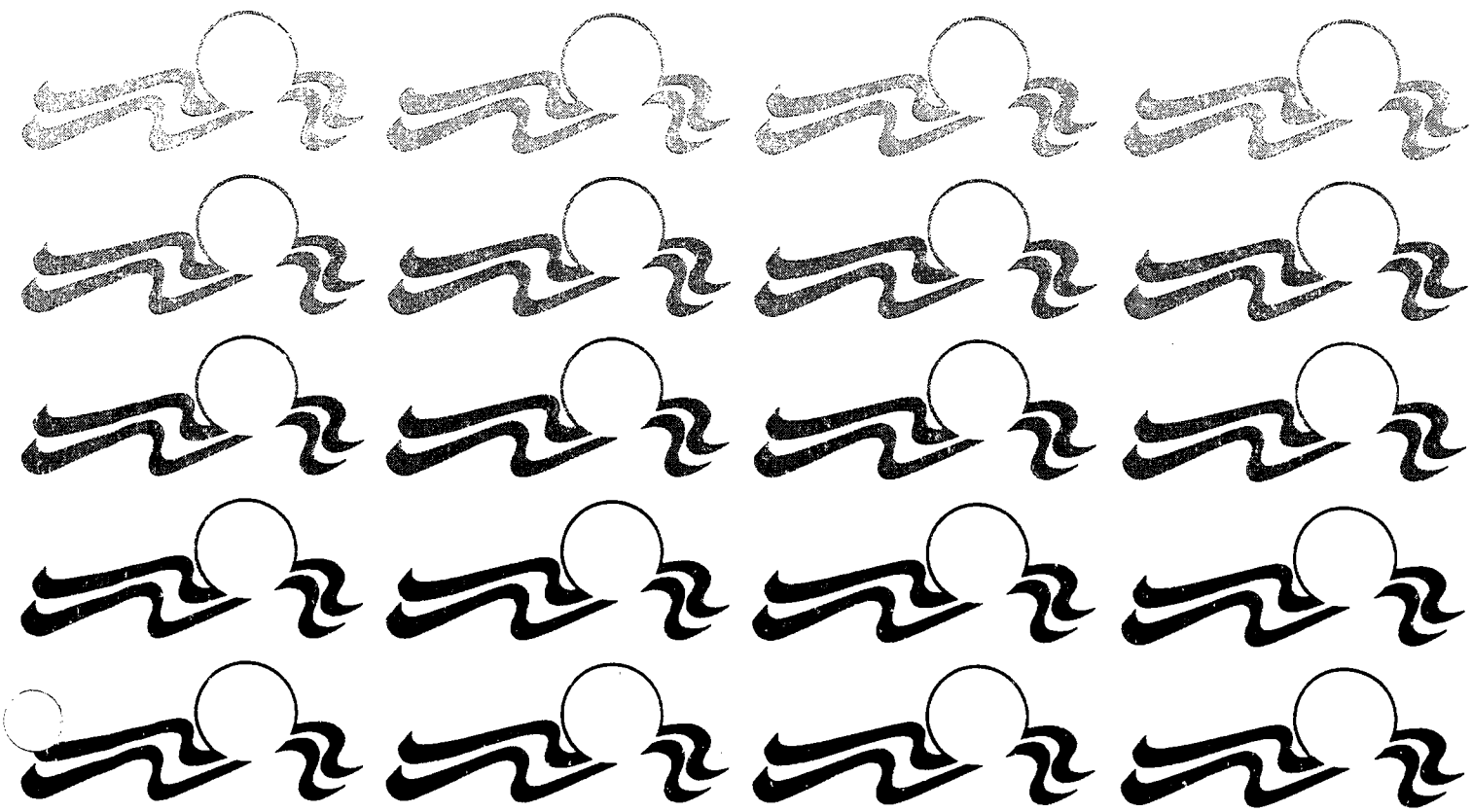
Texas Air Control Board

LABORATORY METHODS

MANUAL



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April 3, 1989

TO: RECIPIENTS OF LABORATORY METHODS MANUAL

This is the latest version of the "Laboratory Methods Manual" from the Sampling and Analysis Division of the Texas Air Control Board. You will note that there is a combination of new and revised methods in addition to some older, unchanged methods. We will provide updated methods to all organizations on our mailing list at regular intervals.

Note that the introduction to the manual refers to both inorganic and organic methods of analysis, but the latter are not yet available.

Sincerely,

J. Scott Mgebroff, Director
Sampling and Analysis Division

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Introduction

This laboratory manual is prepared by the Sampling and Analysis Division at the Texas Air Control Board (TACB) and includes analyses for both inorganic and organic materials in environmental samples. It is designed to provide standardized methods for the analysis of chemical substances in samples that are obtained directly from ambient air or from sources that are vented into the atmosphere, or from materials, or their combustion products, that might find their way into the atmosphere. We will attempt to maintain these methods as current as possible and to provide revisions as needs arise.

The methods described in this manual are available for use by any suitably equipped laboratory. We will approve equivalent methods for analysis upon consultation with the appropriate laboratory section at the TACB and if an adequate quality assurance plan is included in the proposed equivalent method of analysis.

All laboratory methods include measures of both precision and accuracy. The measure of precision usually means the analysis of duplicate samples, preferably by taking duplicate aliquots of the crude material or sample through any extraction or concentration procedures that are called for by the method. The measure of accuracy usually means the analysis of standard or reference materials and these also should be processed through any preliminary procedures. The United States National Institute of Standards and Technology (NIST) is an excellent source for Standard Reference Materials (SRM's) although there are other commercial sources of comparable materials. The laboratories at the TACB are ready to cooperate with any interlaboratory study that is designed to produce quality data on standard materials. The limits of precision and accuracy, usually expressed as a percent difference between two quantities, are given for each method as applicable, and the experiences of the TACB laboratory with precision and accuracy for the method are given, where applicable.

This manual is in a state of transition. The older methods are being reviewed and rewritten. All organizations in the mailing list will receive revised and new analytical methods as they become available. Please destroy all other versions of this laboratory manual.

Information on a particular method of analysis may be obtained from the appropriate laboratory section at the TACB. Additional copies of this manual may be obtained through the mailroom of the TACB upon receipt of a fee of $10.00. The manual is free for public agencies.

We welcome any comments or suggestions on any matter relating to this manual.

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the µg CH_2O/ml from the least squares standard curve.

In some property-line sampling, the concentration of aldehydes can be high. In such cases, the absorbance developed may be too high for accuracy. If the absorbance, when checked at ten minutes, is over 0.5, take an aliquot of the sample being developed, quickly dilute with part of the blank of the same age to obtain 12 ml total diluted sample. Exactly 12 minutes after adding the oxidizing solution to the original sample (and blank), read the absorbance on the spectrophotometer, using the remaining blank as reference. Determine the µg CH_2O/ml absorbing solution in the diluted sample from the standard curve.

G. CALCULATIONS

$$\frac{\mu g\ CH_2O}{M^3} = \frac{\mu g\ CH_2O/ml \times \text{volume absorber (ml)}}{M^3\ air} \times \frac{12\ ml}{ml\ aliquot\ taken}$$

If no dilution is required, drop the last term from the calculation.

NOTE: If a method is being applied to the determination of aldehyde other than formaldehyde, a gravimetric factor $\left[\frac{MW\ Aldehyde}{MW\ CH_2O}\right]$ can be added to the calculation to determine µg/M^3 of aldehyde.

H. QUALITY CONTROL

Seven percent of the samples should be run in duplicate. These samples should agree within 5%. If not, analysis procedures, flow rates, etc., should be checked, and the analysis should be rerun.

Spiked samples should be run to control the accuracy of the analysis. Spiked samples are prepared by adding a known quantity of a standard to an aliquot of sample. Percent recovery can be calculated from the concentrations of the spiked sample, the sample and the standard.

A suitable spike would be prepared as follows: Place a 4 ml aliquot of the 0.4 µg CH_2O/ml standard in a test tube. Add 6 ml of sample to the test tube. Add 2 ml oxidizing reagent. Mix. Wait exactly 12 minutes and read the absorbance on the spectrophotometer, using the blanks as a reference.

$$\text{Percent Recovery} = \frac{\text{conc(spike + sample)} - \text{conc (sample)}\ \frac{6}{10}}{\text{conc (spike)}} \times 100$$

$$\text{where conc(spike)} = \frac{(4\ ml)(0.4\ \mu g\ CH_2O/ml)}{10\ ml} = 0.16\ \mu g\ CH_2O/ml$$

A standard curve should be run each time the analysis is done. MBHT absorber should be discarded if any brown coloration appears.

I. References

Hauser, T. R. and Cummins, R. L., "Increasing Sensitivity of 3-Methyl-2-Benzothiazolone Hydrazone Test for Analysis of Aliphatic Aldehydes in Air", Anal. Chem. 36, 679 (1964).

Sawicki, Hauser, Stanley and Elbert, "The 3-Methyl-2-Benzothiazolone Hydrazone Test", Anal. Chem. 33, 1, 93-96 (1961).

Modified May 25, 1979
Laboratory Division
Texas Air Control Board

ALDEHYDES METHOD

Modified MBTH Method

A. GENERAL

The aliphatic aldehydes in ambient air are collected in a dilute acid solution. In the laboratory, the trapped aldehydes are reacted with MBTH (3-methyl-2-benzo-thiazolinone hydrazone hydrochloride) to form an azine. Oxidation of excess MBTH forms a reactive cation which adds to the azine to give a brilliant blue cationic dye. The intensity of the blue dye is directly proportional to the concentration of the aldehydes and gives a sensitive colorimetric method for aldehyde determination.

B. APPLICABILITY

This laboratory has found that the standard MBTH absorber is too unstable for accurate network aldehyde determination. Immediate color development and/or cold storage are prerequisites for successful application of the standard MBTH method. To utilize the high sensitivity of the aldehyde-MBTH reaction for network determinations, it is necessary to trap the aldehyde in an interim absorber and then carry out the aldehyde-hydrazone reaction in the lab analysis. The same dilute acid absorber used to trap ammonia can be used to trap aldehydes. Thus two pollutants can be analyzed from one sample. In addition, these samples are fairly stable, losing approximately 1% aldehyde per day during a two week storage period.

Sampling for the Texas Air Sampling Network (TASN) should be at the rate of 0.4 liters/minute for 24 hour sampling periods. This appears to be the upper limit for optimal absorption for the aldehydes. Trapping efficiency at 0.4 l/min is 90%. (If sampling for aldehydes alone, a rate of 0.2 l/min would be preferable and if sampling for NH_3 alone, a 0.6 l/min flow would be optimal.) At the rate of 0.4 l/min, sensitivity is down in the 2 ppb range for aldehydes. Telmatic sampling is not recommended with this modified MBTH method as the solution does not efficiently absorb aldehydes at the 2 l/min flow rate.

For property line sampling, it is recommended that the regular MBTH method be used. Using 20 ml absorber and sampling from 1 1/2-2 l/min for thirty minutes, the sensitivity range of that method is 20-200 ppb.

In addition to being the predominant aldehyde in the air, formaldehyde (HCHO) reacts about 25% greater than other aliphatic aldehydes and about 300% greater than branched chain and unsaturated aldehydes.

The following compounds react with MBTH to produce blue or green colored products: aromatic amines, azo dyes, imino heterocyclics, and dinitrohydrazone aldehyde derivatives. However, since most of these are not gaseous or water soluble, they will not generally interfere in analysis of atmospheric samples.

C. APPARATUS

Suitable sampling apparatus
4 - 1000 ml volumetric flasks
9 - 100 ml volumetric flasks
Suitable test tubes for number of samples and standards
Sufficient cuvettes
1 - 2 ml graduated pipet
2 - 0.5 ml graduated pipets
8 - 10 ml volumetric pipets
2 - 5 ml volumetric pipets
1 - 4 ml volumetric pipet
1 - 3 ml volumetric pipet
1 - 2 ml volumetric pipet
3 - 1 ml volumetric pipets
1 - 0.5 ml volumetric pipet
Spectrophotometer capable of operation at 626 nm.

For Formaldehyde standardization:
1 - 50 ml buret
1 - 10 ml buret
3 - 300 ml beakers
3 - 125 ml Erlenmeyer flasks
Ice Bath

D. REAGENTS

All reagents should be ACS reagent grade.

(1) Absorbing Solution
Add 0.5 ml formic acid (88%) to approximately 900 ml deionized water in a 1 liter volumetric flask. Bring up to volume.

(2) Formaldehyde Standard

(a) Concentrated Standard
Pipet 2.7 ml 37% HCHO (should be standardized quarterly to determine strength) into a 1 liter volumetric flask and dilute to the mark with deionized water. This solution has approximately 1,000 µg/ml. This solution is very stable.

(b) Working Standard
Pipet 1 ml of standard (a) into a 100 ml volumetric flask and bring up to volume with deionized water. This solution has approximately 10 µg CHO^-/ml and should be made fresh daily.

(3) MBTH Reagent
Dissolve 0.05 g 3-methyl-2-benzothiazolinone hydrazone hydrochloride in approximately 70 ml of deionized water. Dilute to 100 ml. This reagent must be prepared daily. (Enough for 20 samples) Solution should be clear. Do not use a cloudy solution.

(4) Oxidizing Reagent
Dissolve 0.5 g ferric chloride ($FeCl_3$) and 0.8 g sulfamic acid (NH_2SO_3H) in approximately 70 ml deionized water in a 100 ml volumetric flask. Dilute to the mark. This reagent must be prepared daily.

(5) Reagents for Formaldehyde Standardization

(a) 0.1 N Iodine Solution
Dissolve 25 g KI in approximately 25 ml deionized H_2O. Add 12.7 g I_2 and dilute to 1 liter.

(b) .01 N Iodine Solution
Dilute 100 ml of solution (a) to 1 liter.

(c) Sodium Thiosulfate (0.1 N)
Weigh 15.8 grams of anhydrous sodium thiosulfate ($Na_2S_2O_3$) and dilute to 1 liter.

(d) Potassium Dichromate (0.100 N)
Accurately weigh 4.9036 g of oven-dried $K_2Cr_2O_7$. Dissolve in deionized H_2O and dilute to 1 liter. This solution is 0.1 N and is stable.

(e) Starch Solution
Dissolve 2 g reagent grade soluble starch in 500 ml of boiling deionized water. Filter while the solution is still warm and add a crystal or two of mercuric chloride to inhibit mold growth.

(f) Sodium Carbonate Buffer Solution
Dissolve 80 grams of anhydrous sodium carbonate in about 500 ml of deionized water in a 1000 ml volumetric flask. Slowly add 20 ml glacial acetic acid and dilute to 1 liter. Chill solution.

(g) Sodium Bisulfite - 1% Solution
Dissolve 1 g of $NaHSO_3$ in 100 ml deionized H_2O.

(h) Glacial Acetic Acid

E. COLLECTION OF SAMPLE

The aldehydes are trapped in 50 ml of absorbing solution using a suitable impinger and pumping apparatus. The flow should be approximately 0.4 l/min for a period of 24 hours. Sampling lines should either be Teflon or glass.

F. TEST PROCEDURE

(1) Standardization of Sodium Thiosulfate (0.1 N)

Into each of three Erlenmeyer flasks or beakers pipet 50 ml of 0.100 N $K_2Cr_2O_7$ using a 50 ml volumetric pipet. Add 8 ml of concentrated HCl to each flask. From this point, handle each flask individually through the titration. To the first flask add 2 g KI, swirl to hasten dissolution. Titrate the liberated iodine at once with thiosulfate until the color begins to lighten. Add 2 ml starch solution and continue the titration. There is a blue to emerald green color change at the end point. Determine the blank by use of the same amount of KI and HCl in the same volume of water. Correct the volume of thiosulfate for any blank and calculate the normality of the thiosulfate solution.

(2) Standardization of 0.1 N Iodine

Into each of three Erlenmeyer flasks or three beakers, pipet accurately 20 ml of the iodine solution. Add about 30 ml of distilled water and 1 ml acetic acid. Titrate with the 0.1 N sodium thiosulfate solution until the yellow color of the solution is almost gone. Then add 2 ml starch solution and continue the titration until the blue color just disappears. Titrate the second and third samples of the iodine solution in the same way. Calculate the normality of the iodine.

(3) Standardization of Formaldehyde

Pipet 1 ml of concentrated formaldehyde standard, solution (a) of Section D. (2), into an Erlenmeyer flask. Pipet 1 ml distilled H_2O into another flask for a blank. Add 10 ml of 1% sodium bisulfite and 1 ml of starch solution. Swirl to mix.

Add dropwise with a pipet, 0.1 N I_2 to a dark blue color (approximately 15-20 ml). Destroy the excess iodine with 0.1 N sodium thiosulfate (1-2 drops). Add 0.01 N iodine until a faint blue end point is reached (3-5 drops). The excess inorganic bisulfite is now completely oxidized to sulfate and solution is ready for determination of the formaldehyde bisulfite addition product. Chill the flask in an ice bath and add 25 ml of chilled sodium carbonate buffer. Using a microburet, titrate the liberated sulfite with 0.01 N iodine to a faint blue end point (approximately 5-10 ml).

NOTE: The amount of iodine added in this step must be accurately measured and recorded.

(4) Standard Curve Preparation

Pipet 1.0, 2.0, 3.0, 4.0, and 5.0 ml of standard formaldehyde solution (b), Section D. (2), into 100 ml volumetric flasks. Dilute to volume with absorbing solution. These solutions contain about 0.1, 0.2, 0.3, 0.4, and 0.5 µg HCHO/ml, assuming HCHO used to make standard (a) is indeed 37%. (Use value obtained from HCHO standardization to ascertain true concentration of standards).

Pipet 10 ml from each standard into a 1" test tube. Prepare a blank using 10 ml absorbing solution. To each add 5 ml MBTH solution. Mix well. Wait 30 minutes. Add 1.0 ml oxidizing reagent. Mix well. After a 30 minute development time, read absorbance at 626 nm. Plot absorbance against concentration of standards.

(5) Sample Analysis

Bring volume of absorber back to the original volume used for sampling, using deionized water, to correct for any evaporation during sampling. Place a 10 ml aliquot of each sample in a 1" test tube; prepare a blank using 10 ml absorbing solution. Add 5 ml MBTH solution to each and mix well. Wait 30 minutes. Then add 1.0 ml oxidizing reagent and mix well. After 30 minutes development time, read the absorbance at 626 nm. Determine the concentration of aldehydes from the least squares standard curve.

G. CALCULATIONS

(1) Standardization of 0.1 N Sodium Thiosulfate

$$\text{Normality } Na_2S_2O_3 = \frac{(\text{Normality } K_2Cr_2O_7)(\text{Volume } K_2Cr_2O_7)}{\text{Volume } Na_2S_2O_3} = \frac{(0.100\ \underline{N})(50\text{ ml})}{\text{Volume } Na_2S_2O_3 \text{ in ml}}$$

(2) Standardization of 0.1 N Iodine

$$\text{Normality } I_2 = \frac{(\text{Normality } Na_2S_2O_3)(\text{Volume } Na_2S_2O_3)}{\text{Volume } I_2} =$$

$$\frac{(\text{Normality } Na_2S_2O_3)(\text{Volume } Na_2S_2O_3 \text{ in ml})}{20\text{ ml}}$$

(3) Standardization of Formaldehyde

One ml of 0.01 N I_2 is equivalent to 0.15 mg of HCHO.
Thus, 1 ml of concentrated HCHO contains:

(ml 0.01 N I_2 to titrate sample - ml 0.01 N I_2 to titrate blank)* x
(0.15 mg x 1000 µg/(ml) = µg/ml HCHO

NOTE: If water and buffer are reductant free, the blank will be zero.

(4) Sample Analysis

$$\frac{\mu g}{M^3} = \frac{\mu g/ml\ HCHO \times 50\ ml\ absorber}{M^3}$$

$$\text{where } M^3 = \frac{(liters/minute) \times (minutes)}{1000\ liters/M^3}$$

1 ppm (total aldehydes as HCHO) = 1228 $\mu g/M^3$
(at 760 mm Hg and 25° c)

H. QUALITY CONTROL

All titrations should be run in triplicate. The sodium thiosulfate and iodine should be standardized before each use. The relative deviation in the volume of titrant used should be less than 5 parts per thousand (5 °/oo). The relative deviation is calculated as follows:

$$\text{Relative Deviation (R.D.)} = \frac{\bar{d}}{\bar{v}} \qquad \bar{d} = \frac{\Sigma|v_i - \bar{v}|}{N}$$

where $\bar{d}$ = average deviation

$\bar{v}$ = arithmetic average of all individual volumes

v_i = individual measurement values

N = number of measurements

for example:

Three titration volumes, v_i, were found to be 49.80 ml., 49.91 ml, 49.89 ml for the standardization of $Na_2S_2O_3$

$49.80 + 49.91 + 49.89 = 149.60 \qquad \bar{v} = 49.87$ ml

$|v_1-\bar{v}| \quad |49.80-49.87| = 0.07 \qquad \Sigma|v_i-\bar{v}| = 0.13$

$|v_2-\bar{v}| \quad |49.91-49.87| = 0.04$

$|v_3-\bar{v}| \quad |49.89-49.87| = 0.02 \qquad \bar{d} = \frac{0.13}{3} = 0.04$

$$R.D. = \frac{0.04}{49.87} = 0.8\ ^{o}/oo$$

therefore the three titrations are acceptable.

Duplicates should be run on 7% of the samples or at least one duplicate per batch of 15 or less. These will test the precision of the procedure. The relative deviation should be less than 5% if the absorbance reading is greater than 0.100

$$R.D. = \frac{\bar{d}}{\bar{v}} \quad \text{where} \quad \bar{d} = |v_1 - v_2| \qquad \bar{v} = \frac{v_1 + v_2}{2}$$

Spiked samples should be run to control the accuracy of the analysis. Spiked samples are prepared by adding a known quantity of a standard to an aliquot of sample. Percent recovery can be calculated from the concentrations of the spiked sample, the sample, and the standard.

A suitable spike would be prepared as follows: Place 4 ml of the 0.4 µg HCHO/ml standard in a test tube. Add 6 ml of sample to the test tube. Add 5 ml MBTH solution to each and mix well. Wait 30 minutes. Then add 1.0 ml oxidizing reagent and mix well. After 30 minutes development time, read the absorbance at 626 nm.

$$\text{Percent recovery} = \frac{\text{conc (spike + sample)} - \text{conc (sample)}}{\text{conc (spike)}} \times 100$$

for example:

A sample had a concentration of 0.25 µg HCHO/ml. The spike of the same sample had a measured concentration of 0.305 µg/ml. The spike was prepared as above. The calculated concentration of the spike was 0.160 µg HCHO/ml.

$$\text{Percent recovery} = \frac{(0.305\ \mu g/ml) - [0.25\ \mu g/ml\ (\frac{6\ ml}{10\ ml})]}{0.160\ \mu g/ml} \times 100$$

$$= \frac{0.155}{0.160} \times 100 = 97\%$$

A spiked sample should be run with each set of samples. The percent recovery should be between 90-110%. If not, all steps of the analysis should be examined carefully and the analysis repeated.

A standard curve must be run with each set of samples.

I. REFERENCES

Methods of Air Sampling and Analysis, Intersociety Committee #112 Tentative Method for HCHO Content of the Atmosphere (MBTH - Colorimetric Method - Applications to Other Aldehydes) (43502-02-70T), American Public Health Association, Inc., 1972, pp. 199.

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Hauser, T R., and Cummins, R. L., Increasing Sensitivity of 3-Methyl-2-Benzothiazolone, Hydrazone Test for Analysis of Aliphatic Aldehydes in Air, Anal. Chem., 36, 679 (1964).

Modified July 26, 1979
Laboratory Division
Texas Air Control Board

DETERMINATION OF AMMONIA

Phenol-Nitroprusside Method

A. GENERAL

Ammonia is collected in very dilute acid solution. The trapped ammonia reacts with phenol-nitroprusside and alkaline hypochlorite solutions to produce a blue complex that is measured colorimetrically. The intensity of the blue color is proportional to the amount of NH_3 absorbed.

B. APPLICABILITY

For ambient air sampling at a flow rate of 0.2 liters per minute, the lower limit for detection is 4.4 $\mu g/M^3$; increasing the flow rate to 0.6 liters per minute lowers the limit to 1.4 $\mu g/M^3$. The addition of the nitroprusside catalyst greatly increases the sensitivity of the method.

In addition to being highly dependent upon time and temperature for proper color development, this reaction is pH critical and hypochlorite ion concentration dependent. If the sample pH is less than 11, the color development will be drastically reduced. Also, if the NaOCl has deteriorated as a result of aging, the color will not develop properly.

It has been found that urea interferes positively as do monoalkylamines. Formaldehyde interferes negatively when present in amounts equal to 20% of the NH_3.

C. APPARATUS

Suitable sampling apparatus
2 - 1,000 ml volumetric flasks
2 - 500 ml volumetric flasks
8 - 100 ml volumetric flasks
8 - 10 ml volumetric pipets
3 - 5 ml volumetric pipets
1 - 3 ml volumetric pipet
1 - 2 ml volumetric pipet
1 - 1 ml volumetric pipet
1 - 0.5 ml volumetric pipet
2 - 5 ml graduated pipets
1 - 1 ml graduated pipet
Sufficient storage bottles
Sufficient 1" test tubes
10 mm cuvettes
Spectrophotometer capable of operating at 626 nm
Water bath or oven capable of operation at 37° C.

D. REAGENTS

(1) Absorbing Solution
Add 1 ml formic acid (88%) to 2 liters deionized water.

(2) Phenol-Nitroprusside Solution
Dissolve 5 grams of phenol in 50 ml deionized water. Add 0.025 grams sodium nitroprusside (sodium nitroferricyanide). Transfer to a 500 ml volumetric flask and bring up to volume with deionized water.

NOTE: This solution may be kept up to one month if kept refrigerated in an amber bottle. However, if solution turns yellow, it should be discarded.

(3) Alkaline Hypochlorite
Transfer 4.2 ml of commercially prepared NaOCl (such as "Clorox") and 6.25 ml of 10 N NaOH (or 2.5 grams NaOH pellets) to a 500 ml volumetric flask. Dilute with deionized water to the proper volume.

NOTE: This reagent may be stored up to one month if kept refrigerated in an amber bottle.

(4) Standard Stock Ammonia Solution
Dissolve 3.880 grams $(NH_4)_2SO_4$ in 1 liter deionized water. This solution contains 1000 µg NH_3/ml.

(5) Working Standard Ammonia Solution
(a) Dilute 10 ml of the Standard Stock Ammonia solution to 100 ml with absorbing solution. This solution has 100 µg/ml NH_3.

(b) Dilute 10 ml of the above solution (a) to 100 ml with absorbing solution. This solution has 10 µg/ml and will be used to prepare standards for the standard curve.

E. COLLECTION OF SAMPLE

The sample is collected using a known volume of dilute acid solution in a suitable impinger. When midget impingers are used for property line samples, air may be bubbled through at a rate of 1.5 - 2 liters per minute. Glass or plastic sampling lines are acceptable; galvanized, brass, or copper sampling lines should be avoided. Use 20 ml of absorber in a midget impinger. For ambient sampling use 50 ml of absorber in a NASN bubbler.

F. TEST PROCEDURE

(1) Preparation of Standard Curve
Using the second working standard (see Section D.(5)(b)), pipet 0.5, 1, 2, 3, 5, and 10 ml into a series of 100 ml volumetric flasks.

Make up to volume with absorbing solution. These solutions contain 0.05, 0.1, 0.2, 0.3, 0.5, and 1.0 µg/ml respectively.

Pipet 10 ml of each of the above standard solutions into test tubes. To each add 5 ml of the phenol-nitroprusside solution, mix, and then add 5 ml of the alkaline hypochlorite and mix well.

Prepare a blank using 10 ml absorbing solution and 5 ml of each developing reagent.

Heat standards and blank to 37° C for 30 minutes. Cool to room temperature. Measure the absorbance at 626 nm versus the blank. Plot the absorbance vs. µg NH_3/ml. The absorbance is stable for several hours.

(2) Sample Determination

Correct for any evaporation loss during sampling by bringing the sample back to the original volume with deionized water. Place a 10 ml aliquot of the sample into a test tube; add 5 ml of the phenol-nitroprusside and mix. Add 5 ml of the alkaline hypochlorite solution. Mix thoroughly after addition of each reagent. Heat the samples and the blank to 37° C for 30 minutes. Cool to room temperature and read absorbance at 626 nm versus blank. Calculate µg NH_3/ml from the least squares standard curve.

In some cases samples may yield final colors too intense for accurate reading. If the absorbance is over 0.8, take an aliquot of the sample and dilute with a part of the developed blank. Read the diluted sample versus the remaining blank. Calculate µg/ml for the diluted sample from the standard curve.

NOTE: The time and temperature of incubation are critical if reproducible results are to be obtained. It is considered good practice to prepare a new set of standards each time a set of samples is run. The standards, samples, and quality control samples are then all heated simultaneously; an oven with an internal fan to circulate air or a water bath may be used.

G. CALCULATION

$$\mu g\ NH_3/M^3 = \frac{(\mu g\ NH_3/ml) \times (\text{total ml absorber used})}{M^3 \text{ air sampled}} \times \frac{(20\ ml)^*}{(\text{ml developed sample tak}\\ \text{for aliquot}}$$

*If no dilutions are required, the last factor is deleted.

H. QUALITY CONTROL

Duplicates should be run on 7% of the samples or at least one duplicate per batch of 15 or less. These will test the precision of the procedure. The relative deviation should be less than 5% if the absorbance reading is greater than 0.100.

$$\text{Relative Deviation (R.D.)} = \frac{\bar{d}}{\bar{v}} \quad \text{where } \bar{d} = |v_1 - v_2| \qquad \bar{v} = \frac{|v_1 + v_2|}{2}$$

v_1 and v_2 are the individual measurements.

Spiked samples should be run to control the accuracy of the analysis. Spiked samples are prepared by adding a known quantity of a standard to an aliquot of sample. Percent recovery can be calculated from the concentrations of the spiked sample, the sample, and the standard.

A suitable spike would be prepared as follows: Place 4 ml of the 1.0 µg/ml standard in a test tube. Add 6 ml of sample to the test tube. Add 5 ml of the phenol-nitroprusside solution, mix, then add 5 ml of the alkaline hypochlorite and mix well. Heat to 37° C for 30 minutes. Cool to room temperature. Measure the absorbance at 626 nm versus the blank.

$$\text{Percent recovery} = \frac{\text{conc (spike + sample)} - \text{conc (sample)}}{\text{conc (spike)}} \times 100$$

For example,

A sample had a concentration of .300 µg NH_3/ml. The spike of the same sample had a measured concentration of 0.575 µg/ml. The spike was prepared as above. The calculated concentration of the spike was 0.400 µg/ml.

$$\text{Percent Recovery} = \frac{(0.575\ \mu g/ml) - (0.300\ \mu g/ml)\left(\frac{6\ ml}{10\ ml}\right)}{0.400\ \mu g/ml} \times 100$$

$$= \frac{0.395}{0.400} \times 100 = 99\%$$

A spiked sample should be run with each set of samples. The percent recovery should be between 90-110%. If not, all steps of the analysis should be examined carefully and the analyses repeated.

A standard curve must be run with each set of samples.

I. REFERENCES

Leithe, W., The Analysis of Air Pollutants, 1970, p. 172, 5.6.1.5. Special Topics, Nitrogen Containing Pollutants.

Weatherburn, M. W., "Phenol-Hypochlorite Reaction for the Determination of Ammonia", Anal. Chem. 39, 971 (1967).

Hanshu, Mollie L., Payne, Jim S., Texas Air Control Board

The Analysis of Filters from High-Volume Air Samplers for Arsenic by Inductively-Coupled Plasma Spectroscopy

1.0 PRINCIPLE AND APPLICABILITY.

1.1 Particulate matter suspended in the ambient air is collected on a glass fiber filter for 24 hours using a high-volume (hi-vol) air sampler (Reference 1) or for shorter times on a glass fiber filter using a property-line hi-vol sampler (Reference 2).

1.2 There are several analytical tools which may be used to analyze for arsenic collected as particulate matter on glass fiber filters. These include X-ray fluorescence spectrometry (XRF), atomic absorption (AA) with hydride generation, furnace AA, and inductively-coupled plasma emission (ICP) spectroscopy. However, only high-resolution inductively-coupled plasma spectroscopy is free of the interferences inherent in measuring arsenic by AA without hydride generation (References 3-6), and ICP has detection limits much lower than those usually encountered in using XRF.

1.3 The arsenic content of the sample is measured by pretreating a portion of the filter, usually four filter circles of 37-mm diameter each, with boiling chloroform and then with boiling concentrated nitric acid to liberate any arsenic which might be trapped by tire rubber dust or other solid organic material. Then the filter circles are extracted with a 5 N nitric acid solution. The extraction is facilitated by ultrasonication; the extract is filtered, and the arsenic concentration is determined by ICP.

2.0 RANGE AND LOWER DETECTABLE LIMIT.

2.1 The typical lower limit of the range is 0.01 $\mu g/m^3$ at a total volume of 1800 m^3 of air sampled if the four filter circles are extracted. An upper limit has not yet been observed.

2.2 The lower detectable limit (LDL) is three times the signal-to-noise ratio as determined by a program supplied with the instrument. The LDL is optimized at the start of each analysis, and is of the order of 0.10 $\mu g/mL$ for the solution to be analyzed, which translates to 0.01 $\mu g/m^3$ at a total volume of 1800 m^3 of air sampled.

3.0 PRECISION.

The precision of the method is measured by performing duplicate extractions and analyses on the same particulate-laden filter. The mean precision for this method calculated for 27 duplicate sets having concentrations greater than the LDL is -1% with a standard deviation of

9%. The concentrations for the duplicate sets ranged from 0.08 µg/mL to 9.74 µg/mL arsenic.

4.0 ACCURACY.

The accuracy of the method is measured by analyzing arsenic audit samples. These samples are prepared (by someone other than the analyst) by spotting (spiking) 0.5 mL of either 45 or 90 µg/mL arsenic on four stacked, 37-mm-diameter, blank filter circles supported by four glass spikes anchored in a styrofoam base and drying the filter circles for one hour under an infrared lamp. The mean percent difference (accuracy) for this method calculated for 30 audit samples is 3% with a standard deviation of 3%.

5.0 INTERFERENCES.

Two types of interferences are possible: the overlap of spectral lines and matrix effects.

5.1 There are no overlap interferences when using an instrument with a 3600-group gradient (which has a resolution of 0.01 nM) and the 193.696-nM line or the 197.197-nM line of arsenic.

5.2 Matrix effects have not been seen in the detection of arsenic following the extraction procedures described here, except that a broad-band interference (assumed to be a matrix effect) has been noticed at 193.696 nM for extracts of certain filter papers.

6.0 REAGENTS.

All reagents should be ACS reagent grade or better.

6.1 Glass-distilled water. Water that has been passed through a mixed-bed ion exchanger is distilled from an all-glass still. The water should exhibit a conductivity of ≤ 10 µS/cm.

6.2 Glass-distilled chloroform.

6.3 Concentrated, reagent-grade nitric acid.

6.4 5 N nitric acid. A solution that is 5 N in nitric acid is prepared by mixing 333 mL of reagent-grade nitric acid with enough glass-distilled water to make 1000 mL of solution in a volumetric flask.

6.5 1000-ppm arsenic solution. A solution that contains 1000 ppm arsenic is prepared by dissolving 1.7340 g of reagent-grade sodium arsenite in

enough glass-distilled water to make 1000 mL in a volumetric flask. A commercially available standard prepared for atomic absorption spectroscopy is acceptable.

6.6 Solution containing 20 ppm arsenic in 5 N nitric acid. This standard is prepared by adding 20 mL of the 1000-ppm standard to 333 mL of reagent-grade nitric acid in a 1000-mL volumetric flask and diluting to the mark with distilled water.

6.7 Working standards containing 0.50, 1.00, 5.00, and 10.00 ppm arsenic in 5 nitric acid. These standards are prepared by diluting 2.50, 5.00, 25.00, and 50.00 mL, respectively, of the 20-ppm standard to 100 mL in a volumetric flask with 5 N nitric acid.

7.0 APPARATUS.

7.1 Glassware.

Volumetric flasks, 1000-mL.
Volumetric flasks, 100-mL.
Beakers, 100-mL.
Beakers, 50-mL.

7.2 Shearless punch.

The shearless punch was designed to cut a circle having a diameter of 37 mm from a filter paper. The punch cuts the circle without fraying the filter paper.

7.3 Hotplate.

7.4 Ultrasonic bath.

The ultrasonic bath has tank dimensions of 19.75" x 11.5" x 6" deep.

7.5 Inductively-coupled plasma emission spectrometer (ICP).

The ICP is a model JY38PI as manufactured by Instruments S.A. of Metuchen, N.J. The instrument is equipped with an argon plasma source; a 3600-group gradient; an automated sampler; a data system from Columbia Data Products, Inc., and its complementary software; a flow controller for the nebulizer argon; and a 10-roller peristaltic pump set for delivery of 1.3 mL/min.

7.6 Miscellaneous items.

Pipettor, 4-mL.
Pipettor, 10-mL.

Parafilm.
Plastic or glass funnels.
Whatman No. 50 hardened filter paper, or equivalent, 9-cm diameter.

8.0 PROCEDURE.

8.1 Four filter circles of 37-mm diameter (if possible) are cut from the filter using a shearless punch. The filter is folded exposed side inward and lengthwise (or diametrically if circular).

8.2 The four circles are carefully placed into a 100-mL beaker and covered with 4 mL of chloroform. The beaker is then placed on a hotplate (low-heat setting) to evaporate the chloroform completely by boiling. This process requires about 30 minutes.

8.3 The four circles are next covered with 4 mL of concentrated nitric acid. The beaker is left on the hotplate until the nitric acid has completely evaporated by boiling. This process requires about 90 minutes.

8.4 Finally, the beaker is removed from the hotplate. The four circles are covered with 10 mL of 5 N nitric acid. The beaker is covered with a piece of Parafilm and allowed to sit overnight.

8.5 The beaker is ultrasonicated for one hour.

8.6 The mixture is filtered through Whatman No. 50 hardened filter paper into a 50-mL beakers.

8.7 The filtrate is now ready for analysis for arsenic.

9.0 CALIBRATION.

9.1 A first-order calibration curve is calculated by the software supplied with the instrument from emission data using a 5 N nitric acid blank and three non-zero arsenic standards. Choose the non-zero arsenic standards according to the arsenic concentrations expected for the samples to be analyzed.

9.2 The LDL is also calculated by the software, in this case using the 5.00-µg/mL standard.

10.0 SAMPLE ANALYSIS.

Read and record the concentration in µg/mL of each sample to be analyzed for arsenic.

11.0 CALCULATION.

Calculate the concentration of arsenic in $\mu g/m^3$ as follows:

$$\mu g/m^3 = (C)(10mL)(A)/(4)(10.75\ cm^2)(V)$$

where:

C = concentration of arsenic in µg/mL from Step 10.0;
A = total area of exposed filter in cm^2;
4 = the number of filter circles;
10.75 cm^2 = area of one 37-mm diameter filter circle; and
V = total volume of air sampled in m^3.

Modify the calculation accordingly if four filter circles are not used or if the diameters are not 37 mm.

12.0 QUALITY ASSURANCE.

12.1 Precision of the method is measured by analyzing duplicate samples from the same exposed filter paper.

12.1.1 Duplicate analyses must be performed on at least 10% of the samples.

12.1.2 The percent difference must be less than 20% for arsenic concentrations which are ≥0.50 µg/mL.

12.2 Recoverability of the method is measured by analyzing spiked samples. Prepare spiked samples like audit samples, except use exposed filter papers.

12.2.1 A spiked sample must be analyzed for each ten or fewer samples.

12.2.2 The percent recoverability must be 85-115% for the spiked samples.

12.3 Accuracy of the instrument is determined by analyzing a standard as an unknown.

12.3.1 A standard must be analyzed as an unknown during the analyses of each set of ten or fewer samples.

12.3.2 The percent difference from the true value must be less than 10% for standards ≥0.50 µg/mL.

12.4 An audit sample must be analyzed for each set of ten or fewer samples.

13.0 REFERENCES.

1. United States Environmental Protection Agency, "Reference Method for the Determination of Suspended Particulates in the Atmosphere (High Volume Method)," Code of Federal Register, Title 40, Appendix B, 12-16 (July 1, 1975).

2. Texas Air Control Board, Sampling Procedures Manual, Chapter 11, January 1983.

3. Riley, K.W., "Spectral Interferences by Aluminum in the Determination of Arsenic Using the Graphite Furnace: Choice of Resonance Lines," At. Spectrosc. 3, 120-1 (1982).

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5. Poldoski, J.E., "Molecular Spectral Interference in the Determination of Arsenic by Furnace Atomic Absorbance," At. Absorpt. Newsl. 16, 70-3 (1977).

6. Pierce, F.D., and Brown, H.R., "Inorganic Interference Study of Automated Arsenic and Selenium Determination with Atomic Absorbance Spectrometry," Anal. Chem. 48, 693-5 (1976).

THE ANALYSIS OF LEAD IN GASOLINE BY ATOMIC ABSORPTION SPECTROMETRY

1.0 PRINCIPLE AND APPLICABILITY.

Lead (as tetraethyl lead) in gasoline is stabilized as an inorganic compound (presumably lead iodide) with iodine (Reference 1), evaporated to dryness, and then brought up in dilute nitric acid for analysis by atomic absorption (AA) spectrometry.

2.0 RANGE AND LOWER DETECTABLE LIMIT.

2.1 The typical lower limit of the range is 0.50 µg/g of lead. The upper limit is dependent upon the mass of the iodine used to stabilize the lead; for this method the upper limit is 300 µg/g of lead.

2.2 The lower detectable limit (LDL) is optimized at the start of each analysis, and is of the order of 0.05 µg/mL of lead for the solution to be analyzed, which translates to 0.50 µg/g of lead in gasoline.

3.0 PRECISION.

The precision of the method is measured by performing duplicate extractions and analyses on the same gasoline sample. The mean precision for this method calculated for 10 duplicate sets having concentrations greater than the LDL is 1% with a standard deviation of 1%. The concentrations for the duplicate sets ranged from 10.0 µg/g to 91.7 µg/g of lead in gasoline.

4.0 ACCURACY.

The accuracy of the method is measured by analyzing lead-in-gasoline audit samples. These samples are prepared (by someone other than the analyst) by diluting (as necessary) National Institute of Standards and Technology (NIST) lead-in-gasoline standards with xylenes. The mean percent difference (accuracy) for this method calculated for 12 audit samples is 3% with a standard deviation of 1%.

5.0 INTERFERENCES.

No interferences have been observed for this method.

6.0 REAGENTS.

All reagents should be ACS reagent-grade or better.

6.1 Milli-Q water. Deionized water is passed through a Milli-Q reverse-osmosis system. The water should exhibit a conductivity of ≤10 µS/cm.

6.2 Xylenes (solvent).

6.3 Iodine (resublimed).

6.4 Concentrated nitric acid.

6.5 Solution containing 1000 µg/mL of lead (AA standard).

6.6 Nitric acid (1:1). This solution is prepared by adding 500 mL of concentrated nitric acid to 500 mL of water in a 1000-mL volumetric flask and then mixing.

6.7 Iodine solution. This solution is prepared by dissolving 0.600 g of iodine in about 40 mL of xylenes solvent and then diluting to 100 mL with xylenes solvent in a volumetric flask.

6.8 Solution containing 10 µg/mL of lead in 10% nitric acid. This standard is prepared by adding 5 mL of the 1000-µg/mL lead standard to about 300 mL of water and exactly 50 mL of concentrated nitric acid in a 500-mL volumetric flask and diluting to the mark with water.

6.9 Solution containing 0 µg/mL of lead in 10% nitric acid. This standard is prepared by adding 50 mL of concentrated nitric acid to about 300 mL of water in a 500-mL volumetric flask and diluting to the mark with water.

6.10 Solution containing 5 µg/mL of lead in 10% nitric acid. This standard is prepared by mixing 50 mL of the 10-µg/mL lead standard with 50 mL of the 0-µg/mL lead standard in a 100-mL volumetric flask.

7.0 APPARATUS.

7.1 Glassware.

Pasteur pipets.
Graduated cylinder, 500-mL.
Graduated cylinder, 50-mL.
Volumetric flask, 1000-mL.
Volumetric flasks, 500-mL.
Volumetric flasks, 100-mL.
Beakers, 100-mL.
Watch glasses.

7.2 Top-loading balance.

7.3 Hotplate.

7.4 AA spectrometer.

The AA spectrometer is a Perkin-Elmer Model 3030.

7.5 Miscellaneous items.

Scoopula.
Pipettor, 5-mL.
Pipettor, 10-mL.
Beaker forceps.
Water squirt bottle.
Plastic funnels.
Whatman No. 40 filter paper, or equivalent, 15-cm diameter.
Plastic, screw-cap bottles, 4-oz.

8.0 PROCEDURE.

8.1 Pipet 10 mL of the iodine solution into a 100-mL beaker; cover the beaker with a watch glass.

8.2 Place the beaker on the top-loading balance, and remove the watch glass. Using a Pasteur pipet, weigh 10.00 g of the gasoline sample into the 10 mL of iodine solution. Carefully swirl the beaker, and replace the watch glass.

8.3 Place the beaker on the hotplate (medium-heat setting) in a laboratory hood. Turn on the hood. Remove the watch glass.

8.4 Evaporate the mixture to dryness (this process will require about 40 minutes). A dark residue will coat the bottom and the lower portions of the inside of the beaker.

8.5 Remove the beaker from the hotplate.

8.6 Pipet 10 mL of the 1:1 nitric acid into the beaker; cover the beaker with the watch glass.

8.7 Place the beaker back on the hotplate, and reflux for 30 minutes.

8.8 Remove the beaker from the hotplate.

8.9 Pipet another 10 mL of the 1:1 nitric acid into the beaker; cover the beaker with the watch glass.

8.10 Place the beaker back on the hotplate, and reflux for 30 minutes. The dark residue should now be broken up into tiny flakes, and the extracting solution should be yellowish-orange.

8.11 Remove the beaker from the hotplate. Allow the contents of the beaker to cool.

8.12 Using the water squirt bottle, quantitatively transfer the contents of the beaker into a 100-mL volumetric flask, and dilute to the mark with water. Mix the sample well.

8.13 Filter the sample through Whatman No. 40 filter paper into a 4-oz. plastic, screw-cap bottle. Secure the cap on the bottle, and shake the contents well. The sample is now ready for analysis by AA spectrometry.

9.0 CALIBRATION.

A calibration curve is calculated by the software supplied with the AA instrument from the results obtained from the 0-µg/mL lead standard and either just the 5-µg/mL standard or both of the non-zero standards.

10.0 SAMPLE ANALYSIS.

Read and record the concentration in µg/mL of lead for each sample to be analyzed. Correct for zero drift as necessary.

11.0 CALCULATION.

Calculate the concentration of lead in the gasoline sample in µg/g as follows:

$$\mu g/g = (C)(100\ mL/10.00\ g) \text{ or}$$

$$\mu g/g = 10C$$

where:

C = the concentration of lead in µg/mL from Step 10.0,
100 mL = the final volume of the extracting solution, and
10.00 g = the weight of the gasoline sample.

12.0 QUALITY ASSURANCE.

12.1 Precision of the method is measured by extracting and analyzing duplicate samples from the same gasoline sample.

12.1.1 Duplicate analyses must be performed on at least 10% of the samples.

12.1.2 The percent difference must be less than 20% for lead concentrations which are ≥0.50 µg/mL.

12.2 Recoverability of the method is measured by analyzing spiked samples. Prepare a spiked sample by adding 5.00 g of the appropriate NIST standard (diluted if necessary) and 5.00 g of a gasoline sample to the iodine solution.

12.2.1 A spiked sample must be analyzed for each ten or fewer samples.

12.2.2 The percent recoverability must be 85-115% for each spiked sample.

12.3 Accuracy of the instrument is determined by analyzing standards as unknowns.

12.3.1 A standard must be analyzed as an unknown during the analyses of each set of ten or fewer samples.

12.3.2 The percent differences from the true values must be less than 10% for standards ≥1.0 µg/mL.

12.4 An audit sample must be analyzed for each set of ten or fewer samples.

13.0 REFERENCE.

1. American Society for Testing and Materials (ASTM) Method D 3237 - 79 (Reapproved 1984), "Standard Test Method for Lead in Gasoline by Atomic Absorption Spectrometry," 1988 Annual Book of ASTM Standards, Vol. 05.02, Section 5, pp. 648-650.

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Determination of Beryllium By Flameless Atomic Absorption

A. GENERAL

Particulate containing beryllium is collected using an 8" x 10" cellulose filter and a HiVol sampler. A 1/8" circle of the filter is placed in the flameless atomizer of the atomic absorption spectrophotometer and heated slowly to ash the cellulose and remove the organic components of the sample. The sample is then heated quickly to a high temperature to atomize any beryllium present. The amount of beryllium in the sample is determined by comparing the peak height of the sample generated on a high-speed recorder to the peak heights of a set of standards.

B. APPLICABILITY

This method is applicable to both ambient and property line samples. The method is very sensitive and capable of measuring natural background levels of beryllium. The detection limit for 24-hour samples is approximately 1.0 pg/M^3. For shorter sampling periods, the detection limit is proportionately higher.

C. APPARATUS

Suitable sampling apparatus
Atomic absorption spectrophotometer with flameless atomizer
Microboat manipulator
1 - 1 liter volumetric flask
1 - 1 ml pipet
1 - 2 ml pipet
1 - 4 ml pipet
1 - 6 ml pipet
1 - 8 ml pipet
1 - 10 ml pipet
5 -100 ml volumetric flasks
1 - 1 1 pipet
1 - 1/8" paper punch

D. REAGENTS

All reagents should be ACS reagent grade.

(1) Stock Beryllium Solution
Beryllium and most of its compounds are extremely toxic. Therefore, this laboratory purchases 1000 ppm beryllium solution standards from one of several commercial sources.

(2) Dilute Beryllium Solution
Dilute 1.0 ml of the 1000 ppm standard to 1 liter using distilled water. This solution contains 1 µg/ml of beryllium. Prepare fresh daily.

(3) Working Beryllium Standard
Dilute 0.0, 2.0, 4.0, 6.0, 8.0, and 10.0 ml of the 1 µg/ml standard to 100 ml using distilled water. These standards contain 0.00, 0.02, 0.04, 0.06, 0.08, and 0.10 µg/ml of beryllium, respectively. Prepare fresh daily.

E. COLLECTION OF SAMPLE

The sample is collected using an 8" x 10" Whatman 41 cellulose filter on a HiVol sampler. Other types of filter media, such as cellulose ester or Teflon membrane filters may be suitable, but these have not been tested by this laboratory.

F. TEST PROCEDURE

(1) Instrumental Parameters
NOTE: The instructions given in this section are for an IL 251 Atomic Absorption Spectrophotometer equipped with an IL 455 Flameless Atomizer and an IL 114 Laboratory Recorder. The IL 455 can use either cylindrical or rectangular graphite cuvettes. For this work the rectangular cuvette with a microboat was used. For other brands of spectrophotometers, the instructions will be different. The use of a brand name is done for convenience and does not constitute an endorsement of the product.

The parameters given in this section are meant only as a guide as parameters may change from day-to-day. Specific operating instructions should be obtained from the instruction manuals provided by the manufacturer before any analysis is attempted.

(a) IL 455
The IL 455 consists of a control module and an atomizer cell. The control module provides electrical power, cooling water, argon flow control, temperature readout, and time and temperature programming for the atomizer cell. The atomizer cell contains the graphite cuvette. The two units are connected with an umbilical cord carrying water, argon, and electrical power. The following table lists the IL 455 instrumental parameters used in the analysis of beryllium:

Power	-	ON
Operation Mode	-	AUTO
Auto. Clean	-	OFF
Argon Flow Rate	-	15 CFH at 40 psi
Water Flow Rate	-	1.0-1.5 LPM
Air Pressure	-	40 psi
Power Setting	-	0 0 25 30 0 100
Time Setting	-	0 0 2 6 0 1

(b) IL 251

The IL 251 is a double beam atomic absorption spectrophotometer with background correction capabilities using a continuum lamp. The instrumental parameters for the IL 251 are listed in the following table:

Power	-	ON
Lamp Current	-	7.0 mA
Wavelength	-	234.9 nm
Slit Width	-	320
PM tube voltage	-	800
Analysis Mode	-	SB/A-B
Integration Time	-	1/16 second
Readout mode	-	AUTO
Intensity	-	0.2-0.8
mA/count	-	1.0
Curve Correct	-	0
Wavelength Scan	-	OFF

(c) IL 114

The IL 114 is a high speed recorder with a full scale response time of 0.05 seconds which is necessary in order to measure the transient peaks generated during the analysis. The following table lists the instrumental parameters for the IL 114 recorder:

Power	-	ON
Damping	-	ON
Chart Speed	-	1.0 mm/second

(2) Sample Analysis

Following the manufacturers' instructions and using the instrumental parameters given in the preceeding section, prepare the instrument for use. Start up, shut down, and routine maintenance procedures for IL 251, 114, and 455 systems should be in accordance with the manufacturers' recommendations.

Take a clean sheet of filter media and using the paper punch, cut out several circles for blanks. Using the microboat manipulator, remove the microboat from the atomizer cell. Using tweezers, place one of the blanks in the microboat and return the microboat to the atomizer cell. Press the START/ADVANCE button on the IL 455 and turn on the recorder chart drive. After the analysis cycle is finished, turn off the recorder chart drive and remove the microboat. Invert the microboat to remove the carbon residue left from the paper. Repeat this process at least three times or until there is no peak on the recorder when the paper is atomized. Place another blank in the microboat and add 1.0 µl of the distilled water blank to wet the paper. Press the START/ADVANCE button on the IL 455 and start the recorder chart drive. Again, there should be no peak on the recorder. Place another blank in the microboat and add 1.0 µl of the 0.02 µg/ml Be standard. Press the START/ADVANCE button on the IL 455 and the ZERO button on the IL 251 and start the recorder chart drive. Repeat the preceding step for each of the other standards.

Using the paper punch, punch out a circle from each of the filters to be analyzed. This laboratory has investigated the variation in beryllium concentration with location on the filter from which the hole punch sample is taken for analysis. Analysis of a large number of 1/8" diameter samples from a large number of filters indicates that the beryllium is evenly distributed over the surface of the filter. Therefore, the location from which the sample is taken is not a critical factor. Place a circle in the microboat. Press the START/ADVANCE button on the IL 455, the ZERO button on the IL 251, and then start the recorder chart drive. After the analysis cycle is finished, turn off the recorder chart drive, remove the microboat, and invert it to remove the remaining ash. Analyze subsequent samples similarly.

G. QUALITY CONTROL

If 10 or more samples are run, 10% should be run in duplicate. If fewer than 10 are run, than one sample in the batch should be rerun. Using the paper punch, punch out a second circle from the filter to be run in duplicate. Run as a regular sample. There should not be more than 10 percent difference between duplicates.

If 10 or more samples are run, 10% should be spiked to check the accuracy of the method. If fewer than 10 are run, then the one sample in the batch should be spiked. Using a paper punch, punch out a second circle from the filter to be run. Place the circle in the microboat and add 1.0 µl of the 0.04 µg/ml standard. Press the START/ADVANCE button on the IL 451 and the ZERO button on the IL 251 and start the recorder drive. Calculate the percent recovery from the following equation:

$$\% R = \frac{(\text{pg Be in sample + spike}) - \text{pg Be in sample}}{\text{pg Be in spike}}$$

Ideally, the percent recovery should be 100%. A variation of $\pm$ 10% is acceptable.

H. CALCULATIONS

Using the recorder trace of the standards, construct a curve of peak height vs. µg of Be present in the standard. For the 0.02, 0.04, 0.06, 0.08, 0.10 µg/ml Be standards the amount of Be present is 20, 40, 60, 80, and 100 pg respectively. Using the peak height of the sample and the calibration curve, determine the pg of Be present in the sample.

$$\text{pg/M}^3 \text{ Be} = \frac{(\text{pg Be in sample analyzed}) (\text{area of total sample})}{(\text{M}^3 \text{ of air sampled}) (\text{area of sample analyzed})}$$

I. REFERENCES

Emmel, R.H., Bancroft, M.F., Corum, T.L., Atomic Absorption Methods Manual, Vol 2. "Flameless Operations," Instrumentation Laboratory Inc., 1976.

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DETERMINATION OF CELLULOSE
Modification of Anthrone Method

A. GENERAL

Cellulosic materials entrained on glass fiber filters are dissolved in sulfuric acid. A green color is then developed by using anthrone. The intensity of the color is proportional to the concentration of cellulose. The intensity of the color is measured using a spectrophotometer capable of operating at 625 nm.

B. APPLICABILITY

This method is applicable to cellulosic materials such as sawdust and cotton lint. The range of analysis is from 20 µg/ml of extracted solution to 200 µg/ml of extracted solution. The collection efficiency of the glass fiber filter is assumed to be 100%. Other carbohydrates also give a positive response.

C. APPARATUS

Suitable sampling apparatus
Adequate and sufficient storage bottles
1 - 1000 ml volumetric flask
1 - 250 ml volumetric flask
8 - 100 ml volumetric flasks
1 - 100 ml volumetric pipet
1 - 50 ml volumetric pipet
1 - 40 ml volumetric pipet
1 - 25 ml volumetric pipet
1 - 20 ml volumetric pipet
1 - 15 ml volumetric pipet
1 - 10 ml volumetric pipet
1 - 8 ml volumetric pipet
1 - 5 ml volumetric pipet
1 - 4 ml volumetric pipet
10 - 1 ml volumetric pipets
Sufficient Soxhlet extractors, hotplates, cuvettes, and test tubes for the number of samples and standards analyzed
1 - Spectrophotometer capable of measuring a wavelength of 625 nm
1 - Filtering flask
1 - Fritted glass funnel.

D. REAGENTS

All reagents should be ACS reagent grade.

(1) Sulfuric Acid (60 %)
Slowly pipet 600 ml of concentrated sulfuric acid into a 1 liter volumetric flask containing approximately 300 ml of distilled water. Stir during addition of the acid and if the flask becomes hot to the touch, allow to cool to room temperature before adding more acid. Cooling can be hastened by running water over the outside of the flask. After the addition of the acid and cooling to room temperature, make up to the mark with distilled water.

CAUTION!!! Sulfuric Acid is extremely corrosive and will produce severe burns. Handle with gloves and flood skin with water if contact occurs. Do not breathe fumes. Store in a tightly closed bottle. All equipment should be glass or teflon. Tygon, etc. dissolves in the solutions used.

(2) Anthrone (0.1 %)
Dissolve 0.1 gram of anthrone in 100 ml of concentrated sulfuric acid. Store in a tightly closed container. This reagent should be stored for 24 hours before use and discarded after nine days.

(3) Benzene

(4) Stock Cellulose Solution
Dissolve 0.1000 g of Whatman Column Chromedia, CF 11, fibrous cellulose powder in 200 ml of 60% sulfuric acid in a 250 ml volumetric flask. When dissolution is complete, make up to the mark with additional 60% sulfuric acid. This solution contains 400 µg of cellulose/ml.

E. COLLECTION OF SAMPLE

Collect the sample on an 8" x 10" glass fiber filter using a hi-volume air sampler. Air is drawn through the filter at approximately 600 CFM. A total of 2500 µg of cellulose should be collected before reliable results can be obtained. The filter should then be removed and adequately identified.

F. TEST PROCEDURE

(1) Preparation of Standard Curve
Using 100 ml volumetric flasks, make the following dilutions of the stock cellulose solution using 60% sulfuric acid.

Dilution	Final Concentration (µg/ml)
5:100	20
10:100	40
15:100	60
20:100	80
25:100	100
40:100	160
50:100	200

Pipet 1.0 ml of 60% sulfuric acid into a 1" test tube for the blank. Pipet 1.0 ml of each standard into 1" test tubes. Add 8.0 ml of the 0.1% anthrone solution and 4.0 ml of distilled water to each test tube. Mix. Allow to cool for at least 15 minutes. Time between mixing and cooling should be consistent for all standards and samples. Read the absorbance at 625 nm. Plot a curve of absorbance vs. concentration of cellulose.

(2) Sample Determination

Filter Samples - Cut a 2" x 8" strip from the middle of the filter. Fold into a small bundle and tie with a copper wire. Place the bundle in a Soxhlet extractor and extract with benzene for 6 to 8 hours. This removes most of the glucose and starch. Remove the copper wire and place the filter in a test tube. Add 30 ml of 60% sulfuric acid and digest for 30 minutes. During digestion the filter should be broken apart with a glass stirring rod. Filter the sample through fritted glass or a glass fiber filter. Take a 1.0 ml aliquot, add 8.0 ml of 0.1% anthrone and 4.0 ml of distilled water. Mix. Cool for the same length of time as the standards. Measure the absorbance at 625 nm. Determine µg cellulose/ml of extract from the standard curve.

G. CALCULATIONS

The concentration of cellulose in the air is:

$$\mu g \text{ cellulose}/M^3 = \frac{(\mu g \text{ cellulose/ml of extract})(\text{ml extract})(\text{area of filter exposed})}{(M^3 \text{ of air sampled})(\text{area of filter extracted})}$$

H. QUALITY CONTROL

Duplicates should be run on 7% of the samples or at least one duplicate per batch of 15 or less. These will test the precision of the procedure. The relative deviation should be less than 5% if the absorbance reading is greater than 0.100.

$$\text{Relative Deviation (R.D.)} = \frac{\bar{d}}{\bar{v}} \quad \bar{d} = \frac{|v_1 - v_2|}{2}$$

where $\bar{d}$= average deviation

$\bar{v}$= arithmetic average of all individual volumes

v= individual measurement

Spiked samples should be run to control the accuracy of the analysis. Spiked samples are prepared by adding a known quantity of a standard to an aliquot of sample. Percent recovery can be calculated from the concentrations of the spiked sample, the sample, and the standard.

A suitable spike would be prepared as follows: Place 5 ml of the 100 ug/ml standard in a test tube. Add 5 ml of sample to the test tube. Mix well. Take a 1.0 ml aliquot of this mixture, add 8.0 ml of 0.1% anthrone and 4.0 ml of distilled water. Mix. Allow to cool for the same length of time as the standards. Read the absorbance at 625 nm.

$$\text{Percent recovery} = \frac{\text{conc (spike + sample)} - \text{conc (sample)}}{\text{conc (spike)}} \times 100$$

A spiked sample should be run with each set of samples. The percent recovery should be between 90-110%. If not, all steps of the analysis should be examined carefully and the analysis repeated.

A standard curve must be run with each set of samples.

I. REFERENCES

(1) Unfred, David, Unpublished.

(2) Viles, F. J., and Silverman, L., Determination of Starch and Cellulose with Anthrone, Anal. Chem. 21, 950 (1949).

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Texas Air Control Board

DETERMINATION OF CHLORINE AND/OR CHLORIDES

Turbidimetric Method

A. GENERAL

Gaseous chlorides (HCl) are absorbed in distilled or deionized water and treated with silver nitrate solution. The turbidity resulting from the formation of insoluble silver chloride is measured on a spectrophotometer at 360 nm.

NOTE: Free chlorine (Cl_2) is not trapped by deionized water.

When free chlorine (Cl_2) is sought, two impingers in series must be used. The first impinger contains deionized water to trap chlorides (HCl), and the second contains $NaAsO_2$ to trap chlorine (Cl_2). (If used alone, the arsenite impinger would absorb total chlorine, i.e., HCl and Cl_2) The arsenite reduces Cl_2 to chloride which can again be measured turbidimetrically. For high levels of chlorine, the unreacted arsenite may be titrated with standard iodine solution to determine the amount of chlorine trapped.

B. APPLICABILITY

The lower limit of detection for chlorides is approximately 0.12 µg Cl^-/ml of absorber. The absorption efficiency for chlorides is 100% for a 30 minute sample at 2 L/min. in 20 cc of absorbing solution. Possible interferences in chlorine analysis come from the formation of insoluble silver salts such as those of iodine, bromine, and phosphate.

C. APPARATUS

Suitable sampling apparatus
Adequate and sufficient storage bottles
1 - 1000 ml volumetric flask
8 - 100 ml volumetric flasks
1 - 15 ml volumetric pipet
1 - 2 ml volumetric pipet
3 - 1 ml volumetric pipets
1 - 0.5 ml volumetric pipet
Sufficient 1" test tubes and cuvettes for the number of samples and standards
Vortex-type test tube stirrer
Spectrophotometer or nephelometer capable of operating at 360 nm.

D. REAGENTS

(1) Silver Nitrate Solution (0.5 N)
Place 8.5 grams $AgNO_3$ in a 100 ml volumetric flask and dilute to the mark with distilled or deionized water. Store in a dark brown bottle.

(2) Nitric Acid (2.5 N)
Dilute 16 ml of concentrated HNO_3 to the mark in a 100 ml volumetric flask with deionized water.

(3) Ethanol
Reagent Grade. USP 95% or denatured formula 23A or 1.

NOTE: Isopropyl alcohol may be used instead, provided that it is used consistently throughout a run for both samples and standards.

(4) Stock Standard Chloride Solution
Weigh out 0.1648 gram of NaCl which has been dried at 110° C for one hour and place in a 100 ml volumetric flask. Dilute to the mark with deionized water. This solution contains 1000 µg Cl^-/ml.

(5) Dilute Chloride Standards
Pipet 0.5, 1, 2, 3 and 4 ml of the stock chloride standard solution into 100 ml volumetric flasks and dilute each to the mark with distilled water. These solutions contain respectively 5, 10, 20, 30, and 40 µg Cl^-/ml.

(6) Absorbing Solution for Chlorine
Place 4 grams NaOH and 0.65 gram $NaAsO_2$ in a 1000 ml volumetric flask and dilute to the mark with deionized water.

E. COLLECTION OF SAMPLES

(1) For collection of chlorides (HCl), a midget impinger containing 20 ml deionized water should be used with a telmatic sampler. A known volume of air is bubbled through the impinger at a rate of 1.5-2 L/min. for 30 minutes.

(2) For collection of free chlorine (Cl_2), two impingers should be connected in series. The first should contain 20 ml deionized water (to trap HCl) and the second should contain 20 ml of alkaline arsenite absorber (to trap Cl_2). A known volume of air should be bubbled through these impingers at a rate of 1.5-2 L/min. for 30 minutes.* Sample lines, as always, should be Teflon or glass.

*It should be apparent that using two impingers in a series is equivalent to sampling for chlorides and chlorine simultaneously. If the analysis requested is for chlorides (deionized water absorber) and chlorine (arsenite absorber), an aliquot is taken from each impinger. If the analysis is for chlorine alone, an aliquot is taken from the arsenite impinger alone.

(3) Particulate chlorides are collected on a HiVol by pulling a known volume of air through a glass fiber filter, using a flow rate of 40-60 cubic feet/minute.

F. TEST PROCEDURE

(1) Preparation of Standard Curve

Using volumetric pipets, place 15 ml ethanol or isopropyl alcohol and 1 ml 2.5 N nitric acid in each of six 1" test tubes. To the first test tube (the blank), add 5 ml deionized water. To the other five, add 5 ml of the respective dilute chloride standards. Mix, using a vortex type stirrer. Add 1 ml 0.5 N $AgNO_3$ to each test tube. Add 3 ml deionized water to all test tubes. Mix. Store in the dark for one hour. Read the absorbance of the standards against the blank in 20 mm cuvettes, using a spectrophotometer at 360 nm. Plot a curve of absorbance versus µg Cl^-/ml. A nephelometer may be used if greater sensitivity is desired.

CAUTION!!! Do not mix these reagents in advance, nor store the samples or standards. Some combinations of these reagents will form compounds that undergo violent spontaneous explosions.

(2) Sample Analysis

If any absorbing reagent has evaporated during sampling, restore it to its original volume with deionized water and mix thoroughly. Place 15 ml of ethanol or isopropyl alcohol and 1 ml 2.5 N nitric acid in a 1" test tube. Add a 5 ml aliquot of sample to the test tube. Add 1 ml 0.5 N $AgNO_3$. Add 3 ml deionized water. Mix. Store in the dark for one hour. Read the absorbance of the sample against the blank from the standard curve using a spectrophotometer at 360 nm.

A larger aliquot may be taken, but no more than 8 ml. The sum of the volumes of sample aliquot and distilled water added to the test tube should be 8 ml.

A portion of the glass fiber filter used to collect particulate chlorides should be boiled in 50 ml deionized water for two hours and then filtered. An equal portion of a clean filter should likewise be extracted for a blank. The filter extract can then be analyzed as described above.

G. CALCULATIONS

(1) Gaseous Chlorides (DI water impinger)

$$\mu g\ Cl^-/M^3 = \frac{\mu g\ Cl^-/ml \times \frac{5\ ml}{ml\ aliquot} \times ml\ absorber}{M^3\ sampled}$$

$$\mu g\ HCl/M^3 = \frac{\mu g\ Cl^-/ml \times \frac{5\ ml}{ml\ aliquot} \times ml\ absorber}{M^3\ sampled} \times \frac{36.45}{35.45}$$

(2) Particulate Chlorides (Filter extract)

$$\mu g\ Cl^-/M^3 = \frac{\mu g\ Cl^-/ml \times \frac{5\ ml}{ml\ aliquot} \times ml\ extract}{M^3\ sampled} \times \frac{area\ filter\ exposed}{area\ filter\ extracted}$$

(3) Chlorine (Arsenite impinger*)

$$\mu g\ Cl_2/M^3 = \frac{\mu g\ Cl^-/ml \times \frac{5\ ml}{ml\ aliquot} \times ml\ absorber}{M^3\ sampled}$$

*Must be in series with DI water impinger for Cl_2 determination. Use of arsenite impinger alone will result in determination of <u>total</u> gaseous chlorine ($HCl + Cl_2$).

H. <u>QUALITY CONTROL</u>

Duplicates should be run on 7% of the samples or at least one duplicate per batch of 15 or less. These will test the precision of the procedure. The relative deviation should be less than 5% if the absorbance reading is greater than 0.100.

$$R.D. = \frac{\bar{d}}{\bar{v}} \quad \text{where} \quad \bar{d} = |v_1 - v_2| \qquad \bar{v} = \frac{v_1 + v_2}{2} \qquad v_i = \text{measured value i}$$

Spiked samples should be run to control the accuracy of the analysis. Spiked samples are prepared by adding a known quantity of a standard to an aliquot of sample. Percent recovery can be calculated from the concentrations of the spiked sample, the sample, and the standard.

A suitable spike would be prepared as follows: Place 15 ml of ethanol or isopropyl alcohol and 1 ml 2.5 N nitric acid in a test tube. Add a 4 ml aliquot of the 40 $\mu g\ Cl^-/ml$ standard. Add 4 ml of sample. Mix, using a vortex type stirrer. Add 1 ml 0.5 N $AgNO_3$ to each test tube. Mix. Store in the dark for one hour. Read the absorbance using a spectrophotometer set at 360 nm.

$$\text{Percent recovery} = \frac{\text{conc(spike + sample)} - \text{conc (sample)}}{\text{conc(spike)}} \times 100$$

A spiked sample should be run with each set of samples. The percent recovery should be between 90-110%. If not, all steps of the analysis should be examined carefully and the analysis repeated.

A standard curve must be run with each set of samples.

I. REFERENCES

(1) Standard Methods of Chemical Analysis, 6th Edition, Volume I, D. Van Nostrand Company, 1962, pp. 333-334.

(2) "Atmospheric Emissions from Hydrochloric Acid Manufacturing Processes", AP-54, United States Department of Health, Education, and Welfare, Public Health Service, September 1969, pp. 34-41.

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Laboratory Division
Texas Air Control Board

DETERMINATION OF CHLORINE AND/OR CHLORIDES IN STACK GAS

Turbidimetric Method

A. GENERAL

Chlorine (Cl_2) and chlorides (HCl) are trapped in an impinger containing alkaline arsenite solution which reduces chlorine to chloride. Gaseous chlorides (HCl) are absorbed in distilled or deionized water. Both solutions are treated with silver nitrate and the resulting turbidity from the formation of insoluble silver chloride is measured on a spectrophotometer at 360 nm.

When free chlorine (Cl_2) alone is sought, two impingers in series must be used. The first impinger contains deionized water to trap chlorides (HCl), and the second contains arsenite ($NaAsO_2$) to trap chlorine (Cl_2). (Used alone, the arsenite impinger traps both chlorine and chlorides. Deionized or distilled water does not trap chlorine.) For high levels of chlorine, the unreacted arsenite may be titrated with standard iodine solution to determine the chloride concentration. (The titration should be carried out at a pH between 4 and 9).

B. APPLICABILITY

The lower limit of detection for chlorides is approximately 0.30 µg Cl^-/ml of absorber. Possible interferences in chlorine sampling are insoluble silver salts formed from iodine, bromine, and phosphate. A sulfate concentration greater than 0.3 N will cause the silver chloride suspension to coagulate.

C. APPARATUS

Suitable sampling apparatus
Adequate and sufficient storage bottles
1 - 1000 ml volumetric flask
4 - 500 ml volumetric flasks
12- 100 ml volumetric flasks
3 - 20 ml volumetric pipets
1 - 15 ml volumetric pipet
1 - 2 ml volumetric pipet
3 - 1 ml volumetric pipets
1 - 0.5 ml volumetric pipet
Sufficient 1" test tubes and cuvettes for the number of samples and standards
Vortex type test tube stirrer
Spectrophotometer or nephelometer capable of operating at 360 nm.

D. REAGENTS

(1) Silver Nitrate Solution (0.5 N)
Place 8.5 grams $AgNO_3$ in a 100 ml volumetric flask and dilute to the mark with distilled or deionized water. Store in a dark brown bottle.

(2) Nitric Acid (2.5 N)
Dilute 16 ml of concentrated HNO_3 to the mark in a 100 ml volumetric flask with distilled or deionized water.

(3) Ethanol
Reagent grade. USP 95% or denatured formula 23A or 1. NOTE: Isopropyl alcohol may be used instead, provided that it is used consistently throughout a run for both samples and standards.

(4) Stock Standard Chloride Solution
Weigh out 0.1648 gram of NaCl which has been dried at 110°C for one hour and place in a 100 ml volumetric flask. Dilute to the mark with deionized or distilled water. This solution contains 1000 µg Cl^-/ml.

(5) Dilute Chloride Standards
Pipet 0.5, 1, 2, 3, and 4 ml of the stock chloride standard solution into 100 ml volumetric flasks and dilute each to the mark with deionized water or with the appropriately diluted absorber. The weaker absorber must be diluted 2:5 with distilled or deionized water. The stronger absorber must be diluted 2:25 with distilled or deionized water. The chloride solutions contain 5, 10, 20, 30, and 40 µg Cl^-/ml, respectively. (If chlorides are run separately from chlorine, one set of dilute standards must be made for chlorine and one for chlorides with the appropriate absorbers.)

(6) Absorbing Solution for Chlorine
(a) Chlorine or chlorine and chloride concentrations less than 1000 ppm --- (1 N NaOH and 0.1 N $NaAsO_2$)

Place 40 grams NaOH and 6.5 grams $NaAsO_2$ in a liter volumetric flask and dilute to the mark with distilled or deionized water.

(b) Chlorine or chlorine and chloride concentrations greater than 1000 ppm --- (2.5 N NaOH and 0.5 N $NaAsO_2$)

Place 100 grams NaOH and 32.5 grams $NaAsO_2$ in a 1000 ml volumetric flask and dilute to the mark with distilled or deionized water.

E. COLLECTION OF SAMPLES

Samples should be collected according to accepted stack sampling procedures using a series of impingers with the appropriate absorbing solutions. For the collection of chlorides (HCl), 200 ml of deionized or distilled water should be used. For collection of free chlorine (Cl_2), two impingers should be connected in series. The first should contain 200 ml of

deionized or distilled water (to trap HCl) and the second should contain 200 ml of alkaline arsenite absorber (to trap Cl_2*). Sample lines, as always, should be Teflon or glass.

*It should be apparent that using two impingers in a series is equivalent to sampling for chlorine and chlorides simultaneously. If the analysis requested is for chlorides (deionized water absorber) and chlorine (arsenite absorber), each impinger is analyzed. If the analysis is for chlorine alone, only the arsenite impinger is analyzed.

G. Test Procedure

(1) Preparation of the Standard Curve

(a) Chlorides

Using volumetric pipets, place 15 ml ethanol or isopropyl alcohol and 1 ml 2.5 N nitric acid in each of six 1" test tubes. To the first test tube (the blank) add 5 ml deionized or distilled water. To the other five, add 5 ml of the respective dilute chloride standards (made up in water). Mix, using a vortex-type stirrer. Add 1 ml 0.5 N $AgNO_3$ to each test tube. Add 3 ml deionized or distilled water to all test tubes. Mix. Store in the dark one hour. Read the absorbance of the standards against the blank, using a spectrophotometer at 360 nm. Plot a curve of absorbance vs. µg Cl^-/ml. A nephelometer may be used if greater sensitivity is desired.

(b) Chlorine (or chlorine and chlorides)

Using volumetric pipets, place 15 ml ethanol or isopropyl alcohol and 2 ml 2.5 N nitric acid in each of six 1" test tubes. To the first test tube (the blank) add 5 ml deionized or distilled water. To the other five, add 5 ml of the respective dilute chloride standards (made up in the appropriately diluted absorber)*. Mix, using a vortex-type stirrer. Add 1 ml 0.5 N $AgNO_3$ to each test tube. Add 2 ml deionized or distilled water to all the test tubes. Mix. Store in the dark one hour. Read the absorbance of the standards against the blank using a spectrophotometer at 360 nm. Plot a curve of absorbance vs. µg Cl^-/ml. A nephelometer may be used if greater sensitivity is desired.

*NOTE: The absorber used for the standards must be identical to the one used in sampling. Therefore, enough absorber should be prepared for both standards and samples. Also, the dilution of the absorber must be the same for both standards and samples.

CAUTION!!! Do not mix these reagents in advance, nor store the samples or standards. Some combinations of these reagents will form compounds that undergo violent spontaneous explosions.

(2) Sample Analysis

Transfer contents of the impinger or sample bottle to a 500 ml volumetric flask. Dilute to the mark with deionized or distilled water.

(a) Chlorides

Take a 5 ml or other aliquot (but no more than 8 ml) and proceed with analysis as described in the standard curve preparation, F(1)a. The sum of the volumes of sample aliquot and deionized water added to the test tube should be 8 ml.

(b) Chlorine (or chlorine and chlorides)

If the weaker arsenite absorber was used, no further dilution of the absorber is needed. Take a 5 ml or other aliquot (but no more than 7 ml) and proceed with the analysis as described in the standard curve preparation, F(1)b. The sum of the volumes of sample aliquot and deionized water added to the test tube should be 7 ml.

If the stronger arsenite absorber was used, another dilution of the absorber must be made. Place a 20 ml aliquot in a 100 ml volumetric flask, and dilute to the mark with distilled or deionized water. From this diluted solution, take a 5 ml or other aliquot (but no more than 7 ml) and proceed with the analysis as described in the standard curve preparation F(1)b. The sum of the volumes of sample aliquot and distilled or deionized water added to the test tube should be 7 ml.

G. CALCULATIONS

(1) Chlorides (distilled or deionized water impinger)

$$\mu g\ Cl^-/M^3 = \frac{\mu g\ Cl^-/ml \times \frac{5\ ml}{ml\ aliquot} \times 500\ ml}{M^3\ sampled}$$

$$\mu g\ HCl/M^3 = \frac{\mu g\ Cl^-/ml \times \frac{5\ ml}{ml\ aliquot} \times 500\ ml}{M^3\ sampled} \times \frac{36.45}{35.45}$$

(2) Chlorine (arsenite impinger)*

Weaker absorber (1 N NaOH + 0.1 N $NaAsO_2$)

$$\mu g\ Cl_2/M^3 = \frac{\mu g\ Cl^-/ml \times \frac{5\ ml}{ml\ aliquot} \times 500\ ml}{M^3\ sampled}$$

Stronger absorber (2.5 N NaOH and 0.5 N $NaAsO_2$)

$$\mu g\ Cl_2/M^3 = \frac{\mu g\ Cl^-/ml \times \frac{5\ ml}{ml\ aliquot} \times 500\ ml \times 5}{M^3\ sampled}$$

H. QUALITY CONTROL

Duplicates should be run on 7% of the samples or at least one duplicate

per batch of 15 or less. These will test the precision of the procedure. The relative deviation should be less than 5% if the absorbance reading is greater than 0.100.

$$R.D. = \frac{\bar{d}}{\bar{v}} \qquad \text{where} \quad \bar{d} = |v_1 - v_2|$$

$$\bar{v} = \frac{v_1 + v_2}{2}$$

v_i = measured value i

Spiked samples should be run to control the accuracy of the analysis. Spiked samples are prepared by adding a known quantity of a standard to an aliquot of sample. Percent recovery can be calculated from the concentrations of the spiked sample, the sample, and the standard.

A suitable spike would be prepared as follows: Place 15 ml of ethanol or isopropyl alcohol and 1 ml 2.5 N nitric acid in a test tube. Add a 4 ml aliquot of the 40 µg Cl^-/ml standard. Add 4 ml of sample. Mix, using a vortex type stirrer. Add 1 ml 0.5 N $AgNO_3$ to each test tube. Mix. Store in the dark for one hour. Read the absorbance using a spectrophotometer set at 360 nm.

$$\text{Percent recovery} = \frac{\text{conc (spike + sample)} - \text{conc (sample)}}{\text{conc (spike)}}$$

A spiked sample should be run with each set of samples. The percent recovery should be between 90-110%. If not, all steps of the analysis should be examined carefully and the analysis repeated.

A standard curve must be run with each set of samples.

I. REFERENCES

Standard Methods of Chemical Analysis, 6th Edition, Volume I, D. Van Nostrand Company, 1962, pp. 333-334.

"Atmospheric Emissions from Hydrochloric Acid Manufacturing Processes" AP-54, United States Department of Health, Education, and Welfare, Public Health Service, September 1969, pp. 34-41.

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Laboratory Division
Texas Air Control Board

DETERMINATION OF CYANIDE

Pyrazolone Method

A. GENERAL

Cyanide (CN^-) is absorbed in 2% zinc acetate solution. Cyanide is converted to cyanogen chloride with chloramine T, and then the cyanogen chloride is reacted with a pyridine-pyrazolone reagent to form a blue dye. The intensity of the color measured at 620 nm is proportional to the amount of cyanide collected.

B. APPLICABILITY

The lower limit of detectability has been found to be approximately 0.2 µg/ml of CN^- in the absorbing solution. If 20 ml of absorber is used and approximately 60 liters of air is sampled, the lower limit of detection will be approximately 60 $\mu g/M^3$ of CN^-. Epstein reports that thiocyanate and hydrogen sulfide interfere. However, hydrogen sulfide is removed as zinc sulfide by filtration and thiocyanate interference is eliminated by keeping the reaction time with chloramine T to less than 5 minutes. No interferences are produced by $PO_4^{\equiv}$, $CO_3^{\equiv}$, Cl^-, NH_4^+, BO_3^{+++}, $SO_4^{\equiv}$, cyanates, oxalates, ferri-cyanides, or ferrocyanides.

C. APPARATUS

Suitable sampling apparatus
Adequate and sufficient storage bottles
1 - hotplate stirrer
Sufficient 1" test tubes for all samples and standards
1 - Spectrophotometer capable of operating at 620 nm
1 - analytical balance
Sufficient filter papers and funnels to filter samples
or a centrifuge
1 - fume hood
1 - 50 ml graduated cylinder
1 - 2 liter volumetric flask
3 - 1 liter volumetric flasks
2 - 250 ml volumetric flasks
2 - 100 ml volumetric flasks
7 - 50 ml volumetric flasks
4 - 10 ml pipets and sufficient number for samples and standards
1 - 8 ml pipet
1 - 6 ml pipet
2 - 5 ml pipets
1 - 4 ml pipet
1 - [illegible] pipet
1 - [illegible] pipet
2 - 1 ml graduated pipets

D. REAGENTS

All reagents should be ACS reagent grade.

(1) Chloramine T Solution
Dissolve 1.0 g of chloramine T in 100 ml distilled or deionized. Make fresh daily.

(2) Pyridine

(3) Bis-pyrazolone (3,3' Dimethyl-1,1'-diphenyl - [4,4'-bi-2-pyrazoline] - 5,5'-dione)

Dissolve 0.05 g bis-pyrazolone in 50 ml pyridine. Several minutes of mixing are usually necessary to dissolve bis-pyrazolone in pyridine.

(4) Pyrazolone (3-methyl-1-phenyl-2-pyrazolin-5-one)
Dissolve 0.75 g of pyrazolone in 250 ml distilled or deionized water by heating to approximately 80° C while stirring.

(5) Mixed pyridine - pyrazolone reagent
Mix 50 ml of bis-pyrazolone with 250 ml of pyrazolone. Store in a brown bottle. Prepare fresh every three days.

Caution!!! All pyridine solutions should be pipetted in a good fume hood.

(6) Glacial Acetic Acid

(7) Absorbing Reagent, Zinc Acetate
Dissolve 40 g zinc acetate in 2 liters deionized water.

(8) Sodium Hydroxide Solution (0.2 N NaOH)
Dissolve 8 g of NaOH in 1 liter of distilled or deionized water.

(9) Buffer Solution
Dissolve 3.1 g of boric acid in 1 liter of distilled or deionized water. Add 13 ml of 0.2 M NaOH. Stir. The pH of this solution should be 7.8.

(10) Standard Cyanide Stock Solution
Dissolve 2.51 g of KCN in 1 liter of distilled or deionized water. This solution contains 1,000 µg CN^-/ml.

Caution!!! TOXIC!!! All cyanide solutions should be made in a fume hood. Keep amyl nitrite ampoules on person as an antidote for cyanide poisoning.

E. COLLECTION OF SAMPLE

CN^- is collected in a known volume of absorber (usually 20 ml) using a suitable impinger and pumping arrangement. After collection, identify the sample adequately.

F. TEST PROCEDURE

(1) Working Standard

Dilute 10 ml of stock cyanide solution to 1000 ml in a volumetric flask using zinc acetate absorber. This solution contains 10 µg CN^-/ml. This solution must be prepared fresh daily.

(2) Standard Curve Preparation

Pipet 2, 4, 6, 8, 10, and 12 ml of the working standard solution into separate 50 ml volumetric flasks and bring to volume using zinc acetate absorber. These final standards now contain 0.4, 0.8, 1.2, 1.6, 2.0, and 2.4 µg CN^-/ml respectively.

Place 10 ml of absorber in a 1" test tube. In addition, place 10 ml of each standard in a 1" test tube. To each add 5 ml of buffer and swirl. Add 0.2 ml of chloramine T to each tube and swirl. Wait one minute. Add 5 ml of the mixed pyridine-pyrazolone reagent to each tube and swirl. Wait twenty minutes. Add 0.2 ml of glacial acetic acid and swirl. Measure the absorbance at 620 nm using developed blank to zero. Plot a curve of absorbance vs. µg CN^-/ml absorbing solution.

(3) Sample Analysis

Filter or centrifuge a 20 ml aliquot of sample to remove any zinc sulfide.* Place 10 ml of sample in a 1" test tube. Proceed with analysis as described under "Standard Curve Preparation". From the absorbance, determine the concentration of CN^- in the sample using the calibration curve. If the absorbance is greater than 0.8, it may be necessary to dilute a portion of the sample with absorber before running the test.

*Before doing this step, one may wish to measure the amount of H_2S present in the sample using the Molybdenum Blue Method.

G. CALCULATIONS

$$\mu g\ CN^-/M^3 = \frac{\mu g\ CN^-/ml \times \text{volume of absorber in ml}}{M^3 \text{ of air sampled}} \times \text{dilution factor}$$

If no dilution is required, drop the last term from the calculation.

H. QUALITY CONTROL

Duplicates should be run on 7% of the samples or at least one duplicate per batch of 15 or less. These will test the precision of the procedure. The relative deviation should be less than 5% if the absorbance reading is greater than 0.100.

$$\text{Relative Deviation (R.D)} = \frac{\bar{d}}{\bar{v}} \quad \text{where} \quad \bar{d} = |v_1 - v_2|, \quad \bar{v} = \left|\frac{v_1 + v_2}{2}\right|$$

v_1 and v_2 are the individual measurements.

Spiked samples should be run to control the accuracy of the analysis. Spiked samples are prepared by adding a known quantity of standard to an aliquot of sample. Percent recovery can be calculated from the concentration of the spiked sample, the sample, and the standard.

$$\text{Percent Recovery} = \frac{\text{conc (spike + sample)} - \text{conc (sample)}}{\text{conc spike}} \times 100$$

A suitable spike would be prepared as follows: Place 5 ml of the working standard in a 1" test tube. Add 5 ml of sample. Add 5 ml of buffer and swirl. Add 0.2 ml of chloramine T to the tube and swirl. Wait one minute. Add 5 ml of the mixed pyridine - pyrazolone reagent to each tube and swirl. Wait 20 minutes. Add 0.2 ml glacial acetic acid and swirl. Measure the absorbance at 620 nm versus the developed blank.

A spiked sample should be run with each set of samples. The percent recovery should be between 90-110%. If not, all steps of the analysis should be examined carefully and the analyses repeated.

A standard curve must be run with each set of samples.

I. REFERENCES

Standard Methods for the Examination of Water and Wastewater, 13 Ed., p. 404.

Epstein, J., "Estimation of Microquantities of Cyanide", Analytical Chemistry, 19, 272, 1947.

Fluorides In Ambient Samples

1.0 PRINCIPLE AND APPLICABILITY.

1.1 Particulate and gaseous fluorides in the ambient atmosphere are trapped on separate membrane filters.

1.2 The filter train consists of three 47-mM membrane filters in series and is described in Reference 1.

1.3 The first filter is soaked in a citric acid solution and is used to capture particulate fluoride but not gaseous fluorides.

1.3.1 The citrate ion in the first filter complexes interfering metal cations found in the atmosphere, such as aluminum, to prevent them from reacting with the HF as it passes through to the second filter.

1.3.2 The particulate fluoride retained by the first filter is fused with sodium hydroxide and the concentration of the solubilized product measured with a specific ion fluoride electrode.

1.4 The second and third filters are soaked in a sodium formate solution.

1.4.1 When the gaseous fluorides contact the filters, they are trapped as sodium fluoride.

1.4.2 The gaseous fluoride retained by the second and third formate filters is extracted by soaking the filters in an ionic buffer and measuring the fluoride with a specific ion fluoride electrode.

1.4.3 Alternately, two midget impingers containing 0.01 N sodium hydroxide can be used in place of the sodium formate filters to trap gaseous fluorides.

1.5 Method 12 does not measure the fluoride in fluorocarbons.

2.0 RANGE AND LOWER DETECTABLE LIMIT.

2.1 Elfers and Decker (Reference 2) report a lower detectable limit (LDL) of 0.25 ppb fluoride in air with the sodium formate-soaked filters.

2.1.1 Also, they report on a system of two sodium formate impregnated filters which were tested with 28 µg of fluoride as HF that resulted in all the fluoride being collected by the first filter with no significant HF breakthrough to the second filter.

2.2 The Texas Air Control Board laboratory has found that, when using the three filters in series under field conditions, gaseous fluoride breakthrough from the first to the second sodium formate filter may occur at 5 µg of fluoride or lower.

2.2.1 However, under normal sampling conditions (humidity, temperature), the first sodium formate filter should trap approximately 80% of the gaseous fluoride.

3.0 PRECISION.

3.1 The precision of the specific ion fluoride electrode can be measured by daily analysis of unknown solutions.

3.1.1 On five fluoride solutions (1.7 - 110 ppm) over a six-day period, Elfers and Decker report a standard deviation of less than 5% and, in most cases, less than 2%.

3.2 The precision of the method can be measured by analysis of samples collected simultaneously in the field.

4.0 ACCURACY.

4.1 The accuracy of the specific ion fluoride electrode can be measured by daily analysis of unknown solutions.

4.1.1 On the same five fluoride solutions (Section 3.1.1), Elfers and Decker report an average error of less than 4%.

5.0 INHERENT SOURCES OF ERROR AND INTERFERENCE.

5.1 Fluoride activity in the samples is reduced by complexing with aluminum, other polyvalent cations, and hydrogen, as well as by pH effects.

5.1.1 These interferences can be removed by adding an ionic buffer to the fluoride solutions before the concentration is measured with a specific ion fluoride electrode (Section 7.1).

5.2 EPA states that the main cause of error has been found to be distillation during sample analysis (Reference 5).

5.2.1 The Texas Air Control Board's laboratory utilizes the McQuaker and Gurney method (Reference 3) of filtering the sample under slightly alkaline conditions to remove interfering cations as insoluble oxides. This makes the distillation step unnecessary (See 8.3.10).

5.3 Samples and standards should be close to the same temperature. At the 10^{-3} level, a 1° C change in temperature will cause a 2% error (Reference 6).

5.4 Lack of stability in the electrometer will cause significant error in the results.

5.5 Three nickel crucible blanks are run to account for possible fluoride contamination from the crucibles during the sodium hydroxide fusion.

6.0 APPARATUS.

6.1 Plasticware.

1000-mL polypropylene volumetric flask for the stock fluoride standard.
100-mL polypropylene volumetric flasks for samples and standards.
Plastic filtering funnels.
Polypropylene beakers (50-100 mL) for use with samples and standards during analysis.
Plastic storage bottles for samples.

6.2 Filters.

Gelman Versapor supported membrane filters. 0.8 µM, 47 mM
Whatman No. 40 filter paper or equivalent.

6.3 pH indicator strips.

Test 0-14 pH range with no bleeding into solution.

6.4 Nickel crucibles with covers.

50-100 mL capacity.

6.5 Evaporating oven.

Temperature range: ≥ 150° C.
Recirculating airflow.

6.6 Muffle furnace.

Temperature range: ≥ 700° C.
Desired temperatures can be reached within one hour.

6.7 Specific ion fluoride electrode.

7.0 REAGENTS.

All reagents should be ACS reagent grade.

7.1 Total Ionic Strength Adjustment Buffer (TISAB).

7.1.1 Place approximately 500 mL of distilled water in a 1-liter beaker. Add 57 mL glacial acetic acid, 58 g sodium chloride and 4 g CDTA (Cyclohexylene dinitrilotetraacetic acid).

7.1.2 Stir to dissolve.

7.1.3 Place the beaker in a water bath to cool.

7.1.4 Slowly add 5 M NaOH to the solution, measuring the pH continuously with a calibrated pH/reference electrode pair, until the pH is 5.3.

7.1.5 Cool to room temperature.

7.1.6 Pour into a 1-liter flask and dilute to volume with distilled water.

7.1.7 NOTE: Buffers for the purpose are available commercially. TISAB II, a product of Orion Research, is the one currently used in this laboratory.

7.2 Ethanol. Either USP ethanol or denatured ethanol is acceptable.

7.3 Isopropyl Alcohol.

7.4 Sodium Hydroxide (5 N).

7.4.1 Weigh out 200 grams of sodium hydroxide and place in a 1000-mL volumetric flask.

7.4.2 Add about 700 mL of distilled water and stir until the NaOH is completely dissolved.

7.4.3 Allow the solution to cool and dilute to the mark with distilled water.

7.5 Sodium Hydroxide (0.01 N).

7.5.1 Dilute 2 mL 5 N sodium hydroxide to 1 liter with distilled water.

7.5.2 Prepare solution only if the two formate filters are to be replaced with impingers.

7.6 Stock Standard Fluoride Solution (100 µg F^-/mL).

7.6.1 Dissolve 0.2210 grams of sodium fluoride (NaF) (oven dried for two hours at 110° C), in distilled water contained in a 1000-mL plastic volumetric flask and dilute to the mark.

7.6.2 Alternately, a commercial fluoride standard may be used.

7.7 Sodium Formate Solution.

7.7.1 To 10 g sodium formate in a beaker add 50 mL distilled water and 50 mL ethanol and stir to dissolve.

7.7.2 This should be prepared fresh on the day of use.

7.8 Citric Acid (0.1 M in 50% isopropyl alcohol).

7.8.1 To 1.92 g anhydrous citric acid or 2.10 g citric acid monohydrate in a beaker, add 50 mL distilled water and 50 mL isopropyl alcohol and stir to dissolve.

7.8.2 This should be prepared fresh on the day of use.

7.9 Hydrochloric Acid (3 N). Dilute 125 mL concentrated HCl to 500 mL with distilled water.

8.0 PROCEDURE (Specific Ion Electrode Method).

8.1 Collection of sample.

8.1.1 See Chapter 12 of the Texas Air Control Board's Sampling Procedures Manual under Determination of Fluorides (Reference 1).

8.1.2 Fluoride collection using membrane filters should not be attempted above 90% relative humidity or visible atmospheric dust conditions.

8.1.3 The membrane filter method should not be used to test stack gases.

8.1.4 If the filters are removed from their holders, use plastic tweezers or disposable gloves and place them in individually labeled plastic bags.

8.1.5 Subject blank filters to the same field conditions that the sample filters experience except for having air drawn through them.

8.1.6 If the impinger method is used, a citric acid-treated filter should be mounted ahead of two midget impingers, each containing 15 or 20 mL of 0.01 N NaOH.

8.2 Preparation of filters.

8.2.1 The same type of nylon-reinforced 0.8-µm membrane filters are used for both the trapping of particulate fluoride and gaseous fluoride.

8.2.2 Place the filters to be used for particulate fluoride in a beaker containing the citric acid solution and the filters for gaseous fluorides in the sodium formate solution.

8.2.3 Allow the filters to soak for at least one hour.

8.2.4 Remove the filters with plastic tweezers taking care not to damage the collecting surface of the filter.

8.2.5 Keeping the sodium formate and citric acid filters separate, place the filters on plastic netting to dry.

8.2.6 Fold the netting over the filters and place tissue paper over the netting to protect the filter from dust while they dry.

8.3 Citric acid filter (particulate fluoride).

8.3.1 After sampling has been completed, the particulate fluoride on the citric acid-treated filter must be made water soluble before it can be analyzed.

8.3.2 Place the folded citric acid-treated filter in a nickel crucible. (Also run blank field filters in three separate crucibles and take the average reading.)

8.3.3 Add 10 mL 5 N NaOH, then sufficient distilled water to cover the filter.

8.3.4 Allow the filters to soak for one hour.

8.3.5 Place the crucible in an oven at 120° C until the liquid has completely evaporated.

8.3.6 Cover the crucible and place it in a muffle furnace at 300° C for two hours. (Slowly raise the temperature to minimize smoking of the filters.)

8.3.7 Raise the temperature to 600° C and let the sample fuse for at least one hour.

8.3.8 Remove the crucible from the muffle furnace and allow it to cool.

8.3.9 Add 20 mL of distilled water to the crucible, replace the cover, and warm on a hotplate so as to dissolve the sodium hydroxide fusion cake. (With some samples this may still leave a residue even after hours of heating.)

8.3.10 After cooling, use 3 N HCl, 1 N NaOH if necessary, and pH indicator strips (pH 0-14 sticks) to bring the pH of the solution to 8-9. (This step creates insoluble oxides from interfering metal cations such as aluminum or iron that are later removed by filtration.)

8.3.11 Do not produce neutral or acidic conditions during step 8.3.10, as some of the fluoride could be lost.

8.3.12 Transfer the solution in the crucible to a 100-mL polypropylene volumetric flask and use 100 mL as the total volume in the calculations (See 11.0).

8.3.13 Rinse the crucible with distilled water and pour rinsings into the volumetric flask.

8.3.14 Fill the volumetric flask to the mark with distilled water.

8.3.15 Filter the solution through dry Whatman No. 40 paper or equivalent into a polypropylene beaker and discard the filter paper.

8.3.16 The filtrate solution is now ready to be analyzed for particulate fluoride from the citric acid-treated filter (See 10.0).

8.4 Sodium formate filter (gaseous fluoride).

8.4.1 Place each sodium formate-treated filter in a small plastic beaker large enough to allow the filter to lie flat on the bottom of the beaker.

8.4.2 To each beaker add 10 mL TISAB and 10 mL distilled water.

8.4.3 Cover the beakers with parafilm and either ultrasonicate for two hours or stir with a teflon-coated magnetic stirrer for three hours.

8.4.4 Decant the solution into a second plastic beaker.

8.4.5 The solution is now ready to be analyzed for gasesous fluorides from the sodium formate-treated filter. (See 10.0 but do not add any more TISAB. Millivolt readings can be made directly on the solution. When doing the calculations, use a total volume of 10 mL for the sodium formate-treated filters.)

8.5 0.01 N NaOH impingers (gaseous fluorides. Alternate method).

8.5.1 Using a plastic graduated cylinder, measure the volume of the sample. If the volume is <90% of the preshipment volume, then void the sample.

8.5.2 Transfer the solution to a clean, dry plastic beaker and use distilled water to rinse the inside of the container and graduated cylinder into the plastic beaker.

8.5.3 Using 3 N HCl, 1 N NaOH if necessary, and pH indicator strips (ph 0-14 strips), bring the pH of the solution to 8-9. (In a separate plastic beaker place approximately 20 mL of unused 0.1 N NaOH field absorber and use as a field blank.)

8.5.4 Do not produce neutral or acidic conditions during Step 8.5.3 because some of the fluoride could be lost.

8.5.5 Measure the volume of the solution in a clean, dry, plastic graduated cylinder and use this as the total volume in the calculations (See 11.0).

8.5.6 Filter the solution through dry Whatman No. 40 filter paper or equivalent and discard the filter paper.

8.5.7 The filtrate is now ready to be analyzed for gaseous fluorides from the impinger (See 10.0).

9.0 STANDARD PREPARATION.

9.1 Working standards containing 0.1, 1.0 and 10 µg F^-/mL can be prepared as follows:

9.2 Pipet 0.1, 1.0 and 10 mL, respectively, of the the 100 µg F^-/mL stock standard into separate 100 mL polypropylene volumetric flasks.

9.3 Fill each flask to the mark with distilled water. (Make the working standards fresh each day.)

9.4 The standard curve consists of six calibration solutions containing 0.05, 0.1, 0.5, 1.0, 5.0 and 10.0 µg F^-/mL.

9.5 For 0.1, 1.0 and 10.0 µg F^-/mL, place 10 mL of the 0.1, 1.0 and 10.0 µg F^-/mL working standards, respectively, in small plastic beakers and add 10 mL of TISAB buffer.

9.6 For 0.05, 0.50 and 5.0 µg F^-/mL, place 5 mL of the 0.1, 1.0 and 10.0 µg F^-/mL working standards, respectively, in small plastic beakers and add 5 mL distilled water and 10 mL TISAB buffer.

9.7 A new calibration curve should be run with each batch of samples and read in the order of increasing concentration.

9.8 A plot of millivolts or relative millivolts vs. the log of the concentration should give a straight line. If it does not, then the electrode is not operating properly.

9.9 Since the log of the concentration is used do not start the standard curve with a zero concentration, but rather use the 0.05 standard as the first point on the curve.

10.0 SAMPLE ANALYSIS.

10.1 To a 10-mL aliquot of sample in a small plastic beaker, add 10 mL TISAB buffer.

10.2 Obtain a millivolt or relative millivolt reading in the same way as the calibration solutions.

10.3 If the sample is too concentrated, it may be diluted with distilled water.

10.3.1 The diluted solution should contain 10 mL(sample + water) and 10 mL TISAB.

10.3.2 Be sure to include the dilution factor in the calculations.

10.4 Between measurements, rinse the fluoride electrode with distilled water and blot dry.

10.5 Keep samples and standards at the same temperature during analysis.

11.0 CALCULATIONS.

11.1 $\mu g\ F^-$ in sample (impinger or filter) = (concentration in $\mu g/mL$ of the sample measured by the fluoride electrode) X (total volume of filtrate or impinger contents in mL) X (dilution factor, if any).

11.2 $$\mu g\ F^-/m^3 = \frac{\mu g\ F^- \text{ in sample}}{\text{volume of air sampled in } m^3}$$

11.3 $$\mu g\ HF/m^3 = \frac{\mu g\ F^-}{m^3} \frac{MW\ HF}{MW\ F^-} = \frac{\mu g\ F^-}{m^3} \frac{20}{19}$$

11.4 ppb gaseous fluoride as HF

$$= \frac{\mu g\ F^-}{m^3} \frac{20}{19} \frac{24.04}{MW\ HF}$$

$$= \frac{\mu g\ F^-}{m^3} \frac{20}{19} \frac{24.04}{20}$$

$$= \frac{\mu g\ F^-}{m^3}\ 1.265$$

The particulate fluoride should be calculated using equation 11.2. The gaseous fluorides are calculated as HF using equation 11.4. The constant 24.04 in equation 11.4 takes into account the conversion from weight to volume using the Gas Law.

12.0 QUALITY ASSURANCE.

12.1 Precision is determined by duplicate aliquots of the same filtrate that have been measured for fluoride concentration by an ion electrode.

12.1.1 These duplicates determine the precision of the ion electrode.

12.1.2 The average of the relative deviation of all the duplicates in an analysis should not be more than five percent.

Relative Deviation (R.D.) = $\bar{d}/\bar{c}$

c_i = individual value of the concentration in $\mu g\ F^-/mL$

$\bar{d}$ = average deviation of the two duplicate concentrations in $\mu g\ F^-/mL$. $\bar{d} = \frac{c_1 - c_2}{2}$

$\bar{c}$ = arithmethic average of the two duplicate concentrations. $\bar{c} = \frac{c_1 + c_2}{2}$

12.1.3 At least one duplicate should be run for every ten or less samples.

12.2 Accuracy of the fluoride electrode is determined by audits.

12.2.1 The concentration of the audit should be unknown to the analyst at the time of the analysis.

12.2.2 A suitable audit would be a solution of NaF at a concentration between 1 and 10 $\mu g\ F^-/mL$.

12.2.3 The average error should be less than 5%.

12.2.4 At least one audit should be run per analysis.

12.3 Recoverability of a sample is measured with spikes.

12.3.1 Spikes determine whether the fluoride ion is being complexed in the filtrate.

12.3.2 Prepare a spiked sample by adding a known quantity of a standard (the spike) to an aliquot of sample filtrate.

12.3.3 EXAMPLE: 5 mL of a 10 µg F^-/mL standard are added to 5 mL of a sample with a concentration of 8.6 µg F^-/mL. (The volume of the standard and sample should equal the volume of TISAB.) With the ion electrode, the concentration of the spiked sample was found to be 9.4 µg F^-/mL.

$$\text{Percent recovery} = \frac{\text{Conc(spike + sample)} - \text{Conc(sample)}}{\text{Conc(spike)}} \times 100$$

Conc(spike + sample) = 9.4 µg F^-/mL.
Conc(sample) = 1/2(8.6 µg F^-/mL) = 4.3 µg F^-/mL.
Conc(spike) = 1/2(10 µg F^-/mL) = 5 µg F^-/mL.

Note that the concentration of the sample and standard used as a spike are half of the original value because each was diluted with the other by half.

$$\text{Percent recovery} = \frac{9.4\ \mu g\ F^-/mL - 1/2(8.6\ \mu g\ F^-/mL)}{1/2(10\ \mu g\ F\text{-}/mL)} \times 100 = 102\%$$

12.3.4 The percent recovery should be between 90-110%.

12.3.5 At least one spike should be run for every ten or less samples.

13.0 REFERENCES.

1. Texas Air Control Board, Sampling Procedures Manual, Chapter 12.

2. Elfers, L.A. and Decker, C.E., "Analysis of Fluoride in Air and Stack Gas Samples by Use of a Specific Ion Electrode," Anal. Chem., 40, 1658 (1968).

3. McQuaker, N.R. and Gurney, M., "Determination of Total Fluoride in Soil and Vegetation Using an Alkali Fusion-Selective Ion Electrode Technique," Anal. Chem. 49, 53 (1977).

4. Thompson, R.J., and McMullen, T.B. and Morgan, G.B., "Fluoride Concentrations in the Ambient Air," J. Air Poll. Control Assoc., 21, 8 (1971).

5. EPA Quality Assurance Handbook for Air Pollution Systems. Volume III - Stationary Source Specific Methods. Method 13B. Revision No. 0, January 4, 1980.

6. Orion Instruction Manual for Fluoride Electrodes. Model 96-09, p. 27, 1977.

Fluorides In Stack Gases

1.0 PRINCIPLE AND APPLICABILITY.

1.1 In the Hydrogen Fluoride Gas (HF) stack sampling procedure (Reference 1), a filter is used immediately after the probe to trap particulate fluorides while the 0.1 N NaOH impingers in back of the filter capture the gaseous fluorides.

1.2 The filter may be analyzed for both water soluble and water insoluble particulate fluorides or only for total particulate fluoride by a sodium hydroxide fusion.

1.3 The impingers containing sodium hydroxide are analyzed by a specific ion electrode for gaseous fluorides which are assumed to be HF.

1.4 Method 13 does not measure the fluoride in fluorocarbons.

2.0 RANGE AND LOWER DETECTABLE LIMIT.

2.1 The concentration range of the procedure is from 0.02 to 2,000 μg F^-/mL (Reference 2).

2.2 The lower detectable limit (LDL) by Method 13 is 0.05 μg F^-/mL.

3.0 PRECISION.

3.1 A collaborative test done at a primary aluminum smelter showed that fluoride concentrations from 0.1 to 1.4 μg F^-/m^3 could be determined with a within-laboratory precision of 0.037 μg F^-/m^3 (Reference 2).

4.0 ACCURACY.

4.1 The accuracy of the method measured as interlaboratory precision has been shown to be 0.056 μg F^-/m^3 for fluoride concentrations from 0.1 to 1.4 μg F^-/m^3 (Reference 2).

5.0 INHERENT SOURCES OF ERROR AND INTERFERENCE.

5.1 Fluoride activity in the samples is reduced by complexing with aluminum, other polyvalent cations, and hydrogen, as well as by pH effects.

5.1.1 These interferences can be removed by adding an ionic buffer to the fluoride solutions before the concentration is measured with a specific fluoride electrode (See 7.1).

5.2 EPA states that the main cause of error has been found to be distillation during sample analysis (Reference 2).

5.2.1 The Texas Air Control Board Laboratory utilizes the McQuaker and Gurney method (Reference 3) of filtering the samples under slightly alkaline conditions to remove interfering cations as insoluble oxides (See 8.2.3). This makes the distillation step unnecessary.

5.3 Samples and standards should be close to the same temperature. At the 10^{-3} M level, a 1°C change in temperature will cause a 2% error (Reference 4).

5.4 Lack of stability in the electrometer will cause significant error in the results.

5.5 Fluoride absorption into the grease on sample-exposed surfaces when sampling can cause low results.

5.6 Three nickel crucible blanks are run to account for possible fluoride contamination from the crucibles during the sodium hydroxide fusion.

6.0 APPARATUS.

6.1 Plasticware.

1000-mL polypropylene volumetric flask for the stock fluoride standard.
100-mL polypropylene volumetric flask for samples and standards.
Plastic filtering funnels.
Plastic storage bottles for samples.

6.2 pH indicator strips.

Test 0-14 pH range. No bleeding from pH strip into solution.

6.3 Nickel crucibles with cover.

50-100 mL capacity.

6.4 Evaporating oven.

Temperature range: ≥150° C.
Recirculating airflow.

6.5 Muffle furnace.

Temperature range: ≥700° C.
Desired temperature can be reached quickly.

6.6 Whatman No. 40 filter paper or equivalent.

6.7 Specific ion fluoride electrode.

6.8 Parafilm or other plastic film for sealing beakers.

7.0 REAGENTS.

All reagents should be ACS reagent grade or better.

7.1 Total Ionic Strength Adjustment Buffer (TISAB).

7.1.1 Place approximately 500 mL of distilled water in a 1-liter beaker. Add 57 mL glacial acetic acid, 58 g sodium chloride, and 4 g CDTA (Cyclohexylene dinitrilotetraacetic acid).

7.1.2 Stir to dissolve.

7.1.3 Place the beaker in a water bath to cool.

7.1.4 Slowly add 5 N NaOH to the solution, measuring the pH continuously with a pH electrode, until the pH is 5.3.

7.1.5 Cool to room temperature.

7.1.6 Pour into a 1-liter flask and dilute to volume with distilled water.

7.1.7 NOTE: Buffers for the purpose are available commercially. TISAB II, a product of Orion Research, is the one currently used in this laboratory.

7.2 Sodium Hydroxide (5 N).

7.2.1 To about 700 mL distilled water in a 1-liter volumetric flask, add 200 g NaOH pellets and stir until dissolved.

7.2.2 Allow solution to cool, then dilute to the mark with distilled water.

7.3 Sodium Hydroxide (1 N). Dilute 20 mL 5 N NaOH to 100 mL with distilled water.

7.4 Sodium Hydroxide Absorber (0.1 N). Dilute 20 mL 5.0 N sodium hydroxide to 1 liter with distilled water.

7.5 Stock Standard Fluoride Solution (100 μg F^-/mL).

7.5.1 Dissolve 0.2210 g of sodium fluoride (oven dried for two hours at 110° C.) in distilled water contained in a 1000-mL plastic volumetric flask and dilute to volume.

7.5.2 Alternatively, a commercial fluoride standard may be used.

7.6 Hydrochloric Acid (3 N). Dilute 125 mL concentrated (approximately 12 N) hydrochloric acid to 500 mL.

8.0 PROCEDURE (Specific Ion Electrode Method).

8.1 Collection of sample.

8.1.1 Do not use glass fiber filter for stack sampling fluorides because of high F^- blank values.

8.1.2 The filter used in sampling can be unheated if a paper or membrane medium is used (Reference 2); however, an unheated filter may cause condensation problems.

8.1.3 According to EPA, the filter should have a ≥95% collection efficiency (≤5% penetration) for 0.3 micron dioctyle phthalate smoke particles. (Consult the manufacturer's quality control test data.)

8.1.4 Prior to sampling, determine the average F^- blank value of at least three filters from the lot to be used for sampling and reject if the blank value is ≥0.015 mg F/cm^2 of filter area.

8.1.5 This laboratory recommends the use of Whatman Ultra-Pure QM-A quartz filters which exceed EPA criteria and can be heated up to 500° C.

8.1.6 Reject filters with pin holes or flaws.

8.1.7 Subject filter blanks and 0.1 N NaOH blanks to the same field conditions that the samples experience except for being used in sampling.

8.1.8 Use plastic bottles (plastic petri dishes for filters) as shipping containers for the samples.

8.1.9 After sampling, mark the level of liquid on the plastic container to determine sample loss during shipment.

8.2 Impinger (gaseous fluorides).

8.2.1 Using a plastic graduated cylinder, measure the volume of the sample. If the volume is <90% of the preshipment volume (See 8.1.9), then void the sample.

8.2.2 Transfer the solution to a clean, dry plastic beaker and use distilled water to rinse the inside of the container and graduated cylinder into the plastic beaker. (In a separate plastic beaker place approximately 20 mL of unused 0.1 N NaOH field absorber and use as a blank.)

8.2.3 Using 3 N HCl, 1 N NaOH if necessary, and pH indicator strips (pH 0-14 sticks), bring the pH of the solution to 8-9. (This step creates insoluble oxides from interfering metal cations such as aluminum or iron that are later removed by filtration.)

8.2.4 Do not produce neutral or acidic conditions during Step 8.2.3 because some of the fluoride could be lost.

8.2.5 Measure the volume of the solution in a clean, dry, plastic graduated cylinder and use this as the total volume in the calculations (See 11.0).

8.2.6 Filter the solution through dry Whatman No. 40 filter paper or equivalent and discard the filter paper.

8.2.7 The filtrate is now ready to be analyzed for gaseous fluorides from the stack (See 10.0).

8.3 Filter (particulate fluorides).

8.3.1 The particulate fluoride on the filter can be analyzed in two steps as
A. Water-soluble fluorides (Steps 8.4-8.4.6) and
B. Water-insoluble fluorides (Steps 8.5-8.5.15); or it can be analyzed in one step as
C. Total particulate fluorides (Steps 8.6-8.6.4).

8.4 A. Water-Soluble Fluorides (on the filter).

8.4.1 Place the sample filter in a plastic beaker with 30 mL of distilled water. (In separate beakers, run three clean field filters as samples and take the average for a blank reading.)

8.4.2 Cover the beaker with parafilm and either ultrasonicate for two hours or stir with a teflon-coated magnetic stirrer for three hours.

8.4.3 Filter the sample in the beaker through dry Whatman No. 40 filter paper or equivalent into a second plastic beaker. (Do not discard the pair of sample filter and Whatman filter because they will be used in Step 8.5.1.)

8.4.4 With distilled water, rinse the inside of the first beaker from Step 8.4.1 into the Whatman filter and then rinse the last traces of the water soluble sample on the Whatman filter into the filtrate in the second plastic beaker.

8.4.5 At this point for the filtrate in the second beaker, follow Steps 8.2.3 through 8.2.6 in this procedure.

8.4.6 The filtrate is now ready to be analyzed for water soluble particulate fluoride from the filter (See 10.0).

8.5 B. Water-Insoluble Fluorides (on the filter).

8.5.1 Place the sample and Whatman filter from Step 8.4.3 in the same crucible. (Put the three pairs of clean field filters and Whatman filters in three separate crucibles and take the average as a blank reading.)

8.5.2 Add 10 mL 5 N NaOH, then sufficient distilled water to cover the filters.

8.5.3 Allow the filters to soak for one hour.

8.5.4 Place the crucible in an oven at 120° C until the liquid has completely evaporated.

8.5.5 Cover the crucible and place it in a muffle furnace at 300° C for two hours. (Slowly raise the temperature to minimize smoking from the filters.)

8.5.6 Raise the temperature to 600° C and let the sample fuse for at least 1 hour.

8.5.7 Remove the crucible from the muffle furnace and allow it to cool.

8.5.8 Add 20 mL of distilled water to the crucible, replace the cover and warm on a hotplate so as to dissolve the sodium hydroxide fusion cake. (With some samples this may still leave a residue even after hours of heating.)

8.5.9 After cooling, use 3 N HCl, 1 N NaOH if necessary, and pH indicator strips (pH 0-14 sticks) to bring the pH of the solution to 8-9. (This step creates insoluble oxides from interfering metal cations such as aluminum or iron that are later removed by filtration.)

8.5.10 Do not produce neutral or acidic conditions during Step 8.5.9, as some of the fluoride could be lost.

8.5.11 Transfer the solution in the crucible to a 100-mL polypropylene volumetric flask and use 100 mL as the total volume in the calculations (See 11.1).

8.5.12 Rinse the crucible with distilled water and pour the rinsings into the volumetric flask.

8.5.13 Fill the volumetric flask to the mark with distilled water.

8.5.14 Filter the solution through dry Whatman No. 40 paper or equivalent into a polypropylene beaker and discard the filter paper.

8.5.15 The filtrate is now ready to be analyzed for water insoluble particulate fluoride from the filter (See 10.0).

8.6 C. Total Particulate Fluorides (on the filter).

8.6.1 To analyze for the total particulate fluoride on the filter, disregard sections 8.4 A & 8.5 B and place the folded sample filter in a nickel crucible. (Also run three clean field filters in three separate crucibles as a blank and take the average as a blank reading.)

8.6.2 Add 10 mL 5 N NaOH then sufficient distilled water to cover the filter.

8.6.3 At this point, follow steps 8.5.3 through 8.5.14 in this procedure.

8.6.4 The filtrate is now ready to be analyzed for total particulate fluoride from the filter (See 10.0).

8.7 Probe Wash (distilled water).

8.7.1 The probe wash can be analyzed for:
A. Water-soluble fluorides (gaseous and water soluble particulate) (Steps 8.8-8.8.4)
B. Water-insoluble fluorides (particulate) (Steps 8.9-8.9.4)

8.8 A. Water-Soluble Fluorides (gaseous and water soluble particulate)

8.8.1 Filter the probe wash through dry Whatman No. 40 filter paper or equivalent into a plastic beaker. (Do not discard the filter because it will be used in Step 8.9.1.)

8.8.2 With distilled water rinse the last traces of the water soluble fluorides on the filter into the filtrate in the plastic beaker.

8.8.3 At this point follow Steps 8.2.3 through 8.2.6 of this procedure.

8.8.4 The filtrate is now ready to be analyzed for water-soluble fluorides from the probe wash (See 10.0).

8.9 B. Water-Insoluble Fluorides (particulate).

8.9.1 Place the folded Whatman filter from Step 8.8.1 into a nickel crucible. (Also run a blank Whatman filter in a separate crucible.)

8.9.2 Add 10 mL 5 N NaOH, then sufficient distilled water to cover the filter.

8.9.3 At this point follow Steps 8.5.3 through 8.5.14 in this procedure.

8.9.4 The filtrate is now ready to be analyzed for water-insoluble particulate fluoride from the probe wash (See 10.0).

9.0 STANDARD PREPARATION.

9.1 Working standards containing 0.1, 1.0 and 10 µg F^-/mL can be prepared as follows:

9.2 Pipet 0.1, 1.0 and 10 mL, respectively, of the the 100 µg F^-/mL stock standard into separate 100 mL polypropylene volumetric flasks.

9.3 Fill each flask to the mark with distilled water. (Make the working standards fresh each day.)

9.4 The standard curve consists of six calibration solutions containing 0.05, 0.1, 0.5, 1.0, 5.0 and 10.0 µg F^-/mL.

9.5 For 0.1, 1.0 and 10.0 µg F^-/mL, place 10 mL of the 0.1, 1.0 and 10.0 µg F^-/mL working standards, respectively, in small plastic beakers and add 10 mL of TISAB buffer.

9.6 For 0.05, 0.50 and 5.0 µg F^-/mL, place 5 mL of the 0.1, 1.0 and 10.0 µg F^-/mL working standards, respectively, in small plastic beakers and add 5 mL distilled water and 10 mL TISAB buffer.

9.7 A new calibration curve should be run with each batch of samples and read in the order of increasing concentration.

9.8 A plot of millivolts or relative millivolts vs. the log of the concentration should result in a straight line. If it does not, then the electrode is not operating properly.

9.9 Since the log of the concentration is used, do not start the standard curve with a zero concentration, but rather use the 0.05 standard as the first point on the curve.

10.0 SAMPLE ANALYSIS.

10.1 To a 10-mL aliquot of sample in a small plastic beaker, add 10 mL TISAB buffer.

10.2 Obtain a millivolt or relative millivolt reading in the same way as the calibration solutions.

10.3 If the sample is too concentrated, it may be diluted with distilled water.

10.3.1 The diluted solution should contain 10 mL(sample + water) and 10 mL TISAB.

10.3.2 Be sure to include the dilution factor in the calculations.

10.4 Between measurements, rinse the fluoride electrode with distilled water and blot dry.

10.5 Keep samples and standards at the same temperature during analysis.

11.0 CALCULATIONS.

11.1 $\mu g\ F^-$ in sample(impinger or filter) = (concentration in $\mu g/mL$ of the sample measured by the fluoride electrode) X (total volume of filtrate or impinger contents in mL) X (dilution factor, if any).

11.2 $$\mu g\ F^-/m^3 = \frac{\mu g\ F^-\ \text{in sample}}{\text{volume of stack gas sampled in } m^3}$$

11.3 $$\mu g\ HF/m3 = \frac{\mu g\ F^-}{m3}\ \frac{MW\ HF}{MW\ F^-} = \frac{\mu g\ F^-}{m^3}\ \frac{20}{19}$$

11.4 $$\text{ppb gaseous flouride} = \frac{\mu g\ F^-}{m^3}\ \frac{20}{19}\ \frac{24.04}{MW\ HF}$$

$$= \frac{\mu g\ F^-}{m^3}\ \frac{20}{19}\ \frac{24.04}{20}$$

$$= \frac{\mu g\ F^-}{m^3}\ 1.265$$

The particulate fluoride should be calculated using equation 11.2.
The gaseous fluorides are calculated as HF using equation 11.4
The constant 24.04 in equation 11.4 takes into account the conversion from weight to volume using the Gas Law.

12.0 QUALITY ASSURANCE.

12.1 Precision is determined by duplicate aliquots of the same filtrate that have been measured for fluoride concentration by an ion electrode.

12.1.1 These duplicates determine the precision of the ion electrode.

12.1.2 The average of the relative deviation of all the duplicates in an analysis should not be more than five percent.

Relative Deviation (R.D.) = $\bar{d}/\bar{c}$

c_i = individual value of the concentration in µg F^-/mL.

$\bar{d}$ = average deviation of the two duplicate concentrations in µg F^-/mL. $\bar{d} = \frac{c_1 - c_2}{2}$

$\bar{c}$ = arithmetic average of the two duplicate concentrations. $\bar{c} = \frac{c_1 + c_2}{2}$

12.1.3 At least one duplicate should be run for every ten or less samples.

12.2 Accuracy of the fluoride electrode is determined by audits.

12.2.1 The concentration of the audit should be unknown to the analyst at the time of the analysis.

12.2.2 A suitable audit would be a solution of NaF at a concentration between 1 and 10 µg F^-/mL.

12.2.3 The average error should be less than 5%.

12.2.4 At least one audit should be run per analysis.

12.3 Recoverability of a sample is measured with spikes.

12.3.1 Spikes determine whether the fluoride ion is being complexed in the filtrate.

12.3.2 Prepare a spiked sample by adding a known quantity of a standard (the spike) to an aliquot of sample filtrate.

12.3.3 EXAMPLE: 5 mL of a 10 µg F^-/mL standard are added to 5 mL of a sample with a concentration of 8.6 µg F^-/mL. (The volume of the standard and sample should equal the volume of TISAB.) With the ion electrode, the concentration of the spiked sample was found to be 9.4 µg F^-/mL.

$$\text{Percent recovery} = \frac{\text{Conc(spike + sample)} - \text{Conc(sample)}}{\text{Conc(spike)}} \times 100$$

Conc(spike + sample) = 9.4 μg F^-/mL.
Conc(sample) = 1/2(8.6 μg F^-/mL) = 4.3 μg F^-/mL.
Conc(spike) = 1/2(10 μg F^-/mL) = 5 μg F^-/mL.

Note that the concentration of the sample and standard used as a spike are half of the original value because each was diluted with the other by half.

$$\text{Percent recovery} = \frac{9.4\ \mu g\ F^-/mL - 1/2(8.6\ \mu g\ F^-/mL)}{1/2(10\ \mu g\ F^-/mL)} \times 100 = 102\%$$

12.3.4 The percent recovery should be between 90-110%.

12.3.5 At least one spike should be run for every ten or less samples.

13.0 REFERENCES.

1. Texas Air Control Board, Sampling Procedures Manual, Chapter 6.

2. EPA Quality Assurance Handbook for Air Pollution Measurement Systems, Volume III--Stationary Source Specific Methods, Method 13B, Revision No. 0, January 4, 1982.

3. McQuaker, N.R. and Gurney, M., "Determination of Total Fluoride in Soil and Vegetation Using an Alkali Fusion-Selective Ion Electrode Technique," Anal. Chem., 49, 53 (1977).

4. Orion Instruction Manual for Fluoride Electrode Model 96-09, p. 27

5. Elfers, L.A. and Decker, C.E., "Analysis of Fluoride in Air and Stack Gas Samples by Use of a Specific Ion Electrode," Anal. Chem., 40, 1658 (1968).

6. Thompson, R.J., and McMullen, T.B. and Morgan, G.B., "Fluoride Concentrations in the Ambient Air," J. Air Poll. Control Assoc., 21, 8 (1971).

Total Fluorides In Vegetation And Other Solid Material

1.0 PRINCIPLE AND APPLICABILITY.

1.1 This technique applies to fluorides that have been absorbed by or deposited on a material. Also, as in the case of bricks, it applies to fluorides that are held in an inorganic matrix that render them water-insoluble.

1.2 After grinding the samples to a fine consistency, a sodium hydroxide fusion is used, followed by measurement of the fluoride content of the solutions with a specific ion electrode.

1.3 According to EPA, the main cause of error in fluoride analysis is the distillation step (Reference 1).

1.3.1 This laboratory uses the McQuaker and Gurney method (Reference 2) of filtering the samples under slightly alkaline conditions which makes the distillation step unnecessary (see 8.9).

2.0 RANGE AND LOWER DETECTABLE LIMIT.

2.1 McQuaker and Gurney report a detection limit of 3 ppm (3 μg F^-/ gram dried sample) for a 0.5 g sample.

2.2 The theoretical upper limit of the range is in excess of 4000 ppm (Reference 2).

3.0 PRECISION.

3.1 Replicate samples are used to measure the precision of the method (see 12.1).

3.2 This laboratory has found the average precision of this method to be 10%.

4.0 ACCURACY.

4.1 Audits or standards analyzed as unknowns are used to measure the accuracy of the method (see 12.5).

4.2 This laboratory has found the average accuracy of the method to be 92%.

5.0 INHERENT SOURCES OF ERROR AND INTERFERENCE.

5.1 Fluoride activity in the sample is reduced by complexing with aluminum, other polyvalent cations, and hydrogen, as well as by pH effects.

5.1.1 These interferences can be removed by adding an ionic buffer to the fluoride solutions before the concentration is measured with a specific ion fluoride electrode (see 7.1).

5.2 Samples and standards should be close to the same temperature. At the 10^{-3} M level, a 1° C change in temperature will cause a 2% error (Reference 3).

5.3 Lack of stability in the ionalyzer meter will cause significant error in the results.

5.4 See 1.3 and 1.3.1.

5.5 Three nickel crucible blanks are run to account for possible fluoride contamination from the crucibles during the sodium hydroxide fusion.

6.0 APPARATUS.

6.1 Plasticware.

1000-mL polypropylene volumetric flask for the stock fluoride standard.
100-mL polypropylene volumetric flask for samples and standards.
Plastic filtering funnels.
Plastic storage bottles for samples.

6.2 pH indicator strips.

(1) Cover a 0-14 pH range.
(2) Do not bleed from pH strip into the solution.

6.3 Nickel crucibles with cover.

50-100 mL capacity.

6.4 Evaporating oven.

Temperature: ≥150° C.
Recirculating airflow.

6.5 Muffle furnace.

Temperature range: ≥ 700° C.
Desired temperature can be reached quickly.

6.6 Whatman No. 40 filter paper or equivalent.

6.7 Specific ion fluoride electrode.

6.8 Parafilm or other plastic film for sealing beakers.

7.0 REAGENTS.

All reagents should be ACS reagent grade or better.

7.1 Total Ionic Strength Adjustment Buffer (TISAB).

7.1.1 Place approximately 500 mL of distilled water in a 1-liter beaker. Add 57 mL glacial acetic acid, 58 g sodium chloride, and 4 g CDTA (cyclohexylene dinitrilotetraacetic acid).

7.1.2 Stir to dissolve.

7.1.3 Place the beaker in a water bath to cool.

7.1.4 Slowly add 5 N NaOH to the solution, measuring the pH continuously with a pH electrode, until the pH is 5.3.

7.1.5 Cool to room temperature.

7.1.6 Pour into a 1-liter flask and dilute to volume with distilled water.

7.1.7 NOTE: Buffers for this purpose are commercially available. TISAB II, a product of Orion Research, is the one currently used in this laboratory.

7.2 Sodium Hydroxide (5 N).

7.2.1 To about 700 mL distilled water in a 1-liter volumetric flask, add 200 g NaOH pellets and stir until dissolved. Allow solution to cool, then dilute to the mark with distilled water.

7.3 Sodium Hydroxide (1 N). Dilute 20 mL 5 N NaOH to 100 mL.

7.4 Stock Standard Fluoride Solution (100 µg F^-/mL).

7.4.1 Dissolve 0.2210 g of sodium fluoride (oven dried for 2 hours at 110° C) in distilled water contained in a 1000-mL plastic volumetric flask and dilute to volume.

7.4.2 Alternatively, a commercial fluoride standard may be used.

7.4.3 The standard must be stored in a plastic bottle.

7.5 Hydrochloric Acid (3 N). Dilute 125 mL concentrated (approximately 12 N) hydrochloric acid to 500 mL.

8.0 PROCEDURE (Specific Ion Electrode Method).

8.1 Place the sample or a representative portion of it in a polypropylene beaker and dry in an oven at 105° C for three hours.

8.1.1 With some samples, such as bricks, it will be necessary to first crush them to a powder in order to expose enough surface to the drying process.

8.2 After drying, homogenize the sample so as to pass through a fine mesh sieve. (A 100 mesh sieve or finer is recommended.)

8.3 In a tared nickel crucible, weigh a sample portion of 0.50-1.00 g.

8.4 Add 10 mL 5 N NaOH to the sample in the crucible.

8.4.1 To determine an average blank reading, add 10 mL 5 N NaOH to each of three empty nickel crucibles and take them through the analysis. (If the fluoride is collected on filters, use blank filters as specified in the instructions in Methods 12 and 13 in order to obtain the blank reading.)

8.5 With a plastic stirring rod ensure that the sample is uniformly dispersed in the sodium hydroxide solution.

8.6 Place the crucible in an oven at 120° C until the liquid has completely evaporated.

8.7 Cover the crucible and place it in a muffle furnace at 300° C for 2 hours. (If a fluoride determination is done on filters, slowly raise the temperature to minimize smoking of the filters.)

8.7.1 Raise the temperature to 600° C and let the sample fuse for at least 1 hour.

8.7.2 Remove the crucible from the muffle furnace and allow it to cool.

8.8 Add 20 mL of distilled water to the crucible, replace the cover and warm on a hot plate for two hours so as to dissolve the sodium hydroxide fusion cake. (With some samples this may still leave a residue even after hours of heating.)

8.9 After cooling, use 3 N HCl, or 1 N NaOH if necessary, to bring the pH of the solution to 8-9. Measure with pH indicator strips (0-14 sticks). (This step creates insoluble oxides from interfering metal cations such as aluminum or iron that are later removed by filtration.)

8.9.1 Do not produce neutral or acidic conditions during step 8.9, as some of the fluoride could be lost.

8.10 Transfer the solution from the crucible to a 100-mL polypropylene volumetric flask. Use 100 mL as the total volume in the calculations (see 11.0).

8.10.1 Rinse the crucible with distilled water and pour the rinsings into the volumetric flask.

8.11 Fill the volumetric flask to the mark with distilled water; shake well.

8.12 Filter the solution through dry Whatman No. 40 paper or equivalent into a polypropylene beaker and discard the filter.

8.13 The filtrate is now ready to be analyzed for total fluorides (see Section 10.0).

9.0 STANDARD PREPARATION.

9.1 Working standards containing 0.1, 1.0 and 10 µg F^-/mL can be prepared as follows:

9.2 Pipet 0.1, 1.0 and 10 mL respectively of the 100 µg F^-/mL stock standard into separate 100 mL polypropylene volumetric flasks.

9.3 Fill each flask to the mark with distilled water. (Make the working standards fresh each day.)

9.4 The standard curve consists of six calibration solutions containing 0.05, 0.1, 0.5, 1.0, 5.0 and 10.0 µg F^-/mL.

9.5 For 0.1, 1.0 and 10.0 µg F^-/mL, place 10 mL of the 0.1, 1.0 and 10.0 µg F^-/mL working standards, respectively, in small plastic beakers and add 10 mL of TISAB buffer.

9.6 For 0.05, 0.50 and 5.0 µg F-/mL, place 5 mL of the 0.1, 1.0 and 10.0 µg F-/mL working standards, respectively, in small plastic beakers and add 5 mL distilled water and 10 mL TISAB buffer.

9.7 A new calibration curve should be run with each batch of samples and read in order of increasing concentration.

9.8 A plot of millivolts or relative millivolts vs. the log of the concentration should give a straight line. If it does not, then the electrode is not operating properly.

9.9 Since the log of the concentration is used, do not start the standard curve with a zero concentration but rather use the 0.05 standard as the first point on the curve.

10.0 SAMPLE ANALYSIS.

10.1 To a 10-mL aliquot of the sample in a small plastic beaker, add 10 mL TISAB buffer.

10.2 Obtain a millivolt or relative millivolt reading in the same way as was done for the calibration solutions.

10.3 If the sample is too concentrated, it may be diluted with distilled water.

10.3.1 The diluted solution should contain 10 mL (sample + water) and 10 mL TISAB.

10.3.2 Be sure to include the dilution factor in the calculations.

10.4 Between measurements, rinse the fluoride electrode with distilled water and blot dry.

10.5 Keep samples and standards at the same temperature during analysis.

11.0 CALCULATIONS.

$$\mu g\ F^-/\text{gram dried sample} = \frac{(\text{conc. of aliquot analyzed in } \mu g\ F^-/mL) \times (100\ mL) \times (\text{Sample dilution factor})}{\text{Weight of dried sample in grams}}$$

12.0 QUALITY ASSURANCE.

12.1 Precision of the method is measured by replicate aliquots of the same dried sample in two different crucibles that have been taken through the analysis.

12.1.1 The average of the relative deviation of all the replicates in an analysis should not be more than 15 percent for concentrations greater than 50 $\mu g\ F^-/g$ dried sample.

12.1.2 Relative deviation (R.D.) = $\bar{d} / \bar{c}$ $\quad \bar{d} = \frac{c_1 - c_2}{2}$

$$\bar{c} = \frac{c_1 + c_2}{2}$$

ci = individual value of the replicate concentration in µg F^-/gram dry weight.

$\bar{d}$ = average deviation of the two replicate concentrations in µg F^-/gram dry sample.

$\bar{c}$ = arithmetic average of the two replicate concentrations.

12.2 Precision of the ion electrode is determined by measuring the F^- concentration of duplicate aliquots from the same crucible filtrate.

12.2.1 The average of the relative deviation of all the duplicates in an analysis should not be more than five percent.

12.2.2 Relative deviation (R.D.) = $\bar{d} / \bar{c}$ $\quad \bar{d} = \frac{c_1 - c_2}{2}$

$\bar{d}$ = average deviation of the two duplicate concentrations in µg F^-/mL.

$\bar{c}$ = arithmetic average of the two duplicate concentrations. $\quad \bar{c} = \frac{c_1 + c^2}{2}$

c_i = individual value of the concentration in µg F^-/mL.

12.3 Determine the precision of the method and the precision of the electrode for every ten or less samples.

12.4 Recoverability of a sample is measured with spikes.

12.4.1 Spikes determine whether the fluoride ion is being complexed in the filtrate.

12.4.2 Prepare a spiked sample by adding a known quantity of a standard (the spike) to an aliquot of sample filtrate.

12.4.3 EXAMPLE: 5 mL of a 10 µg F^-/mL standard are added to 5 mL of a sample with a concentration of 8.6 µg F^-/mL. (The volume of the standard and sample should equal the volume of TISAB.) With the ion electrode, the concentration of the spiked sample was found to be 9.4 µg F^-/mL.

$$\text{Percent recovery} = \frac{\text{Conc (spike + sample)} - \text{Conc (sample)}}{\text{Conc (spike)}}$$

Conc (spike + sample) = 9.4 µg F^-/mL
Conc (sample) = 1/2 (8.6 µg F-/mL) = 4.3 µg F^-/mL
Conc (spike) = 1/2 (10 µg F^-/mL) = 5 µg F^-/mL

Notice that the concentration of the sample and standard used as a spike are half the original value because each was diluted with the other by half.

$$\text{Percent recovery} = \frac{9.4\ \mu g\ F^-/mL - 1/2\ (8.6\ \mu g\ F-/mL)}{1/2\ (10\ \mu g\ F^-ml)} \times 100 = 102\%$$

12.4.4 The percent recovery should be between 90-110%.

12.4.5 At least one spike should be run for every ten or less samples.

12.5 Accuracy of the method is determined by fluoride standards that are placed in crucibles and taken through the analysis.

12.5.1 Standards determine if any fluoride was complexed or lost during the fusion/extraction process.

12.5.2 Any stable fluoride compound such as NaF may be used as a standard.

12.5.3 An audit is a standard whose concentration is unknown to the analyst.

12.5.4 At least one audit should be run per analysis.

13.0 REFERENCES.

1. EPA Quality Assurance Handbook for Air Pollution Measurement Systems. Volume III - Stationary Source Specific Methods, Method 13B. Revision No. 0, January 4, 1982.

2. McQuaker, N.R., and Gurney, M., "Determination of Total Fluoride in Soil and Vegetation Using an Alkali Fusion-Selective Ion Electrode Technique," Anal Chem., 49, 53 (1977).

3. Orion Instruction Manual for Fluoride Electrodes Model 96-09, p. 27, 1977.

4. Elfers, L.A., and Decker, C.E., "Analysis of Fluoride in Air and Stack Gas Samples by Use of a Specific Ion Electrode," Anal Chem., 40 1658 (1968).

5. Thompson, R.J., McMullen, T.B., and Morgan, G.B., "Fluoride Concentrations in the Ambient Air," J. Air Poll. Control Assoc., 21, 8 (1971).

Modified June 25, 1979
Laboratory Division
Texas Air Control Board

DETERMINATION OF FORMALDEHYDE

Modification of West-Gaeke Technique

A. GENERAL

Formaldehyde is absorbed in a sodium tetrachloromercurate solution. A pinkish color is produced by the addition of reagents at a later time. The intensity of the developed color is a function of the moles of formaldehyde absorbed. The concentration is measured using a spectrophotometer or colorimeter capable or operation at a wavelength of 557 nm.

B. APPLICABILITY

The efficiency with which formaldehyde is absorbed is assumed to be 100%. The test has a lower limit of detection of less than 0.05 µg of formaldehyde per milliliter of absorbing solution. Assuming a concentration in solution of 0.1 µg of formaldehyde/ml of absorbing solution and a volume of air sampled of 60 liters, the concentration of formaldehyde on a gaseous volume basis would be about 10 parts per billion. Standards have been analyzed having concentration up to 0.32 µg of formaldehyde/ml of absorbing solution. Changes in pH of the sample will affect the consistency of the absorbance. The distilled water used in the analysis must be at high quality or color formation will be inhibited. High concentrations of sulfur dioxide will interfere with the analysis and so will nitrogen dioxide if present in 25-100 fold excess.[1] Leithe[1] states that acrolein will undergo the same reactions as formaldehyde, so this would be a positive interference if it is present. Concerning aldehydes higher than formaldehyde, Leithe[1] states that the interference is only slight for the three hour development period while Lyles[2], et al, makes no mention of high aldehyde reactions.

C. APPARATUS

Suitable sampling apparatus
Adequate and sufficient storage bottles
4 - 1000 ml volumetric flasks
1 - 250 ml volumetric flask
2 - 100 ml volumetric flasks
4 - 50 ml volumetric flasks
1 - 100 ml volumetric pipet
6 - 10 ml volumetric pipet
1 - 0.5 ml volumetric pipet
2 - 1 ml volumetric pipet
2 - 2 ml volumetric pipets
2 - 5 ml graduated pipets
1 - 50 ml graduated cylinder
Sufficient 50 ml test tubes and cuvettes for the number of standards

and samples being analyzed.
1 - Spectrophotometer capable of operating at 557 nm.

D. REAGENTS

All reagents should be ACS reagent grade.

(1) Absorbing Solution

NOTE!!! These absorbing solutions are different from the West-Gaeke SO_2 absorbing solutions. Do not substitute for SO_2 analysis.

(a) Stock Solution
Dissolve 16.3 grams of mercuric chloride and 7.3 grams of sodium chloride in 1 liter of distilled water.

(b) Working Solution
Using a 100 ml volumetric pipet, place 100 ml of the stock absorbing solution in a 1 liter volumetric flask and dilute to the mark with distilled water.

CAUTION!!! Mercury compounds are toxic and caution should be used when handling such compounds or solutions. Pipeting should be done only with a bulb and if the solutions are spilled on the skin, flush and wash thoroughly. When handling mercury solutions, use good personal hygiene and always wash before eating or smoking.

The mercury can be recovered by placing the used or unused absorbing solution in a covered polyethylene container along with shreds of aluminum plates or containers. The mercury will amalgamate with the aluminum and after a period of several weeks, the aqueous liquid can be decanted. Retain the aluminum-mercury sludge for reclamation.

(2) Sodium Sulfite
Place 0.25 grams of sodium sulfite in a 1 liter volumetric flask and dilute to the mark with distilled water. The sodium sulfite concentration will weaken with time. Prepare fresh before each analysis.

(3) Pararosaniline Hydrochloride Dye

NOTE!!! These solutions are significantly different from the dye solutions used for the West-Gaeke SO_2 analysis. Label them carefully and do not attempt any substitutions.

(a) Stock Solution
Place 0.2 grams of the dye in a 100 ml volumetric flask and dilute to the mark with distilled water. Permit the solutions to stand for three days and then filter.

(b) Working Solution

Place 42.5 ml of the concentrated dye solution in a 250 ml volumetric flask. Add 12.5 ml of concentrated hydrochloric acid.

Allow this mixture to stand for five minutes. Then dilute to the mark with distilled water. This working solution has performed well for up to three days in this laboratory. It should be relatively stable and should have a life of several weeks if kept refrigerated.

NOTE: This laboratory has obtained very satisfactory results using Allied Chemicals Basic Fuchsin Dye.

E. COLLECTION OF SAMPLE

The sample is collected using a known volume of the sodium tetrachloromecurate absorbing solution placed in a suitable impinger. Air flow rates should not exceed 2.0 - 2.5 liters/minute for one to two hour samples. For 24-hour samples, the flowrate should be approximately 200 milliliters/minute. Approximately 0.05 µg of aldehyde or formaldehyde per milliliter of absorbing solution must be collected for a reliable analysis.

F. TEST PROCEDURE

(1) Preparation of Standards

(a) Concentrated Stock Formaldehyde Solution

Place 1 ml of 40% formaldehyde in a 100 ml volumetric flask and dilute to the mark with distilled water.

(b) Dilute Stock Solution

Place 2 ml of the concentrated stock solution in a 1 liter volumetric flask and dilute to the mark with distilled water.

(c) Working Standards

Place 0.5 ml, 1.0 ml, 1.5 ml, and 2.0 ml respectively in separate 50 ml volumetric flasks. Dilute to the mark with the working absorber solution. Mix the prepared standards thoroughly. These standards contain 0.08, 0.16, 0.24, and 0.32 µg formaldehyde/ml. Prepare fresh working standards with each analysis.

(2) Preparation of Standard Curve

Using volumetric pipets, place 10 ml of the working absorber solution and 10 ml of each of the four working standards in five separate test tubes. To each add 1 ml of the sodium sulfite solution; mix thoroughly. Next, add 1 ml of the working pararosaniline solution to each test tube. Again, mix thoroughly. Set the test tubes aside and wait 2 1/2 to 3 hours for the color development to reach its maximum. Then read the absorbance at 557 nm on a suitable spectrophotometer, using the blank as reference. Plot absorbance versus concentration of formaldehyde in the working standards.

(3) Sample Analysis

If any of the absorber solution has evaporated during the sampling period, restore the sample to its original volume using working absorber solution. Mix thoroughly. Place 10 ml of working absorber solution in a test tube. Place 10 ml of each of the samples in separate test tubes. Add 1 ml of sodium sulfite and mix thoroughly. Next, add 1 ml of the working pararosaniline solution to each of the cuvettes. Mix thoroughly. Set the cuvettes aside for a 2 1/2 to 3 hour waiting period for color development. Read the absorbance of the samples using the working absorber blank to set the spectrophotometer for zero absorbance. Using the observed absorbance, determine the concentration of each sample from a standard curve.

G. CALCULATIONS

In order to determine concentration of the aldehyde in the volume of air sampled, determine the concentration of the sample in µg of aldehyde/ml of absorbing solution and substitute in the following formula:

$$\mu g \text{ aldehyde}/M^3 = \frac{(\mu g \text{ aldehyde/ml})(\text{total milliliters of absorbing solution used})}{M^3 \text{ of air sampled}}$$

H. QUALITY CONTROL

Duplicates should be run on 7% of the samples or at least one duplicate per batch of 15 or less. These will test the precision of the procedure. The relative deviation should be less than 5% if the absorbance reading is greater than 0.100.

$$R.D. = \frac{\bar{d}}{\bar{v}} \quad \text{where} \quad \bar{d} = |v_1 - v_2| \qquad v_i = \text{measured value } i$$

$$\bar{v} = \frac{v_1 + v_2}{2}$$

Spiked samples should be run to control the accuracy of the analysis. Spiked samples are prepared by adding a known quantity of a standard to an aliquot of sample. Percent recovery can be calculated from the concentrations of the spiked sample, the sample, and the standard.

$$\text{Percent recovery} = \frac{\text{conc (spike + sample)} - \text{conc (sample)}}{\text{conc (spike)}} \times 100$$

A spiked sample should be run with each set of samples. The percent recovery should be between 90-110%. If not, all steps of the analysis should be examined carefully and the analysis repeated.

A standard curve must be run with each set of samples.

I. REFERENCES

Leithe, W., The Analysis of Air Pollutants, Ann Ailuer-Humphrey Science Publishers, London, 1970.

Lyles, G. R., Dowling, F. B., and Blanchard, V. J. Quantitative Determination of Formaldehyde in Parts per Hundred Million Concentration Level, J. A. P. C. A. 15, 106, 1965.

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Laboratory Division
Texas Air Control Board

DETERMINATION OF HYDROGEN SULFIDE

Molybdenum Blue Method

A. GENERAL

Hydrogen sulfide (H_2S) is absorbed in alkaline cadmium sulfate ($3CdSO_4 \cdot 8H_2O$) or 2% zinc acetate solution [$Zn(C_2H_3O_2)_2$]. At a later time, a blue color is developed by the addition of reagents. The intensity of the blue color is a function of the sulfide concentration. The concentration is then measured using a spectrophotometer or colorimeter.

B. APPLICABILITY

The lower limit of detectability has been found to be approximately 0.02 µg/ml of H_2S in the absorbing reagent. If 20 ml of absorbing solution is used and approximately 60 liters of air is passed through the absorbing solution, the lower detectable limit will be approximately 0.01 ppm of H_2S by gaseous volume in ambient air assuming 100% collection efficiency, Jacobs, et. al., reports that the collection efficiency is at least 90% at 0.1 ft^3/min. (2.8 liters). Buck, et. al.,[3] report no significant interferences due to SO_2, CS_2, or ethyl mercaptan. This laboratory has found that SO_2, NO_2, CS_2, NH_3 and formaldehyde do not interfere with this method.

NOTE: This laboratory uses only alkaline cadmium sulfate for ambient and property line sampling. Loss of sulfide by oxidation occurs with zinc acetate and is significant at low sulfide levels. However, zinc acetate is recommended as an absorber for high levels of sulfide such as in stack sampling, since it absorbs H_2S more efficiently than does alkaline cadmium sulfate at high H_2S levels.

C. APPARATUS

Suitable sampling apparatus
Adequate and sufficient storage bottles
4 - 1000 ml volumetric flasks
1 - 200 ml volumetric flask
1 - 100 ml volumetric flask
1 - 1000 ml beaker
9 - 250 ml Erlenmeyer flasks or beakers
2 - 100 ml graduated cylinders
1 - magnetic stirrer
1 - 50 ml buret
1 - 50 ml pipet
2 - 25 ml pipets
8 - 10 ml pipets
1 - 5 ml pipet

1 - 4 ml pipet
2 - 5 ml pipets

Sufficient cuvettes for the number of standards and samples to be analyzed
1 - Spectrophotometer capable of operating at a wavelength of 570 nM.

D. REAGENTS

All reagents should be ACS reagent grade.

(1) Hydrochloric Acid, conc.

(2) Iodine, 0.1 N
Dissolve 12.691 grams of resublimed iodine in 25 ml of a solution containing 15 grams of potassium iodide. Stir until all the iodine is dissolved. Dilute to one liter with distilled or deionized water and store in a dark bottle.

(3) Sodium Thiosulfate, 0.1 N
Weigh 16.0 grams of anydrous sodium thiosulfate ($Na_2S_2O_3$) (or 25 grams of $Na_2S_2O_3 \cdot 5\ H_2O$) and dilute to one liter. Use this solution to standardize the iodine solution. Sodium thiosulfate is fairly unstable and should be standardized before each use.

(4) Potassium Dichromate, 0.100 N
Using an analytical balance, weigh accurately 4.9036 grams of oven-dried (110° C) $K_2Cr_2O_7$. Dissolve this in distilled water and dilute to one liter. This solution is 0.100 N and is stable.

(5) Potassium Iodide (KI)

(6) Starch Indicator Solution
Prepare by dissolving 2 grams of reagent grade soluble starch in 500 ml of boiling distilled water, and then filtering while the solution is still warm. Add a crystal or two of mercuric chloride to inhibit mold growth.

(7) Absorbing Reagent
Alkaline Cadmium Sulfate
Dissolve 0.6 grams of sodium hydroxide (NaOH) in approximately 100 ml of distilled water. Dissolve 8.60 grams of cadmium sulfate ($3CdSO_4 \cdot 8\ H_2O$) in a separate 100 ml aliquot of distilled water. Add the cadmium sulfate to the sodium hydroxide solution while mixing well. Dilute this suspension to two liters in a volumetric flask with distilled water. Before withdrawing any of this solution to be used in sampling, agitate the solution well in order to get the precipitate suspended in the solution.

CAUTION!!! Cadmium compounds are toxic. Do not pipet these solutions by mouth. In the event of spillage upon the skin, wash the areas thoroughly with warm soapy water.

Use good personal hygiene when working with any toxic materials.

The alkaline cadmium sulfate absorber and cadmium sulfide (formed when H_2S is absorbed) adhere to glass surfaces. All glassware which has been in contact with any of these should be rinsed with a little dilute acid before any other use.

(8) Ammonium Molybdate Solution
Dissolve 15.0 grams of ammonium molybdate [$(NH_4)_6Mo_7O_{24} \cdot 4\ H_2O$] in 50 ml of distilled water. A magnetic stirrer will help greatly. This solution must be prepared fresh daily. Preparation of this solution should be begun first because dissolution is very slow.

(9) Glacial Acetic Acid

(10) Sulfuric Acid, 12 N
To approximately 30 ml distilled water in a 100 ml volumetric flask; add cautiously, 33 ml reagent grade (35.9 N) sulfuric acid (H_2SO_4). Allow the mixture to cool, then dilute to the mark with distilled water.

(11) Sulfide Stock Solution
Prepare either one of the two sulfide stock solutions detailed below:

a. Hydrogen Sulfide Stock Standard
A lecture bottle of commercial H_2S is a convenient source of gas from which to prepare your standards. Into 125-150 ml of the appropriate absorbing reagent, bubble H_2S from the lecture bottle. Bubble at the rate of approximately one bubble per second for approximately one minute. This should produce a stock standard of adequate concentration.

b. Sodium Sulfide Stock
Dissolve 0.750 grams sodium sulfide nonadhydrate ($Na_2S \cdot 9\ H_2O$) in 200 ml of the appropriate absorbing reagent. Stir until the solution is complete. The concentration of $S^=$ ion in this solution should be approximately 500 µg $S^=$/ml.

NOTE: After preparation, stock sulfide solutions should be stored in a tightly stoppered glass container. These solutions are unstable and must be standardized each time before preparing the dilute standards.

E. COLLECTION OF SAMPLE

The H_2S is collected in a known volume of absorber (usually 20 ml for property-line sampling) using a suitable impinger and pumping arrangement. Do not bubble air through the solution at a rate in excess of 2.0-2.5 L/min. After collecting the sample, identify the sample adequately. Keep sample in dark.

The sampling lines should be made of FEP® Teflon or glass. Rubber or metal lines should be avoided.

F. TEST PROCEDURES

NOTE: For stack samples, see "Determination of Hydrogen Sulfide in Stack Gas".

(1) Standardization of 0.1 N Sodium Thiosulfate
Into each of three Erlenmeyer flasks or beakers, pipet 50 ml of 0.100 N $K_2Cr_2O_7$ using a 50 ml volumetric pipet. Add 8 ml of concentrated HCl to each flask. From this point, handle each flask individually through the titration. To the first flask, add 2 g KI, swirl to hasten dissolution. Titrate the liberated iodine at once with thiosulfate until the color begins to lighten. Add 2 ml starch solution and continue the titration. There is a blue to emerald green color change at the end point. Titrate the second and third samples of dichromate in the same way. Determine the blank by use of the same amount of KI and HCl in the same volume of water. Correct the volume of thiosulfate for any blank and calculate the normality of the thiosulfate solution.

(2) Standardization of 0.1 N Iodine
Into each of three Erlenmeyer flasks or three beakers, pipet accurately 20 ml of the iodine solution. Add about 30 ml of distilled water and 1 ml acetic acid. Titrate with the 0.1 N sodium thiosulfate solution until the yellow color of the solution is almost gone. Then, add 2 ml starch solution and continue the titration until the blue color just disappears. Titrate the second and third samples of the iodine solution in the same way. Calculate the normality of the iodine.

(3) Standardization of the Sulfide Stock Solution
Using a volumetric pipet, place 25 ml of the standardized 0.1 N iodine solution in a beaker or Erlenmeyer flask. Using another volumetric pipet, place 25 ml of the sulfide stock solution to be standardized in the same container. (Keep solutions in the dark until ready to titrate). Titrate the excess iodine with the standardized 0.1 N thiosulfate solution to the yellow color of dilute iodine. Then add 2 ml of the starch solution and continue the titration until the blue color just disappears. Calculate the concentration of the stock sulfide solution.

(4) Working Standard
Using the known concentration of the stock standard, immediately prepare a working standard. A dilution of 10 ml stock solution to 100 ml with absorber will usually give a working standard of 50-60 µg H_2S/ml.

(5) Dilute Standards
Immediately prepare the dilute standards from your working standard. Using volumetric pipets, add 0.5, 1, 2, 3, 4, and 5 ml of working standard into six separate 100 ml volumetric flasks.

Dilute to the mark with the appropriate absorbing reagent. These Solutions will contain approximately 0.25, 0.50, 1.0, 1.5, 2.0, 2.5 µg H_2S/ml. Calculate the exact concentrations.

NOTE: Immediately before withdrawing an aliquot from the standards, thoroughly agitate the solution to assure an even distribution of the precipitate. Use a magnetic stirrer if available. Solution stirring speed should produce a barely perceptible vortex.

(6) Standard Curve Preparation

Place 10 ml of the absorbing reagent in a 1" test tube. In addition, place 10 ml of each standard in separate 1" test tubes. To each add 3 ml of the ammonium molybdate solution and 1 ml of 12 N sulfuric acid, thoroughly agitating the solution after each addition. Wait 30 minutes and read the absorbance at 570 nm. Plot a curve of absorbance versus µg H_2S/ml of absorbing solution. The resulting "curve" is easily reproduced. If a blue precipitate forms in the developed solution, new $Na_2S \cdot 9H_2O$ may be needed.

(7) Sample Analysis

Place 10 ml of the absorbing reagent in a 1" test tube. Prepare a reagent blank and a set of standards, using the same absorber. Proceed with the analysis as described under "Standard Curve Preparation". Determine the concentration of H_2S from the calibration curve. If the samples are taken from a high H_2S source, it is good practice to prepare a blank using twice the quantities of reagents specified above. If the absorbance of the developed sample is over 0.7, take an aliquot, and dilute to 14 ml with developed blank. Read the absorbance and calculate the H_2S concentration.

G. CALCULATIONS

(1) Standardization of 0.1 N Sodium Thiosulfate

$$\text{Normality } Na_2S_2O_3 = \frac{(\text{Normality } K_2Cr_2O_7)\ (\text{Volume } K_2Cr_2O_7)}{(\text{Volume } Na_2S_2O_3)}$$

$$= \frac{(0.100\ \text{N})\ (50\ \text{ml})}{\text{Volume } Na_2S_2O_3 \text{ in ml}}$$

(2) Standardization of 0.1 N Iodine

$$\text{Normality } I_2 = \frac{(\text{Normality } Na_2S_2O_3)(\text{Volume } Na_2S_2O_3)}{\text{Volume } I_2}$$

$$= \frac{(\text{Normality } Na_2S_2O_3)(\text{Volume } Na_2S_2O_3 \text{ in ml})}{20 \text{ ml}}$$

(3) Standardization of Sulfide Stock Solution

$$\text{Grams } H_2S/\text{ml of stock} = \frac{(\text{N } I_2 \times \text{Volume } I_2) - (\text{N } Na_2S_2O_3 \times \text{Volume } Na_2S_2O_3)}{58.82 \times \text{Volume } S^= \text{ stock aliquot}}$$

where:

(a) (N of I_2 x volume I_2) - (N of $Na_2S_2O_3$ x volume $Na_2S_2O_3$ used) = Meq I_2 used by stock $S^=$ solution.

(b) Meq I_2 used by stock $S^=$ solution $\times \frac{16 \text{ g/eq}}{1000 \text{ meq/eq}}$ = g $S^=$ in the aliquot

(c) $\frac{\text{grams } S^= \text{ in the aliquot}}{\text{vol. stock } S^= \text{ aliquot used in ml}} \times \frac{34 \text{ g/mole}}{32 \text{ g/mole}}$ = grams H_2S/ml of stock $S^=$ solution

(4) Total H_2S in Sample

$$\text{g } H_2S/M^3 = \frac{(\text{g } H_2S/\text{ml})(\text{Volume of absorber in ml})}{M^3 \text{ of air sampled}} \times \frac{14 \text{ ml}}{\text{ml aliquot of developed sample}}$$

H. QUALITY CONTROL

All titrations should be run in triplicate. The sodium thiosulfate, iodine, and stock sulfide should be standardized before each use. The relative deviation in the volume of titrant used should be less than 5 parts per thousand (5 °/oo). The relative deviation is calculated as follows:

$$\text{R.D.} = \frac{\bar{d}}{\bar{v}} \qquad \bar{d} = \Sigma \frac{|v_i - \bar{v}|}{N}$$

where: $\bar{d}$ = average deviation

$\bar{v}$ = arithmetic average of all individual volumes

v_i = individual measurement

N = number of measurements

for example:

Three titration volumes, v_i, were found to be 49.80 ml, 49.91 ml, 49.89 ml for the standardization of $Na_2S_2O_3$.

49.80 + 49.91 + 49.89 = 149.60 $\qquad \bar{v}$ = 49.87

$|v_1 - \bar{v}| = |49.80 - 49.87| = 0.07 \quad \Sigma|v_i - \bar{v}| = 0.13$

$|v_2 - \bar{v}| = |49.91 - 49.87| = 0.04 \quad \bar{d} = \frac{0.13}{3} = 0.04$

$|v_3 - \bar{v}| = |49.89 - 49.87| = 0.02$

$$R.D. = \frac{0.04}{49.87} = 0.8\ ^{o}/oo$$

therefore, the three titrations are acceptable.

Another example:

19.40, 19.39, 19.40 $\quad \bar{v} = 19.40 \quad \bar{d} = 0.003$

$$R.D. = \frac{0.003}{19.40} = 0.2\ ^{o}/oo$$

therefore, the titration is acceptable.

Duplicate analyses of 7 percent of the samples should be run to test the precision of the procedure. The relative deviation should be less than 5% if the absorbance reading is greater than 0.100.

$$R.D. = \frac{\bar{d}}{\bar{v}} \quad \text{where } \bar{d} = |v_1 - v_2| \quad \bar{v} = \frac{v_1 + v_2}{2}$$

Spiked samples should be run to control the accuracy of the analysis. Spiked samples are prepared by adding a known quantity of a standard to an aliquot of sample. Percent recovery can be calculated from the concentrations of the spiked sample, the sample, and the standard.

A suitable spike would be prepared as follows: Place a 4.0 ml aliquot of the 2.5 µg/ml dilute standard in a test tube. Add 6.0 ml of sample to the test tube. Add 3 ml of ammonium molybdate solution and 1 ml of 12 N sulfuric acid, thoroughly agitating the solution after each addition. Wait 30 minutes and read the absorbance at 570 nm.

$$\text{Percent recovery} = \frac{\text{conc (spike + sample)} - \text{conc (sample)}}{\text{conc (spike)}} \times 100$$

For example,

A sample had a concentration of 0.75 µg H_2S/ml. The spike of the same sample had a measured concentration of 1.43 µg/ml. The spike was prepared as above. The calculated concentration of the spike was 1.00 µg H_2S/ml.

$$\text{Percent recovery} = \frac{(1.43\ \mu g/ml) - (0.75\ \mu g/ml)\ (6/10)}{1.0\ \mu g/ml} \times 100 =$$

$$\frac{(1.43\ \mu g/ml) - (.45\ \mu g/ml)}{1.0\ \mu g/ml} \times 100 = 98\%$$

A spiked sample should be run with each set of samples. The percent recovery should be between 90% - 110%. If not, all steps of the analysis should be examined carefully and the analysis repeated.

A standard curve must be run with each set of samples.

I. REFERENCES

(1) Jacobs, M.D., M.M. Braverman and S. Hochheiser, "Ultramicro-determination of Sulfides in Air", Anal. Chem. 29: 1349 (September, 1957).

(2) Sands, A. E., Grafius, M. A., Wainwright, H. W., Wilson, M. W., "The Determination of Low Concentrations of Hydrogen Sulfide in Gas by the Methylene Blue Method", United States Department of the Interior, Bureau of Mines Report of Investigations, R. I. 4547, (September, 1949).

(3) Buck, M. and H. Stratmann, "Bestimmung von Schwefelwasserstoff in der Atmosphare", Staub 24: 241, (July, 1964).

Modified May 21, 1979
Laboratory Division
Texas Air Control Board

DETERMINATION OF HYDROGEN SULFIDE IN STACK GAS

A. GENERAL

Hydrogen sulfide (H_2S) is absorbed in a zinc acetate [$Zn(C_2H_3O_2)_2$] absorber. The sulfide in the absorber is measured by titration of excess iodine with standard thiosulfate using a starch indicator.

B. APPLICABILITY

The lower limit of detectability has been found to be 0.1 mg/ml of H_2S in the absorbing reagent. If levels lower than this are desired, then the molybdenum blue method should be used. Zinc acetate is recommended as the absorber for high levels of sulfide such as in stack sampling, since it absorbs H_2S more efficiently than does alkaline cadmium sulfate at high H_2S levels. Loss of sulfide by oxidation occurs with zinc acetate but is significant only at low sulfide levels. Therefore, alkaline cadmium sulfate is used for ambient and property line sampling. (See Determination of Hydrogen Sulfide - Molybdenum Blue Method.)

C. APPARATUS

Suitable sampling apparatus
Adequate and sufficient storage bottles
4-1000 ml volumetric flasks
1-1000 ml beaker
9-250 ml Erlenmeyer flasks or 250 ml beakers
1-50 ml pipet
2-25 ml pipets
1-50 ml buret

D. REAGENTS

All reagents should be ACS reagent grade.

(1) Iodine, 0.1 N
Dissolve 12.7 grams of resublimed iodine in 25 ml of a solution containing 15 grams of potassium iodide. Stir until all the iodine is dissolved. Dilute to one liter with distilled or deionized water. Store in a dark bottle.

(2) Sodium Thiosulfate, 0.1 N
Weigh 16.0 grams of anhydrous sodium thiosulfate ($Na_2S_2O_3$) (25g $Na_2S_2O_3 \cdot 5\ H_2O$) and 1g Na_2CO_3 and dilute to one liter. Use this solution to standardize the iodine solution. Sodium thiosulfate is fairly unstable and should be standardized before each use.

(3) Potassium Dichromate 0.100 N
Using an analytical balance, accurately weigh out 4.9036 grams of oven-dried $K_2Cr_2O_7$. Dissolve this in distilled or deionized water in a 1000 ml volumetric flask and dilute to the mark with distilled or deionized water. This solution is 0.100 N and is stable.

(4) Starch Indicator Solution
Dissolve 2 grams of reagent grade soluble starch in 500 ml of boiling distilled water. Then filter while the solution is still warm and add a crystal or two of mercuric chloride to inhibit mold growth.

(5) Absorbing Reagent - Zinc Acetate, 2%*
Dissolve 20 grams zinc acetate [$Zn(C_2H_3O_2)_2$] in approximately 100 ml of deionized or distilled water and dilute to 1 liter. A precipitate will form. Before withdrawing any of this solution, agitate the solution well in order to get the precipitate suspended so that a representative aliquot will be obtained.

*Zinc sulfide (formed when H_2S is absorbed) adheres to glass surfaces. All glassware which has been in contact with this should be rinsed with a little dilute acid before any other use.

(6) Sodium Sulfide Stock
Dissolve 0.750 grams sodium nonahydrate ($Na_2S \cdot 9\ H_2O$) in 200 ml of zinc acetate absorber. Stir until solution is complete. The concentration of $S^=$ ion in this solution is approximately 500 µg $S^=$/ml.

E. COLLECTION OF SAMPLE

Samples should be collected according to accepted stack sampling procedures. The sampling lines should be made of FEP® Teflon or glass. Rubber or metal lines should be avoided.

F. TEST PROCEDURE

(1) Standardization of 0.1 N Sodium Thiosulfate
Into each of three Erlenmeyer flasks or beakers pipet 50 ml of 0.100 N $K_2Cr_2O_7$ using a 50 ml volumetric pipet. Add 8 ml of concentrated HCl to each flask. From this point, handle each flask individually through the titration. To the first flask add 2 g KI, swirl to hasten dissolution. Titrate the liberated iodine at once with thiosulfate until the color begins to lighten. Add 2 ml starch solution and continue the titration. There is a blue to emerald green

color change at the end point. Titrate the second and third samples of thiosulfate the same way. Determine the blank by use of the same amount of KI and HCl in the same volume of water. Correct the volume of thiosulfate for any blank and calculate the normality of the thiosulfate solution.

(2) Standardization of 0.1 N Iodine

Into each of three Erlenmeyer flasks or three beakers, pipet accurately 20 ml of the iodine solution. Add about 30 ml of distilled water and 1 ml acetic acid. Titrate with 0.1 N sodium thiosulfate solution until the yellow color of the solution is almost gone. Then add 2 ml starch solution and continue the titration until the blue color just disappears. Titrate the second and third samples of the iodine solution in the same way. Calculate the normality of the iodine.

(3) Standardization of the Sulfide Stock Solution

Using a volumetric pipet, place 25 ml of the standardized 0.1 N iodine solution in a beaker or Erlenmeyer flask. Using another volumetric pipet, place 25 ml of the stock sulfide solution in the same container. (Keep solutions in the dark until ready to titrate). Titrate the excess iodine with the standardized 0.1 N thiosulfate solution to the yellow color of dilute iodine. Then add 2 ml of the starch solution and continue the titration until the blue color just disappears. Do in triplicate.

(4) Sample Analysis

Using a graduated cylinder, measure the volume of each sample. Using a volumetric pipet, place 25 ml of the standardized 0.1 N iodine solution in a beaker or Erlenmeyer flask. Using another volumetric pipet, place a 25 ml aliquot of the sample in the same container. (Keep solutions in the dark until ready to titrate). Titrate the excess iodine with the standardized 0.1 N thiosulfate solution to the yellow color of dilute iodine. Then add 2 ml of the starch solution and continue the titration until the blue color just disappears.

NOTE: For low concentrations the Molybdenum Blue Method should be used.

G. QUALITY CONTROL

All titrations should be run in triplicate. The sodium thiosulfate, iodine, and stock sulfide should be standardized before each use. The relative deviation in the volume of titrant used should be less than 5 parts per thousand (5 °/oo). The relative deviation is calculated as follows:

$$R.D. = \frac{\bar{d}}{\bar{v}} \qquad \bar{d} = \frac{\Sigma |v_i - \bar{v}|}{N}$$

where $\bar{d}$ = average deviation

$\bar{v}$ = arithmetic average of all individual volumes

v_i = individual measurement

N = number of measurements

For example:

Three titration volumes, v_i, were found to be 49.80 ml, 49.91 ml, 49.89 ml for the standardization of $Na_2S_2O_3$.

$49.80 + 49.91 + 49.89 = 149.60 \qquad \bar{v} = 49.87$

$|v_1 - \bar{v}| = |49.80 - 49.87| \qquad \Sigma|v_i - \bar{v}| = 0.13$

$|v_2 - \bar{v}| = |49.91 - 49.87|$

$|v_3 - \bar{v}| = |49.89 - 49.87| \qquad \bar{d} = \frac{0.13}{3} = 0.04$

$$\text{R.D.} = \frac{0.04}{49.87} = 0.8\ ^{o}/oo$$

therefore the three titrations are acceptable.

Another example:

19.40, 19.39, 19.40 $\qquad \bar{v} = 19.40 \qquad \bar{d} = 0.003$

$$\text{R.D.} = \frac{0.003}{19.40} = 0.2\ ^{o}/oo$$

therefore the titration is acceptable.

Spiked samples should be run to control the accuracy of the analysis. Spiked samples are prepared by adding a known quantity of a standard to an aliquot of sample. Percent recovery can be calculated from the concentrations of the spiked sample, the sample, and the standard.

A suitable spike would be prepared as follows: Using a volumetric pipet, place 25 ml of the standardized 0.1 N iodine solution in a beaker or Erlenmeyer flask. Using volumetric pipets, place 10 ml of stock sulfide solution and 15 ml of sample in the same container (Keep solutions in the dark until ready to titrate). Titrate the excess iodine with the standardized 0.1 N thiosulfate solution to the yellow color of dilute iodine. Then add 2 ml of the starch solution and continue the titration until the blue color just disappears.

$$\text{Percent recovery} = \frac{\text{conc (spike + sample)} - \text{conc (sample)}}{\text{conc (spike)}} \times 100$$

For example:

A sample took 10.00, 10.05, 9.95 ml thiosulfate to titrate. The spike of the same sample took 12.92 ml, 12.87 ml, 12.85 ml thiosulfate. The normality of the I_2 solution was 0.0988 N; the thiosulfate was 0.1003 N.

The spike was prepared as above. The concentration of the stock sulfide was 500.0 µg $S^{=}$/ml

$$\text{conc (spike + sample)} = \frac{(0.09888 \times 25\ \text{ml}) - (0.1003 \times 12.88\ \text{ml})}{(58.82)\ (25\ \text{ml})} =$$

$$\frac{2.472 - 1.292}{(58.82)\ (25)} = 0.0008024\ \text{g/ml} \qquad 802.4\ \mu\text{g } H_2S\text{/ml}$$

$$\text{conc (sample)} = \frac{(0.09888 \times 25\ \text{ml}) - (0.1003 \times 10.00\ \text{ml})}{(58.82)\ (25\ \text{ml})} = \frac{1.469}{(58.82)\ (25)} =$$

999.0 µg H_2S/ml

$$\text{conc spike} = \frac{500\ \mu\text{g } S^{=}\text{/ml} \times 10\ \text{ml} \times 34\ \text{g } H_2S\text{/mole}}{25\ \text{ml} \qquad\qquad 32\ \text{g } S^{=}\text{/mole}} = 212.5\ \mu\text{g } H_2S\text{/ml}$$

$$\%\ R = \frac{(802.4\ \mu\text{g/ml}) - 999.0\ (\frac{15}{25})}{212.5\ \mu\text{g/ml}} = \frac{802.4 - 599.4}{212.5\ \mu\text{g/ml}}$$

$$\%\ R = \frac{203\ \mu\text{g/ml}}{212.5\ \mu\text{g/ml}} = 1.015 \times 100 - 96\%$$

A spiked sample should be run with each set of samples. The percent recovery should be between 90%-110%. If not, all steps of the analysis should be examined carefully and the analysis repeated.

H. CALCULATIONS

(1) Standardization of 0.1 N Sodium Thiosulfate

$$\text{Normality of } Na_2S_2O_3 = \frac{(\text{Normality of } K_2Cr_2O_7 \text{ solution})(\text{Volume } K_2Cr_2O_7)}{\text{Volume } Na_2S_2O_3} =$$

$$\frac{(0.100\ \text{N})(50\ \text{ml})}{\text{volume } Na_2S_2O_3 \text{ in ml}}$$

(2) Standardization of 0.1 N Iodine

$$\text{Normality of } I_2 = \frac{(\text{Normality } Na_2S_2O_3)(\text{Volume } Na_2S_2O_3)}{\text{volume } I_2} =$$

$$\frac{(\text{Normality } Na_2S_2O_3)(\text{Volume } Na_2S_2O_3 \text{ in ml})}{20\ \text{ml}}$$

(3) Standardization of Sulfide Stock Solution

$$g\ H_2S/ml\ of\ stock = \frac{(N\ I_2 \times volume\ I_2) - (N\ Na_2S_2O_3 \times volume\ Na_2S_2O_3)}{58.82 \times volume\ stock\ S^{=}\ aliquot}$$

where

a) ($\underline{N}$ of I_2 x volume I_2) - ($\underline{N}$ of $Na_2S_2O_3$ x volume $Na_2S_2O_3$ used) = Meq I_2 used by stock $S^{=}$ solution

b) Meq I_2 used by stock $S^{=}$ solution x $\frac{16\ g/eq}{1000\ meq/eq}$ = g $S^{=}$ in the aliquot

c) $\frac{\text{grams } S^{=} \text{ in the aliquot}}{\text{volume stock } S^{=} \text{ used in ml}} \times \frac{34\ g\ H_2S/mole}{32\ g\ S^{=}/mole}$ = grams H_2S/ml of stock $S^{=}$ solution

All volumes are in milliliters

(4) Sample Concentration

$$g\ H_2S/ml = \frac{(N\ I_2 \times ml\ I_2) - (N\ Na_2S_2O_3 \times ml\ Na_2S_2O_3)}{(58.82) \times (sample\ aliquot\ volume\ in\ ml)}$$

where

a) ($\underline{N}$ I_2 x ml I_2) - ($\underline{N}$ $Na_2S_2O_3$ x ml $Na_2S_2O_3$) = Meq I_2 used by sample aliquot

b) Meq I_2 used by sample aliquot x $\frac{16\ g/eq}{1000\ meq/eq}$ = g $S^{=}$ in the aliquot

c) $\frac{\text{grams } S^{=} \text{ in the aliquot}}{\text{sample aliquot volume in ml}} \times \frac{34\ g\ H_2S/mole}{32\ g\ S^{=}/mole}$

g H_2S/ml in sample aliquot

$$g\ H_2S/M^3 = \frac{g\ H_2S/ml \times volume\ of\ absorber\ in\ ml}{M^3\ of\ air\ sampled}$$

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Laboratory Division
Texas Air Control Board

DETERMINATION OF NITRATE

Reduction-Diazotization Method

A. GENERAL

Nitrate (NO_3^-) is extracted from a Hi Vol filter by reluxing with water. The extracted nitrate is subsequently reduced to nitrite and treated with diazotizing reagents. This results in the formation of a colored compound the concentration of which is measured using a spectrophotometer.

B. APPLICABILITY

The range of analysis for a 24-hour Hi Vol sample is from 0.02 $\mu g/M^3$ to 1.0 $\mu g/M^3$. The filter collection efficiency is assumed to be greater than 99%. Because some instability had been noted, several tests varying heating, reagent concentration, reaction time, etc., were conducted. Heating the solutions at different temperatures and/or different lengths of time made no improvement. When the samples were allowed to stand for thirty minutes at room temperature, the results were reproducible and stable. Reducing the amount of the acetone-water mixture added to stop the reaction also increased stability. An average percent recovery in tests in this laboratory of 95% has been achieved without heating the final solution.

C. APPARATUS

Suitable sampling apparatus
Adequate and sufficient storage bottles
125 ml Erlenmeyer flasks with standard taper joints, matching air condensers, filtering funnels, and test tubes sufficient for the number of samples to be analyzed
Whatman #41 filter paper
4 - 1000 ml volumetric flasks
2 - 500 ml volumetric flasks
2 - 250 ml volumetric flasks
6 - 100 ml volumetric flasks
6 - 50 ml volumetric flasks
1 - 50 ml pipet
1 - 25 ml pipet
8 - 10 ml pipets
2 - 8 ml pipets
1 - 6 ml pipet
1 - 4 ml pipet
1 - 3 ml pipet
3 - 2 ml pipets
5 - 1 ml pipets
1 - 10 mm cuvette
1 - Spectrophotometer capable of operating at 540 nm

D. REAGENTS

(1) Stock Copper Reagent
Dissolve 1.25 g of $CuSO_4 \cdot 5H_2O$ in deionized water in a 500 ml volumetric flask and dilute to the mark with deionized water.

(2) Working Copper Reagent
Place 10 ml of stock copper reagent in a 1000 ml volumetric flask and dilute to the mark with deionized water.

(3) Stock Hydrazine Sulfate Reagent
Dissolve 10.4 g of hydrazine sulfate in deionized water in a 500 ml volumetric flask and dilute to the mark with deionized water.

(4) Working Hydrazine Sulfate Reagent
Place 50 ml of stock hydrazine sulfate reagent in a 1000 ml volumetric flask and dilute to the mark with deionized water.

(5) Sodium Hydroxide (0.3 N)
Dissolve 12 g of NaOH pellets in deionized water and dilute to 1 liter.

(6) Acetone: Water Mixture
Place 25 ml of acetone in a 250 ml volumetric flask and dilute to the mark with deionized water.

(7) Sulfanilamide Reagent
Dissolve 5 g of sulfanilamide in 95 ml of 85% phosphoric acid (the commercial strength). Rinse into a 250 ml volumetric flask and dilute to the mark with deionized water.

(8) NEDA Reagent (NEDA: N-(1-Naphthyl)-ethylenediamine dihydrochloride)
Dissolve 0.1 g of NEDA in deionized water and dilute to 100 ml in a volumetric flask. Prepare fresh daily.

(9) Stock Nitrate Solution
Accurately weigh out 0.1630 g of KNO_3. Place in a 1000 ml volumetric flask, dissolve and then dilute to the mark with deionized water. This solution contains 100 µg NO_3^-/ml.

E. COLLECTION OF SAMPLE

The sample is collected using a high volume air sampler and an 8" x 10" filter. Air is drawn through the filter at 60 ft^3/min.

F. TEST PROCEDURE

(1) Working Standard

Dilute 10 ml of stock nitrate solution to 100 ml in a volumetric flask with deionized water. This solution is stable for only 24 hours and must be prepared daily. It contains 10 µg NO_3^-/ml.

(2) Standards

Pipet 0, 2, 4, 6, 8, and 10 ml of working nitrate solution into 100 ml volumetric flasks and dilute to the mark with deionized water. These solutions contain 0, 0.2, 0.4, 0.6, 0.8, and 1.0 µg NO_3^-/ml respectively.

(3) Sample Analysis

Cut a 1" x 8" strip from the filter. Cut the strip into small pieces and place in a 125 ml flask equipped with an air condenser. Add 50 ml distilled or deionized water and reflux gently six to eight hours. Filter the resulting extract into a flask. Do not bring back to volume. Pipet a 2 ml aliquot of each extract into a test tube. Pipet 8 ml of distilled or deionized water into each test tube to give a total volume of 10 ml. For sampling periods less than 24 hours, the aliquot size can be increased but the total volume of extract plus water must be 10 ml. In addition, pipet 10 ml of each standard into a set of test tubes. To each test tube of standard or sample add 1.0 ml of working copper reagent. Mix. Add 1.0 ml of 0.3 N NaOH. Mix. Add 1.0 ml of hydrazine reagent. Mix. Wait 30 minutes. Add 1.0 ml of acetone-water mixture to each test tube. Mix. This stops the reduction reaction. Add 1.0 ml of sulfanilamide solution to each test tube. Mix. Add 1.0 ml of NEDA reagent to each test tube. Mix. Let stand for 10 minutes and measure against a blank at 540 nm. Using the absorbance values of the standards, construct a calibration curve. From the standard curve, determine the µg NO_3^-/ml in each of the samples.

G. QUALITY CONTROL

Duplicates should be run on 7% of the samples or at least one duplicate per batch of 15 or less. These will test the precision of the procedure. The relative deviation should be less than 5% if the absorbance reading is greater than 0.100.

$$R.D. = \frac{\bar{d}}{\bar{v}} \qquad \text{where } \bar{d} = |v_1 - v_2| \qquad v_i = \text{measured value } i$$

$$\bar{v} = \frac{v_1 + v_2}{2}$$

Spiked samples should be run to control the accuracy of the analysis. Spiked samples are prepared by adding a known quantity of a standard to an aliquot of sample. Percent recovery can be calculated from the concentrations of the spiked sample, the sample, and the standard.

$$\text{Percent Recovery} = \frac{\text{conc(spike + sample)} - \text{conc(sample)}}{\text{conc(spike)}} \times 100$$

A suitable spike would be prepared as follows: Place 2 ml of the 1.0 µg NO_3^-/ml standard into a test tube. Add a 2 ml aliquot of sample extract. Pipet 6 ml of distilled or deionized water into the test tube to give a total volume of 10 ml. Add 1.0 ml of working copper reagent. Mix. Add 1.0 ml of 0.3 N NaOH. Mix. Add 1.0 ml of hydrazine reagent. Mix. Wait 30 minutes. Add 1.0 ml of acetone-water mixture to each test tube. Mix. Add 1.0 ml sulfanilamide solution. Mix. Add 1.0 ml of NEDA reagent. Mix. Let stand for 10 minutes and measure against the blank at 540 nm.

A spiked sample should be run with each set of samples. The percent recovery should be between 90-110%. If not, all steps of the analysis should be examined carefully and the analysis repeated.

A standard curve must be run with each set of samples.

H. CALCULATIONS

$$\mu g\ NO_3^-/M^3 = \frac{(\mu g\ NO_3^-/ml)\ (ml\ analyzed)^*\ (total\ ml\ extract)\ (total\ area\ of\ filter)}{(ml\ aliquot)\ (area\ of\ filter\ analyzed)\ (volume\ of\ air\ sampled\ in\ M^3)}$$

*ml analyzed = ml aliquot + deionized water added to test tube = 10 ml in above method (ml aliquot, usually 2 ml as noted above)

I. REFERENCES

Water Research, 1 (1967), pp. 205-216

Modified October 22, 1979
Laboratory Division
Texas Air Control Board

DETERMINATION OF NITROGEN DIOXIDE

Modification of the Christie Technique

A. GENERAL

Nitrogen dioxide (NO_2) is absorbed in a sodium hydroxide/sodium arsenite solution which forms sodium nitrite. The concentration of nitrite ion is measured colorimetrically by the addition of a phosphoric acid/ sulfanilamide solution, and NEDA. The intensity of the color is proportional to the concentration of the nitrite ion present.

B. APPLICABILITY

The lower limit of detection has been found to be approximately 0.01 µg NO_2^-/ml. This corresponds to approximately 2 µg/M^3 for a 24-hour ambient sample, and to about 6 µg/M^3 for a 30-minute property line sample at a flow of 1 L/min. This method requires no fritted impinger for flows up to 200 cc/min., but for a higher flowrate, a fritted tip is suggested.

The absorbing solution used in this method is more alkaline than the original Christie method. This was found to be necessary to obtain high sampling efficiency at the end of 24 hours sampling. Sampling efficiency is essentially 100% for ambient sampling.

Nitric oxide (NO) does not appear to interfere to any significant extent. SO_2 interferes slightly, 100 µg/M^3 SO_2 gives a negative response equivalent to 2-3 µg/M^3 NO_2.

This method does not need to include the Saltzman factor of 0.72 as do the Jacobs-Hochheiser and Saltzman methods. Instead there is a "Christie Factor" or an analytical efficiency factor of 0.8 needed in the calculation to obtain the correct amount of nitrogen dioxide gas that actually passed through the absorbing solution.

C. APPARATUS

Suitable sampling apparatus
Adequate and sufficient storage bottles
2- 1,000 ml volumetric flasks
4- 100 ml volumetric flasks
6- 50 ml volumetric flasks
7- 10 ml volumetric pipets
1- 5 ml volumetric pipet
1- 4 ml volumetric pipet
1- 3 ml volumetric pipet
1- 2 ml volumetric pipet
4- 1 ml volumetric pipets
Sufficient test tubes and pipets for the number of analyses
Cuvettes for reading absorbance in the spectrophotometer

Spectrophotometer (capable of operating at 540 nm)

D. REAGENTS

All reagents should be ACS reagent grade.

(1) Absorbing Solution
Add 20 grams of sodium hydroxide (NaOH) to a 1,000 ml volumetric flask. Add 1 gram of sodium arsenite ($NaAsO_2$) and dilute to the mark with distilled water.

This solution is highly toxic and should be washed off if spilled on the skin.

NOTE: This solution is more alkaline than the standard Christie absorber.

(2) Phosphoric Acid/Sulfanilamide Solution
Place 4.0 grams sulfanilamide in approximately 100 ml of distilled water in a 200 ml volumetric flask. Add 75 ml of 85% phosphoric acid, mix, and make up to the mark with distilled water.

NOTE: This solution is used to neutralize the sample instead of HCl because it gives better recovery of absorbed nitrite and surer results.

(3) NEDA: (0.1%)
Dilute 0.10 gram of n-(1-Naphthyl)-ethylenediamine dihydrochloride to 100 ml with distilled water in a volumetric flask. This solution should be prepared fresh daily.

(4) Stock Standard Nitrite Solution
Accurately weigh out 0.1500 gram $NaNO_2$ and dilute to 1,000 ml in a volumetric flask with distilled water. This stock solution contains 100 µg NO_2^-/ml.

E. COLLECTION OF SAMPLE

The sample is collected in a known volume of absorbing solution (50 ml for ambient bubblers and 15 - 25 ml for property line samples) and at a known flowrate (0.2 L/min. for bubblers and 1.0 L/min. for property line samples). Ambient bubbler samples require no fritted impingers, but higher flows do. All sample lines should be glass if possible, as NO_2 will diffuse through Teflon^R and polyethylene. Metal lines are not acceptable.

F. TEST PROCEDURE

(1) Preparation of Standards
Dilute 10 ml of the stock nitrite standard solution to 100 ml in a volumetric flask with distilled water. This intermediate standard solution now contains 10 µg NO_2^-/ml. Pipet 0, 2, 4, 6, 8, and 10 ml of the intermediate standard solution into separate 100 ml volumetric flasks and dilute with absorbing solution. These working standards now contain 0, 0.2, 0.4, 0.6, 0.8, and 1.0 µg NO_2^-/ml respectively.

(2) Preparation of a Standard Curve

Using volumetric pipets, place 10 ml of each of the working standards into separate test tubes. Add 2 ml of phosphoric acid/sulfanilamide solution. Swirl to mix; and add 1 ml of the NEDA solution, swirl. Wait ten minutes for full color development. (If automatic shaker is available, shake samples for full ten minutes.) Read the absorbance of each standard against the blank at 540 nm. Plot a curve of absorbance vs. concentration of the final standards.

(3) Sample Analysis

If any of the absorbing solution has evaporated during the sampling period, restore it to its original volume with distilled water and mix. Place 10 ml of the sample in a test tube. Add 2 ml of phosphoric acid/sulfanilamide solution. Swirl to mix. Add 1 ml of the 0.1% NEDA solution, swirl. Wait ten minutes for full color development. (If possible, shake samples for full ten minutes.) Read the absorbance of the sample against the blank at 540 nm. From the absorbance, determine the concentration of NO_2^- ion. If the absorbance is greater than 0.8, it is advisable to dilute an aliquot of sample with blank of the same age and read the absorbance for the diluted sample vs. the remaining blank.

G. CALCULATIONS

$$NO_2\ \mu g/M^3 = \frac{\mu g\ NO_2^-/ml \times \text{volume of absorber in ml}}{0.8 \times M^3 \text{ air sampled}} \times \frac{13\ ml}{\text{volume aliquot}}$$

If no dilution was made, drop the last term from the calculation.

H. QUALITY CONTROL

Duplicates should be run on 7% of the samples or at least one duplicate per batch of 15 or less. Replicates test the precision of the procedure. The relative deviation should be less than 5% for absorbance readings above 0.100.

$$\text{Relative Deviation (R.D.)} = \frac{\bar{d}}{\bar{v}} \times 100 \qquad \bar{d} = \frac{|v_1 - v_2|}{2}$$

where $\bar{d}$ = average deviation

$\bar{v}$ = arithmetic average of all individual measurements

v_i = individual measurement

For example, duplicates of a sample read 0.205 and 0.217.

$$R.D. = \frac{0.006}{0.211} \times 100 = 3\%$$

If duplicates exceed 5% all steps in the procedure should be reviewed.

NOTE: It is possible to have very good precision and have poor accuracy from interferences, poor reagents, etc.

Spiked samples should be run to control the accuracy of the analysis. Spiked samples are prepared by adding a known quantity of a standard to an aliquot of sample. Percent recovery can be calculated from the concentrations of the spiked sample, the sample, and the standard.

A suitable spike would be prepared as follows: Place 4 ml of the 1.0 µg NO_2^-/ml standard in a test tube. Add 6 ml of a sample to the test tube. (Sample analysis should be simultaneous with spiked sample analysis). Mix well. Add 2 ml of phosphoric acid/sulfanilamide solution. Swirl to mix. Add 1 ml NEDA solution, swirl. Wait ten minutes for full color development. (If possible shake samples for full ten minutes) Read the absorbance of the spiked sample against the blank at 540 nm.

$$\text{Percent Recovery} = \frac{\text{conc(spike + sample)} - \text{conc(sample)}}{\text{conc(spike)}} \times 100$$

For example:

An NO_2 sample had a concentration of 0.311 µg NO_2/ml. The spiked sample, prepared as above, had a concentration of 0.590 µg NO_2^-/ml.

$$\text{conc(spike + sample)} = 0.590 \text{ µg } NO_2^-\text{/ml}$$

$$\text{conc(sample)} = 0.311 \text{ µg } NO_2^-\text{/ml} \times \frac{6 \text{ ml}}{10 \text{ ml}} = 0.187 \text{ µg } NO_2^-\text{/ml}$$

$$\text{conc(spike)} = (1.00 \text{ µg } NO_2^-\text{/ml}) \times \frac{4 \text{ ml}}{10 \text{ ml}} = 0.400 \text{ µg } NO_2^-\text{/ml}$$

$$\text{Percent Recovery} = \frac{0.590 \text{ µg } NO_2^-\text{/ml} - 0.187 \text{ µg } NO_2^-\text{/ml}}{0.400 \text{ µg } NO_2^-\text{/ml}}$$

Percent Recovery = 101%

A spiked sample should be run with each set of samples. The percent recovery should be between 90-100%. If not, all steps in the analysis should be examined carefully, interferences checked for, and the analysis repeated.

A standard curve should be run with each set of samples.

I. REFERENCES

Jacobs, M. B., and Hochheiser, S., "Continuous Sampling and Ultra-Microdetermination of Nitrogen Dioxide in Air", Anal. Chem, 30, p. 426, 1958.

Christie, A. A., Lidzey, R. G., and Radford, D. W. F., "Field Methods of the Determination of Nitrogen Dioxide in Air", The Analyst, May, 1970, Vol. 95, p. 519.

Ginn, W. L., Jr., and Payne, J. S., Jr., Laboratory Division, Texas Air Control Board.

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Laboratory Division
Texas Air Control Board

DETERMINATION OF NITROGEN DIOXIDE

Saltzman Method

A. GENERAL

Nitrogen dioxide (NO_2) is absorbed in a glacial acetic-sulfanilic acid solution to produce a red-violet color directly. The intensity of the color, which is proportional to the amount of NO_2 absorbed, is measured on a spectrophotometer capable of operating at 540 nm.

B. APPLICABILITY

The lower limit of detection for the Saltzman method is about .02 µg NO_2/ml. The absorption efficiency is dependent on both the porosity of the fritted bubbler and the flow rate. An efficiency of 95% has been found using a flow rate of 0.2 liters per minute, a maximum pore diameter of 70-100 microns, and 50 ml of absorbing solution in a standard impinger.

Because of the direct color development, it is immediately apparent when a sufficient amount of NO_2 has been absorbed from the atmosphere. For this reason, the Saltzman method is particularly useful for property-line sampling.

Large excesses of ozone (five-fold) and sulfur dioxide (thirty-fold) will interfere with the color development. Addition of 1% acetone to the absorbing reagent will reduce the interference from sulfur dioxide for 4-5 hours.

This laboratory has found that the developed color is stable for up to one week when kept at room temperature (72° - 75° F) in the absence of absorbed sulfur dioxide. Exposure to heat will cause a deterioration and discoloration of the absorbing reagent.

The Saltzman method can be used to standardize nitrogen dioxide mixtures in the laboratory.

C. APPARATUS

Suitable sampling apparatus
Adequate and sufficient storage bottles
2 - 1000 ml volumetric flasks
2 - 100 ml volumetric flasks
5 - 50 ml volumetric flasks
1 - 20 ml volumetric pipet
1 - 10 ml volumetric pipet
1 - 5 ml volumetric pipet
4 ml volumetric pipet
3 ml volumetric pipet
1 - 2 ml volumetric pipet

1 - 1 ml volumetric pipet
Sufficient cuvettes for reading the absorbance of standards and samples in a spectrophotometer
Spectrophotometer capable of measuring absorbance at 540 nm.

D. REAGENTS

All reagents should be ACS grade.

(1) Absorbing Solution
Dissolve 5 grams of sulfanilic acid in almost a liter of distilled or deionized water (DI H_2O) containing 140 ml glacial acetic acid. Gentle heating is permissible if desired to speed up the process. To the cooled mixture, add 20 ml of the 0.1% stock solution of NEDA (below) and dilute to 1 liter.

(2) N-(1 Naphthyl) Ethylenediamine Dihydrochloride (NEDA)(0.1%)
Dissolve 0.1 grams NEDA in 100 ml DI H_2O.

(3) Standard Solution
Accurately weigh out 0.1500 gram $NaNO_2$ and dilute to 1,000 ml in a volumetric flask with DI H_2O. This stock solution contains 100 µg NO_2^-/ml.

E. COLLECTION OF SAMPLE

The sample is collected in a known volume of absorbing solution (usually 20 ml for property-line sampling and 50 ml for ambient sampling). Air flow rate should not exceed approximately 0.2 liters per minute. An impinger equipped with a frit with a maximum pore diameter of 70-100 microns must be used. All sample lines should be glass if possible, since NO_2 diffuses through Teflon^R and polyethylene. In no case should rubber or metal be used, but if polyethylene must be included, the lines should be made as short as possible. As stated earlier, this method is not suitable for ambient sampling in cases where the actual sample period or the time required to transport the absorbing solution to and from the sample site will cause this reagent to be subjected to temperatures higher than 75° F for extended periods of time. There will be no deterioration of reagent, however, if exposed to hot weather for short periods of time (approximately three hours) as in the case of property-line sampling during summer weather.

Maximum pore diameter of the frit is not as critical in this method as in the Jacobs-Hochheiser method because of the better absorption efficiency of the Saltzman reagent. To insure relative consistency, however, it is advisable to use frits with approximately the same range of maximum pore diameters (70-100 microns). Measure this pore size as follows: set up the fritted impinger in a bubbler with enough water to cover the frit. Attach a vacuum source to the other hole in the bubbler and measure the vacuum required to draw the first perceptible stream of bubbles through the frit. Apply the following equation:

$$\text{Maximum pore diameter, } \mu m = \frac{30S}{P}$$

Where: S = Surface tension of water in dynes/cm (73 at 18° C, 72 at 25° C, and 71 at 36° C)

P = Measured vacuum, mm Hg

For ambient air sampling, needle calibrations (to determine flow rate) should be made with the needle in the train pulling through a fritted impinger to compensate for the pressure drop through the frit.

F. TEST PROCEDURE

(1) Preparation of Standards

Dilute 10 ml of the 100 µg NO_2^-/ml stock solution to 100 ml in a volumetric flask with DI H_2O. This solution now contains 10 µg NO_2^-/ml. Pipette 0, 2, 4, 6, 8, and 10 ml into 100 ml volumetric flasks, then dilute to the mark with absorbing reagent. These standards contain 0, 0.2, 0.4, 0.6, 0.8, and 1.0 µg NO_2^-/ml respectively.

(2) Preparation of Standard Curve

Since the pinkish color appears directly, one need only wait ten minutes for complete color development before reading the intensity at 540 nm on a spectrophotometer using the absorbing reagent as a blank. Plot a curve of absorbance versus concentration.

(3) Sample Analysis

If any absorbing reagent has evaporated during the sample period, restore to original volume with deionized water and mix thoroughly. Read the absorbance on a spectrophotometer at 540 nm. From the observed absorbance, determine the concentration of NO_2^- in the sample from the standard curve. If the samples are taken from a high concentration NO_2 source, the color development may be followed as sampling progresses and the sample can be ended when sufficient color has appeared for accurate reading.

G. CALCULATIONS

In practice, Saltzman found that one mole of NO_2, produces the same color as 0.72 moles of sodium nitrite. For this reason, the amount of NO_2, as read from the standard curve, must be divided by 0.72 to give the true value of NO_2 which actually went through the bubbler.

The stoichiometric factor of 0.72 is disputed by Purdue, Dudley, Clements, and Thompson in an article in the February, 1972, issue of Environmental Science and Technology.

$$\mu g\ NO_2/M^3 = \frac{\mu g\ NO_2^-/ml \times \text{total ml absorbing solution}}{0.72 \times \text{volume air sampled in } M^3}$$

H. QUALITY CONTROL

Duplicates should be run on 7% of the samples or at least one duplicate per batch of 15 or less. Replicates test the precision of the procedure. The relative deviation should be less than 5% for absorbance readings above 0.100.

$$\text{Relative Deviation (R.D.)} = \frac{\bar{d}}{\bar{v}} \times 100 \qquad \bar{d} = \frac{|v_1 - v_2|}{2}$$

$$\bar{v} = \frac{v_1 + v_2}{2}$$

where $\bar{d}$ = average deviation

$\bar{v}$ = average of individual measurements

v_i = individual measurement

If duplicates exceed 5% all steps in the procedure should be reviewed. Note: It is possible to have very good precision but poor accuracy.

Spiked samples should be run to control the accuracy of the analysis. Spiked samples are prepared by adding a known quantity of a standard to an aliquot of sample. Percent recovery can be calculated from the concentration of the spiked sample, the sample, and the standard.

$$\text{Percent Recovery} = \frac{\text{conc(spike + sample)} - \text{conc(sample)}}{\text{conc(spike)}} \times 100$$

where conc(spike + sample) = measured concentration

conc(sample) = measured concentration x dilution factor

conc(spike) = concentration of standard x dilution factor

A spiked sample should be run with each set of samples. The percent recovery should be between 90-110%. If not, all steps in the analysis should be examined carefully, interferences checked for, and the analysis repeated.

A standard curve should be run with each set of samples.

I. REFERENCES

"Selected Methods for the Measurement of Air Pollutants", U. S. Department of Health, Education, and Welfare. Environmental Health Series 999-AP-11, May, 1965, pp. C-1 through C-7.

Modified January 25, 1979
Laboratory Division
Texas Air Control Board

Determination of Nitrogen Oxides
Phenoldisulfonic Acid Method

A. GENERAL

Nitrogen oxides (NO and/or NO_2, or collectively, NO_x) in stack gas are determined as nitrate (NO_3^-) colorimetrically. NO_x is collected in a glass flow-through type bomb and converted to nitrate ion by reaction with aqueous hydrogen peroxide which is injected immediately following collection of the sample. A yellow color is developed at a later time by the addition of reagents. The color intensity developed is a function of the concentration of the nitrate. The intensity is measured using a spectrophotometer capable of operating at 410 nm.

B. APPLICABILITY

This method may be used for stack sampling with a varying ratio of NO to NO_2. Inorganic nitrates, nitrites, and organic nitrogen compounds easily oxidized to nitrate ion may interfere and give high results. Reducing agents such as SO_2 and halides may interfere to give lower results. The range of analysis is from 0.5 µg NO_2/ml of solution to 50.0 µg NO_2/ml of solution.

C. APPARATUS

Suitable sampling apparatus
Adequate and sufficient storage bottles
2 - 1000 ml volumetric flasks
1 - 500 ml volumetric flask
7 - 100 ml volumetric flasks
Sufficient 50 ml volumetric flasks for the number of samples and standards analyzed
Sufficient porcelain crucibles for the number of samples and standards analyzed
Sufficient 10 mm cuvettes for the number of samples and standards analyzed
2 - 10 ml volumetric pipets
1 - 9 ml volumetric pipet
1 - 8 ml volumetric pipet
1 - 7 ml volumetric pipet
1 - 5 ml volumetric pipet
1 - 3 ml volumetric pipet
2 - 2 ml volumetric pipets
2 - 1 ml volumetric pipets
1 - 10 ml graduated pipet
1 - 500 ml graduated cylinder
1 - 100 ml graduated cylinder
1 - Spectrophotometer capable of handling 10 mm cuvettes and measuring at at a wavelength of 410 nm
1 - Analytical balance
1 - Steam bath

D. REAGENTS

All reagents should be ACS reagent grade.

(1) Potassium Hydroxide

a. 12 N KOH:
Using distilled water, dissolve 673 grams of potassium hydroxide (KOH) in a 1000 ml volumetric flask and make up to the mark.

Caution! This reagent is very caustic. Avoid contact with the skin. Store in a plastic bottle closed tightly with a plastic cap. Do not store in a volumetric flask.

b. 1 N KOH:
Dilute 8.3 ml of 12 N KOH to 100 ml with distilled water. Store in plastic bottle.

(2) Phenoldisulfonic Acid
Dissolve 75 grams of pure phenol in 450 ml of concentrated sulfuric acid (H_2SO_4). Add 25 ml of fuming H_2SO_4 (15% free SO_3). Stir well; heat for two hours on a steam bath. This reagent is stable and can be stored for long as desired.

Caution! Phenol is poisonous and caustic. Do not handle with bare hands or allow contact with the skin. Sulfuric acid is extremely corrosive to all body tissues. Avoid contact with the skin as it produces severe burns. Do not breathe fumes as lung damage may occur. Both of these chemicals should be stored in tightly sealed glass containers.

(3) Stock Nitrate Solution
Dissolve 0.5495 grams of dry, anhydrous potassium nitrate (KNO_3) in distilled water in a 500 ml volumetric flask. Fill to the mark with water. This solution contains 500 µg NO_2/ml.

(4) Absorbing Reagent 0.1 M H_2O_2 in 0.05 M H_2SO_4
Prepare by adding 2.8 ml concentrated H_2SO_4 and 10.0 ml 30% H_2O_2 to 500 ml DI water in a 1000 ml volumetric flask. Dilute to 1.0 liter with distilled or DI water. (Caution! Do not mix acid and peroxide before dilution.)

E. COLLECTION OF SAMPLE

A sample is collected in a volumetrically calibrated glass flow-through type bomb. For each sample, a volume of at least ten times the volume of the bomb should be flowed through to purge the sample bomb. After the sample bomb is purged, the sample is taken. Record the temperature and pressure of the gas passing through the bomb. As soon as possible after sampling, inject 25 ml absorbing solution into the bomb. Shake the bomb. After 12 to 16 hours, the oxidation of NO to NO_2 and then to NO_3^- should be complete and the contents of the bomb can be removed.

F. TEST PROCEDURES

(1) Preparation of Standard Curve

Pipet 0.0, 1.0, 2.0, 3.0, 5.0, 7.0, 8.0 ml stock standard (500 µg NO_2/ml) into 100 ml volumetric flasks. Add 50 ml absorber and 10 ml distilled water to each flask. Add 1 N KOH dropwise to each standard to give pH 9-12. Then fill each flask to the mark with distilled water and mix well. Standards are stable at this point.

Place a 10.0 ml aliquot of each standard into a porcelain crucible and evaporate to dryness on a steam bath. Dissolve the residue in 2.0 ml of phenoldisulfonic acid. Using distilled water, rinse this solution into a 50 ml volumetric flask and make up to approximately 30 ml. Add 9.0 ml of 12 N KOH and bring the volume to 50 ml with distilled water. Mix thoroughly.

The equivalent µg NO_2/ml in each flask is:

0.0 ml = 0.0 µg NO_2/ml = blank
1.0 ml = 1.0 µg NO_2/ml
2.0 ml = 2.0 µg NO_2/ml
3.0 ml = 3.0 µg NO_2/ml
5.0 ml = 5.0 µg NO_2/ml
7.0 ml = 7.0 µg NO_2/ml
8.0 ml = 8.0 µg NO_2/ml

Any precipitate formed need not be filtered out as it settles to the bottom and should not interfere. Using 10 mm cuvette, measure the absorbance of each standard against the blank at 410 nm. Plot a curve of absorbance vs. µg NO_2/ml.

(2) Sample Determination

Empty contents of sample bomb into a 100 ml volumetric flask. Rinse bomb twice with approximately 10 ml portions of distilled or deionized water into the volumetric flask. Add 1.0 N KOH dropwise until sample is slightly alkaline to litmus paper. Fill to the mark with distilled water and mix well. Samples are stable at this point although they may slowly evolve oxygen. Continue as under Preparation of Standard Curve, starting with the evaporation step.

G. CALCULATIONS

The amount of NO_2 in the original sample can be calculated:

$$\mu g\ NO_2 = \frac{(\mu g\ NO_2/ml)\ (\text{dilution volume})\ (\text{sample volume})}{(\text{aliquot volume})}$$

$$= \frac{(\mu g\ NO_2/ml)\ (50\ ml)\ (100\ ml)}{10\ ml}$$

Note that NO_x is reported as equivalent of NO_2

H. QUALITY CONTROL

Duplicates should be run on 7% of the samples or at least one duplicate per batch of 15 or less. These will test the precision of the procedure. The relative deviation should be less than 5% if the absorbance reading is greater than 0.100.

$$\text{Relative Deviation (R.D.)} = \frac{\bar{d}}{\bar{v}} \qquad \bar{d} = \frac{|v_1 - v_2|}{2}$$

where $\bar{d}$ = average deviation
$\bar{v}$ = arithmetic average of all individual measurements
v = individual measurement

Spiked samples should be run to control the accuracy of the analysis. Spiked samples are prepared by adding a known quantity of a standard to an aliquot of sample. Percent recovery can be calculated from the concentrations of the spiked sample, the sample, and the standard.

A suitable spike would be prepared as follows: Place a 5 ml aliquot of the 8.0 µg NO_2/ml standard into a porcelain cuicible. Add 5 ml of sample to the crucible. Evaporate to dryness on a steam bath. Dissolve the residue in 20 ml phenoldisulfonic acid. Using distilled water, rinse this solution into a 50 ml volumetric flask and make up to approximately 30 ml. Add 9.0 ml of 12 N KOH and bring the volume to 50 ml with distilled water. Mix thoroughly. Any precipitate formed need not be filtered out as it settles to the bottom and should not interfere. Measure the absorbance against a blank at 410 nm.

$$\text{Percent recovery} = \frac{\text{conc (spike + sample)} - \text{conc (sample)}}{\text{conc (spike)}} \times 100$$

A spiked sample should be run with each set of samples. The percent recovery should be between 90-110%. If not, all steps of the analysis should be reviewed and the analysis repeated.

A standard curve must be run with each set of samples.

I. REFERENCES

"Nitrogen, Nitrate-Phenoldisulfonic Acid Method", Standard Methods for the Examination of Water and Wastewater, 11th Edition, APHA, New York (1965).

"Determination of Nitrogen Oxide Emissions from Stationary Sources", Federal Register, Vol. 36, Number 247, December 23, 1971.

"Improved Phenoldisulfonic Acid Method for Determination of NO_x from Stationary Sources", Martens, H. H., Dee, L. A., Nakamura, J. T., and Jaye, F. C., Environmental Science and Technology, Z, 13, December, 1973.

Adopted January 19, 1979
Laboratory Division
Texas Air Control Board

Ozone
Boric Acid Potassium Iodide Method

A. GENERAL

Ozone is collected in an absorbing solution of 0.1 M boric acid containing 1% potassium iodide. The ozone oxidizes the potassium iodide to free iodine which is measured spectrophotometrically as the tri-iodide ion.

B. APPLICABILITY

This method is recommended solely for ozone generator calibration and not for field sampling because of the many interferences that exist. However, for ozone generator calibration these interferences are negligible.

Using an absorber volume of 10 mls and a flow rate of 0.5 L/min., consistent agreement with uv photometry can be obtained over a range of 0.1 - 3.5 ppm (200 $\mu g/M^3$-7000 $\mu g/M^3$).

In no case should a sampling time of over 30 minutes be used, as the tri-iodide ion is lost by conversion to iodate.

C. APPARATUS

Suitable sampling apparatus (Teflon fittings and tubing)
2 - Mae West or midget impingers
4 - 1 liter volumetric flasks
4 - 100 ml volumetric flasks
5 - 25 ml volumetric flasks
1 - 20 ml volumetric pipet
1 - 15 ml volumetric pipet
3 - 10 ml volumetric pipets
3 - 5 ml volumetric pipets
1 - 3 ml volumetric pipet
1 - 2 ml volumetric pipet
1 - 1 ml volumetric pipet
10 mm cuvettes
Spectrophotometer capable of operating at 352 nM

D. REAGENTS

(1) Hydrogen Peroxide (0.0018%)
Add 3 ml of 30% (30 ml of 3% H_2O_2) hydrogen peroxide (H_2O_2) to approximately 200 ml of distilled water in a 1000 ml volumetric flask and dilute to volume with distilled water. Mix thoroughly. This solution is 0.09% H_2O_2. Add 2 ml of this solution to 50 ml of distilled water in a 100 ml volumetric flask and dilute to the mark with distilled water. Mix thoroughly. This solution is 0.0018% H_2O_2. Prepare fresh daily.

(2) Absorbing Reagent, 0.1 M Boric Acid, 1% Potassium Iodide
Dissolve 6.2 g of boric acid (H_3BO_3) in approximately 750 ml of distilled water in a 1000 ml volumetric flask. Add 10 g of potassium iodide (KI) to the boric acid solution and mix thoroughly. Add 1 ml of 0.0018% H_2O_2 solution and mix thoroughly. Within 5 minutes after adding the peroxide (1) dilute to volume with distilled water and mix and (2) determine the absorbance of this solution at 352 nM against a water blank. The pH of this BAKI solution should be 5.5 ± 0.2.

Let absorbing solution stand for two hours. Remeasure absorbance at 352 nM against a water blank. If this second absorbance is at least 0.010 absorbance units/cm greater than the first reading, the absorber is ready to use. If this amount of increase has not occurred, discard the absorber. Prepare fresh absorber using a different lot of KI.

(3) Sulfuric Acid (1N)
Dilute 28 ml of concentrated H_2SO_4 to volume in a 1000 ml volumetric flask.

(4) Potassium Iodate Solution (0.1N)
Dry potassium iodate at 150°C. Cool. Store in a desiccator. Accurately weigh 3.5667 g of KIO_3 and dissolve in 300 ml distilled water in a 1000 ml volumetric flask. Bring to volume with distilled water. This solution is stable if kept capped.

(5) Standard Iodine Solutions
(a) Using a volumetric pipet, add 10 ml of 0.1 N KIO_3 solution to a 100 ml volumetric flask. Add 1 g KI and 5 ml of 1 N H_2SO_4 and dilute to volume with distilled H_2O. Mix thoroughly.

(b) Immediately before use, pipet 10 ml of solution (a) into a 100 ml volumetric flask and dilute to volume with absorbing reagent.

(c) Pipet 5 ml of (b) into 100 ml volumetric flask and dilute to volume with absorbing reagent. This solution is 50 x 10^{-6} N.

E. COLLECTION OF SAMPLE

Ozone is trapped in 10 ml of absorber in each of two midget or Mae West impingers connected in series. The flow rate should be between 0.4-0.6 liter/minute and remain constant during sampling. Sampling longer than 30 minutes results in poor results as the I_2 formed volatilizes. No metal tubing (no stainless steel lines) or fittings should be used. No rubber tubing should be used as it causes O_3 decomposition. Glass or Teflon fittings and lines should be used.

F. TEST PROCEDURES

(1) Standard Curve Preparation

Pipet 5, 10, 15, 20, and 25 ml of the 50×10^{-6} N iodine solution into a series of 25 ml volumetric flasks. Dilute each to volume with absorbing reagent and mix thoroughly. To prevent I_2 losses by volatilization, the flasks should remain stoppered until abosrbance measurements are made. All absorbance measurements should be taken within 20 minutes after preparation of the iodine standards. These standards are 10×10^{-6} N I_2, 20×10^{-6} N I_2, 30×10^{-6} N I_2, 40×10^{-6} N I_2, and 50×10^{-6} N I_2. This is equivalent to 0.24 µg/ml O_3, 0.48 µg/ml O_3, 0.72 µg/ml O_3, 0.96 µg/ml O_3, and 1.20 µg/ml O_3.

(2) Sample Analysis

Immediately after sampling, measure the absorbance of the solution in the first impinger versus a blank of the absorber. Repeat with the solution from the second absorber. Determine the concentration from the standard curve.

G. CALCULATIONS

$$\mu g\ O_3/M^3 = \frac{\mu g\ O_3/ml\ 1st\ impinger \times 10\ ml\ absorber + \mu g\ O_3/ml\ 2nd\ impinger \times 10\ ml\ abs}{total\ volume\ air\ in\ M^3}$$

H. QUALITY CONTROL

Seven percent of the samples should be run in duplicate. These samples should agree within 2%. If not, analysis procedures, flow rates, etc., should be checked and the analysis should be rerun.

The accuracy of the method should be checked against a calibrated uv photometer. These measurements should agree within 2%. If not, a careful check of procedures, flow rates, etc., should be made and the analysis rerun.

I. REFERENCES

1. Flamm, D.L., "Analysis of Ozone at Low Concentrations with Boric Acid Buffered KI," Environ. Sci. Technol. 11, 978-983 (1977).

2. "Tentative Ozone Calibration Procedure Using Boric Acid - Potassium Iodide (BAKI)" Environmental Monitoring and Support Laboratory, EPA, June, 1977.

3. Flamm, D.L., Paur, R.J., Rehme, K.S., "Further Developments in Ozone Calibration Using Boric Acid Buffered KI," presented at the 71st Annual Meeting of the Air Pollution Control Association.

Particulate in Stack Gases

1.0 PRINCIPLE AND APPLICABILITY.

1.1 This method is applicable for stack samples of particulate matter where no sulfur dioxide, sulfur trioxide, or sulfuric acid are present (Reference 1).

1.2 A preweighed glass fiber filter immediately behind the probe traps the larger particulate matter from the stack.

1.2.1 After sampling, the filter is reweighed and the difference is the total particulate for that filter.

1.3 Smaller particulate is trapped in distilled water impingers in back of the filter. (For a diagram of the sampling train see Figure 3-1 in Reference 2.)

1.3.1 The solutions from the impingers and probe wash are transferred to separate tared beakers and evaporated to dryness. The change in beaker weight is equal to the particulate content of the impinger or probe wash.

2.0 RANGE AND LOWER DETECTABLE LIMIT.

2.1 The upper limit is determined by the point at which a decrease in flow rate is evidenced across the filter.

2.1.1 The point is affected by particle size distribution, moisture from the stack and variablility of the filter.

2.2 The lower limit is determined by the sensitivity of the balance and by inherent sources of error (See Section 5.0).

3.0 PRECISION.

3.1 A collaborative test program showed a within-laboratory deviation of 10.4% (Reference 3).

4.0 ACCURACY.

4.1 The interlaboratory precision has been shown to be 12.1% (Reference 3).

5.0 INHERENT SOURCES OF ERROR AND INTERFERENCE.

5.1 The greatest source of error occurs during the sampling collection and recovery phase instead of the analysis phase (Reference 3).

6.0 APPARATUS.

6.1 Glassware.

250-mL graduated cylinder.
250-mL beakers.

6.2 Glass fiber filters.

There may be no organic binders in the filters.
The filters must have ≤ 0.05% penetration for 0.3 micron dioctyl phthalate smoke particles.
This laboratory uses Whatman EPM 2000 filters supplied by EPA.

6.3 Evaporating oven.

Temperature range: ≥ 150° C.
Recirculating airflow.

6.4 Analytical balance.

Sensitivity of 0.1 mg.
Precisionl 0.1 mg.

6.5 Desiccator or humidity-controlled environment.

7.0 REAGENTS.

All reagents should be ACS reagent grade or better.

7.1 Anhydrous calcium sulfate for the desiccator.

7.2 Distilled water with less than 10 mg particulate/Liter (See 11.0).

7.3 Acetone with less than 8 mg particulate/Liter (See 11.0).

8.0 PROCEDURE.

8.1 Collection of sample.

8.1.1 See Chapter 5, Stack Sampling for Particulate Matter in Reference 2. A description of the the impingers for sampling for particulate matter are described in the same chapter

8.1.2 The competence of the analyst is the main factor affecting the precision of the method.

8.1.3 All surfaces, excluding the filter, that will be in contact with particulate should be rinsed with distilled water.

8.1.4 Filter and solution blanks should be subjected to the same field conditions that the samples experience except for actual sampling.

8.1.5 EPA recommends acetone for the probe wash (Reference 3). Reference 2 describes the acetone wash procedure in Sample Recovery.

8.1.6 Before sampling, check the distilled water and acetone to be used (See 11.0).

8.1.7 After sampling, mark the level of liquid on the sample container in case of loss during shipment.

8.2 Preparation prior to sampling of A. Filters
B. Filters

8.3 A. Filter.

8.3.1 EPA recommends that glass fiber filters without organic binders be used that have <0.05% penetration for 0.3 micron dioctyl phthalate smoke particles. (Consult the manufacturer's quality control test data.)

8.3.2 Filters of the proper filter holder diameter may be obtained from the manufacturer or cut from a larger sheet of filter paper. (This laboratory uses 8 x 10 in. sheets of Whatman glass fiber filter cut to size.)

8.3.3 Visually inspect each filter against a light source for pinholes or other irregularities. (Always use tweezers or disposable gloves when handling filters.)

8.3.4 Number the usable filters near the edge using a numbering machine. (Include enough filters for blanks.)

8.3.5 Oven dry the filters at 105° C for two hours.

8.3.6 Immediately after removing from heat, place the filters in a desiccator containing anhydrous calcium sulfate or in a constant humidity-controlled environment for two hours.

8.3.7 If the filter was placed in a desiccator, weigh the filter to the nearest 0.1 mg and return it to the desiccator for six hours.

8.3.8 Weigh the filter from the desiccator at six hour intervals until filter weight changes of <0.5 mg from the previous weighing are achieved. (The final weight will be the original filter weight.)

8.3.9 If the filter was placed in a humidity-controlled environment, weigh the filter only once to the nearest 0.1 mg and use this as the original filter weight. (The humidity in a humidity-controlled environment is a verifiable quantity and therefore the filter is only weighed once.)

8.3.10 During each weighing in Steps 8.3.7-8.3.9, the filter must not be exposed to the laboratory atmosphere for >2 minutes or to a relative humidity >50% before obtaining a weight.

8.3.11 Place the filters in labeled glass or plastic petri dishes and keep the filters in the containers at all times except during sampling and weighing. The filters will be shipped in these dishes.

8.4 B. Beaker.

8.4.1 Label clean beakers. (Use disposable gloves or tongs when handling beakers.)

8.4.2 Oven dry the beakers at 105° for two hours.

8.4.3 Immediately after removing from heat, place the beakers in a desiccator containing anhydrous calcium sulfate or in a constant humidity-controlled environment for two hours.

8.4.4 If the beaker was placed in a desiccator, weigh the beaker to the nearest 0.1 mg and return it to the desiccator for six hours.

8.4.5 Weigh the beaker from the desiccator at six hour intervals until beaker weight changes of <0.5 mg from the previous weighing are achieved. (The final weight will be the tare weight of the beaker.)

8.4.6 If the beaker was placed in a humidity-controlled environment, weigh the beaker only once to the nearest 0.1 mg and use this as a tare weight.

8.4.7 During each weighing in Steps 8.4.4-8.4.6, the beaker must not be exposed to the laboratory atmosphere for >2 minutes or to a relative humidity of >50% before obtaining a weight.

9.0 ANALYSIS OF FILTER, IMPINGER, AND PROBE WASH (distilled water or acetone).

9.1 Filter.

9.1.1 Using tweezers, put the sample filter in a tared, 250-mL beaker and with a fine, clean brush transfer any loose particulate from the filter shipping container to the tared beaker. (In a separate tared beaker, include a clean field filter as a blank.)

9.1.2 Oven dry the beaker with filter at 105° C for two hours.

9.1.3 Immediately after removing from heat, place the beaker with filter in a desiccator or in a humidity-controlled environment for two hours.

9.1.4 If the beaker with filter was placed in a desiccator, weigh and return to the desiccator for six hours.

9.1.5 Weigh the beaker with filter at six hour intervals until weight changes of <0.5 mg from the previous weighing are achieved. (The final weight will be the filter plus beaker weight.)

9.1.6 If the beaker with filter was placed in a humidity-controlled environment, weigh only once to the nearest 0.1 mg and use this as a final filter plus beaker weight.

9.1.7 During each weighing in Steps 9.1.4-9.1.6, the beaker with filter must not be exposed to the laboratory atmosphere for >2 minutes or to a relative humidity >50% before obtaining a weight.

9.1.8 The final weight of the blank filter should be within ±5 mg of the original filter weight or 2% of the final filter weight, whichever is greater (Reference 2).

9.2 Impinger and probe wash (distilled water).

9.2.1 Using a clean, dry, graduated cylinder measure the volume of the sample. If the amount is <90% of the preshipment volume (See 8.1.7), then void the sample.

9.2.2 Transfer the sample to a clean, tared 250-mL beaker. (In a separate tared beaker, include a distilled water field blank equal to the average volume of the samples.)

9.2.3 Rinse the cylinder and sample container with two 25-mL portions of distilled water and transfer the rinsings to the beaker.

9.2.4 Evaporate the samples to dryness by heating in an oven at 95° C. (Also heat a clean, tared beaker with the samples and carry it through

the analysis to determine if particulate matter was collected from the surroundings.)

9.2.5 Immediately after removing from heat, place the beakers in a desiccator or humidity-controlled environment for two hours.

9.2.6 If the beaker was placed in a desiccator, weigh the beaker and return it to the desiccator for six hours.

9.2.7 Weigh the beaker at six hour intervals until weight changes of <0.5 mg from the previous weighing are achieved. (The final weight will be the particulate plus beaker weight.)

9.2.8 If the beaker was placed in a humidity-controlled environment, weigh the beaker only once and use this as a final particulate plus beaker weight.

9.2.9 During each weighing in Steps 9.2.6-9.2.8, the beaker must not be exposed to the laboratory atmosphere for >2 minutes or to a relative humidity >50% before obtaining a weight.

9.2.10 The weight of the clean, tared beaker should not have changed by >2 mg.

9.3 Acetone probe wash.

9.3.1 According to EPA, acetone evaporations may be performed at elevated temperatures under close supervision if the following precautions are observed (Reference 2):

a. Use adequate ventilation around source to prevent flashing.
b. Evaporate at temperatures below 56p C.
c. Occasionally swirl the acetone solution to maintain an even temperature.

9.3.2 Using a clean, dry, graduated cylinder measure the volume of the sample. If the amount is <90% of the preshipment volume (See 8.1.7), then void the sample.

9.3.3 Transfer the sample to a tared 250-mL beaker. (Include an acetone field blank approximately equal to the average volume of the samples.)

9.3.4 Rinse the cylinder and sample container with 25-mL portions of acetone and transfer the rinsings to the beaker.

9.3.5 Using a vented fan-circulated oven or hot plates and a fume hood, evaporate the acetone samples to dryness by heating at 45° C. (Also heat a clean, tared beaker with the samples.)

9.3.6 Follow Steps 9.2.5 through 9.2.10.

10.0 CALCULATIONS.

10.1 Filter.

Particulate on filter = (weight of filter plus beaker) - (tare weight of beaker) - (original weight of filter).

10.2 Impinger and probe wash.

Particulate = (weight of particulate + beaker) - (tare weight of beaker).

11.0 QUALITY CONTROL.

11.1 Prior to sampling, place 200 mL of distilled water and acetone from the batch that will be used for stack sampling in separate clean, tared beakers.

11.1.1 Evaporate to dryness following the steps outlined in Section 9.2 and 9.3.

11.1.2 The solutions must not be contaminated by more than 0.001% by weight:

Distilled water <10 mg particulate/Liter
Acetone <8 mg particulate/Liter

11.1.3 If the water or acetone blank is contaminated by more than the allowable limit, discard that batch and test a new batch.

11.2 After obtaining a final original filter weight for a batch of clean, heated filters, reweigh 10% or a minimum of four filters.

11.2.1 If the weight of any one filter does not agree within 0.5 mg, reweigh the entire batch of filters.

11.3 Follow Steps 11.2 and 11.2.1 for the batch of clean, tared beakers.

11.4 After sampling, follow the same quality control procedures for the sampled filter with beaker (See 9.1.3) and the beakers used to evaporate the impinger and probe wash samples.

12.0 REFERENCE.

1. "Particulate in Stack Gases Containing Sulfur Oxides," Texas Air Control Board's Laboratory Methods Manual, Revised 1985.

2. Texas Air Control Board, Sampling Procedures Manual, January 1983.

3. EPA Quality Assurance Handbook for Air Pollution Measurement Systems.. Volume III--Stationary Source Specific Methods. Method 5, Revision No. 0, January 15, 1980.

Particulate (Including Ammonium Sulfate and Ammonium Sulfite) in Stack Gases Containing Sulfur Oxides and Ammonia

1.0 PRINCIPLE AND APPLICABILITY.

1.1 This method is applicable for the determination of particulate in stack gases containing sulfur oxides and ammonia and is a modification of the U.S. Environmental Protection Agency (EPA) Method 8 (Reference 1) and Method 5 (Reference 2).

1.2 The sampling train consists of a heated, preweighed glass fiber filter immediately in back of the probe followed by three impingers in series, the first containing 80% isopropanol (IPA) in water and the next two containing 6% hydrogen peroxide (H_2O_2) in water (Reference 3).

1.3 The particulate weight determined by this method includes the weight of ammonium sulfate [$(NH_4)_2SO_4$] and ammonium sulfite [$(NH_4)_2SO_3$] created from the sulfuric acid (H_2SO_4), sulfur trioxide (SO_3), sulfur dioxide (SO_2), and ammonia (NH_3) in the stack gas. However, stack $(NH_4)_2SO_4$ and stack $(NH_4)_2SO_3$ are analyzed and reported by this method, so their contributions to the total particulate weight can be determined. Also, this method provides analyses for free (unreacted with NH_3) H_2SO_4 and free SO_2, so weights for both of these entities are reported.

1.3.1 Most of the particulate is collected on the filter; the remainder is collected in the probe wash and in the IPA absorber. This particulate may be water- or acid-soluble and cannot be determined by a filtration technique.

1.3.2 Note: One mole of H_2SO_4, SO_3, or SO_2 reacts with two moles of NH_3.

1.3.3 Sulfuric acid (H_2SO_4) mist may be caught on the heated filter and combined with NH_3 from the stack to form $(NH_4)_2SO_4$. The remaining H_2SO_4 mist and NH_3 are trapped by the IPA absorber, which also collects SO_3 and converts it to H_2SO_4. (Ammonium sulfate may also be found in the probe wash.)

1.3.4 In the presence of sufficient NH_3, SO_2 forms particulate $(NH_4)_2SO_3$, which is trapped in the probe, on the filter, and in the IPA absorber (Reference 4). The remaining (free) SO_2 from the stack passes through the IPA solution to the second and third (H_2O_2) impingers, where it is converted to H_2SO_4.

1.3.5 In the majority of cases, there will be more sulfur oxides in the stack than NH_3. Therefore, NH_3 will be the limiting factor in the reaction with H_2SO_4, SO_3, and SO_2.

1.3.6 If the stack NH_3 is much greater (by at least a factor of 1.2) than twice the total moles of $H_2SO_4 + SO_3 + SO_2$, then this laboratory addresses the problem on an individual basis, taking into account the stack process and the desired results from the analyses.

1.4 Reported data.

1.4.1 Free SO_2. Each H_2O_2 absorber solution is analyzed for sulfate (as SO_2) by ion chromatography (IC) according to the Texas Air Control Board's (TACB's) Laboratory Methods Manual, Method 26a (Reference 5). From these analyses, the total weight of free SO_2 is reported.

1.4.2 Total stack $(NH_4)_2SO_3$, total stack $(NH_4)_2SO_4$, total free H_2SO_4, and total particulate.

1.4.2.1 The filter is extracted with distilled deionized (DDI) water. A portion of the extracting solution is then analyzed for ammonium, sulfite, and sulfate ions by IC according to the TACB's Laboratory Methods Manual, Methods 26b and 26a (Reference 5). From these analyses stack $(NH_4)_2SO_3$ on the filter, stack $(NH_4)_2SO_4$ on the filter, and free H_2SO_4 on the filter are calculated. The remaining portion of the extracting solution (along with the filter and undissolved particulate) is transferred into a clean, tared beaker, is made basic with ammonium hydroxide (NH_4OH) (to fix any free H_2SO_4), and then is evaporated to dryness. Particulate collected on the filter is then calculated from the final weight of the beaker (plus contents), the tared weight of the beaker, the weight of the clean filter, and the weights of stack $(NH_4)_2SO_3$ on the filter, stack $(NH_4)_2SO_4$ on the filter, and free H_2SO_4 on the filter.

1.4.2.2 The probe wash and the IPA absorber are analyzed separately. Each volume is adjusted with DDI water. Then a portion of each resulting solution is analyzed for ammonium, sulfite, and sulfate ions by IC as in Step 1.4.2.1. From these analyses stack $(NH_4)_2SO_3$ in the probe wash and IPA absorber, stack $(NH_4)_2SO_4$ in the probe wash and IPA absorber, and free H_2SO_4 in the probe wash and IPA absorber are calculated. The remaining portion of each solution is transferred into a clean, tared beaker, evaporated down to 100 mL, made basic with NH_4OH (to fix any free H_2SO_4), and then evaporated to dryness. Particulate collected in the probe wash and the IPA absorber is then calculated from the final weight of each beaker (plus contents), the tared weight of each beaker, and the weights of stack $(NH_4)_2SO_3$ in

the probe wash and IPA absorber, stack $(NH_4)_2SO_4$ in the probe wash and IPA absorber, and free H_2SO_4 in the probe wash and IPA absorber.

1.4.2.3 Total stack $(NH_4)_2SO_3$, total stack $(NH_4)_2SO_4$, total free H_2SO_4, and total particulate are calculated from the analyses described in Steps 1.4.2.1 and 1.4.2.2.

2.0 RANGES AND LOWER DETECTABLE LIMITS.

2.1 According to EPA Method 8 (Reference 1), the minimum detectable limits of the method are 0.00005 g SO_3/m^3 and 0.0012 g SO_2/m^3.

2.2 No upper limits have been established.

2.3 The lower detectable limit for the particulate is limited by the weighing process.

3.0 PRECISION.

3.1 The precision of the method, as determined by interlaboratory tests, was found to be 0.00719 g H_2SO_4/m^3 and 0.0223 g SO_2/m^3 (Reference 1).

3.2 The precision of the particulate measurement in stack gas, as a result of a collaborative test program showed a standard deviation percent of mean value of 10.4% (Reference 2).

4.0 ACCURACY.

4.1 The accuracy of the method measured as interlaboratory precision has been shown to be 0.00803 g H_2SO_4/m^3 and 0.0311 g SO_2/m^3 (Reference 1).

4.2 The accuracy of the particulate measurement in stack gas, as a result of an interlaboratory collaborative test program, showed a standard deviation percent of mean value of 12.1% (Reference 2).

5.0 INTERFERENCES.

5.1 Possible interferences with this method include fluorides and water-soluble, non-ammonium salts of H_2SO_4.

5.1.1 Fluorides react with the preweighed glass fiber filter causing it to lose weight as silicon tetrafluoride, thereby interfering with the gravimetric determination of undissolved particulate on the filter.

5.1.2 Water-soluble, non-ammonium salts of H_2SO_4 (such as Na_2SO_4, $MgSO_4$, and amine sulfates) will be reported as free H_2SO_4, causing the reported free H_2SO_4 to be high and the reported particulate to be low.

5.1.3 The greatest source of error occurs during the sampling and collection phase instead of the analysis phase (Reference 2).

6.0 REAGENTS.

All reagents should be ACS reagent-grade or better.

6.1 DDI water.

6.2 Concentrated NH_4OH.

6.3 Ethanol.

6.4 Phenolphthalein indicator. Dissolve 0.05 g phenolphthalein in 50 mL of ethanol, and add 50 mL of DDI water.

7.0 APPARATUS.

7.1 Glassware.

125-mL Erlenmeyer flasks with air condensers.
250-mL graduated cylinders.
250-mL beakers.
50-mL volumetric flasks.
250-mL volumetric flasks.

7.2 Pipettors, 5- and 10-mL.

7.3 Evaporating oven.

Temperature range: 55 to 100° C.
Recirculating airflow.

7.4 Analytical balance.

Sensitivity of 0.0001 g.
Precision of 0.0001 g.

8.0 PROCEDURES.

8.1 Collection of sample.

8.1.1 Before the sampling trip begins, read Steps 8.3 and 8.4 in the TACB's Laboratory Methods Manual, Method 23 (Reference 5) for the preparation of the glass fiber filters and of the beakers used to evaporate the samples.

8.1.2 Prepare the filter and solution blanks to be analyzed by this procedure.

8.1.3 Subject the filter and solution blanks to the same field conditions that the samples experience except for being used in sampling.

8.1.4 Before sampling, perform quality control checks (see Step 12.0) on the IPA batch to be used in the first impinger and on the batch of DDI water or acetone to be used as the probe wash.

8.1.5 After sampling, the person sampling must mark the level of liquid on each sample container in case of loss during shipment. It is assumed that the probe wash will not exceed a volume of 150 mL and that each impinger will contain slightly less than 100 mL of absorber.

8.2 Preparation of the peroxide absorbers.

8.2.1 Using DDI water, adjust the volume of each H_2O_2 absorber to 100 mL.

8.2.2 Using a pipettor, dilute a 5-mL portion of each absorber to 50 mL with DDI water. Each absorber is now ready for analysis.

8.3 Preparation of the filters.

8.3.1 After sampling has been completed, use tweezers to remove the filter from the shipping container. Cut the filter into several pieces before placing it into a 125-mL Erlenmeyer flask equipped with an air condenser. (Extract a clean field filter in a separate flask as a blank.)

8.3.2 Rinse the filter shipping container with two 25-mL portions of DDI water, and pour the rinsings into the Erlenmeyer flask. (The total volume of the filter extract used in the calculations is 50 mL.)

8.3.3 Reflux gently for six to eight hours. Allow the sample to cool. Then verify that the total volume is still 50 mL; adjust with DDI water if necessary.

8.3.4 Allow the undissolved particulate in the extracting solution to settle. Then pipet a 5-mL aliquot of the filter extract into a 50-mL volumetric

flask and dilute to the mark with DDI water. This sample is now ready for analyses.

8.3.5 Place the remaining 45 mL of the filter extract, the filter, and the undissolved particulate from Step 8.3.3 into a clean, tared 250-mL beaker.

8.3.6 Rinse the Erlenmeyer flask with three 10-mL portions of DDI water, and pour the rinsings into the tared beaker.

8.3.7 Add five drops of the phenolphthalein solution and then enough drops of concentrated NH_4OH to turn the sample pink.

8.3.8 Evaporate to dryness in an oven at 95° C. This sample is now ready for analysis.

8.4 Preparation of the probe wash and the IPA absorber (each separately).

8.4.1 Using a clean, dry graduated cylinder, measure the volume of the IPA absorber. If its volume is less than 90 mL, void the sample.

8.4.2 Pour each sample into a 250-mL volumetric flask. (Include a probe wash and an IPA-absorber field blank equal to the volume of the field sample, and put each into a separate volumetric flask.)

8.4.3 Rinse the sample container and the graduated cylinder with DDI water, and pour the rinsings into the volumetric flask. Dilute the flask to the mark with DDI water.

8.4.4 Pipet a 10-mL aliquot of the sample into a 50-mL volumetric flask, and dilute to the mark with DDI water. This sample is now ready for analyses.

8.4.5 Place the remaining 240 mL of sample from Step 8.4.3 into a clean, tared 250-mL beaker.

8.4.6 Add five drops of the phenolphthalein solution and then enough drops of concentrated NH_4OH to turn the sample pink.

8.4.7 Evaporate to dryness in an oven at 95° C (50° C for the probe wash if it contains acetone). This sample is now ready for analysis.

9.0 CALIBRATION.

Follow the procedures given in the TACB's Laboratory Methods Manual, Methods 26b and 26a (Reference 5) for the calibration of the IC instruments.

10.0 SAMPLE ANALYSIS.

10.1 Peroxide absorbing solutions.

Analyze the samples in the 50-mL flasks from Step 8.2.2 for sulfate ion (to be reported as free SO_2) by using the IC method.

10.2 Filter extract.

10.2.1 Analyze the samples in the 50-mL flasks from Step 8.3.4 for ammonium, sulfite, and sulfate ions by using the IC methods.

10.2.2 Obtain the final (constant) weight on the beakers from Step 8.3.8 by using the procedures in the TACB's Laboratory Methods Manual, Method 23 (Reference 5).

10.3 Probe wash.

10.3.1 Analyze the probe-wash sample in the 50-mL flask from Step 8.4.4 for ammonium, sulfite, and sulfate ions by using the IC method.

10.3.2 Obtain the final (constant) weight on the probe-wash beaker from Step 8.4.7 by using the procedures used in Step 10.2.2.

10.4 IPA absorber.

10.4.1 Analyze the IPA-absorber sample in the 50-mL flask from Step 8.4.4 for ammonium, sulfite, and sulfate ions by using the IC method.

10.4.2 Obtain the final (constant) weight on the IPA-absorber beaker from Step 8.4.7 by using the procedures used in Step 10.2.2.

11.0 CALCULATIONS.

11.1 Peroxide absorbers.

Calculate and report the weight for total free SO_2 given by:

$$A = (B + C)(10)(100)(0.667)$$

where A is the weight of total free SO_2 in μg,
B and C are the sulfate-ion concentrations in the diluted peroxide solutions from Step 10.1 in μg/mL,
10 is the dilution factor for each absorber,
100 is the volume for each absorber in mL, and
0.667 is the ratio of the molecular weight of SO_2 to the ionic weight of sulfate ion.

11.2 Filter extract.

11.2.1 Calculate the μmoles of stack ammonium ion in the filter extract given by:

$$D = E(10)(50) / (18)$$

where D is the μmoles of stack ammonium ion in the filter extract,
E is the stack ammonium-ion concentration in the diluted filter extract from Step 10.2.1 in μg/mL,
10 is the dilution factor,
50 is the volume of the extracting solution in mL, and
18 is the ionic weight of ammonium ion.

11.2.2 Calculate the μmoles of sulfite ion in the filter extract given by:

$$F = G(10)(50) / (80)$$

where F is the μmoles of sulfite ion in the filter extract,
G is the sulfite-ion concentration in the diluted filter extract from Step 10.2.1 in μg/mL,
10 is the dilution factor,
50 is the volume of the extracting solution in mL, and
80 is the ionic weight of sulfite ion.

11.2.3 Calculate the μmoles of sulfate ion in the filter extract given by:

$$H = I(10)(50) / (96)$$

where H is the μmoles of sulfate ion in the filter extract,
I is the sulfate-ion concentration in the diluted filter extract from Step 10.2.1 in μg/mL,
10 is the dilution factor,
50 is the volume of the extracting solution in mL, and
96 is the ionic weight of sulfate ion.

11.2.4 Theoretically, sufficient μmoles of stack ammonium ion will exist in the filter extract to fix all of the sulfite ion in the filter extract, so calculate the weight of stack $(NH_4)_2SO_3$ in the filter extract given by:

$$J = F(116)$$

where J is the weight of stack $(NH_4)_2SO_3$ in the filter extract in μg,
F is the μmoles of sulfite ion in the filter extract from Step 11.2.2, and
116 is the molecular weight of $(NH_4)_2SO_3$.

11.2.5 Calculate the μmoles of stack ammonium ion remaining in the filter extract given by:

$$K = D - 2F$$

where K is the μmoles of stack ammonium ion remaining in the filter extract,
D is the μmoles of stack ammonium ion in the filter extract from Step 11.2.1, and
2F is the μmoles of stack ammonium ion already used to form $(NH_4)_2SO_3$ in the filter extract (F is from Step 11.2.2).

11.2.6 Calculate the weight of stack $(NH_4)_2SO_4$ in the filter extract given by:

$$L = 0.5K(132)$$

where L is the weight of stack $(NH_4)_2SO_4$ in the filter extract in μg,
K is the μmoles of stack ammonium ion remaining in the filter extract (from Step 11.2.5) that can react with 0.5K μmoles of sulfate ion in the filter extract, and
132 is the molecular weight of $(NH_4)_2SO_4$.

11.2.7 Calculate the weight of free H_2SO_4 in the filter extract given by:

$$M = (H - 0.5K)(98)$$

where M is the weight of free H_2SO_4 in the filter extract in μg,
H is the μmoles of sulfate ion in the filter extract from Step 11.2.3,
0.5K is the μmoles of stack $(NH_4)_2SO_4$ from Step 11.2.6, and
98 is the molecular weight of H_2SO_4.

11.2.8 Calculate the weight of particulate (including stack $(NH_4)_2SO_3$ and stack $(NH_4)_2SO_4$) in the filter extract given by:

$$N = P - Q - R + 0.1(J + L) - 0.9M(1.35)$$

where N is the weight of particulate (including stack $(NH_4)_2SO_3$ and stack $(NH_4)_2SO_4$) in the filter extract in μg,
P is the final weight of the filter-extract beaker from Step 10.2.2 in μg,
Q is the tared weight of the filter-extract beaker in μg,
R is the clean weight of the filter in μg,
0.1 is the fraction of the stack $(NH_4)_2SO_3$ and stack $(NH_4)_2SO_4$ removed from the filter extract for analysis,
J is the weight of stack $(NH_4)_2SO_3$ from Step 11.2.4 in μg,
L is the weight of stack $(NH_4)_2SO_4$ from Step 11.2.6 in μg,

0.9 is the fraction of the free H_2SO_4 remaining in the filter extract after removing some of the extract for analyses,
M is the weight of free H_2SO_4 in the filter extract from Step 11.2.7 in µg, and
1.35 is the ratio of the molecular weight of $(NH_4)_2SO_4$ to the molecular weight of H_2SO_4.

11.3 Probe wash.

11.3.1 Calculate the µmoles of stack ammonium ion in the probe wash given by:

$$S = T(5)(250) / (18)$$

where S is the µmoles of stack ammonium ion in the probe wash,
T is the stack ammonium-ion concentration in the diluted probe wash from Step 10.3.1 in µg/mL,
5 is the dilution factor,
250 is the volume of the probe wash in mL, and
18 is the ionic weight of ammonium ion.

11.3.2 Calculate the µmoles of sulfite ion in the probe wash given by:

$$U = V(5)(250) / (80)$$

where U is the µmoles of sulfite ion in the probe wash,
V is the sulfite-ion concentration in the diluted probe wash from Step 10.3.1 in µg/mL,
5 is the dilution factor,
250 is the volume of the probe wash in mL, and
80 is the ionic weight of sulfite ion.

11.3.3 Calculate the µmoles of sulfate ion in the probe wash given by:

$$W = X(5)(250) / (96)$$

where W is the µmoles of sulfate ion in the probe wash,
X is the sulfate-ion concentration in the diluted probe wash from Step 10.3.1 in µg/mL,
5 is the dilution factor,
250 is the volume of the probe wash in mL, and
96 is the ionic weight of sulfate ion.

11.3.4 Theoretically, sufficient µmoles of stack ammonium ion will exist in the probe wash to fix all of the sulfite ion in the probe wash, so calculate the weight of stack $(NH_4)_2SO_3$ in the probe wash given by:

$$Y = Z(116)$$

where Y is the weight of stack $(NH_4)_2SO_3$ in the probe wash in µg,
Z is the µmoles of sulfite ion in the probe wash from Step 11.3.2, and
116 is the molecular weight of $(NH_4)_2SO_3$.

11.3.5 Calculate the µmoles of stack ammonium ion remaining in the probe wash given by:

$$a = S - 2U$$

where a is the µmoles of stack ammonium ion remaining in the probe wash,
S is the µmoles of stack ammonium ion in the probe wash from Step 11.3.1, and
2U is the µmoles of stack ammonium ion already used to form $(NH_4)_2SO_3$ in the probe wash (U is from Step 11.3.2).

11.3.6 Calculate the weight of stack $(NH_4)_2SO_4$ in the probe wash given by:

$$b = 0.5a(132)$$

where b is the weight of stack $(NH_4)_2SO_4$ in the probe wash in µg,
a is the µmoles of stack ammonium ion remaining in the probe wash (from Step 11.3.5) that can react with 0.5a µmoles of sulfate ion in the probe wash, and
132 is the molecular weight of $(NH_4)_2SO_4$.

11.3.7 Calculate the weight of free H_2SO_4 in the probe wash given by:

$$c = (W - 0.5a)(98)$$

where c is the weight of free H_2SO_4 in the probe wash in µg,
W is the µmoles of sulfate ion in the probe wash from Step 11.3.3,
0.5a is the µmoles of stack $(NH_4)_2SO_4$ from Step 11.3.6, and
98 is the molecular weight of H_2SO_4.

11.3.8 Calculate the weight of particulate (including stack $(NH_4)_2SO_3$ and stack $(NH_4)_2SO_4$) in the probe wash given by:

$$d = e - f + 0.04(Y + b) - 0.96c(1.35)$$

where d is the weight of particulate (including stack $(NH_4)_2SO_3$ and stack $(NH_4)_2SO_4$) in the probe wash in µg,
e is the final weight of the probe-wash beaker from Step 10.3.2 in µg,
f is the tared weight of the probe-wash beaker in µg,

0.04 is the fraction of the stack $(NH_4)_2SO_3$ and stack $(NH_4)_2SO_4$ removed from the probe wash for analysis,
Y is the weight of stack $(NH_4)_2SO_3$ from Step 11.3.4 in µg,
b is the weight of stack $(NH_4)_2SO_4$ from Step 11.3.6 in µg,
0.96 is the fraction of the free H_2SO_4 remaining in the probe wash after removing some of the probe wash for analyses,
c is the weight of free H_2SO_4 in the probe wash from Step 11.3.7 in µg, and
1.35 is the ratio of the molecular weight of $(NH_4)_2SO_4$ to the molecular weight of H_2SO_4.

11.4 IPA absorber.

11.4.1 Calculate the µmoles of stack ammonium ion in the IPA absorber given by:

$$h = i(5)(250) / (18)$$

where h is the µmoles of stack ammonium ion in the IPA absorber,
i is the stack ammonium-ion concentration in the diluted IPA absorber from Step 10.4.1 in µg/mL,
5 is the dilution factor,
250 is the volume of the IPA absorber in mL, and
18 is the ionic weight of ammonium ion.

11.4.2 Calculate the µmoles of sulfite ion in the IPA absorber given by:

$$j = k(5)(250) / (80)$$

where j is the µmoles of sulfite ion in the IPA absorber,
k is the sulfite-ion concentration in the diluted IPA absorber from Step 10.4.1 in µg/mL,
5 is the dilution factor,
250 is the volume of the IPA absorber in mL, and
80 is the ionic weight of sulfite ion.

11.4.3 Calculate the µmoles of sulfate ion in the IPA absorber given by:

$$m = n(5)(250) / (96)$$

where m is the µmoles of sulfate ion in the IPA absorber,
n is the sulfate-ion concentration in the diluted IPA absorber from Step 10.4.1 in µg/mL,
5 is the dilution factor,
250 is the volume of the IPA absorber in mL, and
96 is the ionic weight of sulfate ion.

11.4.4 Theoretically, sufficient μmoles of stack ammonium ion will exist in the IPA absorber to fix all of the sulfite ion in the IPA absorber, so calculate the weight of stack $(NH_4)_2SO_3$ in the IPA absorber given by:

$$p = q(116)$$

where p is the weight of stack $(NH_4)_2SO_3$ in the IPA absorber in μg,
q is the μmoles of sulfite ion in the IPA absorber from Step 11.4.2, and
116 is the molecular weight of $(NH_4)_2SO_3$.

11.4.5 Calculate the μmoles of stack ammonium ion remaining in the IPA absorber given by:

$$r = h - 2j$$

where r is the μmoles of stack ammonium ion remaining in the IPA absorber,
h is the μmoles of stack ammonium ion in the IPA absorber from Step 11.4.1, and
2j is the μmoles of stack ammonium ion already used to form $(NH_4)_2SO_3$ in the IPA absorber (j is from Step 11.4.2).

11.4.6 Compare the μmoles of stack ammonium ion remaining in the IPA absorber (r from Step 11.4.5) with the μmoles of stack sulfate ion in the IPA absorber (m from Step 11.4.3). If r is greater than 2m, see Step 1.3.6. Otherwise, continue with Step 11.4.7.

11.4.7 Calculate the weight of stack $(NH_4)_2SO_4$ in the IPA absorber given by:

$$s = 0.5r(132)$$

where s is the weight of stack $(NH_4)_2SO_4$ in the IPA absorber in μg,
r is the μmoles of stack ammonium ion remaining in the IPA absorber (from Step 11.4.5) that can react with 0.5r μmoles of sulfate ion in the IPA absorber, and
132 is the molecular weight of $(NH_4)_2SO_4$.

11.4.8 Calculate the weight of free H_2SO_4 in the IPA absorber given by:

$$t = (m - 0.5r)(98)$$

where t is the weight of free H_2SO_4 in the IPA absorber in μg,
m is the μmoles of sulfate ion in the IPA absorber from Step 11.4.3,
0.5r is the μmoles of stack $(NH_4)_2SO_4$ from Step 11.4.7, and
98 is the molecular weight of H_2SO_4.

11.4.9 Calculate the weight of particulate (including stack $(NH_4)_2SO_3$ and stack $(NH_4)_2SO_4$) in the IPA absorber given by:

$$u = v - w + 0.04(p + s) - 0.96t(1.35)$$

where u is the weight of particulate (including stack $(NH_4)_2SO_3$ and stack $(NH_4)_2SO_4$) in the IPA absorber in µg,
v is the final weight of the IPA-absorber beaker from Step 10.4.2 in µg,
w is the tared weight of the IPA-absorber beaker in µg,
0.04 is the fraction of the stack $(NH_4)_2SO_3$ and stack $(NH_4)_2SO_4$ removed from the IPA absorber for analysis,
p is the weight of stack $(NH_4)_2SO_3$ from Step 11.4.4 in µg,
s is the weight of stack $(NH_4)_2SO_4$ from Step 11.4.7 in µg,
0.96 is the fraction of the free H_2SO_4 remaining in the IPA absorber after removing some of the IPA absorber for analyses,
t is the weight of free H_2SO_4 in the IPA absorber from Step 11.4.8 in µg, and
1.35 is the ratio of the molecular weight of $(NH_4)_2SO_4$ to the molecular weight of H_2SO_4.

11.5 Total weights

11.5.1 Calculate and report the weight for total stack $(NH_4)_2SO_3$ given by:

$$x = J + Y + p$$

where x is the weight for total stack $(NH_4)_2SO_3$ in µg,
J is the weight for stack $(NH_4)_2SO_3$ in the filter extract from Step 11.2.4 in µg,
Y is the weight for stack $(NH_4)_2SO_3$ in the probe wash from Step 11.3.4 in µg, and
p is the weight for stack $(NH_4)_2SO_3$ in the IPA absorber from Step 11.4.4 in µg.

11.5.2 Calculate and report the weight for total stack $(NH_4)_2SO_4$ given by:

$$y = L + b + s$$

where y is the weight for total stack $(NH_4)_2SO_4$ in µg,
L is the weight for stack $(NH_4)_2SO_4$ in the filter extract from Step 11.2.6 in µg,
b is the weight for stack $(NH_4)_2SO_4$ in the probe wash from Step 11.3.6 in µg, and
s is the weight for stack $(NH_4)_2SO_4$ in the IPA absorber from Step 11.4.7 in µg.

11.5.3 Calculate and report the weight for total free H_2SO_4 in the stack given by:

$$z = M + c + t$$

where z is the weight for total free H_2SO_4 in the stack in µg,
M is the weight for free H_2SO_4 in the filter extract from Step 11.2.7 in µg,
c is the weight for free H_2SO_4 in the probe wash from Step 11.3.7 in µg, and
t is the weight for free H_2SO_4 in the IPA absorber from Step 11.4.8 in µg.

11.5.4 Calculate and report the weight for total stack particulate (including $(NH_4)_2SO_3$ and $(NH_4)_2SO_4$) given by:

$$A' = N + d + u$$

where A' is the weight for total stack particulate in µg,
N is the weight for stack particulate in the filter extract from Step 11.2.8 in µg,
d is the weight for stack particulate in the probe wash from Step 11.3.8 in µg, and
u is the weight for stack particulate in the IPA absorber from Step 11.4.9 in µg.

12.0 QUALITY ASSURANCE.

12.1 Follow the quality assurance procedures for the analyses of ammonium, sulfite, and sulfate ions by IC as outlined in the TACB's Laboratory Methods Manual, Methods 26b and 26a (Reference 5).

12.2 Follow the quality assurance procedures for filters and beakers as outlined in the TACB's Laboratory Methods Manual, Method 23 (Reference 5).

12.3 Prior to sampling, evaporate 200 mL of the DDI water (or acetone) probe wash and 200 mL of the IPA from the batches that will be used for stack sampling.

12.3.1 Evaporate each sample to dryness in clean, tared beakers following the procedures outlined in Step 8.4 in the TACB's Laboratory Methods Manual, Method 23 (Reference 5) for the preparation of clean, tared beakers.

12.3.2 The samples must not be contaminated by more than 0.001% by weight:

Distilled water--not more than 10 mg particulate/liter,
Acetone--not more than 8 mg particulate/liter, and
IPA--not more than 8 mg particulate/liter.

12.3.3 If any sample is contaminated by more than its allowable limit, discard that sample, and test a new batch.

13.0 REFERENCES.

1. EPA Quality Assurance Handbook for Air Pollution Measurement Systems. Volume III - Stationary Source Specific Methods. Method 8. Revision No. 0, May 1, 1979.

2. EPA Quality Assurance Handbook for Air Pollution Measurement Systems. Volume III - Stationary Source Specific Methods. Method 5. Revision No. 0, January 15, 1980.

3. Texas Air Control Board, Sampling Procedures Manual, Chapter 5.

4. EPA Quality Assurance Handbook for Air Pollution Measurement Systems. Volume III - Stationary Source Specific Methods. Method 6. Revision No. 0, May 1, 1979.

5. Texas Air Control Board, Laboratory Methods Manual, Revised 1989. (Method 26b, Analysis for Cations by Ion Chromatography, is under development.)

Determination of Common Anions by Ion Chromatography

1.0 PRINCIPLE AND APPLICABILITY.

1.1 This method measures total solvent-soluble levels of chloride, nitrate, sulfate, and other common inorganic anionic species in any aqueous solution or aqueous extract.

1.2 A glass fiber or quartz filter is used to collect particulate in the air using a high-volume air sampler.

1.3 Soluble species are then extracted from an exposed filter with very dilute perchloric acid. Any other aqueous solution may be analyzed directly if it is free of particulate matter or filtered before it is analyzed.

1.4 The ion-chromatographic system may be either of the chemically suppressed type or what is called single column ion chromatography. In either case the sample is injected into the column. The first stage of separation consists of a pre-column and a separator column follows. A conductivity detector, which monitors changes in the conductivity of the effluent, is used to monitor the concentration of the ions. Appropriate electronics convert the signal from the detector into a chromatographic spectrum.

1.5 Peak heights (or peak areas) are recorded and the concentration of each anion is determined using a standard curve.

1.6 Any species which can be chemically altered to an inorganic ion (e.g.,sulfur dioxide oxidized to sulfate ion) may be analyzed by this method. The only restriction is that the chemical species must be the anion of a strong acid. For example, sulfide and cyanide cannot be measured using conductivity detection.

2.0 RANGE AND LOWER DETECTABLE LIMIT (LDL).

2.1 The lower limit for detection of chloride is generally 0.02 μg/mL; the lower limit for nitrate and sulfate is generally 0.05 μg/mL. The LDL may be reduced further by using a more sensitive scale on the conductivity detector or by pre-concentration of the sample.

2.2 There is no upper limit to the method since any sample can be diluted to bring the concentration of the ions within the range of the conductivity scale of the detector.

3.0 PRECISION.

3.1 The average precision of this measurement has historically been ≤ 10% with a maximum acceptable value of 20 %.

4.0 ACCURACY.

4.1 The average accuracy of this measurement has historically been ≤10% with a maximum acceptable value of 20 %.

5.0 INHERENT SOURCES OF ERROR AND INTERFERENCE.

5.1 Many filters (especially the glass fiber type) contain extractable amounts of some ionic species, especially chloride. Contamination can also occur from improperly rinsed containers and even from perspiration. It is very important that all surfaces and utensils be maintained scrupulously clean and that all solvents and diluents be tested for contamination.

5.1.1 The analysis of blanks and other such tests must be included in each analytical run.

5.1.2 A very complex mixture of ions may require special consideration. For example, chloride may interfere with nitrite, phosphate may interfere with sulfate or sulfite. All precautions must be taken to ensure the integrity of the analysis.

6.0 EQUIPMENT/APPARATUS.

6.1 Any chemically-suppressed or single-column ion-chromatograph may be used.

6.2 Proper IC separator column as indicated for the ion(s) being determined.

6.3 A strip chart recorder, an electronic integrator or other device may be used to measure peak area or peak height for each chemical species in the chromatogram.

6.4 Pipettors with disposable plastic tips capable of transferring 0.10- to 10.0-mL quantities, either alone or in combination.

6.5 Sufficient volumetric flasks in which to prepare standards, eluent, and regenerant.

6.6 Sufficient number of test tubes for extracting and storing samples.

6.7 Ultrasonic bath, when needed, for extracting ions from particulates or other solid materials.

6.8 Apparatus for filtration of aqueous solutions and accompanying 0.45-μM pore size membrane filters.

7.0 REAGENTS.

7.1 All reagents should be ACS reagent grade.

7.2 High-quality distilled water for rinsing IC system between samples, and to dilute samples if necessary.

7.3 Extraction reagents.

7.3.2 U.S.P. ethyl alcohol, 95% .

7.3.3 A solution that is 5×10^{-5} M in perchloric acid is used to extract the filters.

8.0 PROCEDURE.

8.1 Extraction of filters.

8.1.1 From each 8" x 10" filter, cut a 3/4" to 1" x 8" strip from the exposed part of the filter. If a 37-mM Teflon filter is to be extracted, the whole filter is used and only 10 mL perchloric acid. is required.

8.1.2 Carefully cut the strip into approximately 1/2" pieces and place them in a scrupulously clean (see "Sources of Error"), dry test tube (40- to 50-mL capacity).

8.1.3 Wet the contents of each tube with 8 to 12 drops 95% ethanol.

8.1.4 Add 20 mL of 5×10^{-5} M perchloric acid solution and shake tubes gently to ensure that all filter surfaces are wet. Distilled water may be used in place of perchloric acid.

8.1.5 Place tubes in an ultrasonic bath for 30 minutes.

8.1.6 Remove tubes from bath and shake individually to loosen any stubborn particulate. Filter each sample through a 0.45-μM pore size membrane filter and store in a clean, covered test tube.

8.2 Preparation of Standard Curve.

8.2.1 Prepare a set of standards that includes each of the ions being analyzed. Choose at least five different concentrations, such that the expected range of the sample concentrations will be bracketed by the highest and lowest standards. For example, at the 10-µS/cm setting, standards ranging from 0.05 ppm chlorine and 0.10 ppm nitrate and sulfate to 0.50 ppm chlorine and 1.0 ppm nitrate and sulfate would be reasonable.

8.2.2 The standards should be prepared with glass-distilled water. The eluent may be used as a diluent if the "water dip" poses a problem.

8.2.3 A calibration of the instrument must be performed at regular intervals especially if major changes are made to the system.

8.3 Refer to the operating manual for the specific instrument being used.

8.3.1 Set the eluent pump to give an eluent solution flow rate which will provide both convenient retention times for the desired ions, and complete separation of ion peaks. The concentration of the eluent may also be varied to optimize peak separation and retention times.

8.3.2 If any samples contain particulate or look cloudy, filter them through a syringe-tip filter.

9.0 ANALYSIS OF SAMPLE.

9.1 For analysis of ion concentrations, record peak heights (or areas) for each ion (consult test chromatogram for your particular column to determine elution order).

9.1.1 If the peak height/area of a sample is more than 5% greater than that of the highest standard, dilute the sample with distilled water or eluent to bring it within the range of the standards.

9.1.2 If the peak height/area of a sample is more than 5% less than that of the lowest standard, prepare and analyze a standard low enough to bracket the sample. If there is no integratable peak, that ion is considered non-detectable in that sample.

9.2 Once the linearity of the response to the ion or ions has been confirmed, a single standard for each analytical run may be used to convert peak area or height to concentration. This standard should be analyzed at least twice during each analytical run and and the average peak height or area used in the calculations.

10.0 CALCULATIONS.

10.1 The total ionic concentration of a sample equals the concentration of the aliquot run on the IC multiplied by the dilution factor. If the sample was not diluted prior to IC analysis, the total concentration is given directly calculation.

10.2 It may be more useful to express concentration in $\mu g/M^3$. This number is given by:

$$\mu g/M^3 = ((\mu g/mL)(F)/V)$$

where $\mu g/mL$ = the total sample concentration;

F = any dilution factor and the total volume of the absorber solution or extracting solution. In the case of a filter that was extracted, the fraction of the whole exposed filter which was actually extracted and analyzed (for example, if a one-inch strip from an 8" x 10" filter was used, and one-half inch on either end of the filter was unexposed, then F = 9, because one-ninth of the exposed filter area was analyzed); and

V = the volume of air sampled in M^3

11.0 QUALITY ASSURANCE.

11.1 Precision of the method is measured by duplicate samples taken throughout the analysis.

11.1.1 For a filter that is extracted, a duplicate sample consists of a second strip from a randomly chosen filter which is extracted, analyzed, and compared to the first strip.

11.1.2 The percent difference between duplicate results must be less than 20 %.

11.1.3 A duplicate analysis must be performed for each set of ten or fewer samples.

11.2 Accuracy of the method is determined analyzing an audit solution or a standard solution treated as an unknown.

11.2.1 An audit or a standard analyzed as an unknown must be included during the analysis of every set of ten or fewer samples.

11.2.2 The percent difference from the true value must be less than 20 %.

11.3 Accuracy of the extraction method, when used, is measured by extracting and analyzing audit samples.

11.3.1 An audit sample consists of a portion of a blank filter (same dimensions as sample strips) which has been spotted with solutions containing known amounts of the desired ions.

11.3.2 An analysis of the audit solution must be performed at least once in each analytical run.

11.3.3 The percent difference from the true value must be less than 20 %.

11.4 Accuracy of the analysis is determined by running spiked samples.

11.4.1 A spiked sample should be run for every set of ten or fewer samples.

11.4.2 A spiked sample is prepared by adding a known quantity of a standard to an aliquot of sample. A suitable spike might be prepared as follows: Place a known volume of a sample in a beaker and add an equal volume of a standard that had a similar peak height or area. Mix well and analyze using the same conditions as used for the sample and the standard.

11.4.3 The µg/mL recovered from the standard used for spiking is obtained from the following equations:

A. $R = aB + cD$ where

R = the result for the spiked sample in µg/mL.
a = the fraction of the spiked sample due to the unknown (sample).
B = the concentration of the unknown, already measured, in µg/mL.
c= the fraction of the spiked sample due to the standard.
D = will give the concentration of the standard as determined in the analysis, in µg/mL.

Solve for D.

B. % recovered = D/S x 100 where

S = the true concentration of the standard.

11.4.4 The percent recovered should be between 90-110%.

12.0 REFERENCES.

1. The Determination of Inorganic Anions in Water by Ion Chromatography. James W. O'Dell, John D. Pfaff, Morris E. Gates, and Gerald D. McKee. U.S. EPA. Test Method 300.0, 1984.

2. Chloride, Orthophosphate, Nitrate, and Sulfate in Wet Deposition by Chemically Suppressed ion Chromatography. Susan R. Bachman, Carla Jo Brennan, Jane E. Rothert , and Mark E. Peden. U.S. EPA. Test Method 300.6, 1986.

3. Standard Test Method for Anions in Water by Ion Chromatography. ASTM Method D 4327-84.

4. Determination of Anions by Ion Chromatography with Conductivity Measurement, Method 429. Standard Methods for the Examination of Water and Wastewater. American Public Health Association, 1015 Fifteenth Street, Washington, D.C. 20005, Sixteenth Edition.

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Laboratory Division
Texas Air Control Board

DETERMINATION OF SULFUR DIOXIDE
by Ion Chromatography

A. GENERAL

Sulfur dioxide is trapped as sulfite ion in a slightly basic, dilute carbonate solution. The sulfite is largely air oxidized to sulfate during sampling, and the subsequent addition of hydrogen peroxide insures that oxidation is complete.

The sulfate is measured by ion chromatography. This consists of passing the sample first through an anion exchange column to separate the sulfate from other anions, next through a cation exchange column to remove cations in order to increase sensitivity, and finally through an electrical conductivity detector. The integrated signal from this detector, which is proportional to the quantity of sulfate, is recorded and the sulfate concentration calculated from a standard curve.

B. APPLICABILITY

The lower limit for the determination is approximately 0.075 µg $SO_4^=$ (= 0.05 µg SO_2)/ml absorber. Occasional interfering peaks have been observed in field samples. The most common anions - fluoride, chloride, nitrite, nitrate, bromide, and phosphate - do not interfere. Arsenite is a serious interference. Its retention time is almost identical to that of sulfate, causing falsely high sulfate results without an interference being suspected. Treatment with hydrogen peroxide as prescribed in this method eliminates the arsenite interference by oxidizing arsenite to arsenate, which does not overlap with sulfate. However, when alkaline arsenite absorber is being used for parallel NO_2 sampling, care should be taken to prevent any contamination of the SO_2 sample.

C. APPARATUS

Dionex Model 10 Ion Chromatograph equipped with 3 x 250 mm anion separator column and 6 x 250 mm cation suppressor column
Electronic filter to suppress the cyclic signal created by pulsating pressure in the detector cell
Electronic integrator
Strip chart recorder
Pipettors with disposable plastic tips capable of transferring 0.10, 0.25, 0.50, 0.75, and 1.0 ml quantities, either alone or in combination

Sufficient disposable 20 ml plastic beakers
1 - 5 ml plastic syringe, with tapered Luer tip
1 - 4000 ml volumetric flask
3 - 500 ml volumetric flasks
6 - 100 ml volumetric flasks
Membrane filters, 0.45 μm pore size, for aqueous solutions
Apparatus for suction filtration of aqueous solutions

D. REAGENTS

All reagents should be ACS reagent grade

(1) Stock $NaHCO_3$ Solution
Dissolve 25.20 g $NaHCO_3$ in distilled water in a 500 ml volumetric flask. Dilute to the mark with distilled water.

(2) Stock Na_2CO_3 Solution
Dissolve 25.44 g Na_2CO_3 in distilled water in a 500 ml volumetric flask and dilute to the mark.

(3) Absorbing Reagent
Pipet 20 ml stock $NaHCO_3$ and 15 ml stock Na_2CO_3 into a 4000 ml flask and dilute to volume with distilled water. This solution is 0.003 M in $NaHCO_3$ and 0.0018 M in Na_2CO_3. Filter the solution through a 0.45 μm pore size membrane filter.

(4) Eluent Buffer Solution
Pipet 20 ml $NaHCO_3$ stock solution and 10 ml Na_2CO_3 stock solution into a 4000 ml volumetric flask and dilute to volume with distilled water. This solution is 0.003 M in $NaHCO_3$ and 0.0012 M in Na_2CO_3. Filter the solution through a 0.45 μm pore size membrane filter and store in a flexible plastic bottle out of contact with air. (To achieve the desired retention time, separation, etc. the eluent buffer may vary from 0.009 M carbonate to 0.0015 M carbonate.)

(5) Sulfur Dioxide Stock Standard
Dissolve 0.1109 g anhydrous Na_2SO_4 in distilled water in a 500 ml volumetric flask and dilute to the mark. This solution contains a concentration of sulfate equivalent to 100 μg SO_2/ml.

(6) 1% Hydrogen Peroxide Solution
Dilute 3.3 ml 30% hydrogen peroxide to 100 ml with distilled water. This solution must be prepared fresh daily.

E. SAMPLING PROCEDURE

Fill the standard bubbler tubes to be used for sampling with SO_2 absorbing solution and allow them to stand overnight, so that any soluble sulfite in the walls will be leached out. Discard the solution. Refill the tubes with 50 ml SO_2 absorbing solution and, using a standard bubbler

train, sample at a rate of about 400 ml/minute for 24 hours. The absorbed SO_2 is air oxidized to $SO_4^=$ ion, in which form it is measured.

F. TEST PROCEDURE

(1) Preparation of Standard Curve
Using the pipettor with disposable tips, transfer 0.10, 0.25, 0.50, 0.75, and 1.0 ml SO_2 stock standard into 100 ml volumetric flasks and dilute to volume with filtered SO_2 absorber. These working standards contain the equivalent of 0.10, 0.25, 0.50, 0.75, and 1.0 µg SO_2/ml respectively.

(2) Sample Analysis
After the sample tubes have been returned to the laboratory for analysis, add to the contents of each 1 ml 1% hydrogen peroxide, mix, cap tightly, and let stand at room temperature for 24 hours. Then place the sample tubes in an oven overnight at 40° C.

Set the pump in the Ion Chromatograph to give an eluent buffer solution flow rate which will provide both a convenient retention time for $SO_4^=$ and complete separation from other ions. (Eluent buffer strength may also have to be varied) The chromatograph output should be connected through the electronic filter and the integrator to the recorder, in that order. Set the electronic filter so that the signal from the pulsating pressure in the detector cell just disappears from the recorder trace. Transfer portions of the standards and samples to disposable plastic beakers which have been pre-rinsed with distilled water. (NOTE: This laboratory has found pre-rinsing of the plastic beakers is necessary because of plastic fragments which will clog the columns.) Inject them into the instrument, taking care to rinse the syringe with eluent or distilled water between solutions and to avoid the introduction of air bubbles into the instrument. Using the integrated values for peak areas of standards and samples, construct a standard curve and calculate the SO_2 concentrations of the samples.

G. CALCULATIONS

$$\mu g\ SO_2/M^3 = \frac{(\mu g\ SO_2/ml)\ (\text{volume of absorber in ml})}{(M^3 \text{ of air sampled})}$$

H. QUALITY CONTROL

Duplicates should be run on 7% of the samples or at least one duplicate per batch of 15 or less. These will test the precision of the procedure. The relative deviation should be less than 5% for concentrations above 0.25 µg SO_2/ml.

$$\text{Relative Deviation (.R.D.)} = \frac{\bar{d}}{\bar{v}} \qquad \bar{d} = \frac{|v_1 - v_2|}{2}$$

$$\bar{v} = \frac{v_1 + v_2}{2}$$

where $\bar{d}$ = average deviation

$\bar{v}$ = arithmetic average

v_i = individual measurement

Spiked samples should be run to control the accuracy of the analysis. Spiked samples are prepared by adding a known quantity of a standard to an aliquot of sample. Percent recovery can be calculated from the concentrations of the spiked sample, the sample and the standard.

A suitable spike would be prepared as follows: Place 5 ml of the 1.0 µg SO_2/ml standard in a test tube. Add 5 ml of the sample to the test tube. Mix well. Run the spike using the same conditions as used for the sample and standards.

$$\text{Percent Recovery} = \frac{\text{conc(spike + sample)} - \text{conc(sample)}}{\text{conc(spike)}} \times 100$$

A spiked sample should be run with each set of samples. The percent recovery should be between 90-110%. If not, all steps in the analysis should be examined carefully and the analysis repeated.

A standard curve must be run with each set of samples.

I. REFERENCES

Sawicki, I., Mulik, J.D., and Wittgenstein, E., Ion Chromatographic Analysis of Environmental Pollutants, Ann Arbor Science Publishers, Inc., Ann Arbor, Michigan, 1978.

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Laboratory Division
Texas Air Control Board

DETERMINATION OF SULFUR DIOXIDE

Modifications of West-Gaeke

A. GENERAL

Sulfur dioxide (SO_2) is absorbed in a solution of potassium tetrachloromercurate. A red-violet color is developed at a later time by the addition of reagents. The color intensity developed is a function of the concentration of absorbed SO_2. Measurement of color intensity is made using a spectrophotometer or colorimeter.

B. APPLICABILITY

The SO_2-tetrachloromercurate complex formed during the absorption is thermally unstable and at temperatures over 40° C, there is a loss of SO_2 of 25%/day. Below 20° C the rate of loss is less than 1%/day. Hence, refrigerated storage and rapid analysis will increase the accuracy of the determination.

The range of the analysis is from .05 µg SO_2/ml of absorber to 5 µg SO_2/ml of absorber. Collection efficiency is assumed to be 100%, but this efficiency can be influenced by collection rate as well as temperature. Using a 3X scale expansion, this laboratory found that we are able to detect a lower limit of 8 µg/M^3 using 10 mm cuvettes. The only interference normally encountered is nitrogen dioxide and this interference is removed by the addition of sulfamic acid during the analysis.

C. APPARATUS NEEDED

Suitable sampling apparatus
Adequate and sufficient storage bottles
3 - 1000 ml volumetric flasks
2 - 500 ml volumetric flasks
1 - 250 ml volumetric flask
2 - 200 ml volumetric flask
7 - 100 ml volumetric flasks
3 - 250 ml beakers
Sufficient 1" test tubes and cuvettes for the number of standards and samples being analyzed
3 - 1 ml volumetric pipets
4 - 2 ml volumetric pipets
1 - 3 ml volumetric pipet
1 - 4 ml volumetric pipet
3 - 5 ml volumetric pipets
8 - 10 ml volumetric pipets
1 - 20 ml volumetric pipet
1 - 50 ml volumetric pipet
3 - glass stirring rods

1 - Spectrophotometer capable of operating at 575 nm

D. REAGENTS

All reagents should be ACS reagent grade.

(1) Absorbing Reagent, Potassium Tetrachloromercurate
Dissolve 10.9 grams of mercuric chloride ($HgCl_2$), 5.96 grams of potassium chloride (KCl), and .066 grams EDTA (disodium salt), and dilute to 1000 ml with distilled or deionized water. The pH of this reagent should be approximately 4.0, but the range of pH 3-5 is acceptable according to the Federal Register. The reagent is stable for up to six months. If a precipitate appears, discard the reagent.

CAUTION!! This absorbing reagent contains mercury which is a health hazard. Avoid pipeting by mouth and wash thoroughly if any is spilled upon the skin. The Hg can be recovered by placing the used or unused absorbing solution in a covered polyethylene container along with shreds of aluminum plates or containers. The Hg will amalgamate with the aluminum and after a period of several weeks, the aqueous liquid can be decanted off. The mercury-aluminum amalgam sludge may be retained in the container for re-use and eventual reclamation of the mercury. Add cut-up aluminum dishes as necessary to have unreacted aluminum on top of the sludge.

(2) Sulfamic Acid
Dissolve 0.6 grams of sulfamic acid (NH_2SO_3H) in 100 ml of distilled water. Do not use this reagent after it is three days old. Results will get lower as the reagent deteriorates.

(3) Formaldehyde
Dilute 1 ml of 37% formaldehyde to 200 ml with distilled water. Prepare this reagent daily.

(4) Hydrochloric Acid (1N)
Dilute 16.6 ml of concentrated hydrochloric acid to 200 ml.

(5) Stock Sulfite Solution
Dissolve 1.91 grams of reagent grade sodium metabisulfite ($Na_2S_2O_5$) in 100 ml of distilled water in a 250 ml volumetric flask. After the $Na_2S_2O_5$ is dissolved, dilute the solution to 250 ml. Prepare and standardize before each use. Dilutions will be made from this stock solution to make the working solutions - 7.65 grams of $Na_2S_2O_5$ per liter should yield a SO_2 concentration of approximately 5000 µg/ml.

(6) Starch Solution

Prepare by dissolving 2 grams of reagent grade soluble starch in 500 ml boiling deionized water, and then filtering while warm. Add one or two drops of the tetrachloromercurate absorbing solution to inhibit mold growth.

(7) Potassium Dichromate Solution

Using an analytical balance, weigh out 2.4518 grams of oven-dried potassium dichromate ($K_2Cr_2O_7$). Dissolve this $K_2Cr_2O_7$ in deionized water in a 500 ml volumetric flask and make up to the mark. The resulting dichromate standard solution is 0.100 N, and may be stored as long as desired. It can increase in strength if any water is allowed to evaporate. Standard 0.100 N dichromate solution can be purchased, if preferred.

(8) Basic Fuchsin[1]

(a) Concentrated Solution

Dissolve 0.2 grams basic fuchsin in 100 ml of 1 N hydrochloric acid. Stir until the basic fuchsin is all dissolved. This solution is stable for up to nine months if kept refrigerated.

(b) Basic Fuchsin Reagent

Place 40 ml of the concentrated basic fuchsin solution in a 500 ml volumetric flask. Add 10.1 ml of 85% H_3PO_4 and then dilute to the mark with distilled water. The reagent is stable for up to nine months if it is kept refrigerated.

E. COLLECTION OF SAMPLE

The sample is collected using a known volume of the potassium tetrachloromercurate absorbing solution placed in a suitable impinger. Air is bubbled through the solution at a rate not to exceed 2-2.5 liters/minute. A total of 0.05 µg SO_2/ml of absorbing solution must be collected before reliable determinations can be made. Since the SO_2-tetrachloromercurate complex is thermally unstable, the SO_2 concentration in an air sample is dependent on the temperature during and after sample collection. The following table shows the SO_2 loss due to temperature.

[1] Either basic fuchsin or pararosaniline hydrochloride may be used, but one should use a calibration curve prepared with the same dye since the pararosaniline produces darker color.

Temperature °C	Rate of SO_2 Loss %/Day
20	0.9
30	5.0
40	25.0
50	75.0

The sample should be kept as cool as possible. Identify the sample adequately after it is taken. Sampling lines should be made of FEP Teflon^R, or glass. Other plastics are acceptable if they cannot be avoided. Metal lines and fittings must not be used. All sampling lines should be as short as possible. Avoid particulate pre-filters if possible, or check the brand of pre-filters used for SO_2 absorption under sampling conditions.

F. TEST PROCEDURE

(1) Preparation of Standard Curve

(a) Standardization of Stock Bisulfite Solution

Fill a burette with the $Na_2S_2O_5$ stock solution to be standardized. Into each of three Erlenmeyer flasks or beakers, pipet 50 ml of 0.100 N $K_2Cr_2O_7$ using a volumetric pipet. Add 8 ml of concentrated HCl to each flask. From this point , handle each flask individually through the titration. To the first flask, add 2g KI, swirl to hasten dissolution. Titrate the liberated iodine at once with the $Na_2S_2O_5$ solution until the color is a dirty green (approximately 30 ml should be needed). Add 2 ml of starch solution and continue the titration. There is a blue to emerald green color change at the end point. The change is sharp and clear. Titrate the second and third samples in the same way. Determine the blank by use of the same amount of KI and HCl in 50 ml of water. Correct the volume of $Na_2S_2O_5$ for any blank and calculate the normality of the $Na_2S_2O_5$ solution. If the $Na_2S_2O_5$ is of good reagent grade, the solution should contain about 5000 µg SO_2/ml.

The average of results from three titrations should be used as the µg SO_2/ml in the stock solution on that day.

(b) Curve Preparation

To a 100 ml volumetric flask, add 1 ml of the standardized stock sulfite solution and dilute to the mark with potassium tetrachloromercurate solution. This intermediate solution contains approximately 50 µg SO_2/ml. Place 0, 1, 2, 3, 4, and 5 ml of the 50 µg SO_2/ml in 100 ml volumetric flasks and dilute to the mark with the potassium tetrachloromercurate solution. The exact amounts of SO_2 per ml are equal to:

conc. of stock sulfite x 1 x 10^{-4} or approx. .5 µg/ml
conc. of stock sulfite x 2 x 10^{-4} or approx. 1.0 µg/ml
conc. of stock sulfite x 3 x 10^{-4} or approx. 1.5 µg/ml
conc. of stock sulfite x 4 x 10^{-4} or approx. 2.0 µg/ml
conc. of stock sulfite x 5 x 10^{-4} or approx. 2.5 µg/ml

These standards and blanks are used to generate a standard curve. The time lapse from titration of the stock sulfite solution to preparation and use of the standard solutions should be held to a minimum, particularly prior to the final dilution with the absorbing solution.

Place 10 ml of each of the standards and the blank in a separate 1" test tube. To each test tube add 1 ml of the sulfamic acid solution, mix thoroughly, and allow to stand for ten minutes. To each of the test tubes, add 2 ml of the formaldehyde solution and 5 ml of the basic fuchsin reagent and mix thoroughly. Develop the color for 30 minutes in the dark. Measure the absorbance of each standard against the reagent blank at 575 nm. Plot a curve of absorbance vs. µg SO_2/ml.

(2) Sample Determination

For ambient samples, measure the amount of absorbing solution remaining after sampling. Add deionized water to offset any evaporation loss that occurred during sampling. For compliance samples do not add water. Place 10 ml of the sample in a 1" test tube. Proceed as described above. Prepare a 20 ml reagent blank using twice the quantities specified in the standard curve preparation. Measure the resulting absorbance and determine the sample concentration of SO_2 in µg/ml from the prepared standard curve.

In some property line sampling, the concentration of SO_2 will be high. In such cases, the absorbance developed may be too high for accuracy. If the absorbance developed is found to be over 0.9, take an aliquot and dilute with a portion of the blank of the same age back to a total volume of 18 ml. Immediately read the absorbance of the diluted sample vs. the remaining blank. From the standard curve, determine the µg SO_2/ml of the diluted sample.

G. CALCULATIONS

(1) Concentration of SO_2 in Stock Bisulfite

$$\text{Normality of } Na_2S_2O_5 = \frac{(\text{Normality of } K_2Cr_2O_7)(\text{Volume of } K_2Cr_2O_7)}{(\text{Volume of } Na_2S_2O_5)} =$$

$$\frac{(0.100\ N)(50\ ml)}{(\text{Volume } Na_2S_2O_5 \text{ in ml})}$$

$\mu g\ SO_2/ml$ = (Normality of $Na_2S_2O_5$) $3.20 \times 10^4\ \mu g\ SO_2/meq\ Na_2S_2O_5$

$$= \frac{(0.100\ N)(50\ ml)\ (3.20 \times 10^4\ \mu g\ SO_2/meq\ Na_2S_2O_5)}{(\text{Volume } Na_2S_2O_5 \text{ in ml})} =$$

$$= \frac{1.60 \times 10^5\ \mu g\ SO_2}{\text{Volume } Na_2S_2O_5 \text{ in ml}}$$

(2) Concentration of SO_2 in Air

$$\mu g\ SO_2/M^3 = \frac{(\mu g\ SO_2/ml)(\text{total volume of absorbing solution})}{M^3 \text{ air sampled}}$$

if dilution is made multiply by $\frac{18\ ml}{ml\ aliquot}$

H. QUALITY CONTROL

All titrations should be run in triplicate. The stock bisulfite must be standardized before each use. The relative deviation in the volume of titrant used should be less than 5 parts per thousand (5 °/oo). The relative deviation is calculated as follows:

$$\text{Relative Deviation (R.D.)} = \frac{\bar{d}}{\bar{v}} \qquad \bar{d} = \frac{\Sigma|v_i - \bar{v}|}{N}$$

where: $\bar{d}$ = average deviation

$\bar{v}$ = arithmetic average of all individual measurements

v_i = individual measurement

N = number of measurements

for example:

Three titration volumes, v_i, were found to be 49.80 ml, 49.91 ml, 49.89 ml for the standardization of $Na_2S_2O_5$.

$\bar{v} = 49.87 \qquad \Sigma|v_i - \bar{v}| = 0.13$

$\bar{d} = \frac{0.13}{3} = 0.04$

R.D. = $\frac{0.04}{49.87} = 0.8$ °/oo

therefore, the three titrations are acceptable

Duplicate analyses of 7 percent of the samples should be run to test the precision of the procedure. The relative deviation should be less than 5% if the absorbance reading is greater than 0.100.

$$\text{R.D.} = \frac{\bar{d}}{\bar{v}} \quad \text{where } \bar{d} = |v_1 - v_2|$$

$$\bar{v} = \frac{v_1 + v_2}{2}$$

Spiked samples should be run to control the accuracy of the analysis. Spiked samples are prepared by adding a known quantity of a standard to an aliquot of sample. Percent recovery can be calculated from the concentrations of the spiked sample, the sample, and the standard.

A suitable spike would be prepared as follows: Place 4 ml of the most concentrated working standard (approximately 2.5 µg SO_2/ml) in a 1" test tube. Add 6 ml of sample. Mix. Add 1 ml of sulfamic acid solution, mix thoroughly, and allow to stand for ten minutes. Add 2 ml formaldehyde solution and 5 ml of basic fuchsin reagent and mix thoroughly. Develop for 30 minutes in the dark. Measure the absorbance of each standard against the reagent blank at 575 nm.

$$\text{Percent Recovery} = \frac{\text{conc(sample + spike)} - \text{conc(sample)}}{\text{conc(spike)}} \times 100$$

For example:

A sample had a concentration of 0.55 µg SO_2/ml. The spike of the same sample had a measured concentration of 1.28 µg SO_2/ml. The spike was prepared as above. The standard used for the spike had a concentration of 2.48 µg SO_2/ml.

$$\text{conc(sample + spike)} = 1.28 \text{ µg } SO_2\text{/ml}$$

$$\text{conc(sample)} = (0.55 \text{ µg } SO_2\text{/ml})\left(\frac{6 \text{ ml}}{10 \text{ ml}}\right) = 0.33 \text{ µg } SO_2\text{/ml}$$

$$\text{conc(spike)} = (2.48 \text{ µg } SO_2\text{/ml})\left(\frac{4 \text{ ml}}{10 \text{ ml}}\right) = 0.99 \text{ µg } SO_2\text{/ml}$$

$$\text{Percent Recovery} = \frac{(1.28 \text{ µg } SO_2\text{/ml}) - (0.33 \text{ µg } SO_2\text{/ml})}{0.99 \text{ µg } SO_2\text{/ml}} \times 100 = 96\%$$

A spiked sample should be run with each set of samples. The percent recovery should be between 90%-110%. If not, all steps of the analysis should be examined carefully and the analysis repeated.

A standard curve must be run with each set of samples.

I. REFERENCES

Scarengelli, F. P., Saltzman, B. E., and Frey, S. A., "Spectrophotometric Determination of Atmospheric Sulfur Dioxide", Analytical Chemistry 39, 1709, (1967).

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Laboratory Division
Texas Air Control Board

Determination of Sulfur Dioxide, Sulfur Trioxide and Sulfuric Acid Mist in Stack Gas Peroxide-Barium Titration Method

A. GENERAL

Sulfuric acid mist (H_2SO_4) and sulfur trioxide (SO_3) are trapped in an impinger containing 80% isopropyl alcohol, in which SO_3 is converted to H_2SO_4. Sulfur dioxide (SO_2) is not absorbed and passes through to a second impinger containing a 6% hydrogen peroxide (H_2O_2) solution which traps it and converts SO_2 to H_2SO_4.

The H_2SO_4 formed in the liquid absorbers is measured by titration with barium perchlorate [$Ba(ClO_4)_2$] using thorin indicator. The results are calculated either as SO_2 or SO_3 as appropriate.

B. APPLICABILITY

The range of analysis for SO_2 is approximately 0.005 g to 14.0 g. This range has been determined from reviewing past SO_2 analyses. About 95% of SO_2 will be collected in the first H_2O_2 impinger. Thorin indicator is a divalent cation indicator so any divalent metal cation such as Cd^{++}, Co^{++}, Fe^{++}, and Zn^{++} will interfere. An interfering ion will turn the thorin pink as soon as it is added to the sample. This titration can only be done on samples that have a filter before the impinger.

C. APPARATUS

Suitable sampling apparatus
Glass fiber filters
Adequate and sufficient storage bottles
Sealable polyethylene bags
1, 2, 3, 4, or 5 ml volumetric pipets depending on sample aliquot to be taken
20 ml volumetric pipet
100 ml beakers (enough for number of samples to be analyzed)
Magnetic stirrer and magnet (optional)
25 ml or 50 ml burets
500 ml volumetric flasks
150 ml Erlenmeyer flasks

D. REAGENTS

(1) Distilled Water

(2) Isopropyl Alcohol (2-propanol)

(3) Ethanol

(4) 80% Isopropyl Alcohol
Dilute 800 ml isopropyl alcohol to 1,000 ml with DI water.

(5) 30% Hydrogen Peroxide (commercial reagent grade H_2O_2)

(6) 6% Hydrogen Peroxide
Dilute 1 volume of 30% H_2O_2 to 5 volumes with distilled water. Prepare as needed daily.

(7) Sodium Carbonate (Na_2CO_3)

(8) Sulfuric Acid, 96% (commercial reagent grade H_2SO_4)

(9) Methyl Orange Indicator
Dissolve 0.01 g of methyl orange in 100 ml distilled water.

(10) 0.1 N Sulfuric Acid
Add 2.8 ml concentrated (96%) sulfuric acid to a little distilled water in a 1000 ml volumetric flask and dilute to the mark.

(11) Barium Perchlorate, anhydrous [$Ba(ClO_4)_2$]

(12) Thorin Indicator
Dissolve 0.2 g thorin in 100 ml distilled water. Store in a polyethylene bottle. (Thorin: o- [(2-hydroxy-3, 6-disulfo-1-naphthyl)azo] benzene-arsonic acid, disodium salt)

(13) 0.01 N Alcoholic Barium Perchlorate
Dissolve 1.7 g $Ba(ClO_4)_2$ in 200 ml distilled water and dilute to 1000 ml with isopropyl alcohol.

E. COLLECTION OF SAMPLE

Samples should be collected according to accepted stack sampling procedures using a series of impingers with the appropriate absorbing solutions. After sampling, the impingers should be carefully stoppered and returned to the laboratory for analysis. If there is a shortage of impingers, the following procedure may be used:

Transfer the contents of impingers into separate clean polyethylene bottles. Care must be taken to spill nothing when washing out the impingers with DI water. A polyethylene wash bottle is convenient for washing impinger tip and tube. Transfer all washings from one impinger to the corresponding sample bottle. Carefully label each bottle for impinger number, test number, date, etc. Place the filter, which must be glass fiber and not cellulose, in a clean polyethylene bag; seal; and label.

F. TEST PROCEDURE

(1) Standardization of 0.1 N Sulfuric Acid

Into each of three numbered 150 ml Erlenmeyer flasks, weigh accurately*, by difference from a weighing boat, 0.1 g samples of primary standard sodium carbonate. (The sodium carbonate should be dried at 105° C for 2 hours and stored in a desiccator before use.) Rinse and fill a buret with the 0.1 N sulfuric acid solution. Dissolve the first sample of standard sodium carbonate in 25 ml distilled H_2O. Add a few drops of methyl orange indicator. Record the initial buret reading, then titrate the solution of sodium carbonate with the 0.1 N sulfuric acid solution. There is a yellow to orange color change at the endpoint. Approximately 20 ml of 0.1 N H_2SO_4 titrates 0.1 g Na_2CO_3. Record the final buret reading. Dissolve and titrate the second and third sodium carbonate solutions in the same way.

*EXAMPLE:

wt. of weighing boat + Na_2CO_3	1.3201 g
wt. of weighing boat - Na_2CO_3	1.2189 g
wt. of Na_2CO_3 in flask I	0.1012 g

(2) Standardization of 0.01 N Alcoholic Barium Perchlorate

Into each of three 100 ml beakers, pipet 1 ml of the standard 0.1 N H_2SO_4 solution. Add 4 ml of distilled water; 20 ml of isopropyl alcohol, and 2 to 4 drops of thorin indicator to each beaker. Rinse and fill a buret with 0.01 N $Ba(ClO_4)_2$ solution. Record the initial buret reading, then titrate the solution of sulfuric acid with the $Ba(ClO_4)_2$ solution. There is a yellow to pinkish yellow color change at the endpoint. Approximately 10 ml of $Ba(ClO_4)_2$ are needed to titrate 1 ml of 0.1 N H_2SO_4. Record the final buret reading. Titrate the second and third sulfuric acid solutions the same way.

(3) Sample Analysis

Transfer the contents of the sample bottle to a 500 ml volumetric flask. Dilute to the mark with the distilled water. Into each of three beakers place a 5 ml aliquot of the sample solution. If the sample contains large amounts of H_2SO_4 (formed from SO_2 or SO_3), a smaller aliquot or a dilution may be necessary. This depends on the ability of the analyst to see the endpoint since the more titrant added, the fainter the endpoint becomes.

For SO_2, H_2SO_4 mist, and SO_3 analysis, if less than 5 ml sample is used, add sufficient distilled water to the beaker to make a total of 5 ml. Add 20 ml of isopropyl alcohol and 2 to 4 drops of thorin indicator**. (The exact alcohol - water ratio is not critical.) Rinse and fill a buret with 0.01 N $Ba(ClO_4)_2$ standard solution. Record the initial buret reading, then titrate the

the sample to a pinkish yellow endpoint. Record the final buret reading. Titrate the second and third aliquots the same way.

**A little methylene blue can be mixed with the thorin for use as the indicator. This makes the endpoint easier for some analysts to see, but does not affect the endpoint.

G. QUALITY CONTROL

Replicate analyses (triplicate preferably) of each sample should be run to control the precision of the analysis. The average deviation in the volume of $Ba(ClO_4)_2$ used should be less than 0.05 ml. The average deviation is calculated as follows:

$$\bar{d} = \frac{\Sigma \mid v_i - \bar{v} \mid}{N}$$

where $\bar{d}$ = average deviation

v_i = individual measurement

$\bar{v}$ = arithmetic average of all individual measurements

N = number of replicates

For example:

Three titration volumes, v_i, were found to be 4.85 ml, 4.87 ml, 4.80 ml.

$4.85 + 4.87 + 4.80 = 14.52 \qquad \bar{v} = 4.84$

$\mid v_1 - \bar{v} \mid = \mid 4.85 - 4.84 \mid = 0.01$

$\mid v_2 - \bar{v} \mid = \mid 4.87 - 4.84 \mid = 0.03$

$\mid v_3 - \bar{v} \mid = \mid 4.80 - 4.84 \mid = 0.04$

$\Sigma \mid v_i - \bar{v} \mid = 0.08 \qquad \bar{d} = \frac{\Sigma \mid v_i - \bar{v} \mid}{N} = \frac{0.08}{3} = 0.03$

Therefore, the three titrations are acceptable.

Another example:

2.63, 2.73, 2.79 $\qquad \bar{v} = 2.72 \qquad \bar{d} = \frac{\Sigma \mid v_i - \bar{v} \mid}{N} = 0.06$

Therefore another titration must be done.

Spiked samples should be run to control the accuracy of the analysis. Spiked samples are prepared by adding a known quantity of a standard to an aliquot of sample. Percent recovery can be calculated from the concentration of the spiked sample, the sample, and the standard.

A suitable spike would be prepared as follows: Place a 4 ml aliquot of sample in a beaker. Add 1 ml of 0.05 N H_2SO_4 to the beaker. (Prepared by mixing 10 ml of 0.1 N H_2SO_4 and 10 ml of distilled H_2O. Use volumetric pipets.) Add 20 ml of isopropyl alcohol and 2 to 4 drops of thorin indicator. Titrate as a normal sample. Do in triplicate.

$$\text{Percent recovery} = \frac{\text{conc. (spike + sample)} - \text{conc(sample)}}{\text{conc (spike)}} \times 100$$

For example:

A sample required 2.43 ml, 2.47 ml, 2.46 ml of 0.010 N $Ba(ClO_4)_2$ for each 5 ml aliquot. Spikes of the same sample required 6.89 ml, 6.91 ml, 6.90 ml $Ba(ClO_4)_2$. The spikes were prepared as above.

$$\text{Conc (spike)} = \frac{(1 \text{ ml})\ (0.05 \text{ N } H_2SO_4)}{5 \text{ ml}} = 0.0100 \text{ N}$$

$$\text{Conc (sample)} = \frac{(2.45 \text{ ml})(0.0100 \text{ N})(4 \text{ ml})}{5 \text{ ml} \qquad (5 \text{ ml})} = 0.0039 \text{ N}$$

$$\text{Conc (spike + sample)} = \frac{(6.90 \text{ ml})(0.0100 \text{ N})}{5 \text{ ml}} = 0.0138 \text{ N}$$

$$\text{Percent Recovery} = \frac{0.0138 \text{ N} - 0.0039 \text{ N}}{0.0100 \text{ N}} \times 100 = 99.0\%$$

A spiked sample should be run with each set of samples. The percent recovery should be between 90% - 110%. If not, all solutions should be standardized again. The samples would be titrated again if the standard solutions have changed.

The 0.1 N H_2SO_4 solution and the 0.01 N $Ba(ClO_4)_2$ solution must be standardized each time they are prepared. The $Ba(ClO_4)_2$ should be standardized every three months.

H. CALCULATIONS

(1) Standardization of 0.1 N H_2SO_4

$$\text{Normality of the } H_2SO_4 = \frac{\text{grams } Na_2CO_3 \times 1000 \text{ ml/l}}{53.00 \text{ g/eq} \times \text{volume } H_2SO_4 \text{ in ml}}$$

(2) Standardization of 0.01 N $Ba(ClO_4)_2$

$$\text{Normality of } Ba(ClO_4)_2 = \frac{\text{volume } H_2SO_4 \text{ in ml} \times \text{normality } H_2SO_4}{\text{volume } Ba(ClO_4)_2 \text{ used in ml}}$$

(3) Samples:

g SO_2 in sample =

$$\frac{[\text{volume } Ba(ClO_4)_2]\ [\text{Normality } Ba(ClO_4)_2]\ [0.032 \text{ g/eq } 1/\text{ml}]\ [\text{sample volume}]}{\text{aliquot volume}}$$

g H_2SO_4 in sample = same, except use 0.049 instead of 0.032.

g SO_3 in sample = same, except use 0.040 instead of 0.032.

I. REFERENCES

Determination of SO_2 and SO_3 in Stack Gas, Emeryville Method 4S16-59a, Analytical Department, Shell Development Company, Emeryville, California, 1959.

Texas Air Control Board Compliance Sampling Manual, as revised.

Environmental Protection Agency. Method 8, Determination of Sulfuric Acid Mist and Sulfur Dioxide Emissions from Stationary Sources.

Determination of Suspended Particulate Matter in the Atmosphere (High-Volume Method) TSP and SSI

1.0 PRINCIPLE AND APPLICABILITY.

1.1 For the purposes of this description, total suspended particulate (TSP) is defined as sampling at the 25-50-μm cutoff point. Size selective inlet (SSI) sampling is sampling at the 10-μm cutoff point.

1.2 This method provides a measurement of the mass concentration of TSP in ambient air for determining compliance with the primary and secondary national ambient air quality standards for particulate matter. The measurement process is nondestructive, and the size of the sample is usually adequate for subsequent chemical or nonchemical, i.e., nondestructive, analysis.

1.3 An air sampler, properly located at the measurement site, draws air into a covered housing and through a filter during a 24-hour (nominal) sampling period. The sampler's flow rate and the geometry of the shelter favor the collection of particles up to 25-50 μm (aerodynamic diameter), depending on wind speed and direction, for TSP sampling. In the case of SSI sampling, the sampler is designed to discriminate against particles larger than 10 μm (aerodynamic diameter). The glass fiber filters used are specified to have a minimum collection efficiency of 99 percent for 0.3-μm (DOP) particles.

1.4 The filter is weighed (after equilibration at constant humidity) before and after use to determine the net weight (mass) gain. The total volume of air sampled, corrected to EPA standard conditions (25° C, 760 mm Hg), is determined from the measured flow rate and the sampling time. The concentration of total suspended particulate matter in ambient air is computed as the mass of collected particles divided by the volume of air sampled, corrected to standard conditions, and is expressed as micrograms per standard cubic meter (μg/std m^3).

2.0 RANGE AND LOWER DETECTABLE LIMIT.

2.1 The approximate concentration range of the method, at least as applied to glass fiber filters, is 2 to 750 μg/std m^3. The upper limit is determined by the point at which the sampler can no longer maintain the specified flow rate due to the increased pressure drop of the loaded filter. This point is affected by particle size distribution, moisture content of the collected particles, and variability from filter to filter, among other things. The lower limit is determined by the sensitivity of the balance and by inherent sources of error (see Section 6.0).

2.2 At wind speeds between 1.3 and 4.5 m/sec (3 and 10 mph), the high-volume air sampler has been found to collect particles up to 25 to 50 μm (TSP sampler), depending on the wind speed and direction, and the SSI sampler up to 10 μm. For the glass fiber filter specified below there is effectively no lower limit on the particle size.

3.0 PRECISION.

3.1 A measure of the precision of the weighing methods with glass fiber filters is a mean weight difference for 48 exposed filters that were reweighed during the first quarter of 1984 which was -0.0006 g with a standard deviation of 0.0006 g. For the same time period and for 53 clean filters that were reweighed, the mean weight difference was 0.0006 g with a standard deviation of 0.0007 g.

4.0 ACCURACY.

4.1 There is no filter standard available for measuring the accuracy of the weighing process. This method describes a procedure for weighing a 1.0000-g, a 3.0000-g, and a 5.0000-g class "S" weight every day when weighing is to be performed and to record this weight in an appropriate log book. An analysis of the weights recorded during the first quarter of 1984 reveals, for the 5.0000-g weight, a mean weight of 5.0000 g for 39 weighings and a standard deviation of 0.0001 g. If these data are expressed as percent difference, the mean, for the same 39 values, becomes -0.00003 % and the standard deviation is 0.0002 %.

5.0 INHERENT SOURCES OF ERROR AND INTERFERENCES.

5.1 Loss of volatiles. Volatile particles collected on the filter may be lost during subsequent sampling or during shipment and/or storage of the filter prior to the post-sampling weighing. Although such losses are largely unavoidable, the filter should be reweighed as soon after sampling as is practical.

5.2 Artifact particulate matter. Artifact particulate matter can be formed on the surface of alkaline glass fiber filters by oxidation of acid gases in the sample air, resulting in a higher-than-true TSP determination. This effect usually occurs early in the sampling period and is a function of the filter's pH and the presence of acid gases. It is generally believed to account for only a small percentage of the filter weight gain, but the effect may become more significant when relatively small particulate weights are collected.

5.3 Humidity. Glass fiber filters are comparatively insensitive to changes in relative humidity, but collected particulate matter can be hygroscopic.

The moisture-conditioning procedure minimizes, but may not completely eliminate, error due to moisture. It is expected that quartz fiber filters will behave in the same manner. Cellulose filters are very sensitive to changes in humidity; therefore, if the humidity cannot be controlled to within 1%, a correction must be made relative to a fixed humidity. The correction is determined experimentally by weighing a set of cellulose filters under several different humidity conditions and then determining the change of weight per unit humidity change.

5.4 Filter handling. Careful handling of the filter between the pre-sampling and post-sampling weighings is necessary to avoid errors due to loss of glass fibers or particles from the filter. A filter paper cartridge or cassette used to protect the filter can minimize handling errors.

5.5 Non-sampled particulate matter. Particulate matter may be deposited on the filter by wind during periods when the sampler is inoperative. It is recommended that errors from this source be minimized by an automatic mechanical device that keeps the filter covered during nonsampling periods or by timely installation and retrieval of filters to minimize the non-sampling periods prior to and following operation.

6.0 APPARATUS.

6.1 Filters. Filters provided by the Texas Air Control Board (generally through the Environmental Protection Agency) can be assumed to meet the following criteria. Additional specifications are required if the sample is to be analyzed chemically.

6.1.1 Size: Filters designed for TSP and SSI are 20.3 ± 0.2 X 25.4 ± 0.2 cm (nominal 8 X 10 in.).

6.1.2 Nominal exposed area: 406.5 cm^2 (63.0 in.).

6.1.3 Material: Glass fiber, quartz fiber, cellulose, or other relatively inert material.

6.1.4 Collection efficiency: The efficiency for glass fiber filters is 99 percent minimum as measured by the DOP test (ASTM-2986) for particles of 0.3 µm-diameter.

6.1.5 Recommended-pressure drop range: For glass fiber filters, the pressure drop should be 42-45 mm Hg at a flow rate of 1.5 std m^3/min through the nominal exposed area.

6.1.6 pH: Glass fiber filters should have a pH of 6 to 10.

6.1.7 Integrity: 2.4 mg maximum weight loss for glass fiber filters.

6.1.8 Pinholes: None.

6.1.9 Tear strength: Glass fiber filters must have a 500-g minimum tear strength for a 20-mm wide strip cut from the filter in its weakest dimension (see ASTM Test D828-60).

6.1.10 Brittleness: No cracks or material separations after a single lengthwise crease.

6.2 Filter conditioning environment.

6.2.1 Controlled temperature: Between 15° and 30° C with less than 3° C variation during the equilibration period.

6.2.2 Controlled humidity: Less than 50 percent relative humidity, and constant within 5 percent.

6.3 Analytical balance.

6.3.1 Sensitivity: 0.1 mg.

6.3.2 Weighing chamber designed to accept an unfolded 20.3 X 25.4 cm (8 X 10 in.) filter.

6.4 Area light source, similar to X-ray film viewer, or an overhead fluorescent light fixture, to backlight filters for visual inspection.

6.5 Numbering device, capable of printing identification numbers on the filters before they are placed in the filter-conditioning environment, if not numbered by the supplier.

6.6 Hi-vol data record cards are provided for each filter sent into the field. The card has blanks for entering pertinent data for each sampling run.

6.7 Prepaid return envelopes are provided for each filter to facilitate the return of the filters to the central laboratory.

6.8 Flow charts, capable of recording flows for 24 hours at flow rates of 20 to 60 cfm, are provided for samplers having recording flowmeters.

7.0 PROCEDURE.

7.1 Number each filter, if not already numbered by the supplier, near its edge with a unique identification number.

7.2 Backlight each filter and inspect for pinholes, particles, and other imperfections; filters with visible imperfections must not be used.

7.3 Equilibrate each filter in the conditioning environment for at least 24 hours.

7.4 Weigh the filter.

7.4.1 At the start of any day when weighings are to be performed, the balance is challenged with 1.0000-g, 3.0000-g, and 5.0000-g class "S" weights. The measured weight is recorded in the log book devoted to that purpose. The balance must be serviced if any challenged result differs by more than 0.0002 g, after repeated re-taring.

7.4.2 Refer to the automated weighing procedure manual if the automated system is being used. Otherwise, weigh the filter to the nearest milligram and record this tare weight (Wi) with the filter's identification number.

7.4.3 After a batch of filters is weighed, the quality control procedures in Section 10.0 prevail. If the filters are weighed using a non-automated procedure, at least four filters must be reweighed for up to a total of 50 filters weighed, and then at least 10% of the total number of filters if more than 50 were weighed. Under computer control, at least four filters will be reweighed if 50 or fewer were weighed initially, or seven must be reweighed if more than 50 clean filters were weighed, or eight reweighed if more than 50 exposed filters were weighed. The reweighing must be performed by a person who did not weigh the filters originally.

7.5 Do not bend or fold the filter before collection of the sample. Package a set of filters equivalent to the number of filters to be used in one quarter, plus several extra, in a plastic bag. For most applications in the network, the computer program will assign the filters. Prepare a complete filter-supplies package for each site and for each quarter, to consist of the filters, hi-vol data record cards, flow charts, and return envelopes, and send the package to the appropriate regional office or hi-vol operator.

7.6 Inspection and validation of exposed filters.

7.6.1 When exposed filters are received, the data card must be stamped with the date of receipt.

7.6.2 The filter and flow charts are inspected; the particular hi-vol run must be considered invalid if any of the following is true (invalidation code in parentheses):

a. There is an audit failure (AF), or the calibration is overdue (CO), or there was a catastrophic equipment failure (CF);
b. The filter assigned to a particular run date is not received (FNR);
c. Any part of the filter is missing, or the filter is torn (TF);

d. The filter was misaligned on the sampler (FM);
e. The gasket on the sampler leaked (BG);
f. The sampler was operated for more than 25 hours (LR) or less than 23 hours (SR) on a 24 hour run, or the sample filter was run on more than one day (MR), or there was no flow chart used for samplers where one is required (NFC), or the flow chart could not be read (BFC);
g. There was an equipment failure which caused the marking pen or the motor not to operate (EF), or there was a power failure (PF);
h. The initial air flow was greater than 60 cfm (FOL), or the final air flow was less than 40 cfm (FOL), under the new conditions to be applied, or the average flow was less than 20 cfm (LF) under the regulations currently in effect. See Section 10.4.2 for a complete description.
i. The sampler was run on a non-scheduled day (WD);
j. The wrong type of filter was used (WT);
k. The filter was contaminated, or particulate was lost from the filter (SD);
l. The laboratory made an error (I);
m. There was not enough information on the data card (IDS), or the sample had not been run (NR), or there was a general operator error (OE), or the sample was received late (RL);
n. There was bias introduced in the sample by external influences (SB).

7.6.3.1 For samplers in the TSP network, the initial flow and the final flow are read from the flow chart. The average flow is determined from five points along the chart, including the initial and final flows, and a simple average is taken.

7.6.3.2 For samplers manufactured by Andersen, which are used in the SSI network, the total flow is determined using a flow chart and a calibration curve.

7.6.3.3 If samplers manufactured by Wedding are used, the total flow is calculated by using the beginning and ending reading on a Magnahelic gage and a calibration curve.

7.6.4.1 For samplers in the TSP network, the total time the sampler operated is determined from the flow chart.

7.6.4.2 For samplers manufactured by Andersen, which are used in the SSI network, the total time is read from the elapsed time meter.

7.6.4.3 If samplers manufactured by Wedding are used, the total time is read from the elapsed time meter.

8.0 CALIBRATION.

8.1 A calibration chart is provided by the Quality Assurance Division of the TACB for each hi-vol. Calibrations must be performed at less than 6-month intervals.

9.0 CALCULATIONS OF TSP CONCENTRATION.

9.1 Determine the average sampler flow rate during the sampling period. Select five points uniformly spaced around the flow chart and average them. Include both an initial and a final flow rate. Convert the flow rate in cfm to m^3 by multiplying by 0.0283 m^3/ft^3.

9.2 Determine the total sampling time from the flow chart. Read the time of the run to the nearest five minutes. If there is tapering at the start of the run, choose the point where the line stops tapering. If the tracing is not stable after one hour, prepare a report to the Logistics Section of the Ambient Monitoring Division. The run is to be invalidated if the tracing is still not stable after two hours, use BFC invalidation code.

9.3 Calculate the total air volume sampled as:

$$V = Q \times t$$

where:

V = total air volume sampled, in standard volume units, std m^3;
Q = average standard flow rate, std m^3/min; and
t = sampling time, min.

Alternatively, the program available on the microcomputer may be used to perform the calculation.

9.4 Calculate and report the particulate matter concentration, as:

$$TSP = ((Wf-Wi) \times 10^6)/V;$$

where:

TSP = mass concentration of total suspended particulate matter, µg/std m^3;
Wi = initial weight of clean filter, g;
Wf = final weight of exposed filter, g;
V = air volume sampled, converted to standard conditions, std m^3;
10^6 = conversion of g to µg.

10.0 QUALITY ASSURANCE.

10.1 Precision. The precision of the weighing method is measured by reweighing a number of both clean and exposed filters as described above. If a reweighing of any clean filter is more than 0.003 g different from the original weight or if a reweighing of an exposed filter is more than 0.005 g different from the original weight, then the entire batch must be reweighed. For cellulose filters all weights must be corrected to a reference humidity point.

10.2 Accuracy The accuracy of the weighing process may be monitored by the one-gram, the three-gram, and the five-gram balance checks. These checks are performed with class "S" weights, and if there is more than a 0.0002-g weight difference with any calibrated weight, the balance must be tared again. If the discrepancy persists, the balance must be serviced. All this information must be recorded in the appropriate log book.

10.3 Clean filters. Clean filters must meet all tests described in Section 6.1.

10.4 Exposed filters. Exposed filters must meet all the applicable tests described in Section 6.1; the run is declared invalid if any of the tests described in Section 7.6.2 for either the filter or the flow chart is failed.

10.4.1 In the case of samplers in the TSP network, the run is declared invalid if the initial flow rate is greater than 60 actual cubic feet per minute (acfm) or if the final flow rate is less than 39 acfm. For samplers operating with Andersen or Wedding samplers, the average flow must be within +/- 10% of 40 acfm.

10.4.2 The run is declared invalid, regardless of the type of sampler used, if the total time is less than 23 hours or greater than 25 hours.

11.0 ACKNOWLEDGEMENTS.

This procedure was adapted from "Reference Method for the Determination of Suspended Particulates in the Atmosphere (High Volume Method)." Code of Federal Regulations, Title 40, Part 50, Appendix B, pp. 12-16 (July 1, 1975) with appropriate modifications to meet the needs of the TACB. The method as described here includes all references mentioned in the "Reference Method..." description and all interested persons are encouraged to refer to the original for further study.

Determination of Suspended Particulate Matter in the Atmosphere (High-Volume Method) Dichotomous Samplers

1.0 PRINCIPLE AND APPLICABILITY.

1.1 A dichotomous sampler is designed to draw air in a 10-μM cutoff and then divide the particulate into two streams: one with an aerodynamic diameter of between 2 μM and 10 μM and another of less than 2 μM.

1.2 The filters (called membrane filters), which are made of Teflon, are 37 mM in diameter with a polyolefin ring on their circumference to keep them stretched and have a 2-μM pore size. The filters are provided to the Texas Air Control Board (TACB) by the United States Environmental Protection Agency (EPA).

1.3 This method provides a measurement of the mass concentration of suspended particulate matter, in the two particle-size ranges, for determining compliance with the primary and secondary national ambient air quality standards for particulate matter.

1.4 If an elemental analysis of the filters is desired, TACB Method 32 is recommended. This method uses X-ray fluorescence spectroscopy to analyze for 31 elements simultaneously (Reference 1) and has also been declared an equivalent method for lead (Reference 2).

1.5 An air sampler, properly located at the measurement site, draws air into a covered housing, separates the air into two streams and thereby divides the particulate into two fractions. One fraction will have an aerodynamic diameter of less than 2 μM and the other fraction will be in the range of 2 to 10 μM.

1.6 The filter is weighed (after equilibration at constant humidity) before and after use to determine the net weight (mass) gain. The total volume of air sampled, corrected to EPA standard conditions (20° C and 760 mM Hg), is determined from the measured flow rate and the sampling time. The concentration of suspended particulate for each size range is computed as the mass of collected particles divided by the volume of air sampled, corrected to standard conditions, and is expressed in micrograms per standard cubic meter (μg/std M^3).

2.0 RANGE AND LOWER DETECTABLE LIMIT.

2.1 The lower limit of particulate that is detectable, which is determined by the limit to the weighing procedure and other inherent sources of error, is approximately 1 ng/M^3. The upper limit to the range of particulate,

and which should be determined by the point at which the sampler can no longer maintain the specified flow rate, has not been determined.

3.0 PRECISION.

3.1 As a measure of the precision of the weighing methods with membrane filters on a microbalance, a mean weight difference for 52 exposed filters that were reweighed during the second and third quarters of 1985 was -2.1 μg with a standard deviation of 5.8 μg. For the same time period and for 52 clean filters that were reweighed, the mean weight difference was -2.8 μg with a standard deviation of 4.3 μg.

4.0 ACCURACY.

4.1 There is no filter standard available for measuring the accuracy of the weighing process. This method describes a procedure for standardizing the balance with a 200-mg class "M" weight and then weighing a specially designated filter, one which is designated for the weight range of the filters to be weighed (either in the 80 or 90-mg range), and recording this weight in a log book. The mean weight of the 90-mg designated filter for 50 weighings in the period of June through August 1985 was 92391.9 μg with a standard deviation of 4.5 μg (5 parts in 92000).

5.0 INHERENT SOURCES OF ERROR AND INTERFERENCE.

5.1 Loss of volatiles. Volatile particles collected on the filter may be lost during subsequent sampling or during shipment and/or storage of the filter prior to the post-sampling weighing. Although such losses are largely unavoidable, the filter should be reweighed as soon after sampling as is practical.

5.2 Humidity. Membrane filters are comparatively insensitive to change in relative humidity, but collected particulate matter can be hygroscopic. The controlled-humidity environment minimizes, but may not completely eliminate, error due to moisture.

5.3 Filter handling. Careful handling of the filter between the pre-sampling and post-sampling weighings is necessary to avoid errors due to loss of filter material or particles from the filter. The stretched membrane material is particularly susceptible to puncture with forceps or any other sharp object. Extreme care must be taken in handling these filters.

6.0 APPARATUS.

6.1 Filters. The filters provided by the TACB (generally through the EPA) can be assumed to meet the following criteria.

6.1.1 Size. Filters designated for dichotomous samplers are 37 mM in diameter and of 2-μM pore size. The filter is stretched and its shape is retained with a polyolefin ring.

6.1.2 Nominal exposed area. 6.605 cM^2.

6.1.3 Material: Teflon or other similar materials.

6.1.4 Pinholes: None.

6.2 Filter conditioning environment.

6.2.1 Controlled temperature: The temperature is maintained between 15° and 30° C with less than 3° C variation during the equilibration period.

6.2.2 Controlled humidity: The humidity is maintained at less than 50% with a 5% variation permitted.

6.3 Analytical Balance with a sensitivity of 0.1 μg.

6.4 Area light source, similar to X-ray film viewer, or an overhead fluorescent light fixture, to backlight filters for visual inspection.

6.5 Data record sheets are provided for each pair of filters sent into the field. The sheet has blanks for entering pertinent data for each sampling run.

6.6 Prepaid return envelopes are provided for each pair of filters to facilitate the return of the filters to the central laboratory.

7.0 APPARATUS. BALANCE AND ACCESSORIES.

7.1 A balance capable of weighing to 0.01 mg.

7.1.1 A 200-mg class "M" weight.

7.1.2 A reserved set of class "S" weights to total 80 mg and 90 mg.

7.1.3 Additional class "S" weights.

7.2 Static-charge eliminator.

7.2.1 A radioactive material enclosed in a non-destructive case can be used to eliminate any static charge collected on the filters. A Po source is commercially available.

7.3 Test filters.

7.3.1 At least two designated filters are kept in Petri dishes and are used in the quality assurance procedure described in Section 10. One filter should weigh between 80 and 90 mg, and the other should weigh more than 90 mg.

7.4 Anti-magnetic forceps.

7.5 Disposable plastic Petri dishes. 49 mM in diameter and 9 mM deep and with a tight-fitting lid.

7.6 A clock or watch which reads in seconds.

8.0 PROCEDURE.

8.1 Standardizing the balance. The following applies to a Cahn microbalance.

8.1.1 The response should be on 1 and the tare should be off.

8.1.2 Only the special anti-magnetic forceps are to be used. These forceps have a "Cahn" imprinted on them and they are kept in a drawer near than balance.

8.1.3 Zero the balance using the zero adjustment on first the 20 scale and then the 200 scale.

8.1.4 Carefully remove the 200-mg class "M" weight from its container, close the balance door, and wait for the weight to stabilize. The balance should read 199.99 ± 0.01 mg. If an adjustment is necessary use the "calibrate" adjustment to do so. Remove the weight from the balance and return it to its special container.

8.1.5 Place 80 mg of weights from those in the "tare" weights container, or 90 mg if the filters will weigh more than 90 mg, on the tare pan, and a similar weight on the sample side from the weights in the class "S" container, and close the door to the balance.

8.1.6 Do not rezero the balance; instead, use the tare button to bring the balance to zero.

8.1.7 Add the class "M" 200-mg weight to the sample pan. The balance should read 199.99 ± 0.01 mg. If not, use the calibrate adjustment to bring the balance to the correct weight. Remove the 200-mg weight.

8.1.8 Change the balance to the 20-mg scale and use the "tare" button to rezero the balance if necessary.

8.1.9 Remove the 80-mg (or 90-mg) weight from the sample pan.

8.2 Weighing the test filter.

8.2.1 Place the test filter on the radioactive source-static eliminator for 30 seconds.

8.2.2 Place the test filter on the sample pan and after 30 to 45 seconds record the weight in the log book.

8.3 Weighing the filters.

8.3.1 Number each Petri dish with a unique number.

8.3.2 Place a filter on the radioactive source static eliminator for 30 seconds.

8.3.3 Weigh the filter.

8.3.4 Record the weight on the data sheet.

8.3.5 Place the filter in the Petri dish.

8.4 Restoring the balance to its original state.

8.4.1 Release the tare by hitting the tare button twice in rapid succession.

9.0 CALCULATION OF PARTICULATE CONCENTRATION.

9.1 Determine the average sampler flow rate during the sampling period.

9.2 Determine the total sampling time.

9.3 Calculate and report the particulate matter concentration for each fraction as:

$$P.C. = (W_f - W_i)/V$$

where:

P.C. = particulate matter concentration in μg/std. M^3.

W_i = initial weight of clean filter, μg.

W_f = final weight of exposed filter, μg.

V = air volume sampled, converted to standard conditions.

10.0 QUALITY ASSURANCE.

10.1 Precision. The precision of the weighing method is measured by reweighing a number of both clean and exposed filters as described above. If a reweighing of any filter, clean or exposed, is more than 20 μg difference from the original weight, then the entire batch must be reweighed.

10.2 Accuracy. The accuracy of the weighing process may be monitored by the 200-mg class "M" weight checking procedure. If the balance cannot be adjusted to within the limits described, then no weighings are to be made until the balance is serviced. In addition, limits may be established on weighings of the test filter. If any weighing exceeds these limits, then the balance should be recalibrated.

Procedure for the Collection of Wet Deposition Samples at a Precipitation Monitoring Site

1.0 PRINCIPLE AND APPLICABILITY.

1.1 An event monitoring system for the collection of precipitation samples is described in this procedure. The samples collected following this method are analyzed as part of the Texas Air Control Board's (TACB's) wet deposition event monitoring network.

1.2 Anyone operating a precipitation monitoring site must be aware that rain samples are extremely sensitive to contamination. For example, skin oils, perspiration, extraneous dust and dirt, cigarette ash, etc. will cause erroneous results. Containers and bottles must be kept in their protective bags until they are used. During handling of the containers, the inner surfaces must not be touched nor should material be allowed to fall into the containers.

2.0 SITING OF COLLECTOR.

2.1 The sampling collector and its stand shall be located in an open area such that the container does not collect water that has contacted trees, bushes, building roofs, electric power lines or other surfaces that might contaminate the sample.

2.2 The container shall be placed on a stand that is at least three (3) feet above ground level or, if the container is on a building roof, at least three (3) feet above roof level. The container must be in a position which prevents splashing from the ground from contaminating the precipitation sample.

3.0 APPARATUS.

3.1 Samples of precipitation are collected in the collection assembly that is provided by the TACB laboratory in Austin. The assembly is prepared from a "Corning 25932 Disposable Filter System", a polypropylene powder funnel with a 55-mM mouth, and a "Nalgene MitYvac" hand pump that is fitted with a length of "Tygon" tubing that is stoppered at its open end. The cover to the filter system is pierced to accommodate the stem of the funnel which is then held to the base with two large rubber bands.

3.2 The TACB laboratory in Austin will also provide 60-mL and 120-mL bottles, foam mailing boxes and postage-paid return labels. The bottles will have been rinsed with good quality glass-distilled water.

3.3 The containers provided for the collection of the sample will have been rinsed with glass-distilled water having a specific conductance of 1.5

µS/cM or less. And particular attention would have been given to rinsing the filter in the collection assembly since our studies have shown that the filters contain material, probably binders, that contribute to the pH and the conductivity of the solutions that are passed through.

3.4 The container support device can be a support stand with a 3-foot rod and a rectangular base (a ring stand). The sampling assembly is then supported in some manner, an extension ring on a long rod for example, which may be mounted to the support stand with a clamp holder. The base of the support stand may be reinforced with a weight to improve the stability of the stand in high winds. The top of the sampling assembly should be three feet from the ground and the assembly should be three feet from the vertical support.

4.0 COLLECTION OF SAMPLES.

4.1 At the onset of a rainstorm, the collection assembly is removed from its protective bag and placed on the stand.

4.2 Complete Section I of the Field Record Form.

4.3 If at all possible, collect enough rain to fill the bottom container of the collection assembly. If the rain is intermittent, and if there is not yet 100 mL in the container, discontinue the sampling if the sampler has been exposed to a non-raining condition for more than 30 minutes. However, the collector may be left sampling during a rain episode of up to eight hours, provided that no non-raining period lasts more than 30 minutes.

4.4 At the end of the sampling period, remove the assembly from the stand. Attach the vacuum pump to the assembly and draw the remaining rain into the bottom part of the assembly. Keep in mind that the hand pump has two settings--one for pressure and one for vacuum. Make sure it is operating in the vacuum mode.

4.5 Transfer the sample into a 60-mL or 120-mL bottle and seal it tightly. The transfer can be accomplished by simply pouring the precipitation sample from the sampling assembly into the bottle. Do not use a funnel or any other device, and try to fill the bottle as completely as possible.

4.6 Complete Section II of the Field Record Form.

4.7 Send the bottle, in the mailing container, to Austin for analysis.

4.8 Remove excess rain from the sampling assembly by shaking and store it in a plastic wrapper.

4.9 If at any time it is felt that the sampling assembly is contaminated, it must be replaced.

Precipitation Event Monitoring Network

Field Record Form

I. Region_____ City_____

SAROAD Number _____

Location _____

Date _____ Start Time _____

II. Stop Time _____ Duration _____ min.

Sampling Weather Conditions (check all that apply):

Frontal System___ First Half of Event___

Thundershower___ Last Half of Event___

Other___ Entire Event___

Light Rain___

Heavy Rain___

III. Comments

Procedure for the Preliminary Analysis of Wet Deposition Samples at the Precipitation Monitoring Site

1.0 PRINCIPLE AND APPLICABILITY.

1.1 An event monitoring system for the collection of precipitation samples is described in this procedure. An aliquot of the sample is analyzed for conductivity and pH at the local laboratory and the remaining sample is forwarded to the Austin laboratory for analysis as part of the wet deposition event monitoring network.

1.2 Anyone who is performing analyses on precipitation samples must be aware that the samples are extremely sensitive to contamination. For example, skin oils, perspiration, extraneous dust and dirt, cigarette ash, etc., will cause erroneous results. Electrodes, beakers, and other containers and bottles must be rinsed thoroughly in glass-distilled water. During handling of any container, the inner surface must not be touched nor should material be allowed to fall into the container. pH paper may not be used to measure the pH of rain samples because of the very weak buffering capacity of the rain sample. pH paper responds slowly and erratically. In addition, the sample leaches the active materials from the paper.

2.0 FIELD MEASUREMENTS FOR pH AND CONDUCTIVITY.

2.1 The conductivity is measured on an appropriate conductivity meter having a dipping conductivity cell with a cell constant of 1.0 cM.

2.1.1 Conductance is defined as the reciprocal of the resistance. It is measured on an instrument that is basically a Wheatstone bridge with one arm of the bridge being a cell containing the solution that is being measured. The cell consists of two platinized electrodes and the cell is calibrated by measuring the resistance (conductance) of a solution whose conductance is well documented. The calibration constant for the cell is called the cell constant and it will be provided for each cell by the laboratory in Austin.

2.1.2 Specific conductivity is defined as the product of the conductance and the cell constant.

2.2 The pH is measured using a pH meter that measures to 0.01 pH unit and an electrode that is designed to slip into a 13x100-mM disposable culture tube. Other electrodes may be used with suitable modifications to the procedures.

2.3 The conductivity and pH should be measured as soon as possible following collection of the sample.

3.0 REAGENTS.
All reagents should be ACS reagent grade or better.

3.1 The laboratory will supply standard buffers at a pH of 4 and 7 for precipitation samples or buffers at a pH of 3 and 6 if precipitation samples with a pH of less than 4 are anticipated. The buffer solutions will be traceable to National Bureau of Standards (NBS) materials.

3.2 The laboratory will also supply solutions that will be used to check the performances of the pH meter and the conductivity meter prior to their use. Each solution will be of low ionic strength; one will have a pH of about 4.3 and the other a conductivity of about 75 µS/cM.

3.3 The laboratory will also, if requested, provide glass-distilled water that will be certified to have a conductivity of 1.5 µS/cM or less.

4.0 PROCEDURE.

4.1 All solutions and a beaker of water (water blank) must be equilibrated to room temperature. The water blank will be used as a measure of the temperature of all the solutions.

4.2 Measure the conductivity of the sample.

4.2.1 The conductivity of the sample should be measured as soon as possible after the event. The conductivity meter is calibrated according to the manufacturer's directions, and the calibration is confirmed using the test solution provided by the laboratory. The conductivity of all water used to rinse glassware must not exceed 1.5 µS/cM.

4.2.2 Measurements of conductivity are recorded in Section IV of the Analysis Report Form.

4.2.3 Measure and record the temperature of the water blank.

4.2.4 If the conductivity meter has a temperature compensation, adjust the meter to the recorded temperature.

4.2.5 Rinse the conductivity probe with 20 mL of glass-distilled water at least twice.

4.2.6 Record the conductivity of the test solution provided by the TACB Austin laboratory on the form.

4.2.7 Rinse the probe in the test solution; then measure the conductance of the solution and record its value on the form. Use the cell constant of the probe to calculate the conductivity, and then correct the conductivity as described on the form.

4.2.8 Rinse the conductivity probe repeatedly and record the conductivity of the last rinse solution on the form.

4.2.9 Without rerinsing the cell, determine the conductance of 20 mL of the precipitation sample in a clean and rinsed 50-mL beaker, and record the result (to the nearest 0.1 µS) on the form. Follow the directions on the form to calculate the conductivity using the cell constant for the conductance probe. The cell constant is provided with the cell.

4.2.10 Use the same sample for measuring the pH.

4.3 Measure the pH of the precipitation sample.

4.3.1 The pH of the sample should be measured as soon as possible after the conductivity is measured. The pH meter should have been calibrated and ready for use by the time the sample is ready to be analyzed.

4.3.2 Measurements of pH of the sample are recorded in Section V of the Analysis Report Form.

4.3.3 Measure and record the temperature of the water blank.

4.3.4 If the pH meter has a temperature compensator, adjust the meter to the recorded temperature.

4.3.5 The pH meter is calibrated according to the manufacturer's directions using buffers of pH 4 and 7. If a pH of less than 4 is anticipated, then buffers of pH 3 and 6 should be used.

4.3.6 It is important that each electrode be conditioned according to the manufacturer's specifications prior to the measurement.

4.3.7 The special pH electrode that is recommended for precipitation studies is rinsed with the solution to be measured, a solution for calibration or for test, or the precipitation sample, using the culture tubes described above. The tube is filled to 1/3 its capacity and the electrode dipped into it and washed. This procedure is repeated at least once. The pH of the check pH solution and of the precipitation sample are recorded in their appropriate places on the form.

4.3.8 If a typical combination glass electrode or a pair of electrodes is used, then the electrode must be rinsed with glass-distilled water and wiped with a lint-free, paper disposable wipe prior to each measurement.

4.3.9 If the pH of the check solution differs by more than 0.2 pH units from the previous value or from the expected value, or if the pH meter takes more than 60 seconds to stabilize, then seek assistance before the pH of the precipitation sample is measured.

5.0 CALCULATIONS.

5.1 Correct the conductivity of the precipitation sample according to the directions on the form, and record the corrected value.

5.2 Complete the Analysis Report Form and return it, the other aliquot of the sample, and the Field Record Form to the laboratory in Austin.

Precipitation Event Monitoring Network
Analysis Report Form

I. Bucket Number _____ Conductivity of Rinse Water _____.
II. Location of Monitor or Site Number _____.
III. Analyst _____.

IV. Measurement of the Conductivity of the Sample

	Field Measurement	Laboratory Measurement
Date		
Time		
Temperature of Blank		
Conductivity of Last Rinse		
Cell Constant (1)		
Conductance of Standard (2)		
Conductivity of Standard = (Conductance x Cell Constant)		
Ratio = 75/(Conductivity of Standard)		
Conductance of Sample (2)		
Conductivity of Sample = (Conductance x Cell Constant)		
Corrected Conductivity of Sample = (Conductivity of Sample x Ratio)		

V. Measurement of the pH of the Sample

	Field Measurement	Laboratory Measurement
Date		
Time		
Temperature of Blank		
pH of Check Solution (3)		
pH of Sample		

VI. Comments on the Sample or the Procedure (Use the Reverse Side of This Sheet).

(1) The cell constant is certified by the laboratory in Austin, and except for special cases, will have a value of 1 cM^2.
(2) The conductance is the value obtained from the meter. The conductivity is conductance times the cell constant.
(3) The pH of the check solution must be within 0.20 pH units of the previous measurement or of the expected value.

THE ANALYSES OF FILTERS FROM HIGH-VOLUME AIR SAMPLERS OR OF BUBBLER SAMPLES FOR CHROMIUM (VI) BY SPECTROPHOTOMETRY

1.0 PRINCIPLE AND APPLICABILITY.

1.1 Filters from high-volume (hi-vol) air samplers.

1.1.1 Particulate matter suspended in air is collected on a glass fiber or a quartz filter using a 24-hour hi-vol air sampler (References 1 and 2).

1.1.2 The chromium (VI) content of the sample is determined by extracting a portion of the exposed filter with an alkaline, aqueous extracting solution containing sodium sulfate (Na_2SO_4), sodium chloride (NaCl), and sodium hydroxide (NaOH). The extraction is facilitated by brisk stirring. The extract is filtered; then a portion of the filtered extract is treated with 1,5-diphenylcarbazide (DPC) solution and dilute sulfuric acid (H_2SO_4) to develop the violet-pink color which is specific for chromium (VI). Finally, the intensity of the color is determined by using a spectrophotometer (References 3, 4, 5, and 6).

1.2 Bubbler samples.

1.2.1 Chromium (VI) in ambient air is collected in an alkaline, aqueous absorbing solution.

1.2.2 The chromium (VI) content of the sample is determined by the DPC spectophotometric method.

2.0 RANGE AND LOWER DETECTABLE LIMIT.

2.1 Filters from hi-vol air samplers.

2.1.1 For concentrations expressed in units of ng/m^3, an air-sample volume of 2,000 m^3 for the hi-vol sampler is assumed.

2.1.2 The lower limit of the range for chromium (VI) is 0.5 ng/m^3. An upper limit has not yet been observed, although it is greater than 40 ng/m^3. With appropriate dilutions, the upper limit can be extended to 4,000 ng/m^3.

2.1.3 The lower detectable limit (LDL) for chromium (VI) is determined as the concentration of the most dilute chromium (VI) solution for which a definite absorbance can be observed over the signal for a blank. The LDL is 0.007 µg/mL of chromium (VI) in the solution to be analyzed; 0.007 µg/mL of chromium (VI) produces an absorbance of about 0.005 absorbance units. This solution concentration corresponds to an air concentration of 0.5 ng/m^3.

2.2 Bubbler samples.

2.2.1 For concentrations expressed in units of ng/m^3, an air-sample volume of 5.76 m^3 for the bubbler is assumed.

2.2.2 The lower limit of the range for chromium (VI) is 33 ng/m^3. An upper limit has not yet been observed, although it is greater than 2,800 ng/m^3. With appropriate dilutions the upper limit can be extended to 280,000 ng/m^3.

2.2.3 The lower detectable limit for chromium (VI) is 0.007 µg/mL of chromium (VI) in solution. This solution concentration corresponds to an air concentration of 33 ng/m^3.

3.0 PRECISION.

3.1 Filters from hi-vol air samplers.

3.1.1 The precision is measured by performing duplicate extractions and analyses on the same exposed filter.

3.1.2 The average percent difference between duplicate results (precision), calculated from 10 sets of duplicates having concentrations greater than the LDL, is 0% with a standard deviation of 3%. The chromium (VI) concentrations ranged from 0.011 to 0.293 µg/mL.

3.2 Bubbler samples.

3.2.1 The precision is measured by performing duplicate analyses on portions of bubbler sample taken from the same bubbler. (Overall method precision is measured by performing duplicate analyses on portions of bubbler samples taken from different bubblers which were run during the same time period.)

3.2.2 The average percent difference between duplicate results (same bubbler precision), calculated from 6 sets of duplicates having concentrations greater than the LDL, is 0% with a standard deviation of 2%. The chromium (VI) concentrations ranged from 0.118 to 0.139 µg/mL.

3.2.3 The average percent difference between duplicate results (overall method precision), calculated from 6 sets of duplicates having concentrations greater than the LDL, is 1% with a standard deviation of 7%. The chromium (VI) concentrations ranged from 0.122 to 0.136 µg/mL.

4.0 ACCURACIES.

4.1 The two types of accuracies involved in this procedure are method accuracy and instrument accuracy.

4.2 For filters from hi-vol air samplers, the method accuracy is measured by performing extractions and analyses on audit samples (prepared by someone other than the analyst). For bubbler samples, the method accuracy is measured by performing analyses on audit samples (prepared by someone other than the analyst).

4.2.1 Filters from hi-vol air samplers.

4.2.1.1 An audit sample is prepared by extracting a blank portion of either a glass fiber or a quartz filter with extracting solution containing a known concentration of chromium (VI).

4.2.1.2 The average percent difference between the reported and the true values for audit samples (method accuracy), calculated from 10 audit samples, is -2% with a standard deviation of 1%. The chromium (VI) concentrations ranged from 0.075 to 0.300 µg/mL.

4.2.2 Bubbler samples.

4.2.2.1 An audit sample is prepared in the same manner as a standard, except that the person preparing the audit is not the analyst.

4.2.2.2 The average percent difference between the reported and the true values for audit samples (method accuracy), calculated from 10 audit samples, is -2% with a standard deviation of 1%. The chromium (VI) concentrations ranged from 0.075 to 0.300 µg/mL.

4.3 For filters from hi-vol air samplers or for bubbler samples, the instrument accuracy is measured by analyzing chromium (VI) standards (not used to prepare the calibration curves) as unknowns.

4.4 For filters from hi-vol air samplers or for bubbler samples, the average percent difference between the reported and the true values for standards analyzed as unknowns (instrument accuracy), calculated from 10 standards, is 1% with a standard deviation of 1%. The chromium (VI) concentrations ranged from 0.075 to 0.300 µg/mL.

5.0 RECOVERABILITY.

5.1 The recoverability is measured by determining the percent of chromium (VI) recovered from spiked samples.

5.2 Filters from hi-vol air samplers.

5.2.1 A spiked sample is prepared by extracting a portion of an exposed glass fiber or quartz filter with extracting solution containing a known concentration of chromium (VI).

5.2.2 The concentration of recovered chromium (VI) is the difference in the chromium (VI) concentrations for the spiked and unspiked versions of the exposed filter extracts.

5.2.3 The average percent recoverability for chromium (VI), calculated from 10 spiked samples, is 83% with a standard deviation of 6%. Chromium (VI) is difficult to recover quantitatively from exposed filters, because exposed filters contain many species which can be oxidized by chromium (VI). The chromium (VI) spiking concentrations ranged from 0.071 to 0.300 µg/mL.

5.3 Bubbler samples.

5.3.1 A spiked sample is prepared by adding a known amount of chromium (VI) to the absorbing solution containing 0.000 µg/mL chromium (VI).

5.3.2 The concentration of recovered chromium (VI) is the concentration found for the spiked version of the absorbing solution.

5.3.3 The average percent recoverability for chromium (VI), calculated from 6 spiked samples, is 96% with a standard deviation of 4%. The chromium (VI) spiking concentrations ranged from 0.129 to 0.139 µg/mL.

6.0 INTERFERENCES.

6.1 Three types of interferences are possible: interferences in the filter matrix or in the collected particulate matter which can reduce chromium (VI) or oxidize chromium (III), interferences which can precipitate chromium (VI), and interferences which can increase the spectrophotometrically measured color intensity of the complex species formed by chromium (VI) and DPC.

6.2 For the situations involved in this procedure, chromium (VI) is much more likely to be reduced than chromium (III) is likely to be oxidized. The possibility for the reduction of chromium (VI) is minimized by using an alkaline extracting or absorbing solution.

6.3 Filters from hi-vol air samplers.

6.3.1 Both lead and barium can precipitate chromium (VI). In this procedure, lead is tied up as its hydroxy complex or precipitated as lead hydroxide by the alkaline extracting solution. Barium in collected particulate matter is usually

present as insoluble barium sulfate; any soluble barium salts will be converted to barium sulfate by the presence of Na_2SO_4 in the extracting solution. Neither lead nor barium at concentrations equivalent to 4,000 ng/m^3 (produced from depositions of lead nitrate and barium nitrate solutions) causes an interference with the determination of chromium (VI). Other cations forming insoluble chromium (VI) salts, such as silver, are not expected to be in particulate matter collected from ambient air.

6.3.2 The following species can cause interferences by increasing the spectrophotometrically measured color intensity of the chromium (VI) complex: chromium (III), molybdenum, mercury (I and II), vanadium (V), and iron (III) (References 5 and 6).

6.3.2.1 Chromium (III) can cause an increase in the measured color intensity because of its intrinsic blue-green color; however, most (75%) of the chromium (III) will be precipitated as chromium (III) hydroxide in the alkaline extracting solution. Chromium (III) at concentrations up to an equivalent of 10,000 ng/m^3 (produced from depositions of chromium (III) nitrate) has no appreciable effect on the chromium (VI) determination. Any chromium (III) surviving the extraction will cause the following interference ratio: 53 µg/mL of chromium (III) will show up as 0.01 µg/mL of chromium (VI).

6.3.2.2 Molybdenum is not expected to be in particulate matter collected from ambient air; even if present, molybdenum produces no interference with the determination of chromium (VI) in this particular procedure.

6.3.2.3 Mercury (I and II) are not expected to be in particulate matter collected from ambient air; even if present, the presence of NaCl in the extracting solution will produce mercury chloride complexes, eliminating the possible interferences of mercury (I and II).

6.3.2.4 Vanadium (V) is not expected to be in particulate matter collected from ambient air. If it is present and it survives extraction, its interference will be minimized by allowing 15 minutes for color development, during which time the color of the vanadium (V)-DPC complex will fade. Any vanadium (V) surviving the extraction will cause the following interference ratio: 6.0 µg/mL of vanadium (V) will show up as 0.01 µg/mL of chromium (VI).

6.3.2.5 Almost all of the iron (III) in the collected particulate matter will precipitate as iron (III) hydroxide in the alkaline extracting solution. Any iron (III) surviving the extraction will cause the following interference ratio: 570 µg/mL of iron (III) will show up as 0.01 µg/mL of chromium (VI).

6.4 Bubbler samples.

6.4.1 The interferences for chromium (VI) on filters from hi-vol air samplers will also be interferences for chromium (VI) in bubbler samples.

6.4.2 The concentration equivalents (ng/m^3 and µg/mL values) determined for chromium (VI) on filters from hi-vol air samplers are expected to be valid for chromium (VI) in bubbler samples as well.

7.0 REAGENTS.

7.1 All reagents should be ACS reagent-grade or better.

7.2 Filters from hi-vol air samplers and bubbler samples.

7.2.1 Milli-Q water. Milli-Q water is deionized water that has been treated with a Milli-Q water-purification system. The water exhibits a conductivity of ≤ 10 µS/cm.

7.2.2 Deionized (DI) water.

7.2.3 Acetone.

7.2.4 Chemicals.

Na_2SO_4
NaCl
NaOH
DPC
H_2SO_4 (concentrated)
Primary-standard grade potassium dichromate ($K_2Cr_2O_7$)

7.2.5 Solutions. The following solutions should be prepared:

7.2.5.1 Solution containing 5.0 M NaOH. This solution is prepared by dissolving 20.0 g of NaOH in about 60 mL of water and then diluting to 100 mL with water in a volumetric flask. Transfer this solution to a plastic bottle.

7.2.5.2 Extracting or absorbing solution. This solution contains 0.02 M Na_2SO_4, 0.02 M NaCl, and 0.02 M NaOH and is prepared by dissolving 2.84 g of Na_2SO_4 and 1.17 g of NaCl in about 50 mL of water, adding 4.00 mL of 5.0 M NaOH, and diluting to 1,000 mL with water in a volumetric flask. Transfer this solution to a plastic bottle.

7.2.5.3 Solution containing 5.0 M H_2SO_4. This solution is prepared by diluting 27.8 mL of concentrated H_2SO_4 to 100 ml with water in a volumetric flask.

7.2.5.4 Solution containing 2.5 M H_2SO_4. This solution is prepared by diluting 50.0 mL of the 5.0 M H_2SO_4 to 100 mL with water in a volumetric flask.

7.2.5.5 DPC solution. This solution is prepared by dissolving 0.200 g of DPC in about 15 mL of acetone and diluting to 25.0 mL with acetone in a volumetric flask. This solution should be stored in the refrigerator and should remain fresh for 2 weeks.

7.2.5.6 Standard containing 1,000 µg/mL of chromium (VI). This solution is prepared by dissolving 1.415 g of primary-standard grade $K_2Cr_2O_7$ in about 100 mL of water and diluting to 500 mL with water in a volumetric flask. Transfer this solution to a plastic bottle.

7.2.5.7 Standard containing 100 µg/mL of chromium (VI). This solution is prepared by diluting 10.00 mL of the 1,000 µg/mL chromium (VI) solution to 100 mL with water in a volumetric flask. Transfer this solution to a plastic bottle.

7.3 Filters from hi-vol air samplers.

7.3.1 Working standard containing 0.600 µg/mL of chromium (VI) in extracting solution. This solution is prepared by dissolving 2.84 g of Na_2SO_4 and 1.17 g of NaCl in about 50 mL of water, adding 4.00 mL of 5.0 M NaOH and 6.00 mL of 100 µg/mL chromium (VI), and diluting to 1,000 mL with water in a volumetric flask. Transfer this solution to a plastic bottle.

7.3.2 Working standard containing 0.300 µg/mL of chromium (VI) in extracting solution. This solution is prepared by diluting 100.0 mL of 0.600 µg/mL chromium (VI) with 100.0 mL of extracting solution. Transfer this solution to a plastic bottle.

7.3.3 Working standard containing 0.150 µg/mL of chromium (VI) in extracting solution. This solution is prepared by diluting 50.0 mL of 0.600 µg/mL chromium (VI) with 150.0 mL of extracting solution. Transfer this solution to a plastic bottle.

7.3.4 Working standard containing 0.075 µg/mL of chromium (VI) in extracting solution. This solution is prepared by diluting 25.0 mL of 0.600 µg/mL chromium (VI) with 175.0 mL of extracting solution. Transfer this solution to a plastic bottle.

7.4 Bubbler samples.

7.4.1 Sodium bicarbonate ($NaHCO_3$).

7.4.2 Concentrated absorbing solution (corresponding approximately to the absorbing solution after it is brought in from the field and brought up to a

27.0-mL volume). This solution contains 0.04 M Na_2SO_4, 0.04 M NaCl, and 0.04 M $NaHCO_3$ and is prepared by dissolving 5.68 g of Na_2SO_4, 2.34 g of NaCl, and 3.36 g of $NaHCO_3$ in about 100 mL of water and diluting to 1,000 mL with water in a volumetric flask. Transfer this solution to a plastic bottle. (The $NaHCO_3$ is produced by bubbling air containing carbon dioxide through the absorbing solution.)

7.4.3 Working standard containing 0.600 µg/mL of chromium (VI) in concentrated absorbing solution. This solution is prepared by dissolving 5.68 g of Na_2SO_4, 2.34 g of NaCl, and 3.36 g of $NaHCO_3$ in about 100 mL of water; adding 6.00 mL of 100 µg/mL chromium (VI); and diluting to 1,000 mL with water in a volumetric flask. Transfer this solution to a plastic bottle.

7.4.4 Working standard containing 0.300 µg/mL of chromium (VI) in concentrated absorbing solution. This solution is prepared by diluting 100.0 mL of 0.600 µg/mL chromium (VI) with 100.0 mL of concentrated absorbing solution. Transfer this solution to a plastic bottle.

7.4.5 Working standard containing 0.150 µg/mL of chromium (VI) in concentrated absorbing solution. This solution is prepared by diluting 50.0 mL of 0.600 µg/mL chromium (VI) with 150.0 mL of concentrated absorbing solution. Transfer this solution to a plastic bottle.

7.4.6 Working standard containing 0.075 µg/mL of chromium (VI) in concentrated absorbing solution. This solution is prepared by diluting 25.0 mL of 0.600 µg/mL chromium (VI) with 175.0 mL of concentrated absorbing solution. Transfer this solution to a plastic bottle.

8.0 APPARATUS.

8.1 Filters from hi-vol air samplers and bubbler samples.

8.1.1 Glassware.

Test tubes, 1-inch
Beakers, 100-mL
Beakers, 250-mL
Volumetric flask, 25-mL
Volumetric flasks, 100-mL
Volumetric flasks, 500-mL
Volumetric flasks, 1000-mL
Graduated cylinders, 50-mL
Graduated cylinders, 100-mL

8.1.2 Plasticware.

Test-tube holder.
Plastic bottles, 250-mL
Plastic bottles, 500-mL
Plastic bottles, 1000-mL
Squeeze bottle for water
Squeeze bottle for acetone

8.1.3 Vacuum-filtration system with cellulose nitrate filters having 0.45-µm pore sizes (47-mm diameters).

8.1.4 Liquid dispensers.

Pipettor, 200-µL, with appropriate dispenser tips
Pipettor, 250-µL, with appropriate dispenser tips
Pipettor, 5-mL to 10-mL, with appropriate dispenser tips

8.1.5 Vortex mixer.

8.2 Filters from hi-vol air samplers.

8.2.1 Erlenmeyer flasks, 125-mL.

8.2.2 Plasticware.

Stir bars, 1-inch
Stir bar, 2-inch
Stirring rod

8.2.3 Magnetic stirrers.

8.2.4 Paper cutter with ruler edge.

8.2.5 Parafilm.

9.0 PROCEDURE FOR EXTRACTION OF FILTERS.

9.1 Blank filter paper has a positive interference for chromium (VI), so establish the blank value for the particular series of exposed glass fiber or quartz filters to be analyzed by performing this extraction and analysis procedure on at least 3 blank filters for each series and using the average absorbance value (converted to units of µg/mL) as the blank value. For example, the average value for Series 88 quartz filters is 0.004 µg/mL with a standard deviation of 0.002 µg/mL (average of 3 filter strips), and the average value for Series 90 fiber glass filters is 0.006 µg/mL with a standard deviation of 0.001 µg/mL (average of 7 filter strips).

9.2 Using the paper cutter and its ruler, cut off a 1.125-inch strip from the exposed portion of the folded hi-vol filter; this strip is one eighth of the entire exposed area of the filter.

9.3 Fold the filter strip in half lengthwise three times, so that it forms a coil which will fit into the opening of a 1-inch test tube.

9.4 Place the coiled strip into a 1-inch test tube; tamp the filter coil to the bottom of the test tube with the plastic stirring rod.

9.5 Place a 1-inch stir bar on the filter coil in the test tube.

9.6 Using the 5-mL to 10-mL pipettor on a setting of 8.5, add 17.0 mL of extracting solution to the test tube.

9.7 Using the plastic stirring rod, macerate the filter strip until a pulpy suspension results.

9.8 Cover the test tube with Parafilm.

9.9 Place the test tube into a 125-mL Erlenmeyer flask.

9.10 From Parafilm fashion 2-inch, wormlike shims. Use one of these shims to hold the test tube firmly in place in the mouth of the Erlenmeyer flask.

9.11 Place the Erlenmeyer flask containing the test tube on a magnetic stirrer.

9.12 Stir the contents of the test tube briskly for 30 minutes. Supervise the stirring process to verify that it remains under control.

9.13 Remove the Parafilm from the test tube; remove the shim from the Erlenmeyer flask.

9.14 By dragging the 2-inch stir bar up the outside of the test tube, remove the 1-inch stir bar from the test tube.

9.15 Vacuum filter the contents of the test tube through a cellulose nitrate filter.

9.16 Using the 5-mL to 10-mL pipettor on a setting of 6.0, transfer 12.0 mL of the filtrate into a clean 1-inch test tube. This sample is now ready for color development along with the calibration standards.

10.0 COLLECTION AND PREPARATION OF BUBBLER SAMPLES.

10.1 Collect the sample by bubbling ambient air through 50 mL of absorbing solution at about 2 liters per minute (measure to the nearest 0.01 liter per minute) for at least 48 hours. Use plastic bubbler tubes with glass impingers. Place a filter and an empty bubbler tube between the sample tube and the vacuum pump. During the collection period check the bubbler three times a day; add DI water as necessary. During the first day keep the absorber volume between 40 and 55 mL. During the second day add DI water as required so that the final absorber volume will be about 25 mL. This final absorber volume will contain about 0.04 M Na_2SO_4, 0.04 M NaCl, and 0.04 M $NaHCO_3$. Operate two bubbler tubes per site (for the determination of overall method precision).

10.2 After the samples arrive in the laboratory, measure each absorbing solution's volume with a graduated cylinder, and adjust the volume to 27.0 mL with water. Mix each resulting sample well.

10.3 Using the vacuum-filtration system, filter each absorbing solution through a cellulose nitrate filter. Mix each resulting sample well.

10.4 Analyze each absorbing solution in duplicate.

10.5 Using the 5-mL to 10-mL pipettor on a setting of 6.0, transfer 12.0 mL of the absorbing solution into a clean 1-inch test tube. This sample is now ready for color development along with the calibration standards.

11.0 CALIBRATION.

11.1 Set the spectrophotometer's wavelength at 540 nm.

11.2 The spectrophotometer is calibrated before and after analyzing the unknown samples using two standards--the extracting (or concentrated absorbing) solution containing 0.000 µg/mL chromium (VI) and the working standard containing either 0.300 or 0.600 µg/mL chromium (VI). The average from the two calibrations is used to draw the calibration curve.

11.3 Prepare 3 clean test tubes each containing 12.0 mL of extracting (or concentrated absorbing) solution.

11.4 Prepare 1 clean test tube containing 12.0 mL of the working standard containing either 0.300 or 0.600 µg/mL chromium (VI).

11.5 Develop the color in these 4 test tubes along with the color in the test tubes containing the unknown samples according to the procedures given in Section 12 (except don't filter the standards).

11.6 Use one of the developed solutions containing 0.000 µg/mL chromium (VI) to fill the spectrophotometer's reference cell.

11.7 Fine tune the spectrophotometer at 540 nm.

11.8 Calibrate the spectrophotometer before and after analyzing the unknown samples using the remaining 2 test tubes containing 0.000 µg/mL chromium (VI) and the one test tube containing either 0.300 or 0.600 µg/mL chromium (VI). Average the four results for the standards containing 0.000 µg/mL chromium (VI) and the two results for the standard containing 0.300 µg/mL or 0.600 µg/mL chromium (VI). Use these average results to prepare the calibration curve.

12.0 SAMPLE ANALYSIS.

12.1 To each test tube containing 12.0 mL of standard or unknown sample, add 250 µL of the DPC solution.

12.2 Using the vortex mixer, thoroughly mix the standard or sample.

12.3 Add 200 µL of 2.5 M H_2SO_4 to the standard or sample (200 µL of 5.0 M H_2SO_4 for bubbler standards or samples.)

12.4 Again using the vortex mixer, thoroughly mix the standard or sample.

12.5 Vacuum filter the sample through a cellulose nitrate filter.

12.6 Transfer the filtrate to a clean 1-inch test tube.

12.7 Allow 15 minutes for color development.

12.8 Analyze the unknown samples on the calibrated spectrophotometer.

12.9 Use the calibration curve to determine the chromium (VI) concentration in µg/mL.

12.10 From the above concentration value, subtract the appropriate blank value given in µg/mL (for chromium (VI) on filters from a hi-vol air sampler); this yields the corrected chromium (VI) value.

12.11 Clean the spectrophotometer's reference cell.

13.0 CALCULATIONS.

13.1 Filters from hi-vol air samplers.

13.1.1 The chromium (VI) concentration for the unknown sample in ng/m^3 is given by:

$ng/m^3 = (\mu g/mL)(17.0)(8)(1{,}000/m^3)$,

where µg/mL is the corrected chromium (VI) concentration from Step 12.10,
8 is from the extraction of one eighth of the exposed filter,
1,000 converts µg to ng, and
m^3 is the total air volume which was sampled by the hi-vol sampler.

13.1.2 The above equation simplifies to:

$ng/m^3 = (136{,}000)(\mu g/mL)/m^3$.

13.2 Bubbler samplers.

13.2.1 The chromium (VI) concentration for the unknown sample in ng/m^3 is given by:

$ng/m^3 = (\mu g/mL)(27.0)(1{,}000/m^3)$,

where µg/mL is the corrected chromium (VI) concentration from Step 12.9,
1,000 converts µg to ng, and
m^3 is the total air volume which was sampled by the bubbler.

13.2.2 The above equation simplifies to:

$ng/m^3 = (27{,}000)(\mu g/mL)/m^3$.

14.0 QUALITY ASSURANCE.

14.1 Precision of the method is measured by duplicate samples taken through the extraction and analysis procedures (for filters from hi-vol samplers) or duplicate samples taken from the same or duplicate bubbler tubes (for bubbler samples).

14.1.1 Duplicate analyses must be performed on at least 10% of the samples.

14.1.2 The percent difference between duplicate results must be less than 10% for chromium (VI) concentrations > 0.075 µg/mL (20% for chromium (VI) concentrations > 0.075 µg/mL for duplicate bubbler samples for the determination of overall method precision).

14.2 Accuracy of the instrument is determined by a standard analyzed as an unknown.

14.2.1 A standard must be analyzed as an unknown during the analyses of each set of 10 or fewer samples.

14.2.2 The percent difference from the true value must be less than 5% for standards > 0.075 µg/mL.

14.3 Accuracy of the method is determined by analyzing an audit sample. An audit sample must be analyzed for each set of 10 or fewer samples.

14.4 Recoverability of the method is measured by analyzing a spiked sample.

14.4.1 A spiked sample must be analyzed during the analyses of each set of 10 or fewer samples.

14.4.2 The percent recoverability must be 65 to 105% for filters from hi-vol samplers and 75 to 115% for bubbler samples.

15.0 REFERENCES.

1. Texas Air Control Board, Sampling Procedures Manual, Chapter 11, January, 1983.

2. United States Environmental Protection Agency, Reference Method for the Determination of Suspended Particulate Matter in the Atmosphere (High-Volume Method), Code of Federal Register, Title 40, Part 50, Appendix B, (July 1, 1988).

3. Standard Methods of Chemical Analysis, N.H. Furman, ed., Sixth Edition, Volume 1, March, 1962, pp. 351-352.

4. Butler, F. E., Knoll, J. E., and Midgett, M. R., "Chromium Analysis at a Ferrochrome Smelter, a Chemical Plant and a Refractory Brick Plant," JAPCA 36, May, 1986, pp. 581-584.

5. "Procedure for the Sampling and Analysis of Atmospheric Hexavalent Chromium (VI)," Method 106, Jan. 1985, California Air Resources Board, Haagen-Smit Laboratory Division, State of California, 9528 Telstar Ave., El Monte, CA 91731.

6. "Determination of Hexavalent and Total Chromium in Effluent Samples from Electrolytic Chrome Plating Operations," Method 34, Manual of Procedures, Vol. 3, Bay Area Air Quality Management District, 939 Ellis Street, San Francisco, CA 94109.

The Analyses of Soil Samples for Lead by X-Ray Fluorescence Spectrometry

1.0 PRINCIPLE AND APPLICABILITY.

1.1 Soil samples are collected in glass or plastic vials.

1.2 The lead content of each sample is determined by drying the sample in an oven at 105° C for two hours, grinding the sample to 200 mesh, fashioning a 13-mM-diameter pellet from one gram of the sample, and analyzing the pellet by X-ray fluorescence spectrometry (XRF).

2.0 RANGES AND LOWER DETECTABLE LIMITS.

2.1 The lower limit of the range for lead in soil samples is 100 µg/g. The upper limit is approximately 180,000 µg/g; this upper limit is governed by the non-soillike matrix effects caused by high lead concentrations. Soil samples containing lead concentrations greater than 180,000 µg/g may be diluted by lead-free soil before pelletizing and analyzing.

2.2 The lower detectable limits (LDL's) for lead in soil samples are determined as the concentration of the most dilute lead soil sample for which a definite XRF peak can be observed. The LDL for lead in soil samples is 100 µg/g.

3.0 PRECISION.

3.1 The precision of the method is measured by pelletizing and analyzing duplicate one-gram portions of one soil sample.

3.2 The mean precision for lead in soil samples, calculated from 18 sets of duplicates having concentrations greater than the LDL is -5% with a standard deviation of 14%. The lead concentration ranged from 150 to 660,000 µg/g. (The soil sample containing 660,000 µg/g lead was diluted by a factor of 10 with lead-free soil before pelletizing and analysis.)

4.0 ACCURACY.

The accuracy of the method is measured by analyzing pelletized audit samples (prepared by someone other than the analyst). An audit sample is prepared like a standard (see Sections 6.4 through 6.6). The mean percent difference (accuracy) for this method calculated for four audit samples is -3% with a standard deviation of 16%.

5.0 INTERFERENCES.

Two types of interferences are possible: interferences due to matrix effects and the overlap of the Kα arsenic line on the Lα line normally used for the analysis of lead. Interferences due to matrix effects are minimized by analyzing only soil samples containing less than 180,000 µg/g of lead. If a soil sample contains arsenic at a concentration sufficient to interfere with the lead analysis, its presence will be indicated by its Kβ line and by the fact that the lead Lα line is taller than the lead Lβ line. If arsenic is present, then the Lβ line is used for the analysis of lead.

6.0 REAGENTS.

6.1 Lead-free soil, 200-mesh. This soil will have no XRF-detectable lead.

6.2 Lead dioxide powder, 97.4% pure.

6.3 Distilled water.

6.4 Standard containing 180,000 µg/g lead in soil. This standard is prepared by weighing out (on the top-loading balance) 39.33 g of 200-mesh lead-free soil and 10.67 g of lead dioxide (97.4% pure). Weigh these solids out into a 500-mL beaker. Then stir the two solids together well with a scoopula (use at least 250 stirring operations).

6.5 Standard containing 120,000 µg/g lead in soil. This standard is prepared by weighing out into a 500-mL beaker 10.00 g of lead-free soil and 20.00 g of the 180,000 µg/g lead standard. The mixing is performed as described above.

6.6 Standards containing 60,000, 30,000, 10,000, 2,000, 1,000, and 500 µg/g lead in soil. These standards are prepared by making the appropriate dilutions of a higher-concentration standard with lead-free soil and mixing as described above.

7.0 APPARATUS.

7.1 Constant-temperature oven.

7.2 Beakers, 500-mL and 100-mL.

7.3 Scoopulas.

7.4 Top-loading balance.

7.5 Grinder.

7.6 Pellet press.

7.7 Pellet sample holders. These holders are made from polypropylene cups, snap-on collars, and film for XRF samples. The bottom portions of the cups are removed with a jigsaw so that a pellet may be placed on the polypropylene film which is held in place on the remaining portion of the cup with a snap-on polypropylene collar.

7.8 Pasteur pipet with a squeeze bulb.

7.9 XRF instrument. This instrument is manufactured by Columbia Scientific Industries and is a Model 110. Radioactive sources irradiate the samples; X-rays from the sample are sorted and counted by a lithium-drifted silicon detector system. The radioactive source used for the determination of lead is Cd^{109}. The detector results are interpreted and displayed by a Dapple microcomputer system.

7.10 CURFITTER program and an Apple microcomputer.

8.0 PROCEDURES.

8.1 Weigh out each moist sample into a weighed 500-mL beaker. Use the top-loading balance.

8.2 Dry each soil sample in an oven at 105° C for two hours.

8.3 Weigh each beaker with its dried sample. Subtract the weight of the beaker. Determine the percent moisture originally present in each sample.

8.4 Grind each dried sample to 200 mesh. Stir each ground-up sample to ensure homogeneity.

8.5 Using the top-loading balance and the pellet press, fashion a 1.00-g pellet from each ground-up sample. Up to 0.10 g distilled water may be added to each 1.00-g mass before pelletizing if the pellet will not stay intact.

9.0 CALIBRATION.

9.1 Fashion 1.00-g pellets from the lead-free soil (blank) and the standards to be used, using the method described above. Use three or four standards in the range of lead concentrations expected for the soil samples. Other standards may need to be pelletized and used once the samples have been run.

9.2 Place each pellet for the blank and the upscale standards into a pellet sample holder for the XRF. Place the pellet sample holders into the XRF's sample wheel. Using the Cd^{109} source and the Dapple system, determine the intensity for the lead Lα line for each pellet. Use a 250-sec count time. Obtain a printout of each spectrum along with the intensity for the lead Lα line.

10.0 SAMPLE ANALYSIS.

10.1 Place each sample into a pellet sample holder. Place the pellet holders into the XRF's sample wheel. Using the Cd^{109} source and the Dapple system, determine the intensity for the lead Lα line for each sample. Use a 250-sec count time. (Verify that lead Lα and Lβ lines are present for each sample for which a lead concentration greater than its detection limit will be reported.) Obtain a printout of each spectrum along with the intensity for the lead Lα line.

10.2 Prepare a calibration curve using the CURFITTER program. Plot intensity vs. µg/g. A second-order curve is preferable whenever the upscale standards used vary in lead concentrations by more than a factor of two.

10.3 Determine the lead concentrations of the samples in µg/g using the same CURFITTER program. These concentrations will be µg/g on a dry-weight basis.

11.0 CALCULATIONS.

11.1 Report all lead values in µg/g on a dry-weight basis, unless percent lead by weight is required. If percent lead by weight is required, then multiply the concentration in µg/g by 0.0001.

11.2 If any soil samples were diluted with lead-free soil, then correct each µg/g value by multiplying by the dilution factor.

12.0 QUALITY ASSURANCE.

12.1 Precision of the method is measured by duplicate samples pelletized and analyzed.

12.1.1 Duplicate analyses must be performed on at least 10% of the samples.

12.1.2 The percent difference between duplicate results must be less than 25% for lead concentrations > 300 µg/g.

12.2 Recoverability of the method is measured by analyzing spiked samples. Prepare a spiked sample by diluting a regular sample 50:50 with a standard prior to pelletizing and analysis.

12.2.1 Spiked samples must be prepared and analyzed for at least 10% of the samples.

12.2.2 The percent recoverability must be 70-130% for samples containing ≥ 1,000 µg/g lead.

12.3 Accuracy of the instrument is determined by analyzing a standard as an unknown.

12.3.1 A standard must be analyzed as an unknown during the analysis of each set of 10 or fewer samples.

12.3.2 The percent difference from the true value must be less than 10% for standards ≥ 1,000 µg/g.

12.4 An audit sample must be analyzed for each set of ten or fewer samples.

The Analysis of Soil Samples for Elements by Acid Extraction Followed by Inductively-Coupled Plasma Spectrometry

1.0 PRINCIPLE AND APPLICABILITY.

A soil sample is dried and then ground to 100 mesh. A portion of the sample is extracted with 5.0 M nitric acid. The extracting solution is then filtered and analyzed for any acid-extractable element by inductively-coupled plasma spectrometry (ICP).

2.0 RANGE AND LOWER DETECTABLE LIMIT.

The lower limit of the range and the lower detectable limit (LDL) depends upon the analyte and is determined by the ICP instrument. The LDL determined by the ICP is in units of µg/mL; the LDL for the analyte in the soil sample is in units of µg/g and is calculated by multiplying the µg/mL value by 20 (the dilution factor for 5.00 grams of soil extracted with 100 mL of 5.0 M nitric acid). An upper limit of 50,000 µg/mL (1,000,000 µg/g) is theoretically possible. Analytes with concentrations this great can be determined by appropriate dilutions.

3.0 PRECISION.

The precision of the method is measured by performing duplicate extractions and analyses on separate portions of the same soil sample. The precision is analyte-specific. To date, this method has been used to analyze soil samples for lead, arsenic, zinc, manganese, and barium; the average percent difference (precision) for 21 duplicate sets having concentrations greater than the LDL is 1% with a standard deviation of 7%.

4.0 ACCURACY.

The accuracy of the method is measured by analyzing analyte audit or standard solutions as unknown samples. Audit solutions are merely standard solutions prepared by someone other than the analyst. The average percent difference (accuracy) for this method calculated for 27 standard samples analyzed as unknown samples for lead, arsenic, zinc, manganese, and barium was 1% with a standard deviation of 2%.

5.0 INTERFERENCES.

There are no known specific elemental interferences for this method; however, see Section 10.0.

6.0 REAGENTS.

All reagents should be ACS reagent-grade or better.

6.1 Water.

Glass-distilled water (for solution preparations).
Deionized water (for rinsings).

6.2 Concentrated nitric acid.

6.3 Extracting solution consisting of 5.0 M nitric acid. This solution is prepared by adding 667 mL of concentrated nitric acid in a graduated cylinder to a 2000-mL volumetric flask containing approximately 1000 mL of glass-distilled water, letting the solution cool to room temperature, and then diluting to the mark with glass-distilled water.

6.4 Commercially-available standards prepared for atomic absorption spectrometry containing the analyte at 1000 µg/mL.

6.5 Standards containing 0.00, 5.00, 10.00, 20.00, and 40.00 ppm (µg/mL) of the analyte in 5.0 M nitric acid. The 0.00-ppm standard is merely the extracting solution. The 5.00-, 10.00-, 20.00-, and 40.00-ppm standards are prepared by adding 33 mL of concentrated nitric acid in a graduated cylinder to approximately 50 mL of glass-distilled water in a 100-mL volumetric flask and then adding 0.50, 1.00, 2.00, and 4.00 mL, respectively, of the appropriate 1000-ppm standard, letting the solution cool to room temperature, and then diluting to the mark with glass-distilled water. Multi-element standards may be prepared whenever they are needed.

7.0 APPARATUS.

7.1 Glassware.

Graduated cylinder, 1000-mL.
Graduated cylinder, 50-mL.
Volumetric flask, 2000-mL.
Volumetric flasks, 100-mL.
Beakers, 250-mL.
Beakers, 100-mL.

7.2 Miscellaneous items.

Parafilm.
Plastic funnels, powder, 65-mm diameter.

Whatman No. 4 filter paper, 15-cm diameter, or equivalent.
Pipettor, 0.50-mL.
Pipettor, 1.00-mL.
Pipettor, 5.00-mL.
Drying oven.
Grinder, Retch.
Ultrasonic bath.

7.3 ICP.

The ICP is a model JY38PI as manufactured by Instruments S.A. of Edison, NJ. The instrument is equipped with an argon plasma source; a 3600-group grating; a data system from Columbia Data Products, Inc., and its complementary software; and a flow controller for the nebulizer argon.

8.0 PROCEDURE.

8.1 Dry the soil sample for two hours at 105° C in the drying oven.

8.2 Grind the soil sample to 100 mesh using the grinder. Mix the ground-up sample well.

8.3 Accurately weigh out 5.00 g of the soil sample into a 250-mL beaker.

8.4 Carefully (because of bubble formation) add 100 mL of 5 M nitric acid, using a 50-mL graduated cylinder. Cover the beaker with Parafilm.

8.5 Ultrasonicate the covered beaker for one hour. Let the beaker and its contents cool to room temperature.

8.6 Filter approximately 50 mL of the extracting solution through Whatman No. 4 filter paper into a 100-mL beaker. Cover the beaker with Parafilm. The sample is now ready for analysis for acid-soluble elements.

9.0 CALIBRATION.

9.1 A first-order calibration curve is calculated by the software supplied with the ICP instrument from emission data using the 0.00-ppm standard and one or two of the appropriately-selected upscale standards (the ICP instrument's response is linear up to 40 ppm for all elements).

9.2 The LDL is also calculated by the software. Use the 10.00- or 20.00-ppm standard to calculate the LDL in µg/mL.

10.0 SAMPLE ANALYSIS.

Read and record the concentration in µg/mL for each analyte, using the A(nalysis option in the software's Sequential menu.

Note: Certain soils contain acid-soluble compounds which will interfere with the analyses of elements (such as arsenic) having analyte wavelengths below 200 nm. This broad-band interference will be evidenced by the fact that 1) the background for the sample is much greater than that for the standard, 2) the ICP analysis produces a negative concentration whose absolute value is greater than the LDL, or 3) both of the above. If this condition occurs, then use the data disk to store the spectra for the sample and the appropriate standard by using the A(cquire option in the software's P(rofile menu, print out the stored spectra for the sample and the standard by using the G(raph Profiles option in the software's Sequential menu, and perform the analysis by hand using peak heights.

11.0 CALCULATION.

Calculate the concentration of the analyte in the soil samples as follows:

$$\mu g/g = C(20)$$

where C = concentration of the analyte in µg/mL from Step 10.0.

12.0 QUALITY ASSURANCE.

12.1 Precision of the method is measured by performing duplicate extractions and analyses on separate portions of the same soil sample.

12.1.1 Duplicate analyses must be performed on at least 10% of the samples.

12.1.2 The percent differences must be within ±20% for analyte concentrations which are ≥ 0.80 µg/mL.

12.2 Recoverability of the method is measured by extracting and analyzing spiked soil samples. Prepare spiked samples by accurately weighing out 5.00 g of the soil sample in a 250-mL beaker; adding 0.10, 0.20, 0.50, 1.00, or 2.00 mL of the appropriate 1000-ppm standard; drying for 0.5 hour at 105° C in the drying oven; and then proceeding as with an unspiked sample.

12.2.1 A spiked sample must be analyzed for each ten or fewer samples.

12.2.2 The percent recoverability must be 80% to 120% for the spiked samples.

12.3 Accuracy of the instrument is determined by analyzing either an audit solution or a standard solution as an unknown sample.

12.3.1 An audit solution or a standard solution must be analyzed as an unknown sample during the analysis of each set of ten or fewer samples.

12.3.2 The percent difference from the true value must be within ±10% for all audit solutions or standard solutions analyzed as unknowns.