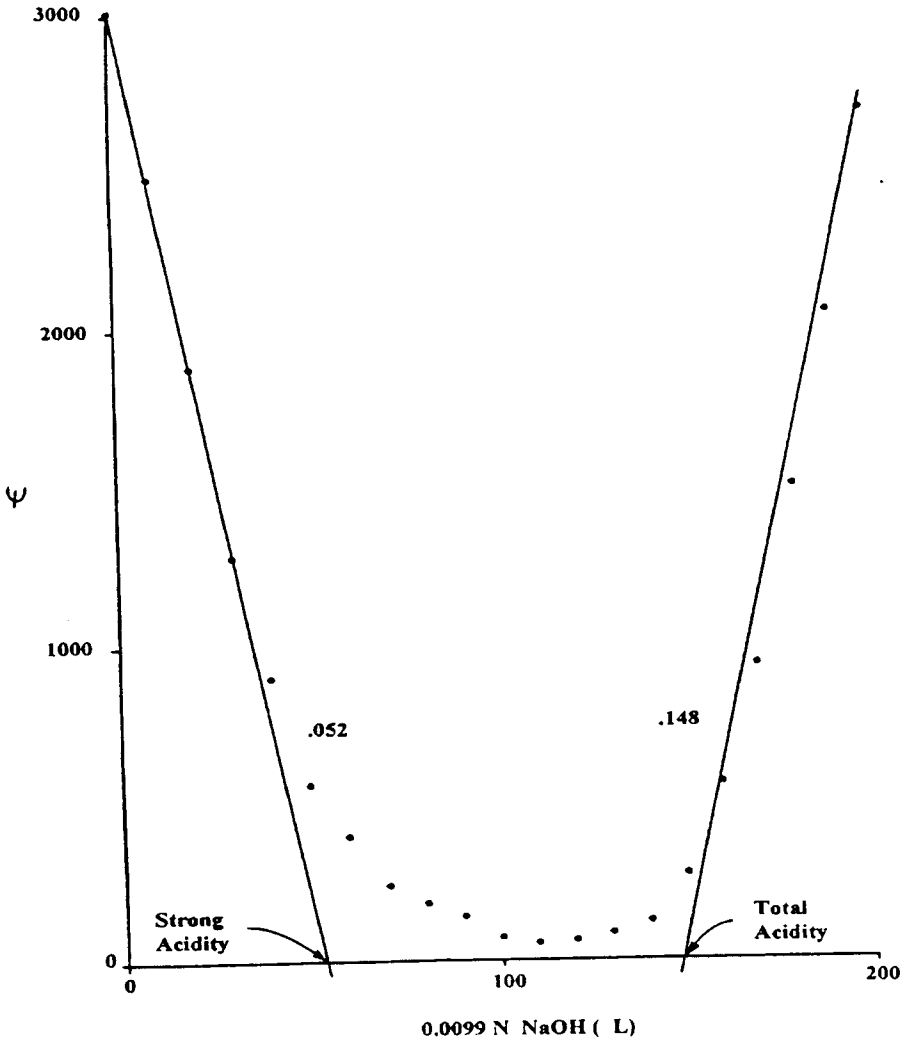
N = normality of the NaOH

9. References

9.1 Gran, Gunner; Determination of the Equivalence Point in Potentiometric Titrations, Analyst, Vol. 77, page 661, 1952.

9.2 McQuaker, Neil R. et al.; Chemical Analysis of Acid Precipitation; pH and Acidity Determinations; Environ. Sci. Technol. Vol. 17, p. 431, 1983.

Figure 1. Gran's Plot
Gran's Function vs Titrant Added



POTASSIUM, DISSOLVED

(Flame Emission)

1. Introduction

1.1 Potassium present in atmospheric precipitation arises from natural sources, such as soil and dust, or from industrial activity.

2. Principle

2.1 The sample is mixed with a solution of cesium and aspirated into an air-acetylene flame. The light energy emitted by potassium is directly proportional to its concentration. The intensity of the light is measured by a spectrophotometer.

3. Scope

3.1 The range is 0.01 to 1.00 mg/L K.

4. Interference

4.1 Cesium is used to prevent ionization of potassium.

5. Apparatus

5.1 Atomic absorption spectrophotometer (operated in the flame emission mode).
5.2 Gas cylinders, compressed air and acetylene.
5.3 Automatic pipet.

6. Reagents

6.1 Distilled water - high purity deionized water.
6.2 Cesium chloride solution (10,000 mg/L Cs): dissolve 12.7 g CsCl in distilled water and dilute to one litre.
6.3 Stock potassium solution (1000 mg/L K): dissolve 1.907 g KCl, dried at 110°C for 2 hours, and dilute to 1000 mL with distilled water.

6.4 Standard potassium solution (100 mg/L K): dilute 100.0 mL potassium stock solution to 1000 mL with distilled water.

6.5 Working standards - prepare as follows:

mL std./1000 mL	conc. mg/L K
0.5	0.05
1.0	0.10
2.5	0.25
5.0	0.50
7.5	0.75
10.0	1.0

7. Procedure

7.1 Measure the sample volume.

7.2 Turn instrument on and allow 30 minutes to warm up.

7.3 Follow manufacturer's instructions for making proper instrument settings.

7.4 Add 2 mL CsCl solution to 100 mL of each sample, standard and blank to be run.

7.5 Run duplicate and spiked sample in accordance with the quality-control program.

8. Instrument Parameters

8.1 Flame emission mode.

8.2 Wavelength: 766.5 nm.

8.3 Fuel: acetylene.

8.4 Oxidant: air.

9. Calculation

9.1 Prepare a calibration curve by plotting peak heights versus mg/L K. Read the concentration of sample from the graph in units of mg/L K.

$$mg\ K = \frac{mg/L\ K \times sample\ volume\ in\ mL}{1000}$$

10. Precision and Accuracy

10.1 In a single laboratory (Alberta Environmental Centre), using snow samples collected in Edmonton and the surrounding area at concentrations of 0.09, 0.44 and 0.88 mg/L K, the coefficients of variation were 1.9%, 1.5% and 1.0%, respectively.

10.2 In a single laboratory (Alberta Environmental Centre), using snow samples collected in Edmonton and the surrounding area at concentrations of 0.10, 0.34 and 0.33 mg/L K, the recoveries were 95%, 104% and 95%, respectively.

11. References

11.1 Analytical Methods for Flame Spectroscopy, Varian Techtron Pty. Ltd.

11.2 Std. Meth. Water and Wastewater, 17th Ed., p. 3-125.

SODIUM, DISSOLVED

(Flame Emission)

1. Introduction

1.1 Sodium present in atmospheric precipitation arises from natural sources such, as soil and dust, or from industrial activity.

2. Principle

2.1 The sample is mixed with a solution of cesium and aspirated into an air-acetylene flame. The light energy emitted at 589.0 nm by the sodium is directly proportional to its concentration. The intensity of the light is measured by a spectrophotometer.

3. Scope

3.1 The range is 0.1 to 1.00 mg/L Na. The detection limit can be extended to 0.004 mg/L, if necessary.

4. Interference

4.1 Cesium is used to prevent the ionization of sodium. Up to 10 mg/L of potassium was found to have no significant effect on sodium concentrations.

5. Apparatus

5.1 Atomic absorption spectrophotometer (operated in the flame emission mode).
5.2 Gas cylinders, compressed air and acetylene.
5.3 Automatic pipet.

6. Reagents

6.1 Distilled water - high purity deionized water.
6.2 Cesium chloride solution (10,000 mg/L Cs): dissolve 12.7 g CsCl in distilled water and dilute to one litre.

6.3 Stock sodium solution (1000 mg/L Na): dissolve 2.542 g NaCl, dried at 140°C for 2 hours, and dilute to 1000 mL with distilled water.

6.4 Standard sodium solution (100 mg/L Na): dilute 100.0 mL sodium stock solution to 1000 mL with distilled water.

6.5 Working standards - prepare as follows:

mL std./1000 mL	conc. mg/L Na
1.0	0.10
2.5	0.25
5.0	0.50
7.5	0.75
10.0	1.00

7. Procedure

7.1 Measure the sample volume.

7.2 Turn instrument on and allow 30 minutes to warm up.

7.3 Follow manufacturer's instructions for making proper instrument settings.

7.4 Add 2 mL CsCl solution to 100 mL of each sample, standard and blank to be run.

7.5 Run duplicate and spiked sample in accordance with the quality-control program.

8. Instrument Parameters

8.1 Flame emission mode.

8.2 Wavelength: 589 nm.

8.3 Fuel: acetylene.

8.4 Oxidant: air.

9. Calculation

9.1 Prepare a calibration curve by plotting peak heights vs mg/L Na. Read the concentration of sample from the graph in units of mg/L Na.

$$mg\ Na = \frac{mg/L\ Na \times sample\ volume\ in\ mL}{1000}$$

10. Precision and Accuracy

10.1 In a single laboratory (Alberta Environmental Centre), using snow samples collected in Edmonton and the surrounding area at concentrations of 0.16, 0.54, and 0.90 mg/L Na, the coefficients of variation were 0.7%, 0.7% and 0.6%, respectively.

10.2 In a single laboratory (Alberta Environmental Centre), using snow samples collected in Edmonton and the surrounding area at concentrations of 0.16, 0.28 and 0.66 mg/L Na, the recoveries were 96%, 99% and 102%, respectively.

11. References

11.1 Analytical Methods for Flame Spectroscopy, Varian Techtron Pty. Ltd.

11.2 Std. Meth. Water and Wastewater, 17th Ed., p. 3-146.

September 1992 Method No. 56565

SPECIFIC CONDUCTANCE

(Conductivity Meter)

1. Introduction

1.1 The conductance of an atmospheric precipitation sample is related to its total concentration of ions. Most inorganic acids, bases and salts are good conductors, whereas most organic compounds do not dissociate in aqueous solution. Therefore, they are poor conductors of current. Freshly distilled water has a specific conductance of 0.5 to 2 microsiemens/cm.

2. Principle

2.1 The measurement of specific conductance is performed by a standard conductivity meter, which consists essentially of a conductance cell and a Wheatstone bridge. The standard unit of electrical resistance is the ohm and the standard unit for the conductance (which is the inverse of the resistance) is the mho (or siemens). Specific conductance is defined as the conductance of a conductor 1 cm long and 1 cm^2 in cross-sectional area.

3. Scope

3.1 The conductivity meter can be used for measuring specific conductance in the range 0.1 µs/cm to 500 µs/cm.

4. Interference

4.1 There are no known interferences.

5. Apparatus

5.1 Direct-reading conductivity meter with a range of 0.1 µs/cm to 500 µs/cm and the capacity for cell constant adjustment.

5.2 Conductivity cell, platinum electrode type.

6. Reagents

6.1 Distilled water: high purity deionized water.

6.2 Standard potassium chloride solution (0.01M): dissolve 0.7456 g of anhydrous KCl in deionized distilled water and make up to 1000 mL. This is a standard reference solution which, at 25°C, has a specific conductance of 1,413 µs/cm.

7. Procedure

7.1 Place 50 mL sample in a 100 mL beaker and allow the sample to reach room temperature.

7.2 Rinse the conductivity cell with deionized distilled water and then rinse with the sample.

7.3 Place the conductivity cell in the standard KCl solution.

7.4 Set the "Measure-Calibrate" switch to "Calibrate".

7.5 Rotate the "Calibration Adjust" until the needle rests at the conductivity cell constant. Check the calibration against the standard potassium chloride solution.

7.6 Set the "Measure-Calibrate" switch to "Measure" and record the conductivity. The range selector is used to bring the needle on scale.

7.7 Store the cell in deionized water after the measurements.

8. Calculation

8.1 The conductivity meter reads directly in conductivity units. Report conductivity in µs/cm.

9. Precision and Accuracy

9.1 Three synthetic unknown samples were tested with the following results:

Conductivity µmhos/cm	No. of Results	Relative Standard Deviation	Relative Error %
147.0	117	8.6	9.4
303.0	120	7.8	1.9
228.0	120	8.4	3.0

With satisfactory equipment, a qualified analyst should be able to obtain results within 1% of the true value (Std. Meth.).

10. Reference

10.1 Std. Meth. Water and Wastewater, 17th Ed., p. 2-59.

LEAD IN SOIL

(Atomic Absorption)

1. Introduction

1.1 The main sources of lead in soil are lead particulates from auto-exhaust and emissions from lead smelters.

2. Principle

2.1 A soil sample is air dried for 30 hours and then dried in an oven at 80°C for 12 hours. The dried sample is pulverized using a mortar and pestle, and sieved through an 80-mesh screen. A suitable aliquot of the soil sample is digested with conc. nitric acid and subsequently analyzed by atomic absorption spectrometry.

3. Scope

3.1 The detection limit is 0.10 mg/kg of the dry sample.

4. Interference

4.1 Chemical: this type of interference occurs when samples are aspirated directly into the flame and when the element is in a molecular combination.

4.2 Non-atomic absorbance: light scattering can occur in samples that have high solids.

4.3 Ionization interference: if the flame is too hot, the neutral atoms become ionized. This interference can be controlled by the addition of an easily ionized element.

4.4 Spectral interference: if the wavelength of another element present in the sample lies close to the wavelength of interest, then the absorbances of both elements will be detected. This leads to erroneously high readings.

5. Apparatus

5.1 Stainless steel borer, 2.5 cm diameter.

5.2 Sieve, 80-mesh size.

5.3 Mortar and pestle.

5.4 Atomic absorption spectrophotometer.

5.5 Analytical balance, sensitivity 0.1 mg.

6. Glassware Handling

6.1 Soak all glassware overnight in dilute HNO_3 to prevent metal contamination.

6.2 Rinse all glassware with distilled water before using.

7. Reagents

7.1 Conc. HNO_3.

7.2 Dilute HNO_3 (3M): dilute 192 mL conc. HNO_3 to 1000 mL with distilled water.

7.3 Stock lead solution (1000 mg/L Pb): weigh 1.599 g of lead nitrate and dissolve in distilled water. Add 10 mL conc. HNO_3 and dilute to 1000 mL.

7.4 Standard lead solution (100 mg/L Pb): pipet 100.0 mL of the stock solution into a 1000 mL volumetric flask and dilute to volume.

7.5 Working standards - prepare as follows:

mL std. sol/1000 mL	conc. mg/L Pb
1.0	0.10
2.5	0.25
5.0	0.50
10.0	1.00
25.0	2.50
50.0	5.00

8. Procedure

8.1 Sampling

8.1.1 Collect samples by using a stainless steel borer.

8.1.2 Collect samples at different soil depths, usually within 10 cm.

8.1.3 Store the sample in a plastic bag.

8.2 Analysis

8.2.1 Dry the sample at room temperature by spreading it in a fumehood for 30 hours. Continue to dry it in an oven at 80°C for 12 hours.

8.2.2 Grind the sample using a mortar and pestle, and sieve it through an 80-mesh screen.

8.2.3 Transfer a weighed sample (approximately 1 g) in a Teflon beaker.

8.2.4 Add 2 mL of conc. nitric acid and heat on a hot plate at 80°C for 2 hours. Keep the sample moist by adding 3M HNO_3.

8.2.5 Adjust the atomic absorption spectrophotometer according to the following setting:

Wavelength:	217.0 nm
Fuel and oxidant:	Acetylene-Air
Flame stoichiometry:	Oxidizing

9. Calculation

9.1 Prepare a calibration curve by plotting peak heights vs mg/l Pb.

9.2 Read the sample concentration from the graph in units of mg/l Pb.

$$mg/kg\ Pb = \frac{mg/L\ Pb \times total\ sample\ volume\ in\ mL}{sample\ weight\ in\ kilogram}$$

10. Precision and Accuracy

10.1 In a single laboratory (Alberta Environmental Centre), using soil samples of concentrations at 26.0 and 922.0 mg/kg, the coefficients of variation were 9% and 5%, respectively.

10.2 In a single laboratory (Alberta Environmental Centre), using soil samples at concentrations of 77.7 and 1847 mg/kg, the recoveries were 88% and 90%, respectively.

11. References

11.1 S.N. Linzon, et al., J. Air. Poll. Control Assoc., Vol. 26, 1976, p. 650.

11.2 J.L. Seeley, et al., Applied Spectroscopy, Vol. 26, 1972, p. 456.

September 1992

Method No. 61011

LEAD IN SOIL

(Direct Current Plasma)

1. Introduction

1.1 The main sources of lead in soil are lead particulates from auto-exhaust and emissions from smelters.

2. Principle

2.1 A soil sample is air dried for 30 hours and dried in an oven at 80°C for 12 hours. The dried sample is pulverized and sieved through a 100-mesh screen. A suitable aliquot of the soil sample is digested with conc. nitric and subsequently analyzed by DCP.

3. Scope

3.1 The detection limit is 0.10 mg/kg of the dry sample.

4. Interference

4.1 Spectral interference: if the wavelength of another element present in the sample lies close to the wavelength of interest, then the emission lines of both elements will be detected, leading to erroneously high readings.

4.2 Molecular background interference, if organic matter is present.

5. Apparatus

5.1 Stainless steel borer, 2.5 cm diameter.

5.2 Sieve, 100-mesh size.

5.3 Rotary grinder and mill.

5.4 DCP (direct current plasma) spectrophotometer.

5.5 Analytical balance, sensitivity 0.1 mg.

6. Glassware handling

6.1 Soak all glassware overnight in dilute HNO_3 to prevent metal contamination.

6.2 Rinse all glassware with distilled water before using.

7. Reagents

7.1 Conc. HNO_3.

7.2 3M HNO_3: dilute 192 mL conc. HNO_3 to 1000 mL with distilled water.

7.3 Stock lead solution (1000 mg/L Pb): weigh 1.599 g of lead nitrate and dissolve in distilled water. Add 10 mL conc. HNO_3 and dilute to 1000 mL.

7.4 Standard lead solution (100 mg/L Pb): pipet 100.0 mL of the stock solution into a 1000 mL volumetric flask and dilute to volume.

7.5 Working standards - prepare as follows:

mL std. sol/1000 mL	conc. mg/L Pb
1.0	0.1
2.0	0.2
10.0	1.0
20.0	2.0
50.0 (or 5.0*)	5.0
10.0*	10.0
20.0*	20.0

*prepare using stock sol'n.

7.6 Quality-control standards: prepare using NBS standard 3128. Make intermediate solution and prepare at least three different concentrations (i.e. 0.1,1,4,16 mg/L).

7.7 QC standard solution: pipet 10.0 mL of NBS 3128 into a 1000 mL volumetric flask, add 100 mL of conc. HNO_3 and dilute to volume with deionized distilled water.

7.8 QC solutions - prepare as follows:

mL std/1000 mL	conc. mg/L Pb
1.0	0.1
10.0	1.0
mL std/100 mL	
4.0	4.0
16.0	16.0

8. Procedure

8.1 Sampling

8.1.1 Collect samples using a stainless steel borer. A minimum of 500 g soil material is required for the sample analysis. The sample is a composite of several cores taken within a one-metre circumference, which is designated as a sampling site. Sampling sites can be located on a transect or grid design, whichever is suitable. A minimum of two control sites and two contaminated sites are required. The control sites should be sampled first to avoid contamination during a sampling procedure. Soil sample cores are normally taken to 15 cm depth; however, deeper sampling may be required if subsoil information is needed.

8.1.2 Store the sample in a jar or plastic bag.

8.1.3 Classify according to type, particle size and foreign material and record all this information.

CSSC (Canada Soil Survey Committee) classification:

< 0.0002 mm	Fine Clay
0.0002-0.002 mm	Coarse Clay
0.002-0.004 mm	Fine Silt
0.006-0.02 mm	Medium Silt
0.02-0.04 mm	Coarse Silt
0.04-0.1 mm	Very Fine Sand
0.1-0.3 mm	Fine Sand
0.3-0.6 mm	Medium Sand
0.6-1.0 mm	Coarse Sand
1.0-2.0 mm	Very Coarse Sand
2.0-80.0 mm	Gravel

Sieve and particle sizes chart at the end of the method.

8.2 Analysis

8.2.1 Spread the smaple in an aluminum pie-plate and dry at room temperature in a fumehood for 30 hours. Continue to dry in an oven at 80°C for 12 hours.

8.2.2 Grind the sample using a rotary grinder with a 20-mesh screen. Separate the aggregate and save it in a plastic bag. Grind the rest using a mill. Wash rollers and screens between samples.

8.2.3 Transfer a weighed portion (approximately 1 g) of the sample in a beaker.

8.2.4 Add 20 mL of conc. HNO_3 and heat on a hot plate at 80°C for 2 hours. Keep sample moist by adding 3M HNO_3.

8.2.5 Filter into a 100 mL volumetric flask and dilute to volume with 3M HNO_3.

8.2.6 Adjust the DCP as follows:

Order:	61
Wavelength:	363.348
Entrance Slit:	50 x 300
Exit Slit:	100 x 300
Plasma Position:	zero
Detection Limit:	0.01 mg/L
Linear Dynamic Range (LDR):	0.1 to 600 mg/L
Background Equivalent Concentration (BEC):	0.4 mg/L
Precision (RSD) at 20 x BEC:	0.8%
Mode:	Internal at 10 seconds and 3 counts
Photomultiplier Tube:	PMT

9. Calculation

$$mg/kg = \frac{mg/L \times total\ sample\ volume\ in\ L}{sample\ weight\ in\ kg}$$

10. Precision and Accuracy

10.1 In a single laboratory (Alberta Environmental Centre), using soil samples of concentrations at 26.0 and 922.0 mg/kg, the coefficients of variation were 9% and 5%, respectively.

10.2 In a single laboratory (Alberta Environmental Centre), using soil samples at concentrations of 77.7 and 1847 mg/kg, the recoveries were 88% and 90%, respectively.

11. References

11.1 S.N. Linzon, et al., J. Air Poll. Control Assoc., Vol. 26, 1976, p. 650.

11.2 Handbook of Spectral Line Characteristics for the DC Plasma Echelle Systems, Spectra Metrics, Inc.

September 1992

Method No. 61113

SAMPLING FOR SOIL ANALYSIS

1. Soil Sampling Procedure

1.1 Soil samples can be taken with a shovel, soil auger, soil probe or soil tube. If sampling with a shovel, dig a hole to the desired depth. Remove a 2.5 cm thick slice from the side of the hole. With a clean knife remove the border and discard, leaving a central core of about 2.5 cm and place the core in a sampling bag. For underwater soil sampling, a soil tube would be more appropriate. Insert the soil tube to the desired depth. Place your palm to seal the tube before lifting it out of the water to prevent excessive loss of soil material. Place the sample in a wide-mouth plastic bottle. A minimum of 500 g soil material is required for the sample analysis. The sample is a composite of several cores taken within a one metre circumference, which is designated as a sampling site. Sampling sites can be located on a transect or grid design (see diagrams, page 24), whichever is suitable. A minimum of two control sites and two contaminated sites are required. The control sites should be sampled first to avoid contamination during a sampling procedure. Soil sample cores are normally taken to 15 cm depth; however, deeper sampling may be required if subsoil information is needed.

2. Sample Containers and Treatment

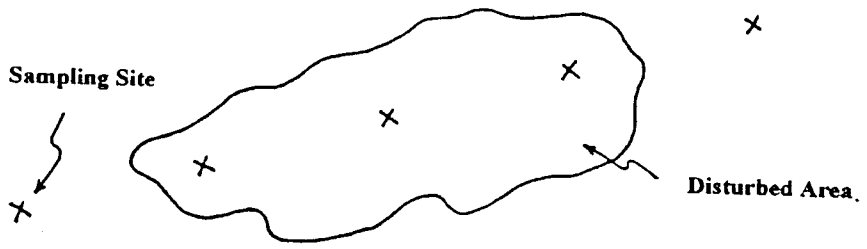
2.1 Double-lined plastic bags are suitable for dry and moist samples, but wide-mouth plastic bottles should be used for saturated samples taken from the bottom of streams and lakes. Soil samples should be kept cool or frozen and delivered the same day for analysis. All sample containers should be labelled clearly with waterproof ink. Soil analysis information should be provided and a drawing of the sample location map included to provide sufficient information for interpreting results.

3. Reference

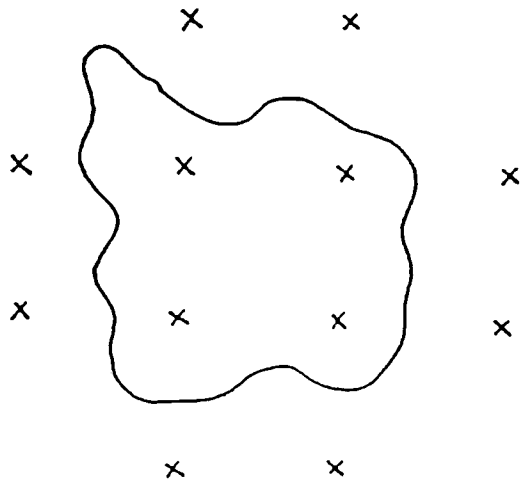
3.1 The Sampling of Water, Soils and Collection of Biological Samples to Analyze Suspected Pollutants, Alberta Forestry, Lands and Wildlife Division, April 1988.

Figure 1. Soil Sampling Design

1. Transect Design



2. Grid Design



SOIL pH

(Electrometric)

1. Introduction

1.1 Soil pH can be determined by several chemical analyses. However, the analysis outlined in procedure 3:13 of the "Manual on Soil Sampling and Methods of Analysis" edited by J.A. McKeague is to be followed.

2. Principle

2.1 A sample of soil is added to distilled water. The mixture is stirred, and the resulting suspension is allowed to settle. The pH is then measured by the glass electrode in combination with a saturated calomel electrode, which provides the reference potential. The glass electrode system is based on the fact that a change of 1 pH unit produces an electrical change of 59.1 mV at 25°C.

3. Interference

3.1 The glass electrode is relatively immune to interference from colour, turbidity, colloidal matter, free chlorine, oxidants or reductants, as well as a high saline content. The exception is a sodium error at high pH. The error caused by high sodium ion concentrations at a pH above 10 may be reduced by using special "low sodium error" electrodes. When employing ordinary glass electrodes, approximate corrections for the sodium error may be made by consulting a chart which the manufacturer furnishes for the particular make and catalog number of the electrode.

3.2 Temperature exerts two significant effects on pH measurements: the electrodes vary in potential, and ionization of the sample varies. The first effect can be negated by an adjustment which is provided on better commercial instruments. The second effect is inherent in the sample and is taken into consideration by recording both the temperature and the pH of each sample.

4. Apparatus

4.1 Equilibrium is shown by the absence of drift, and it should be established between the sample and the electrode system before readings are accepted as final. The analyst should be constantly on the alert for possible erratic results arising from mechanical or electrical failures (eg., weak batteries, cracked glass electrodes, plugged liquid junction and fouling of the electrodes by oily or precipitated materials).

5. Reagents

5.1 Electrode systems are calibrated against a buffer solution of known pH value. It is a good practice to calibrate the electrodes with a buffer, having a pH close to that of the samples, so as to minimize any error resulting from a nonlinear response of the electrode.

5.2 Since buffer solutions may deteriorate because of mold growth or contamination, it is advisable to prepare the solutions just before they are used. This is done by dissolving dry buffer salts in distilled water. Commercially available buffer salts or powders of tested quality may also be used. In making up buffers from solid salts, it is imperative that all the material be dissolved; otherwise the pH may be incorrect. Polyethylene bottles are preferable for storing buffers and samples, although pyrex glassware may be used.

5.3 Information on the preparation of three buffer solutions (pH 4, 7 and 9) is given below. Table 1 lists the pH values of the three buffer solutions at various temperatures.

5.3.1 Buffer solution, pH 4.01 at 25°C: dissolve 10.21 g anhydrous potassium biphthalate, $KHC_8H_4O_4$, in distilled water and dilute to 1000 mL.

5.3.2 Buffer solution pH 6.86 at 25°C: dissolve 3.40 g anhydrous potassium dihydrogen phosphate, KH_2PO_4, and 3.55 g anhydrous disodium hydrogen phosphate, Na_2HPO_4 (both of which have been dried for two hours at 110° to 130°C), in distilled water that has been boiled for 15 minutes and cooled to room temperature. Dilute to 1000 mL.

5.3.3 Buffer solution, pH 9.18 at 25°C: dissolve 3.81 g sodium borate decahydrate (borax), $Na_2B_4O_7$, in distilled water that has been boiled for 15 minutes and cooled to room temperature. Dilute to 1000 mL.

Table 1

EFFECT OF TEMPERATURE ON pH VALUES OF BUFFER SOLUTION

Temperature	pH Value of Buffer Solution		
(°C)	pH 4	pH 7	pH 9
0	4.00	6.98	9.46
5	4.00	6.95	9.40
10	4.00	6.92	9.33
15	4.00	6.90	9.28
20	4.00	6.88	9.23
25	4.01	6.86	9.18
30	4.02	6.85	9.14
35	4.02	6.84	9.10
38	4.03	6.84	9.08
40	4.04	6.84	9.07
45	4.05	6.83	9.04
50	4.06	6.83	9.01
55	4.08	6.83	8.99
60	4.09	6.84	8.96

6. Procedure

6.1 Analysis

6.1.1 Dry soil samples for 24 hours at room temperature.

6.1.2 Run sample through a #10 mesh sieve prior to weighing.

6.1.3 Measure 20 g of soil and place in a small beaker or plastic cup. Add 20 mL of distilled water.

6.1.4 Stir several times during the next half hour. Let settle for one hour.

6.1.5 Measure the pH by immersing the glass electrode into the partly settled suspension (do not immerse it to the bottom of the container) and placing the calomel electrode in the clear supernatant solution. If a combination electrode is used, immerse it in the supernatant solution.

7. Precision and Accuracy

7.1 The precision and accuracy attainable with a pH meter will depend on the type and condition of the instrument used and the technique of standardization and operation. With proper care, a precision of ±0.02 pH unit and an accuracy of ±0.05 pH unit can be achieved with the better battery models. Line-operated instruments, on the other hand, are less accurate; ±0.1 pH unit represents the limits of accuracy under normal conditions. A synthetic unknown sample consisting of a Clark and Lubs buffer solution of pH 7.3 was determined electrometrically with a standard deviation of ±0.13 pH unit in 30 laboratories.

8. Reference

8.1 J.A. McKeague, Manual On Soil Sampling and Methods of Analysis, 2nd Ed., 1978.

September 1992

Method No. 61515

TOTAL SULPHUR IN VEGETATION

(Leco Induction Furnace/Sulphur Titrator)

1. Introduction

1.1 A substantial quantity of elemental sulphur and sulphurous compounds is emitted to the atmosphere from the burning of sulphur-containing oil, gas and coal, and from the sulphur-recovery process of sour gas plants. To assess the level of sulphur pollution in the vicinity of sour gas plants, it is necessary to determine the sulphur content in vegetation adjacent to the plants.

2. Principle

2.1 Samples containing sulphur or sulphur compounds are oxidized in oxygen to SO_2 in a Leco furnace. The SO_2 is allowed to react with iodine liberated from the reaction of KIO_3 and KI with HCl.

The analysis proceeds according to the following equation:

$$KIO_3 + 5KI + 6HCl \longrightarrow 6KCl + 3I_2 + 3H_2O$$

$$SO_2 + I_2 + 2H_2O \longrightarrow H_2SO_4 + 2HI$$

2.2 Dilute HCl is poured into a titration vessel and to it KI and starch solutions are added. A small amount of standard KIO_2 solution is added, and free I_2 is released as indicated by the starch turning blue. An automatic buret containing the KIO_3 is then refilled to the zero or starting point. The sample under test is combusted in oxygen and the resulting SO_2 from the burning sample is directed to the titration vessel where it reacts with free iodine, and the starch turns colourless. More KIO_3 is added to form more free iodine and to bring the solution back to its original colour. This is repeated in a continuous manner until all the sulphur has been oxidized to SO_2 and titrated. The total millilitres of KIO_3 needed for the titration are equivalent to the total micrograms of sulphur in the sample.

3. Scope

3.1 The detection limit is 10 µg/gm of dry sample.

4. Apparatus

4.1 Leco Induction Furnace.
4.2 Leco Sulphur Titrator.
4.3 Leco crucibles.
4.4 Scoop.
4.5 Laboratory oven.
4.6 Vacuum oven.
4.7 Cutting mill, Wiley Intermediate Model, or equivalent.
4.8 10 µL and 100 µL syringes.

5. Reagents

5.1 Accelerators: granular tin, iron chip and copper rings.
5.2 Potassium iodide solution (3%): dissolve 6 g potassium iodide in 200 mL distilled water.
5.3 Starch solution (0.25%): to 800 mL boiling distilled water, slowly add a suspension of 2.5 g starch in 200 mL distilled water. Cool and add 200 mL KI solution.
5.4 Potassium iodate solution (0.0444%): dissolve 0.4440 g potassium iodate in distilled water in a 1000 mL volumetric flask and dilute to the mark with distilled water.
5.5 Dilute HCl solution: dilute 5 mL conc. HCl to 1 litre with distilled water in a volumetric flask.
5.6 Standard sulphur solution (10 mg/mL S): dissolve 1.000 g pure sublimed sulphur in 100 mL spectra-grade benzene.
5.7 Working sulphur standard - use the following volumes of the standard solution to prepare the calibration curve:

µL of 10 mg/L S standard	mg S
10.0	0.1
20.0	0.2
40.0	0.4
80.0	0.8
100.0	1.0

APPENDIX

CONVERSION FACTORS

1. To convert results for gaseous air pollutants from ppm to mg/m^3 and vice versa, use the following equations:

$$ppm \text{ to } mg/m^3: \; mg/m^3 = \frac{ppm \times MW \times 10^3}{MV}$$

$$mg/m^3 \text{ to } ppm: \; ppm = \frac{mg/m^3 \times MV \times 10^{-3}}{MW}$$

where

MW	=	molecular weight of the gas.
MV	=	molar volume of the gas (24.46 L/mole at 25°C and 760 mm Hg).

2. To convert the volume of collected ambient air to that under standard conditions (25°C and 760 mm Hg) use the following equation:

$$V_R = V \times \frac{P}{760} \times \frac{298}{t + 273} \times 10^3$$

where

V_R	=	volume of air in m^3 at 25°C and 760 mm Hg.
V	=	volume of air in litres at sampling conditions.
P	=	barometric pressure in mm Hg during sampling.
t	=	temperature during sampling in °C.
$(10^{-3}$	=	factor to convert litre to m^3).

Note:

1 ft^3	=	28.32 litres.
1 inch of Hg	=	25.4 mm of Hg.

3. To convert the volume of collected source emission gases to that under standard conditions, consult Source Sampling Code, Alberta Environment.

QUALITY ASSURANCE MANUAL

FOR

ATMOSPHERIC POLLUTION MEASUREMENT

AIR ANALYSIS BRANCH
ALBERTA ENVIRONMENTAL CENTRE
1992

TABLE OF CONTENTS

1. INTRODUCTION

1.1 The purpose of this manual is to provide guidelines and procedures for achieving quality data in air pollution measurements in Alberta. Reliable data are necessary for the enforcement of the Clean Air Act and also for licensing industrial operations in the province. This manual is intended to serve as a resource document for the samplers as well as for the analysts.

1.2 The objectives of quality assurance are to produce data that meet the user's requirements in terms of precision, accuracy and representations. Since air pollution measurements are undertaken by government, as well as private and industrial laboratories in the province, quality assurance is essential for establishing and assessing the comparability of data quality among laboratories that contribute to the data base.

1.3 The manual contains a number of elements that are necessary for quality assurance, such as sample collection, preservation and analysis. Since the collection techniques for different air pollutants are not the same, they have been discussed separately. Analyses of the air pollutants have been divided into "Manual" and "Instrumental" analyses.

1.4 In addition, the manual describes the interlaboratory testing and statistical analysis of data.

2. ELEMENTS OF QUALITY ASSURANCE

2.1 Sample Collection

2.1.1 Gaseous Pollutants, Using Candles and Tapes

2.1.1.1 The following gases are monitored by using candles and tapes.

- 2.1.1.1.1 Sulphur Dioxide (sulphation rate)
- 2.1.1.1.2 Hydrogen Sulphide
- 2.1.1.1.3 Fluoride
- 2.1.1.1.4 Nitrogen Dioxide

2.1.1.1.4.1 To maintain quality control, the following steps are followed:

- 2.1.1.1.4.1.1 Maintain uniformity of the gas-reacting medium (viz.PbO_2 in sulphation rate) on all candles and tapes.
- 2.1.1.1.4.1.2 In sample preparation, carry out the drying process at the recommended temperature.
- 2.1.1.1.4.1.3 Record the batch number for all prepared samples and keep blanks in air-tight containers.

2.1.1.1.4.1.4 Expose samples in louvred boxes to protect against strong wind and rain.

2.1.1.1.4.1.5 Ship the samples in boxes to protect against breakage and stripping of the reacting medium.

2.1.2 Dustfall, Using Dust Collectors

The following steps are followed.

2.1.2.1 During winter months, use isopropanol as recommended in the standard method of analysis.

2.1.2.2 During summer months, use copper sulphate.

2.1.2.3 In the field, maintain water level in the dust collectors.

2.1.3 Sampling of Suspended Particulate Matter, Using High-Volume Air Sampler

2.1.3.1 Sampling Station Location

2.1.3.1.1 The meteorological and topographic conditions should be taken into consideration before selecting the location of a sampling station within a monitoring network. Wind speed and wind direction may determine the height of the platform where the samplers should be placed. Any physical obstructions, such as trees, fences, buildings etc., in the immediate area may alter the air flows. The samplers should be placed away from a construction site, dusty roadway or any other sources of dust.

2.1.3.2 Calibration of High-Volume Sampler

2.1.3.2.1 The elapsed-time meter should be checked once every 6 months against a timepiece of known accuracy. A gain or loss of more than 2 minutes/24 hr period warrants an adjustment or replacement. The on/off timer should be calibrated and adjusted at least 3 times a year by using a calibrated elapsed-time meter as a reference.

2.1.3.2.2 The orifice calibration unit should be compared at least once a year against a secondary standard, such as a rotameter. The manufacturer's average calibration curve can be used, provided the calibration does not deviate from it by more than ±4% at any one point along the curve. If the deviation is > ±4%, a new average calibration curve should be constructed using at least five sets of calibration data. A calibrated orifice unit should be used to calibrate a sampler. Samplers should be calibrated after

major maintenance; i.e. after the replacement of motor, motor brushes, rotameter or recorder. Calculate the % deviation from the observed flow rate and the calibration curve flow rate for the same rotameter reading and by using the equation:

$$\% \ deviation = 100 \ \frac{Fo-Fc}{Fc}$$

where

Fo = Observed flow rate

Fc = Flow rate from calibration curve.

The result should fall within ±5%. Rerun or replot if any calibration point has a deviation > ±5%. Consult the operator's manual or EPA's Quality Assurance Handbook for the calibration procedures. Maintain a log book to record all calibrations.

2.1.3.3 Filter Selection and Preparation

2.1.3.3.1 The selection of filter media depends on the type of pollutants to be determined in the suspended particulate matter on the filter. A glass fibre filter is used for the determination of total suspended particulates (TSP), lead (Pb), benzo(a)pyrene (BaP), and other organics, whereas a Teflon or an organic membrane filter should be used for heavy metals, sulphate and nitrate.

2.1.3.3.2 Filters should be conditioned for 24 hours in a constant temperature and humidity chamber or kept in a desiccator before weighing. Each filter is placed in a pre-addressed return envelope which should have sample data recorded on the front.

2.1.3.4 Sample Handling

2.1.3.4.1 Lift the exposed filter from the supporting screen by grasping it gently at the ends, not at the corners. Fold the filter lengthwise at the middle with the exposed side in. Remove the sampler's flow recorder chart and place the chart inside the filter folder with the inked side against the folder and the backside against the filter. Dry the exposed filter at room temperature and 40% humidity, or dry it in a desiccator for 24 hours before weighing.

2.1.4 Volatile Organics Using Solid Adsorbents

2.1.4.1 To analyze low concentrations of ambient air contaminants, the compounds are first concentrated on a solid adsorbent by drawing a large volume of air through an adsorbent tube.

Quality-control procedures consist of:

2.1.4.2 Determining the retention volume for each component and seeing that the retention volume is not exceeded during sampling.

2.1.4.3 Using the correct adsorbent for each type of compound. This can be determined from reference tables issued by EPA and ASTM, provided in the Methods Manual for Chemical Analysis of Atmospheric Pollutants published by Alberta Environment.

2.1.4.4 Storing the sample tube at a low temperature during transport and while waiting to be analyzed. For tubes, such as Tenax, the analysis should be done as soon as possible.

2.1.4.5 Field blanks should consist of tubes that are sent out and opened, but no air drawn through them.

2.1.4.6 Each tube should be clearly labelled with the location, flow rate, sampling duration, sampling time, and operator, as well as clearly specifying the required analysis.

2.1.5 Sampling of Source Emission

2.1.5.1 Calibration of Sampling Apparatus

2.1.5.1.1 Calibration of the sampling system is the most important function in order to achieve quality data. The sampling system consists of (a) S-Type pitot tube/or probe assembly (b) Dry gas meter and orifice meter (c) Rotameter (d) Barometer and (e) Differential pressure gauge. All these units have to be calibrated before taking any sample. Follow the manufacturer's manual, EPA Manual or Alberta Environment's "Source Sampling Code" for these calibrations.

2.1.5.2 Pre-Test Information

2.1.5.2.1 Prior to a stack survey, the sampling crew should have some information regarding the sampling facilities, sampling sites, plant process, stack temperature, gas velocity and the moisture loading. Some of this information may be available from previous surveys conducted under identical operating conditions, or they might be obtained by conducting a preliminary source test. This information is necessary to determine the flow pattern

(cyclonic or non-cyclonic) in the stack, the type of sampling train and the size of the probe nozzle to be used for sampling. As well, this information is needed to help decide whether to conduct isokinetic or proportional sampling, and also to determine the number of sampling points and sampling times per point.

2.1.5.2.2 Check the sampling train and the pitot tube for a possible leak at the conclusion of each sampling run.

2.1.5.3 Sample Collection and Sample Handling

2.1.5.3.1 For sample collection and sample handling, follow the instruction as written in the "Methods Manual" for individual parameters.

2.1.6 Wet Deposition Using Sangamo Sampler

2.1.6.1 Sangamo samplers used by Alberta Environment are wet-only types of sampler. They are equipped with a sensor that detects the presence of moisture (rain, hail, snow, etc.) and causes the lid covering the sampling bucket to be lifted off the bucket, thereby allowing precipitation to fall into it. During dry periods, the lid remains on the sampling bucket. This prevents dry deposition from entering the sampler.

2.1.6.2 Detailed sampling procedures are specified in "Precipitation Quality Sampling Network, Operations Manual", available from Air Quality Control Branch, Alberta Environment. A brief summary of the procedures is presented here.

2.1.6.3 Because of the low concentration of ions inherent in precipitation samples, careful handling procedures are required to keep the sample contaminant-free.

2.1.6.4 Samples are collected on the last working day of the month. If precipitation is occurring, the sample is obtained at the end of the precipitation event.

2.1.6.5 Time is referenced to Mountain Standard Time using the 24 hr. clock.

2.1.7 Sample Collection

2.1.7.1 At month end, the precipitation sampling bucket is taken indoors and decanted into a pre-cleaned sample bottle which is then prepared for shipment to the laboratory. The sample bottle is rinsed three times with distilled water at the laboratory before it is sent to the field sampling site for the sample collection.

2.1.8 Precipitation Sample Handling Procedure

2.1.8.1 Carefully wash the graduated cylinders (for measuring the volume) with distilled deionized water.

2.1.8.2 Remove and carry the sampling bucket indoors.

2.1.8.3 Decant the sampling bucket into the graduated cylinder and record the volume of precipitation. If the sample is frozen, allow it to melt before proceeding.

2.1.8.4 Carefully empty the graduated cylinder into the precleaned shipping bottles. Two 1 L bottles are provided. Discard any excess sample.

2.1.8.5 Thoroughly rinse the collection bucket with distilled deionized water and allow to drain.

2.1.8.6 Return the collection bucket to the Sangamo sampler and store the graduated cylinder in a clean plastic bag.

2.1.8.7 Fill out the precipitation sample log form.

2.1.8.8 Ship to the Alberta Environmental Centre, Air Analysis and Research Branch, Vegreville, Alberta.

2.2 Sample Analysis (Manual Methods)

2.2.1 Gravimetric

2.2.1.1 Gravimetric measurements are used for the determination of dustfall (total and fixed) and suspended particulate matter in air and source emissions.

2.2.1.2 The following steps are followed to maintain quality control:

2.2.1.2.1 Once a month, calibrate the weighing balance against a standard reference weight from NBS.

2.2.1.2.2 Handle material to be weighed with a pair of tongs and keep the balance clean.

2.2.1.2.3 In dustfall analysis (Method No. 32020), after heating and desiccating the crucible, bring it to a constant weight. In high volume filters, desiccate the filters for 24 hours before weighing. For control filter standards, use two high-volume filters; one is used as a blank, and the other is exposed to the ambient air for 24 hours at the sampling site.

2.2.2 Colorimetric

2.2.2.1 A number of parameters, such as chlorine, ammonia, formaldehyde, urea, phosphate, etc., are determined by manual colorimetric methods, using a UV-visible spectrophotometer. prepare working standards fresh from a stock solution. The stock solution is preserved at 4°C in

a refrigerator and is prepared every three months. If the sample is collected in impingers using an absorbing solution, prepare the calibration standards and an internal QC standard using the adsorbing reagent. Develop colouration by adding appropriate reagents to the calibration standards, blank absorbing solution and internal QC standards. Allow 10-15 minutes to develop the colour.

2.2.2.2 Allow at least 5-10 minutes for the spectrophotometer to warm up. Adjust the zero control to bring the meter needle to infinity absorbance on the scale. Standardize the light control by inserting a cell filled with the reagent blank into the sample holder and adjusting the light control until the meter reads zero absorbance. The complete absorbance scale should be checked with a calibrated set of NBS filters any time a control sample can not be measured within ±0.1 µg/mL of its accepted value. Measure a reagent blank and a control sample before each set of determinations. Take at least 4-5 points and use regression analysis to determine the slope and the intercept of the calibration curve. Check each new calibration curve for linearity. The slope of the calibration curve should be within an acceptable accuracy range and the intercept should pass within ±0.2 absorbance units of the origin. Maintain a log book for all the data and calculations.

2.2.3 Titrimetric Analysis

2.2.3.1 Prepare calibration standards from the best available reference material. Standards should be prepared regularly to minimize deterioration with time.

2.2.3.2 Calibrate the instrument according to the procedures in the "Methods Manual for the Analysis of Atmospheric Pollutants".

2.2.3.3 Analyze duplicate and spiked samples on a regular basis to determine the precision and accuracy of the method.

2.2.3.4 Data validation by the supervisor is required.

2.2.3.5 Interlaboratory studies are carried out for Grans plot acidity, ammonia, sulphate and phosphate.

2.2.4 Electrometric

2.2.4.1 Procedures are similar to those for the Titrimetric Analysis.

2.2.4.2 Interlaboratory comparison studies are carried out for pH, fluoride and conductivity. pH and conductivity measurements are part of the Long Range Transport of Air Pollutants (LRTAP) program.

2.3 Sample Analysis (Instrumental Methods)

2.3.1 Ambient Air Analyzers

2.3.1.1 The measurement of NO_x, SO_x, CO and O_3 in ambient air requires the following basic equipment.

2.3.1.1.1 Sampling lines

2.3.1.1.2 Sampling manifold

2.3.1.1.3 NBS calibration standards

2.3.1.1.4 Calibration equipment

2.3.1.1.5 Zero air

2.3.1.1.6 Working gas, traceable to NBS standard

2.3.1.1.7 Strip chart recorder

2.3.1.2 Calibration of Analyzer

2.3.1.2.1 Accurate calibration of the analyzer is very important, since the accuracy and precision of the data derived from an analyzer depends on it.

2.3.1.2.2 Calibration of an analyzer involves the introduction of gas samples of known concentrations into it to adjust the analyzer to a particular sensitivity and to produce a calibration relationship. Samples of different known concentrations are used and the responses are recorded. These standard gas mixtures can be introduced in a decreasing order of at least four different concentrations. The true value of the calibration gas should be traceable to a NBS standard.

2.3.1.2.3 The calibration of an analyzer should be checked once every 3 months. Precision of the analyzers should be determined by a one-point check at least once every two weeks.

2.3.1.3 Calibration Gases

2.3.1.3.1 All commercial calibration standards should be compared with the NBS certified standards.

2.3.2 Auto Analyzer

2.3.2.1 An auto analyzer system is used for some analyses.

2.3.2.2 To maintain quality control, the following steps are followed:

2.3.2.2.1 Follow the instruction manual in assembling the system, and using the given sizes of the tubes and the specified concentrations of reagents.

2.3.2.2.2 Calibrate the system by using standards in ascending order.

2.3.2.2.3 Prepare stock standard solutions every two months, and working standards every week.

2.3.2.2.4 Use two standards, A & B, as external controls to check the performance of the system. The two standards may be prepared once a year.

2.3.2.2.5 The first 5 samples should be the working standards in ascending order and the 6th one is wash sample.

2.3.2.2.6 Every 10th sample should be a wash sample. Spiked samples, duplicates and internal-control standards should be evenly distributed in the sample tray.

2.3.2.2.7 Use Shewhart chart to check precision and accuracy of the system.

2.3.3 Atomic Absorption and Direct Current Plasma

2.3.3.1 Follow the manufacturer's operating instructions. Choose the correct hollow-cathode lamps, and install and align them in the instrument. Select the proper wavelength for the metal to be determined. Select the proper monochromator slit width and regulate the flow of fuel and oxidant. Adjust the burner for maximum absorption and stability. Adjust the instrument span using the highest calibration standard. While aspirating the standard, span the instrument to the desired response. Correct all absorbance values by subtracting the blank absorbance value. Prepare working standards daily by diluting the stock solutions. Run at least four standards plus the reagent blank to cover the linear range indicated by the instrument's manufacturer. Run each sample in duplicate. Run a control standard before the first sample, after every 10th sample and after the last sample. Record all data and the calculations in a log book.

2.3.3.2 Calibration standards are prepared by diluting purchased 1000 ppm standard solutions.

2.3.3.3 Calibration is carried out and checked for linearity. Also, check for interferences in the instrument wavelength tables.

2.3.3.4 By analyzing every fifth sample as a duplicate on a spiked sample, the precision and accuracy of the method can be obtained.

2.3.4 Ion Chromatography

2.3.4.1 Precipitation and ambient air (high-volume filters) samples are analyzed by Ion Chromatography. The following parameters are analyzed.

2.3.4.2 Cations

2.3.4.2.1 Sodium

2.3.4.2.2 Ammonium

2.3.4.2.3 Potassium

2.3.4.3 Anions

2.3.4.3.1 Chloride

2.3.4.3.2 Phosphate

2.3.4.3.3 Nitrate

2.3.4.3.4 Sulphate

2.3.4.4 To maintain quality control, the following steps should be followed:

2.3.4.4.1 Store samples and standards at 4°C.

2.3.4.4.2 Duplicate or spike every fifth sample.

2.3.4.4.3 Use certified reagents.

2.3.4.4.4 Prepare stock standards annually.

2.3.4.4.5 Prepare working standards every four months.

2.3.5 Liquid Chromatography

2.3.5.1 Liquid chromatography is used in the analysis of Poly Aromatic Hydrocarbons (PAH) in high volume filters; Benzo(a)Pyrene is one of the PAHs normally reported.

2.3.5.2 The following steps are to be followed to maintain quality control:

2.3.5.2.1 In the extraction process, use 10 extractions per run. The 10th extraction may alternate between a spiked, or duplicate sample.

2.3.5.2.2 Use certified standards.

2.3.5.2.3 Use HPLC quality solvents.

2.3.5.2.4 Use external certified standards, such as NBS urban dust, and periodically check the efficiency of extraction and check internal standards.

2.3.6 X-Ray Fluorescence (XRF)

2.3.6.1 The XRF system is calibrated against the Ti-Zn standard. This is a two-point calibration that gives the absolute energy of the element emission, as well as the spacing between the emission lines.

2.3.6.2 As the XRF analysis is a comparative procedure, it is important that quality standard elemental references are used. Two sources of reference are used: Columbia Scientific Inductive, and Micromatter. As in any comparative procedure, there is a finite range over which the analyses are accurate.

2.3.6.3 It is important to use thin-film samples. This eliminates the need for alterations and enhancement corrections. Also, the sample must be non-volatile under the x-ray bombardment. This limits the irradiation time to 1000 seconds or less, and the accepted time is usually 200 seconds.

2.3.6.4 The usual precision and accuracy procedures are used, i.e. every 5th sample is a duplicate, or a standard reference material.

2.3.7 Gas Chromatography (VCM)

2.3.7.1 Samples

2.3.7.1.1 Refrigerated on arrival.

2.3.7.1.2 Kept in a box with freezer packs in transit.

2.3.7.2 Tubes

2.3.7.2.1 Preconditioned at 275°C with N_2; flow (~100 cc/min.)

2.3.7.3 Adsorbent

2.3.7.3.1 Spherocarb is used as an absorbent.

2.3.7.4 G.C.

2.3.7.4.1 When the baseline is noisy, the PID lamp is cleaned.

2.3.7.4.2 The valves are cleaned when extra peaks start showing up in the chromatogram.

2.3.7.4.3 The column is temperature-conditioned whenever the GC is shut down.

2.3.7.4.4 The thermal desorber is pressure-tested every day for leaks.

2.3.7.4.5 The volumeter is cleaned whenever mercury is spilled in the tube.

2.3.7.5 Standards

2.3.7.5.1 The main standard is purchased from Matheson, Certified, 100 to 110 ppm concentration.

2.3.7.5.2 This standard is diluted with breathing-quality air to give 1.0, 2.5, and 5.0 ppm working standards. These are run every morning in duplicate, and response factors must agree to within ±4%.

2.3.7.5.3 A calibration standard of 5 ppm (certified) is purchased from Matheson.

2.3.7.5.4 This calibration standard is injected into the GC (in triplicate) without any dilutions and analyzed against the first three standards. The accepted range is 5 ppm ±12%.

2.3.7.6 Sample Analysis

2.3.7.6.1 The sample tubes are taken individually out of the fridge and analyzed. N_2 zero gas is used to flush the samples from the desorber into the volumeter. The diluted sample is mixed in the volumeter with a 50 mL syringe (5 times) before injection .

2.3.7.6.2 The sample is injected in duplicates, or more if required, until the area counts of successive injections is ±10%.

2.3.7.6.3 The system is flushed with N_2 zero gas and an injection is made to ensure no VCM remains in the system. This is the "Blank" value.

2.3.7.7 PID Lamp

2.3.7.7.1 The lamp is cleaned when the baseline is noisy.

2.3.7.7.2 The lamp is changed when the area counts drop to about ⅓ those when the lamp was new. Generally, this takes 3 to 4 months, but can be as little as 1 day or as long as 5 or 6 months.

2.3.7.8 Interlaboratory Studies

2.3.7.8.1 Once a year, 24 calibration standards (8 for each of 3 labs) are made up in the concentration range of 1 to 25 ppb, analyzed and compared.

3. INTERLABORATORY & INTERNAL QUALITY CONTROL TESTS

3.1 There are two types of interlaboratory tests: The first, collaborative testing, involves several laboratories for the purpose of defining the limits of a particular method. This type of interlaboratory study should be undertaken before adopting a method for a routine analysis. The second type, performance testing, also involves several laboratories and provides a means for participating laboratories to compare their results with those of other labs. This type of interlaboratory testing allows the participants to take corrective action when their results are not within the specified limits.

3.2 In addition to interlaboratory testing, internal quality-control procedures should also be followed routinely. The Air Analysis Branch has the following Quality Control-Programs.

3.2.1 External QC

3.2.1.1 LRTAP/Precipitation (Long Range Transport of Air Pollutants)

3.2.1.2 EPA/USA/Source NO_x & SO_2

3.2.1.3 EPS/Canada/High Vol. Air Samples

3.2.1.4 Dow & B.F. Goodrich/VCM

3.2.1.5 Provincial (Private & Industrial Labs) Air & Source

3.2.2 Internal QC

3.2.2.1 The Branch maintains an in-house QC program (approximately 10% of the total tests) of the following:

3.2.2.1.1 Spiking the sample with mid-range standards

3.2.2.1.2 Running the sample in duplicates and triplicates

3.2.2.1.3 Analyzing occasional blind samples

3.2.2.1.4 Analyzing NBS reference materials

3.2.2.1.5 Checking the standards and calibration curves frequently

3.2.2.1.6 Maintaining precision and accuracy-control charts.

3.2.2.1.7 Maintaining log books on analysis and equipment maintenance

4. STATISTICAL PROCEDURES

4.1 Standard Deviation

4.1.1 From a single sample analyzed n times with results x_1 x_2 .....x_n

$$\textit{Average } \bar{x} = \frac{\sum_{i=1}^{n} x_i}{n}$$

$$(S) = \sqrt{\frac{\sum_{i=1}^{n} (x_i - \bar{x})^2}{n-1}}$$

$$\textit{Variance } (S)^2 = \frac{\sum_{i=1}^{n} (x_i - \bar{x})^2}{n-1}$$

4.1.2 From n samples analyzed each in duplicate.

Difference between Results $(x_1 - x_2)_1 \ldots\ldots (x_1 - x_2)_n$

$$(S) = \sqrt{\frac{\sum_{i=1}^{n} (x_1 - x_2)_i^2}{2n}}$$

4.1.3 D.L. The amount of analyte required to be present to ensure that when it is present it will not be reported as absent (i.e. less than the detection criteria).

5. DEFINITION OF TERMS

5.1 Error: Difference between the measured value and the true value.

5.2 Accuracy: The degree of agreement between the measured value and the true value. Accuracy includes precision and bias.

5.3 Precision: A measure of the spread of the data. Usually expressed as one standard deviation.

5.4 Bias: When the error of the limiting mean is not zero.

5.5 Minimum Detection Limit

5.5.1 There are two types of minimum detection limits.

5.5.2 (a) Those based on the stability of the instrument and measured by the prescribed confidence of the signal-to-noise ratio, usually two standard deviations.

5.5.3 (b) Those based on a parameter of the data set and measured at the prescribed confidence level as the dispersion to the low-level standard or low-level duplicate samples. Usually one standard deviation is used.

5.5.4 Range: The interval of measured values over which the procedure is applicable.

5.5.5 Interferences: A component that causes bias or imprecision in the measured value.

6. REFERENCES

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6.5 "Quality Control Handbook", Third Edition by Juran, J.M., McGraw Hill Book Co.

6.6 "Introduction to Statistical Analysis" by Dixon, W. J., and Massey, F.J., McGraw Hill Book Co.