

SOUTH COAST AIR QUALITY MANAGEMENT DISTRICT

METHOD 6.1

**DETERMINATION OF SULFURIC ACID AND SULFUR OXIDES FROM
STATIONARY SOURCES**

**OFFICE OF OPERATIONS
TECHNICAL SERVICES DIVISION
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METHOD 6.1

DETERMINATION OF SULFURIC ACID AND SULFUR OXIDES FROM STATIONARY SOURCES

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METHOD 6.1

DETERMINATION OF SULFURIC ACID AND SULFUR OXIDES FROM STATIONARY SOURCES

Section 1 of 5

1. Overview

1.1 Principle

A gas sample is extracted isokinetically from the stack. The sulfuric acid mist, sulfur trioxide, and sulfur dioxide are separated and measured separately by titration and/or precipitation methods.

1.2 Applicability

This method measures sulfur compound emissions consisting of sulfuric acid mist, sulfur trioxide, and sulfur dioxide from stationary sources. In most instances this method also determines total sulfur compounds (liquid and gaseous) if such determination is required. If reduced liquid and gaseous sulfur compounds (e.g. CS₂, COS, RS) are present in quantities greater

than 2 percent or 5 ppm, whichever is lower, use Method 6.3 in addition to this method.

Sulfuric acid mist is collected on a Whatman thimble preceding the impinger train, maintained above the dew point of moisture but below 200°F. Sulfur trioxide is collected in an impinger containing 2-propanol following the thimble. Sulfur dioxide is collected in two impingers containing hydrogen peroxide (H₂O₂).

If sulfuric acid alone is required, the impingers following the Whatman thimble may contain any desired solution. If total sulfur compounds are required, the thimble and impinger containing 2-propanol are unnecessary. If total sulfur oxides are required, separation of these oxides is unnecessary and an impinger train containing the thimble and impingers with H₂O₂ solution is sufficient.

1.3 Range

Collaborative testing indicates that the lower detectable limits of the method are 0.05 mg/m³ (0.03 x 10⁻⁷ lb/ft³) for sulfur trioxide, and 1.2 mg/m³ (0.74 x 10⁻⁷ lb/ft³) for sulfur

dioxide. No upper limits have been established. Based on theoretical calculations for 200 milliliters of 3 percent hydrogen peroxide solution, the upper concentration limit for sulfur dioxide in a 1.0 m³ (35.3 ft³) gas sample is about 12,500 mg/m³ (7.7 x 10⁻⁴ lb/ft³).

The upper limit can be extended by increasing the quantity of peroxide solution in the impingers.

1.4 Interferences

Possible interfering agents are water soluble cations, fluorides, phosphates, free ammonia, (free ammonia reacts with SO₂ to form particulate sulfite), and dimethyl aniline. If any of these interfering agents are present (this is determined by knowing the process), alternative analytical procedures may be used subject to the approval of the Executive Officer. Three different analytical procedures are included in this method: sodium hydroxide titration, barium perchlorate titration, and barium chloride precipitation.

An alternative procedure, sodium hydroxide titration/barium chloride precipitation, is presented in Section 5.

The sodium hydroxide titration procedure measures sulfuric acid and other strong acids. The barium perchlorate titration procedure and the barium chloride precipitation procedure measure total sulfates.

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2. Field Procedures

2.1 Sampling Apparatus

2.1.1 Sampling Train

A schematic of the sampling train used in this method is shown in Figure 6.1-1.

a. Probe Nozzle

Same as Method 5.1.

b. Probe Liner

Borosilicate or quartz glass. A heating system may be required to prevent moisture condensation during sampling. **DO NOT USE METAL PROBE LINERS.**

c. Pitot Tube

For isokinetic or proportional sampling. Same as Method 2.1.

d. Differential Pressure Gauge

Same as Method 2.1.

e. Filter Holder

Whatman paper thimble filter in a borosilicate glass holder with a dial thermometer as shown in Figure 6.1-1. The holder design provides a positive seal against leakage from the outside or around the filter.

Use a heating box or other means to maintain the desired temperature.

f. Impingers

Six impingers connected in series with leak-free ground glass fittings or any similar leak-free non-contaminating fittings. The first, third, and

fourth impinger must be of Greenburg-Smith design with standard tips. The second, fifth, and sixth impinger must be of Greenburg-Smith design, modified by replacing the tip with 13 mm (1/2 in.) ID glass tube extending to 13 mm (1/2 in.) from the bottom of the flask. The first impinger contains 200 ml of 80 percent 2-propanol, the third and fourth each contains 100 ml of 3 percent H₂O₂ solution and the sixth contains a known weight of silica gel or equivalent desiccant. The second and fifth impingers are empty. The silica gel prevents moisture condensation in the pump and metering devices, eliminating the need to correct for moisture in the metered volume.

The volume of H₂O₂ in the impingers may be increased to 200 ml if the concentration of sulfur oxides in the effluent is expected to be high.

g. Metering System

Same as Method 5.1.

h. Barometer

Same as Method 5.1.

i. Gas Density Determination Equipment

Same as Method 5.1.

2.2 Sampling Reagents

See Section 3.2.1.

2.3 Preliminary Determinations

An uneven distribution of SO_x concentration in the effluent requires traverse sampling per Method 5.1. If H_2SO_4 is present as a mist, perform isokinetic sampling per Method 5.1, unless only total SO_x determination is required and H_2SO_4 is less than 10 percent of total sulfur oxides.

2.4 Non-Isokinetic Sampling

For non-isokinetic sampling, the sampling point in the duct should be either at the centroid of the cross section or at a point no closer than 1.00 m (3.3 ft) to the wall, unless otherwise specified by the Executive Officer.

2.5 Isokinetic Sampling

Select the sampling site and the minimum number of sampling points according to Method 1.1. Determine the stack pressure, temperature, and the range of velocity heads using Method 2.1. Perform a leak check of the Pitot lines as outlined in Method 2.1, Section 2.2.1. To set isokinetic sampling rates, determine moisture content using Method 4.1 or its alternative. Determine the stack gas dry molecular weight as outlined in Method 3.1. If Method 3.1 integrated sampling is used to measure molecular weight, take the integrated bag sample simultaneously with the SO_x sample run.

Select a nozzle size based on the range of velocity heads so that it is not necessary to change the nozzle size to maintain isokinetic

sampling rates. Do not change the nozzle size during the run. Choose the proper differential pressure gauge for the range of velocity heads encountered (see Method 2.1, Section 2.1.2).

Select a probe length suitable for sampling all traverse points. For large stacks, consider sampling from opposite sides of the stack (four sampling ports) to reduce the length of probes.

Select a total sampling time of one hour, or one complete cycle of operation, whichever is greater. The sampling time per point must not be less than 2 minutes, and the total sample volume (corrected to standard conditions) must not be less than 30 ft³.

To avoid timekeeping errors, the number of minutes sampled at each point should be an integer or an integer plus one-half minute. The sampling time must be the same at each point.

In some circumstances (e.g. batch cycles), it may be necessary to sample for shorter times at the traverse points and to obtain smaller gas sample volumes. Such variations require prior approval by the Executive Officer.

2.6 Gas Volume Meter Check and Pretest Leak Check

Follow the basic procedures outlined in Method 5.2, Sections 2.4 and 2.6. During leak checking, adjust the probe and filter heaters to the minimum temperature required to prevent condensation.

2.7 Sampling Train Operation

Follow the basic procedure outlined in Method 5.2, Section 2.7, in conjunction with the following special instructions. Record data on a sheet similar to Figure 6.1-2. The sampling rate should not exceed $0.030 \text{ m}^3/\text{min}$ (1.0 cfm) during the run and should be proportional to the stack flow rate ± 15 percent (for non-isokinetic sampling).

Throughout the test, maintain the probe and filter temperatures above the dew point of moisture but below 200°F . Record the temperature.

If component changes become necessary during a run, perform a leak check immediately before each

change. Record all leak rates. If a leakage rate exceeds the specified rate, either void the run or correct the sample volume as outlined in Chapter X, section on Error Bias Corrections. Conduct leak checks immediately after component changes.

At the conclusion of each run, turn off the pump, record final readings, and remove the probe from the stack. Conduct a post test leak check (mandatory) and record the leak rate. If the post test leakage rate exceeds the specified acceptable rate, either correct the sample volume as outlined in Chapter X, section on error Bias Corrections or void the run.

Conduct a post test check of the gas volume meter check.

Drain the ice bath and, with the probe disconnected, purge the remaining part of the train by drawing clean ambient air through the system for 15 minutes at an average flow rate of 0.5 cfm.

2.8 Calculation of Percent Isokinetic

When sampling isokinetically follow the procedure outlined in Method 5.2, Section 2.8.

2.9 Calibration

Calibrate equipment using the procedures specified in Chapter III. Note that the recommended calibration check of the metering system, described in Method 5.2, Section 2.4, applies to this method.

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3. Laboratory Procedures

3.1 Apparatus

3.1.1 Sampling Train

See Section 2.1.1.

3.1.2 Sample Recovery

a. Wash Bottles

Polyethylene or glass, 500 ml (two).

b. Graduated Cylinders

500 ml, 1 liter with stoppers.

Volumetric flasks may also be used.

c. Storage Bottles

Leak-free polyethylene bottles, 500 ml size (1000 ml, if necessary). Three for each sampling run plus three for reagent blanks.

d. Balance

To measure to ± 0.15 g.

e. Pipet

Class "A", 5.0 ml.

3.1.3 Analysis

a. Pipet

Volumetric Class "A" pipets of various sizes.

b. Buret

10 to 50 ml with 0.02 ml or 0.1 ml divisions. Automatic titrator

accurate to 0.01 ml and 0.1 pH
(optional).

c. Erlenmeyer Flask

250 ml (one for each sample, blank,
and standard).

d. Graduated Cylinder

100 ml.

e. Filtration Apparatus

Suction flask, filter holder, and
vacuum pump.

f. Dropping Bottle

125 ml size, to add indicator
solution.

g. Glass Ion Exchange Column

12-15 mm x approximately 500 mm,
equipped with glass wool plug and

stopcock or clamp to control liquid flow rate.

h. Vibrator

Used for packing the column with ion exchange resin.

3.2 Reagents

Unless otherwise indicated, all reagents are to conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Otherwise, use the best available grade.

3.2.1 Sample Collection Train Preparation

a. Filters

Whatman paper thimble. Cellulose, single thickness.

b. Silica Gel

Indicating- type, fresh or dried at 175°C (350°F) for 2 hours, 6 to 16 mesh.

c. Water

Deionized, distilled to conform to ASTM specification D-1193-74, Type 3. At the option of the analyst, the KMnO_4 test for oxidizable organic matter may be omitted when high concentrations of organic matter are not expected to be present. Reference to water throughout this method implies deionized, distilled water.

d. 2-Propanol, 80 Percent

Mix 800 ml of 2-propanol with 200 ml of water.

NOTE: Experience has shown that only A.C.S. Grade 2-propanol is satisfactory. Tests have shown that

2-propanol from commercial sources occasionally contains peroxide impurities that will cause erroneously high sulfuric acid mist measurement.

Use the following test for detecting peroxides in each lot of 2-propanol: Shake 10 ml of 2-propanol with 10 ml of freshly prepared 10 percent potassium iodide solution. Prepare a blank by similarly treating 10 ml of water. After one minute, read the absorbance on a spectrophotometer at 352 nanometers. If the absorbance exceeds 0.1, the 2-propanol should not be used.

Peroxides may be removed from 2-propanol by redistilling, or by passage through a column of activated alumina. However, since reagent grade 2-propanol with suitable low peroxide levels is readily available from commercial sources, rejection of contaminated lots may be more efficient than following the peroxide removal procedure. Mark the received

lot with the blank value and date of test.

e. Hydrogen Peroxide, 3 Percent

Dilute 100 ml of 30 percent hydrogen peroxide to 1 liter with water.

Prepare fresh daily. Store 30 percent hydrogen peroxide in a refrigerator when not in use.

f. Crushed Ice or Dry Ice

g. Stopcock Grease

3.2.2 Sample Recovery

a. Water

Same as Section 3.2.1 c

b. 2-Propanol, 50 Percent

Mix 500 ml of 100 percent 2-propanol with 500 ml of water.

c. HCl, 0.1N

Dilute 8.3 ml of concentration HCl to
1 liter with water.

3.2.3 Analysis

a. Water

Same as Section 3.2.1 c.

b. 2-Propanol, 100 Percent

c. Thorin Indicator

1-(o-arsenophenylazo)-2-naphthol-3, 6-
disulfonic acid, disodium salt, or
equivalent. Dissolve 0.20 g in 100 ml
of water.

d. Barium Perchlorate [$\text{Ba}(\text{ClO}_4)_2$], 0.01N

Dissolve 1.95 g of barium perchlorate
trihydrate [$\text{Ba}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$] in 200 ml
water, and dilute to 1 liter with 2-
propanol; 1.22 g of barium chloride

dihydrate [$\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$] may be used instead of the barium perchlorate. Standardize with sulfuric acid as in Section 3.9. This solution must be protected against evaporation at all times.

e. Sodium Hydroxide (NaOH), 0.1N

Dissolve 4.00 g of sodium hydroxide in 200 ml of water. Dilute to 1 liter with water. Standardize as in Section 3.9 and protect from exposure to air.

f. Sulfuric Acid Standard (H_2SO_4),
0.0200N

Purchase or standardize to $\pm 0.0002\text{N}$ against 0.0100N NaOH that has previously been standardize against primary standard potassium acid phthalate.

g. Cation Exchange Resin

Rexyn^R, strong acid cation exchange resin; Amberlite^R, cation exchange resin, or equivalent.

h. Hydrochloric Acid (HCl)

Dilute (4-6N).

i. Alternate Indicator for Thorin

Dissolve 0.2 g of thorin and 0.3 g of xylene cyanole FF in 100 ml water. The color change is from green to clear at the end point.

j. Methyl Orange Indicator, Aqueous

Dissolve 1 g of methyl orange in 1 liter of water. Filter if necessary.

3.3 Pretest Preparation

All equipment (including balances, oven temperature, glassware, and safety equipment)

should be checked for readiness before starting the following procedure. Weigh several 200 to 300 g portions of silica gel in airtight containers to the nearest 0.5 g. Record on each container the total weight of the silica gel plus container. As an alternative, the silica gel may be weighed directly in its impinger or sampling holder just prior to train assembly.

Check the thimble visually against light for irregularities, flaws, and pinhole leaks. Label the thimble holder with a thimble identification number. Label the impingers with numbers from 1 (2-propanol) to 6 (silica gel).

Prepare the ion exchange column. Wash the resin three times in a beaker, using stirring and decantation. If not already in the acid form, rinse the resin with dilute (1:1) HCl. Plug the bottom of the column with glass wool. Fill the column about halfway with water, and load the column with resin to about 10 cm.

Caution: The loading must be done in the presence of water without the presence of air bubbles in either the beaker or the column. Water must remain above the top of the resin or

air bubbles will become entrapped. Gentle vibration may help settle the resin. Wash with several 5 ml portions of distilled water until the washing is no longer acidic to pH test paper.

3.4 Preparation of Sample Collection Train

During preparation and assembly of the sampling train, keep all openings covered to prevent contamination until the beginning of sampling.

Place 200 ml of 80 percent 2-propanol in the first impinger, 100 ml of 3 percent H₂O₂ in each of the third and fourth impingers. The second and fifth impingers are left empty. Retain a portion of each reagent for use as a blank solution. Place about 200 g of silica gel in the sixth impinger.

Weigh each of the impingers plus contents to the nearest 0.5 g and record these weights. Place a thimble in the thimble holder and carefully seal the holder. Connect the impingers and thimble holder as shown in Figure 6.1.1. Seal the train, or its components, for transfer to the field. Before transfer the train may be leak checked in the laboratory.

3.5 Sample Recovery

Inspect the train for general condition. Note if the silica gel is completely expended and if the train or its components are sealed. Note any condition which may be reflected in the analysis (e.g. dirty or wet thimble, cloudy solutions, backed-up silica gel, missing items, etc.).

3.5.1 Thimble Catch

In an area protected from wind and free from dust, disconnect the probe from the thimble holder and the thimble holder from the remainder of the train. Wipe down the outside of the probe to prevent sample contamination. Rinse the inside of probe and all connecting glassware to the thimble holder at least three times with 50 percent 2-propanol into a sample container. Contact all of the interior surfaces with each rinse. Add exactly 5.0 ml of approximately 0.1N HCl to the container. Disassemble the thimble holder and remove the thimble. Note its condition. Cut up the thimble and add it

to the solution, being careful not to lose any particulate matter. Tighten the lid on the container and shake it well. Mark the liquid level on the container and label the container to clearly identify its contents.

Process a blank thimble in the same manner at the same time.

3.5.2 2-Propanol Catch

Disconnect the first two impingers from each other and the remainder of the train. Weight each impinger plus contents to the nearest 0.5 g and record these weights.

Transfer the contents of the first and second impingers to a 500 ml graduated cylinder. Rinse the back half of the thimble holder, the impingers, and all connecting glassware with 50 percent 2-propanol into the graduated cylinder at least three times. Dilute the sample to 500 ml with 50 percent 2-propanol, stopper the cylinder, and mix well. Transfer the sample to a container. Tighten the lid on

the container and mark the level of liquid on the container to determine if any sample is lost. Label the container to clearly identify its contents.

Take 200 ml of the 2-propanol reagent blank, add 200 ml of the 50 percent 2-propanol used for recovery, and dilute to 500 ml with water. Stopper the cylinder, mix well, and transfer the blank to a container. Seal the container well, mark the level of the liquid on the container, and label the container to clearly identify its contents.

3.5.3 Peroxide Catch

Disconnect the next three impingers from each other and the remainder of the train. Weigh each impinger plus contents to the nearest 0.5 g and record these weights.

Transfer the contents of these impingers to a 500 ml graduated cylinder (1000 ml, if necessary). Rinse all the impingers plus connecting glassware at least three times with water into the graduated

cylinder. Dilute to 500 ml (1000 ml, if necessary) with water and mix well . Transfer the sample to a container. Seal the container well, mark the level of liquid on the container, and label the container to clearly identify its contents.

Take 200 ml of the peroxide reagent blank and dilute to 500 ml (1000 ml, if necessary) with the water used for sample recovery. Mix well and transfer the blank to a container. Seal the container, mark the level of the liquid on the container, and label it to clearly identify its contents.

3.5.4 Silica Gel

Weigh the spent silica gel (or silica plus impinger) to the nearest 0.5 g and record the weight.

3.6 Analysis

Check the level of liquid in the sample and blank containers and determine if any sample was lost.

Note this on the analytical data sheet. If a noticeable amount of leakage has occurred, void the sample or correct the results using methods approved by the Executive Officer.

3.6.1 Recovery of Thimble Fraction

Quantitatively recover the liquid extract from the thimble fraction for analysis by filtering this fraction, using a suction flask and glass fiber filter. Rinse the thimble at least three times with 50 percent 2-propanol using at least 50 ml per rinse. Quantitatively transfer the combined rinsings to a 500 ml graduated and dilute to 500 ml. Mix well. Transfer to a sample container. Seal the container, mark the level of the liquid on the container, and label it to clearly identify its contents. Recover the blank thimble using the same procedure.

3.6.2 Analysis for Acid

All sample fractions are analyzed for acid using the following procedure. A 100 ml aliquot for the thimble and 2-propanol

fractions, and a minimum 10 ml sample aliquot for the peroxide fraction are recommended.

Thoroughly mix the solution in the sample container. Transfer a sample aliquot into a 250 ml Erlenmeyer flask. Titrate to a pH of 4.2 using standardized 0.1 NaOH and methyl orange as the end point indicator, or a properly operating autotitrator. Record the volume to the nearest 0.01 ml. Repeat the titration with a second sample aliquot and average the titration values. Replicate titrations must agree within 1 percent or 0.05 ml, whichever is greater.

Analyze the thimble and reagent blanks using the same procedure.

3.6.3 Sample Cleanup

Before proceeding with the analysis for sulfate, the thimble and 2-propanol fractions must be treated with a strong-acid cation exchange resin to remove interferences. The peroxide fraction must also be treated with strong-acid cation

exchange resin if the barium-thorin endpoint is slow, shows an off-color, or recurs. Thoroughly mix the solution in the sample container. Drain excess water from the ion exchange column until the resin is just covered. Carefully load 25 ml of sample into the resin and allow the sample to flow slowly through the column. Discard this portion. Load the column with slightly more than 100 ml of sample and allow it to flow through the column at about 3 ml/min collect this portion for analysis. After the sample has been collected, flush the column with 25 ml of water in preparation for the next sample.

Treat the thimble and 2-propanol reagent blanks using the same procedure.

3.6.4 Analysis for Sulfate

All sample fractions are analyzed for sulfate using the following procedure. Use 50 ml aliquots for the thimble and isopropanol fractions, and add 75 ml of 100 percent 2-propanol to each aliquot. Use a 25 ml aliquot for the peroxide

fraction; add 100 ml of 100 percent 2-propanol to each aliquot. Aliquot sizes may be decreased; reduce the 2-propanol proportionately to produce a final solution of 80 percent 2-propanol. Thoroughly mix the solution in the sample container before taking sample aliquots.

Transfer the sample aliquot into 250 ml Erlenmeyer flasks. Add 2-propanol and two to four drops of thorin indicator. Titrate to a pink end point using standardized 0.01N $\text{Ba}(\text{ClO}_4)_2$. Record the volume used to the nearest 0.02 ml. Repeat the titration with a second sample aliquot and average the titration values. Replicate titration must agree within 1 percent or 0.05 ml, whichever is greater.

Titrate the thimble and reagent blanks using the same procedure.

3.7 Calculation and Reporting

Report the data as follows:

Impinger gain, ml (g)

Silica Gel gain, g

Thimble Catch

Acid, as

Sulfate, as SO_3 , mg

Sulfate, as SO_3 , mg

2-Propanol Catch

Acid, as SO_3 , mg

Sulfate, as SO_3 , mg

Peroxide Catch

Acid, as SO_2 , mg

Sulfate, as SO_2 , mg

Calculate the above data as follows:

Impinger Gain = $W_f - W_t$

Silica Gain = $W_f - W_t$

where:

W_f = Final weight of impingers
plus content, g

W_t = Tare weight of impingers
plus content, g

Acid,
as SO₃, mg = (V_S-V_B) x N_N x 80.07/2 x AF

Sulfate,
as SO₃, mg = (V_S-V_B) x N_B x 80.07/2 x AF

where:

V_S = Average sample titration
volume, ml

V_B = Average blank titration
volume, ml

N_N = Normality of NaOH, mg/ml

N_B = Normality of Ba(ClO₄)₂, mg/ml

80.07/2 = Equivalent weight of SO₃

AF = Aliquot factor (sample
volume/analytical aliquot
volume)

3.8 Calibrations

3.8.1 NaOH Standardization

Standardize the 0.1N NaOH. Dry crushed primary grade potassium hydrogen phthalate (KHP) in an oven at 105°C for 2 hours. Cool to room temperature in a desiccator. Weigh 0.95 ± 0.05 g of KHP, to the nearest 0.1 mg, into an Erlenmeyer flask. Dissolve in 70 ml of water, add 2-4 drops

of phenolphthalein indicator, and titrate to faint pink using 0.1N NaOH. Repeat this titration using another portion of KHP. Titrate a 70 ml blank of water and 2-4 drops of phenolphthalein indicator to faint pink end point using 0.1N NaOH. Repeat this procedure and average the results. Replicates must agree within 0.05 ml. Calculate the normality for each aliquot as follows:

$$\begin{array}{r} \text{Normality} \\ \text{of NaOH} = \end{array} \frac{\text{mg KHP}/203.44}{\text{(avg. ml-avg. blank)}}$$

Values must agree within \pm 0.5 percent.

3.8.2 Ba(ClO₄)₂ Standardization

Standardize the Ba(ClO₄)₂ against 0.02N H₂SO₄ that has been purchased (NBS traceable) or standardized against NaOH (see Section 3.8.1).

Transfer 10.0 ml of standard H₂SO₄ into a 250 ml Erlenmeyer flask. Add 40 ml of 100 percent 2-propanol and two to four drops of thurin indicator. Titrate to a pink

end point using 0.01N Ba(ClO₄)₂. Repeat the titration using another aliquot of 0.02N H₂SO₄. Average the titration values. Replicate titrations must agree within 0.05 ml or 0.5 percent.

Transfer 10.0 ml of water into a 250 ml Erlenmeyer flask. Add 40 ml of 100 percent 2-propanol and two to four drops of thurin indicator. Titrate to a pink end point. Repeat this blank titration using another aliquot of water. Average the titration values. Replicate titrations must agree within 0.05 ml.

Calculate the normality of the Ba(ClO₄)₂ as follows:

$$\begin{aligned} \text{Normality of Ba(ClO}_4\text{)}_2 &= \\ &\frac{10.0 \text{ ml} \times N \text{ H}_2\text{SO}_4}{\text{(avg. ml - avg. blank)}} \end{aligned}$$

3.8.3 Autotitrator

If an autotitrator is used, calibrate the pH meter at pH 4 and pH 7 following the manufacturer's instructions.

3.9 Quality Control

3.9.1 Control for Acid Analysis

Titrate 10.0 ml of 0.1N H₂SO₄ with every set of samples, or every ten samples, whichever occurs first. Results must be within \pm 5 percent of the theoretical value. If results are outside of the accepted range, restandardize the NaOH and recalculate the results. If the recalculated results do not fall within range, void the previous results, investigate the procedure until it is under control, and reanalyze the samples.

3.9.2 Control for Sulfate Analysis

Analyze an EPA SO₂ Quality Assurance vial with every set of samples or every ten samples, whichever occurs first. Results must be within \pm 5 percent of theoretical. If results do not fall within the accepted

range, restandardize the $\text{Ba}(\text{ClO}_4)_2$ and recalculate the results. If the recalculated results fall outside of the accepted range, void the previous results, investigate the procedure until it is under control, and reanalyze the samples.

3.9.3 Reweigh one impinger every set of samples and record this weight. Weight must be within 0.5 g of the first weight. If results differ by more than 0.5 g, check the balance calibration and reweigh the entire set.

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4. Engineering Calculations and Reporting

Carry out calculations retaining at least one decimal figure more than that of the acquired data. Round off figures after final calculation.

4.1 Nomenclature

- V_M = Corrected gas volume metered, dscf
- Q = Flow rate, dscfm
- A = Sulfuric acid mist in the probe and thimble, expressed as $H_2SO_4 \cdot 2H_2O$, mg (if reported as SO_3 , multiply by 1.675)
- B = Sulfur trioxide in 2-propanol expressed as SO_3 , mg
- C = Sulfur dioxide in H_2O_2 , mg

4.2 Emissions Calculation

a. Sulfuric Acid Mist

Emission of $\text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$, lb/hr =

$$\frac{(1.32 \times 10^{-4})(A)(Q)}{(V_M)}$$

b. Sulfur Dioxide Concentration

$$\text{Emission of SO}_2, \text{ ppm} = \frac{(835.54)(C)}{(V_M)(64)}$$

c. Total Sulfur Compounds expressed as SO_2

Concentration, ppm =

$$\frac{[(A)(0.4776)+(B)(0.8)+C](835.54)}{(V_M)(64)}$$

d. Total Sulfur Oxides expressed as SO_2

$$\text{Concentration, ppm} = \frac{[(B)(0.8)+C](835.54)}{(V_M)(64)}$$

METHOD 6.1

DETERMINATION OF SULFURIC ACID AND SULFUR OXIDES FROM STATIONARY SOURCES

Section 5 of 5

5. Alternative Laboratory Procedures

This sodium hydroxide titration/barium chloride precipitation procedure is a combined gravimetric and volumetric procedure for determining H₂SO₄ mist plus SO₃, SO₂, and water soluble sulfates in emissions from stationary sources. The lower detection limit is approximately one ppm, by volume, expressed as SO₂, when a sample of 10 dscf is collected.

5.1 Apparatus

5.1.1 Sample Train Preparation

Same as Section 3.1.1.

5.1.2 Sample Recovery

Same as Section 3.1.2.

5.1.3 Sample Analysis

a. Volumetric Pipets

Class A, various sizes.

b. Buret

10 or 50 ml, with 0.02 ml or 0.1 ml divisions; or automatic titrator accurate to 0.01 ml and 0.1 pH.

c. Beakers, 600 ml

d. Gooch Crucibles

40 to 60 ml, prepared with asbestos mat, preignited and preweighed.

e. Analytical Balance

Accurate to within 0.1 mg.

f. Hot Plate

g. Muffle Oven

Capable of operation at 900°C.

h. Rubber Policeman

i. Filtration Apparatus

Consisting of suction flask, filter holder on a vacuum pump.

j. Desiccator

Containing calcium sulfate or silica gel, indicating-type.

k. Crucible Tongs

l. Glass Stirring Rods

m. Watch Glasses

Ribbed, for 600 ml beakers.

5.2 Reagents

Unless otherwise stated, all reagents are to conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Otherwise, use best available grade.

5.2.1 Sample Collection Train Preparation

See Section 3.2.

5.2.2 Sample Recovery

a. Water

See Section 3.2.1 c.

b. HCl 0.1N

See Section 3.2.2 c.

5.2.3 Analysis

a. Water

See Section 3.2.1 c.

b. Methyl Orange Indicator

See Section 3.2.3 j.

c. NaOH 0.1N

See Section 3.2.3 e.

d. Barium Chloride (BaCl_2)

Solution Approximately 10 Percent.

Dissolve 100 of BaCl_2 dihydrate in 900 ml of water.

e. Silver Nitrate Solution

1 Percent (w/w). Dissolve 1 g of AgNO_3 100 ml of water.

f. HCl Concentrated

5.3 Pretest Preparation

See Section 3.3.

5.4 Preparation of Sample collection Train

See Section 3.4.

5.5 Sample Recovery

Note if the silica gel is completely expended and the train or its components are sealed. Note any condition which may be reflected in the analysis (e.g. dirty or wet thimble, cloudy solutions, backed-up silica gel, missing items, etc.).

5.5.1 Thimble Catch, 2-Propanol Catch, Peroxide Catch, and Silica Gel

Perform this recovery using the procedure outlined in Section 3.5.1 through 3.5.4, except use water for sample recovery. Process reagent and thimble blanks.

5.6 Analysis

Check the level of the liquid in the sample and blank containers to determine if any sample was lost. If a noticeable amount of liquid was lost, note this on the data sheet, and either void the sample or correct the results using methods approved by the Executive Officer.

5.6.1 Quantitatively recover the liquid extract from the thimble by filtering this fraction, using a suction flask and glass fiber filter. Rinse the thimble at least three times with water. Quantitatively transfer the combined rinsings to a 500 ml graduated cylinder, dilute to 500 ml, stopper, and mix well. Transfer this sample fraction to a container, seal the container well, mark the level of the liquid on the container, and label it to clearly identify its contents. Recover the blank thimble using the same procedure.

5.6.2 Analysis for Acid

All sample fractions are analyzed for acid using the following procedure. A 100 ml aliquot for thimble and 2-propanol fractions, and a minimum 10 ml sample aliquot for the peroxide fraction is recommended.

Thoroughly mix the solution in the sample container. Transfer a sample aliquot using a pipet into a 250 ml Erlenmeyer flask. Titrate to a pH of 4.2 using standardized 0.1N NaOH and methyl orange indicator, or a properly operating autotitrator. Record the volume to the nearest 0.02 ml. Repeat the titration using another sample aliquot, and average the titration values. Replicate titrations must agree within 1 percent or 0.05 ml, whichever is greater. Analyze thimble and reagent blanks using the same procedure and aliquot sizes as above.

5.6.3 Analysis for Sulfate

Using the titrated samples from above, transfer each aliquot to a 600 ml beaker. Adjust to approximately pH 7 and add 2 ml of concentrated HCl. Place the beaker on a hot plate, insert a stirring rod, and cover with a watch glass. Heat until the contents are nearly boiling. While stirring, slowly add 10 ml of 10 percent BaCl₂ solution, or more if needed. Allow the precipitate to digest several hours on the steam bath. Quantitatively filter through a properly prepared Gooch crucible. Rinse the mat and precipitate thoroughly with hot distilled water and test the rinse for chloride using silver nitrate. When chloride is absent (usually after 300 ml rinse) place the crucible in a furnace and heat at 900°C for one hour. Cool and remove the crucible to the desiccator for at least 6 hours. Weigh until constant weight is reached (6 hours desiccation between weighings). Record to the nearest 0.1 mg.

5.7 Calculations and Reporting

Carry out calculations retaining at least one decimal figure more than that of the acquired data. Round off figures after the final calculations.

Calculate the above data as follows:

$$\text{Impinger Gain, g} = W_f - W_t$$

$$\text{Silica Gel Gain, g} = W_f - W_t$$

where:

$$W_f = \text{Final weight of impingers plus content, g}$$

$$W_t = \text{Tare weight of impingers plus content, g}$$

Acid, as

$$\text{SO}_3, \text{ mg} = (V_s - V_b) \times N \times 80.07/2 \times AF$$

where:

$$V_s = \text{Average sample titration volume, ml}$$

$$V_b = \text{Average blank titration volume, ml}$$

$$N = \text{Normality of sodium hydroxide}$$

80.07/g = Equivalent weight of SO₃

AF = Aliquot factor

NOTE: Values may be expressed as SO₂ using the equivalent weight of SO₂, 64.07/2, in place of the equivalent weight of SO₃.

$$\text{Sulfate, as SO}_3, \text{ mg} = (W_f - W_t) \times \frac{80.07}{223.43} \times \text{AF}$$

where:

W_f = Final weight of crucible plus precipitate, mg

W_t = Tare weight of crucible, mg

$\frac{80.07}{223.43}$ = Conversion factor of BaSO₄ to SO₃

AF = Aliquot factor; sample volume/aliquot volume

Note: Values may be expressed as SO₂ by using

$\frac{64.07}{223.43}$ as the conversion factor.

Summarize the data as follows:

Impinger gain, ml (g)

Silica gel gain, g

Thimble catch

Acid, as SO_3 , mg

Sulfate, as SO_3 , mg

2-Propanol catch

Acid as SO_3 , mg

Sulfate, as SO_3

Peroxide catch

Acid, as SO_2 , mg

Sulfate, as SO_2 , mg

5.8 Calibrations

5.8.1 NaOH, 0.1N

See Section 3.8.1.

5.8.2 pH Meter

If an autotitrator is used, calibrate the pH meter at pH 4 and pH 7 following the manufacturer's instructions.

5.9 Quality Control

5.9.1 Acid Analysis

See Section 3.9.1.

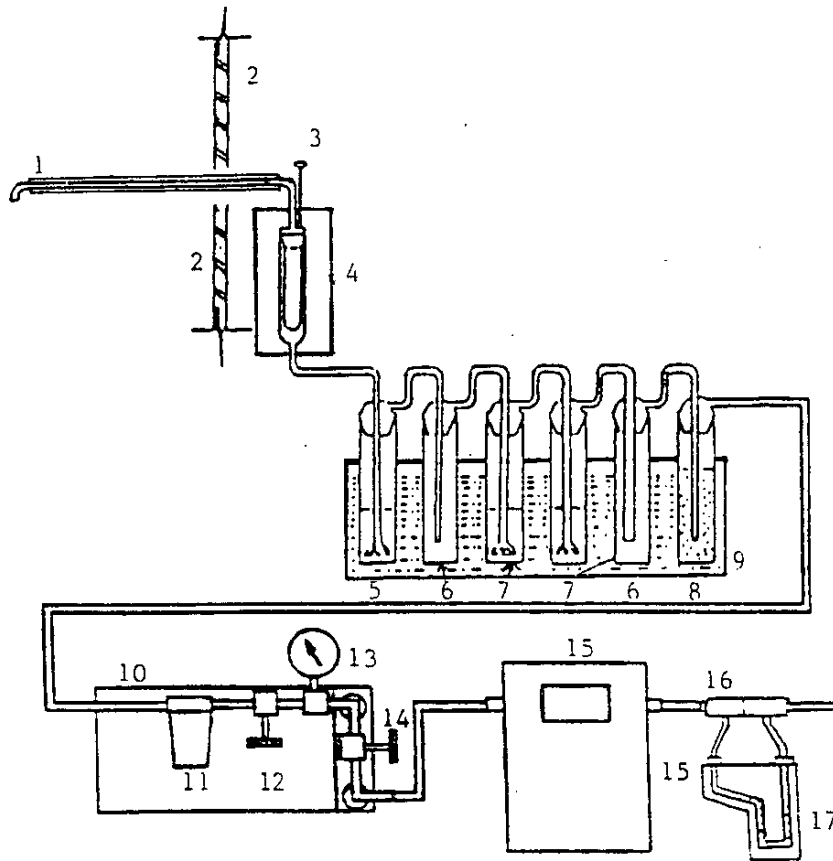
5.9.2 Sulfate Analysis

Use the above titrated solution for sulfate analysis. Results must be within 5 percent of theoretical. If results are out of range, void the previous analysis, investigate the procedure until it is under control, and reanalyze the samples.

5.9.3 Gravimetric Procedures

Redetermine and record one weight for every set of samples or ten samples (whichever occurs first) at each step. Impinger redetermination must be within 0.5 g of the first result. Precipitate redeterminations must be within 0.5 mg of

the first result. If a redetermination falls outside of the range, check the balance calibration and reweigh the entire set.



- | | |
|---|--|
| 1. Heated Glass Probe | 9. Ice Bath |
| 2. Stack Wall | 10. Sealed Pump (Leak Free) |
| 3. Dial Thermometer | 11. Filter for Pump |
| 4. Whatman Thimble Filter
(Inside Hot Box) | 12. Metering Valve |
| 5. Impinger with 200 ml
Isopropanol | 13. Vacuum Gauge |
| 6. Empty Bubbler | 14. By-pass Valve |
| 7. Impinger with 100 ml H_2O_2 (3%) | 15. Temperature Compensated
Dry Gas Meter |
| 8. Bubbler with Silica Gel | 16. Orifice |
| | 17. Orifice Inclined Manometer |

Figure 6.1-1

Sulfur Oxides Impinger Train Setup

