# BAY AREA AIR QUALITY MANAGEMENT DISTRICT

# MANUAL OF PROCEDURES

This Manual of Procedures is designed to give technical assistance and guidance to persons subject to the rules and regulations of the Bay Area Air Quality Management District. Mention of trade names or commercial products does not imply the Bay Area Air Quality Management District's endorsement or recommendation for use.

**VOLUME I — ENFORCEMENT PROCEDURES**
**VOLUME II — ENGINEERING PERMITTING PROCEDURES**
**VOLUME III — LABORATORY POLICY AND PROCEDURES**
**VOLUME IV — SOURCE TEST POLICY AND PROCEDURES**
**VOLUME V — CONTINUOUS EMISSION MONITORING AND PROCEDURES**
**VOLUME VI — AIR MONITORING PROCEDURES**

Adopted by the Board of Directors of the Bay Area Air Quality Management District on September 5, 1979, to become effective on January 1, 1980, and amended on March 19, 1980.

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# MANUAL OF PROCEDURES

## VOLUME I

## ENFORCEMENT PROCEDURES

# MANUAL OF PROCEDURES

## VOL. I

## ENFORCEMENT PROCEDURES

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# 1. EVALUATION OF VISIBLE EMISSIONS

REF: Regs. 6-301, 6-303, 6-304,
10-1-302,
12-4-301, 12-4-302

## 1.1 INTRODUCTION

The following guidelines have been developed to assure the uniform evaluation of visible emissions by a trained observer, and should be utilized with every observation to the extent they are applicable, and to whatever extent time and physical circumstances reasonably permit.

## 1.2 OBSERVER'S LOCATION

1.2.1 Observations shall be made such that the line of sight is approximately at a right angle (90°) to the path of the plume.

1.2.2 The plume should be observed against a suitable background, at its point of maximum obscuration. Whenever possible, black plumes should be evaluated using a blue sky background and white plumes should be evaluated using a dark contrasting background.

1.2.3 Daylight observations should be made with the observer facing away from the sun.

1.2.4 Observations during hours of darkness should be made with the aid of a light source. This source of light may be ambient or artificial depending upon prevailing conditions and should emanate from behind the plume, opposite the observer.

1.2.5 When evaluating an elevated source the observer should be located at a suitable distance from the source. This location, depending upon viewing conditions, should normally fall somewhere between two stack heights and a quarter of a mile from the source.

## 1.3 TIME INTERVAL BETWEEN READINGS

Readings shall be noted at approximately 15 seconds intervals during the observation. Each 15 second momentary observation recorded shall be deemed to represent the average value of emissions for that 15 second period.

Reading intervals up to 1 minute shall be permitted where the appearance of the emission does not vary during such interval.

## 1.4 INTENSITY AND DURATION OF EXCESSIVE VISIBLE EMISSIONS

Regulation 2 states that any visible emission as dark or darker than a Ringelmann #1, for more than 3 minutes in any 60 minute period, is considered to be excessive. Our current policies and procedures, recognizing the subjectivity of the Ringelmann system, specify that a visible emission must be as dark or darker than a Ringelmann 1 1/2 to be considered excessive.

## 1.5 WET PLUMES

Wet plumes are defined as "Those plumes where the presence of uncombined water is the only reason for the failure of an emission to meet the limitations of Regulations 6-301, 6-303 and 10-1-302.

The guidelines for the evaluation of "Wet" plumes are as follows:

1.5.1 Residual plume is that part of the plume which continues to exist after the apparent evaporation of the water droplets emitted.

1.5.2 No violations will be written on wet plume without a residual plume.

1.5.3 Residual plumes which appear, in the judgment of the viewer, to be more than Ringelmann #1 when the relative humidity is less than 60 percent, will be considered to be in violation.

1.5.4 Changes in staff practices will be publicized and made available, particularly to those known to us to be interested in regulations on wet plumes.

## 1.6 QUALIFICATION CRITERIA FOR EVALUATION OF VISIBLE EMISSIONS

1.6.1 Certification. The Inspector must qualify on both black and white plumes at the plume evaluation training school. Qualification on either plume shall consist of meeting the following requirements during both Daylight and Night training sessions.

Observe and successfully evaluate the opacity of one run of black smoke and one run of white smoke in accordance with the following requirements:

1.6.1.1 The deviation of any reading must not be greater than 15%.

1.6.1.2 The average deviation for both black and white runs must be less than 7.5%.

1.6.2 The following definitions apply:

1.6.2.1 A "run" consists of 25 consecutive observations.

1.6.2.2 "Single reading deviation" means the absolute value of the difference between the calibrated meter's reading and the Inspector's record on an individual observation. This single reading deviation is expressed as a percentage on the basis that each full Ringelmann number represents 20%. Each one quarter Ringelmann then represents 5%.

1.6.2.3 "Average deviation" of a run is obtained by adding the absolute values of all the single reading deviations of the run, disregarding plus and minus signs, and dividing by the total number of single readings in the run.

1.6.3 Maintenance of certification -

1.6.3.1 The Inspector must satisfactorily complete the Certification Procedure every 6 months (twice/year) in order to maintain certification.

## 2. INSPECTION CRITERIA FOR PHASE II GASOLINE VAPOR BALANCE SYSTEMS

REF: Reg. 8-7-601

### 2.1 INTRODUCTION

Regulation 8-7-305 requires that all equipment be maintained in good working order. The following criteria have been developed to insure uniformity in the evaluation of Phase II gasoline vapor balance systems and the following procedures are used during the inspection of such systems.

### 2.2 VAPOR BALANCE SYSTEMS

2.2.1 Only two first generation vapor balance systems are approved for use within the BAAQMD, OPE 7VA and Emco Wheaton A300. Any system installed after September 26, 1978 must be certified by the California Air Resources Board (CARB). The first generation systems require only the nozzle, vapor hose, and underground vapor piping. The state certified systems required the nozzle, shorter hoses, an anti-recirculation valve, on retail facilities, swivels at the nozzle and dispenser, and a flow limiter. A further prerequisite for state certification is a maximum allowable pressure drop, through the underground system, of .35 inches of water column at a flowrate of 50 CFH.

### 2.3 THE BAAQMD INSPECTION

2.3.1 Various items are checked by BAAQMD inspectors during the evaluation of Phase II vapor balance systems. Figure I-1 is the inspection sheet (Form I-24-79) used to determine compliance status of the system. The following are the procedures for filling out Form #I-24-79.

2.3.2 Station. Enter the name of the service station.

2.3.3 Address. Enter the street address of the service station.

2.3.4 City. Enter the city in which the service station is located.

2.3.5 Contact. Enter the name of the station owner or manager.

2.3.6 Phone. Enter the telephone number of the service station.

2.3.7 Date. Enter the date of the inspection.

2.3.8 Inspector. Enter the name of the person performing the inspection.

2.3.9 VN #. If a Violation Notice is issued enter the violation notice number. If no VN is issued enter "none". Do not leave this space blank.

2.3.10 Permit. Enter the Permit to Operate number. Do not leave this space blank.

2.3.11 No. of Self-Service Islands. Enter the number of self-service islands.

2.3.12 No. of Full-Service Islands. Enter the number of full-service islands.

2.3.13 Total No. of Dispensers. Enter the total number of dispensers.

2.3.14 No. of Unleaded Dispensers. Enter the number of unleaded dispensers.

2.3.15 No. of Regular Dispensers. Enter the number of regular grade dispensers.

2.3.16 No. of Premium Dispensers. Enter the number of premium grade dispensers.

2.3.17 Pump Number. If a diagram is included on the inspection sheet then enter the number from the diagram (1,2,3, etc.). If a diagram is not included or if the pumps are not numbered then enter the serial number on the dispenser. (Note the dispenser model number.)

2.3.18 Nozzle Type. Enter the manufacturer and model number of the nozzle. The vapor balance nozzles most encountered will be OPW 7VA, OPE 7VC, Emco-Wheaton A300 and Emco-Wheaton A3003.

2.3.19 Gas Grade. Enter P for Premium, R for Regular, UL for unleaded, and D for diesel.

On the following 12 items, enter a Y in the appropriate square on Form I-24-79 if the item is acceptable as installed and enter a N if the item is not acceptable.

2.3.20 Nozzle Type. The following vapor balance nozzles are acceptable: OPE 7VA, Emco-Wheaton A3003, OPW 7VA properly maintained and Emco-Wheaton A300 properly maintained.

2.3.21 Mounting Rack. Nozzle must be mounted securely and in such a manner that the vapor check valve is closed. (Insure that bellows are not compressed.)

2.3.22 Face Seal. The face seal must not be cracked, torn or missing. If the nozzle is not equipped with a separate face seal enter N/A.

2.3.23 Plastic Cup. The OPW 7VA nozzles are equipped with a white plastic cup that pushes against the back surface of the face seal. If the cup is broken or cracked, vapor can leak from the nozzle. For all other nozzle types, enter N/A on I-27-79.

2.3.24 Ring or Rivet. The latch ring shall be secured in its specified position and rivets must not be loose or sheared off.

2.3.25 Bellows. The bellows should be clamped securely to the nozzle barrel and must not have cracks or tears or holes.

2.3.26 Flow Limiter. If the state certified Emco-Wheaton A3003 nozzle is used a flow limiter must be present on the product line. If any other nozzle except the OPW 7VC is being used then enter N/A/ The OPW 7VC is equipped with an internal flow limiter.

2.3.27 Swivels. If a state certified OPW 7VC or Emco-Wheaton A3003 nozzle is used there must be two swivels attached to the nozzle. If a first generation OPW 7VA or Emco-Wheaton A300 nozzle is being used and no swivels are present enter N/A.

2.3.28 Hose 9/8 Length. If a state certified nozzle is used the vapor and product hose lengths must be 8 and 9 feet respectively, or 1/2 the island width plus 6 feet. If a first generation nozzle is used, any hose length is acceptable.

2.3.29 Recirculation Trap. If a state certified balance system is installed, an anti-recirculation valve must be included on commercial retail facilities. Acceptable are OPW 78 series or Emco-Wheaton A-8. These may be installed inside or outside the dispenser and the inlet to the valve must be not greater than 3.5 inches above the island. If a first generation nozzle is used enter N/A.

2.3.30 Swivels. If a state certified system is installed there must be a swivel on the vapor hose at the anti-recirculation valve. The OPW 78-S anti-recirculation valve has a built-in swivel. If a first generation system is used and no swivel is present enter N/A.

2.3.31 Flat, Torn or Kinked. Vapor hoses shall be leak free and kinked or flattened hoses are unacceptable.

2.3.32 Pressure Drop Test, Δ P, Inches of Water Column.

2.3.32.1 Before Draining Hose. See Source Test Method ST-27.

2.3.32.2 After Draining Hose. See Source Test Method ST-27.

2.3.33 Auto Shutoff, Y or N. The automatic shutoff mechanism of the nozzle shall be checked in either of the following ways.

2.3.33.1 Fill a container with gasoline to a depth of approximately 3 inches, begin dispensing gas and dip the spout into the liquid, insuring that the pressure tap is submerged. If the nozzle does not shut off there is a defect in the nozzle.

2.3.33.2 With dispenser OFF engage the nozzle trigger, place finger securely over the pressure tap and use a squeeze bulb to induce a vacuum. If the nozzle trigger does not release, the automatic shut off mechanism is malfunctioning.

2.3.34 Comments. Enter any appropriate comments regarding compliance status of vapor recovery equipment.

2.3.35 After completing the inspection, give the pink copy of Form I-27-79 to the station contact along with the Violation Notice, if one is issued.

# BAY AREA AIR QUALITY MANAGEMENT DISTRICT
# PHASE II VAPOR RECOVERY INSPECTION SHEET

Station ______________________ Address ______________________ City ______________________

Contact ______________________ Phone ______________________ Date ______________________

Inspector ______________________ VN Number ______________________ Permit # ______________________

NO. OF SELF-SERVICE ISLANDS ______________________ NO. OF UNLEADED DISPENSERS ______________________
NO. OF FULL-SERVICE ISLANDS ______________________ NO. OF REGULAR DISPENSERS ______________________
TOTAL NO. OF DISPENSERS ______________________ NO. OF PREMIUM DISPENSERS ______________________

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| PUMP NUMBER | | | | | | | | | |
| NOZZLE TYPE | | | | | | | | | |
| GAS GRADE | | | | | | | | | |

ACCEPTABLE, YES OR NO

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| NOZZLE | 1. NOZZLE TYPE | | | | | | | | | |
| | 2. MOUNTING RACK | | | | | | | | | |
| | 3. FACE SEAL | | | | | | | | | |
| | 4. PLASTIC CUP | | | | | | | | | |
| | 5. RING OR RIVET | | | | | | | | | |
| | 6. BELLOWS | | | | | | | | | |
| | 7. FLOW LIMITER | | | | | | | | | |
| | 8. SWIVELS | | | | | | | | | |
| HOSE | 9. 9/8 LENGTH | | | | | | | | | |
| | 10. RECIRCULATION TRAP | | | | | | | | | |
| | 11. SWIVELS | | | | | | | | | |
| | 12. FLAT, TORN OR KINKED | | | | | | | | | |

PRESSURE DROP TEST, ΔP, INCHES OF WATER COLUMN

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 13. BEFORE DRAINING HOSE | | | | | | | | | |
| 14. AFTER DRAINING HOSE | | | | | | | | | |
| 15. AUTO. SHUTOFF, Y OR N | | | | | | | | | |

COMMENTS: ______________________________________________

______________________________________________

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Figure I-1

FORM I-27-79

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## 5. BOILER, STEAM GENERATOR, AND PROCESS HEATER TUNING PROCEDURE [1]

REF: Reg. 9-7-604 and Proposed Reg. 9-10-605

### 5.1 INTRODUCTION

Regulation 9-7-304.2 and Regulation 9-10-304.2 require that boilers, steam generators, and process heaters be tuned at least once every twelve months by a technician in accordance with the procedure specified in Section 9-7-604 and 9-10-605, respectively. The following tuning procedure has been developed to insure uniformity in the conduct of the tune-ups.

Nothing in this Tuning Procedure shall be construed to require any act or omission that would result in unsafe conditions or would be in violation of any regulation or requirement established by Factory Mutual, Industrial Risk Insurers, National Fire Prevention Association, the California Department of Industrial Relations (Occupational Safety and Health Division), the Federal Occupational Safety and Health Administration, or other relevant regulations and requirements.

### 5.2 THE TUNING PROCEDURE

1. Operate the unit at the firing rate most typical of normal operation. If the unit experiences significant load variations during normal operation, operate it at its average firing rate.

2. At this firing rate, record stack gas temperature, oxygen concentration, and CO concentration (for gaseous fuels) or smoke-spot number [2] (for liquid fuels), and observe flame conditions after unit operation stabilizes at the firing rate selected. If the excess oxygen in the stack gas is at the lower end of the range of typical minimum values [3], and if CO emissions are low and there is no smoke, the unit is probably operating at near optimum efficiency - at this particular firing rate. However, complete the remaining portion of this procedure to determine whether still lower oxygen levels are practical.

3. Increase combustion air flow to the furnace until stack gas oxygen levels increase by one to two percent over the level measured in Step 2. As in Step 2, record the stack gas temperature, CO concentration (for gaseous fuels) or smoke-spot number (for liquid fuels), and observe flame conditions for these higher oxygen levels after boiler operation stabilizes.

4. Decrease combustion air flow until the stack gas oxygen concentration is at the level measured in Step 2. From this level gradually reduce the combustion air flow, in small increments. After each increment, record the stack gas temperature, oxygen concentration, CO concentration (for gaseous fuels) and smoke-spot number (for liquid fuels). Also, observe the flame and record any changes in its condition.

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[1] This tuning procedure is based on a tune-up procedure developed by KVB, Inc. for the EPA.

[2] The smoke-spot number can be determined with ASTM test method D-2156-80 or with the Bacharach method. The Bacharach method is included in a tune-up kit that can be purchased from the Bacharach Company.

[3] Typical minimum oxygen levels for boilers at high firing rates are: 0.5 - 3% for natural gas and 2-4% for liquid fuels. At low firing rates, typical minimum oxygen levels are: 3-8% for natural gas and 5-8% for liquid fuels.

5. Continue to reduce combustion air flow stepwise, until one of these limits is reached:

   a. Unacceptable flame conditions - such as flame impingement on furnace walls or burner parts, excessive flame carryover, or flame instability.
   b. Stack gas CO concentrations greater than 400 ppm.
   c. Smoking at the stack.
   d. Equipment - related limitations - such as low windbox/furnace pressure differential, built in air-flow limits, etc.

6. Develop an $O_2$/CO curve (for gaseous fuels) or $O_2$/smoke curve (for liquid fuels) similar to those shown in Figures 1 and 2 using the excess oxygen and CO or smoke-spot number data obtained at each combustion air flow setting.

7. From the curves prepared in Step 6, find the stack gas oxygen levels where the CO emissions or smoke-spot number equal the following values:

| Fuel | Measurement | Value |
|---|---|---|
| Gaseous | CO Emissions | 400 ppm |
| #1 and #2 oils | smoke-spot number | number 1 |
| #4 Oil | smoke-spot number | number 2 |
| #5 Oil | smoke-spot number | number 3 |
| Other oils | smoke-spot number | number 4 |

The above conditions are referred to as the CO or smoke thresholds, or as the minimum excess oxygen levels.

Compare this minimum value of excess oxygen to the expected value provided by the combustion unit manufacturer. If the minimum level found is substantially higher than the value provided by the combustion unit manufacturer, burner adjustments can probably be made to improve fuel and air mix, thereby allowing operations with less air.

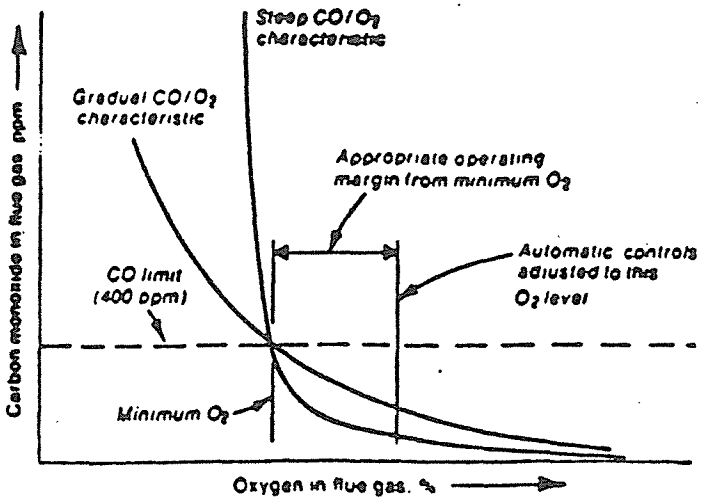
8. Add 0.5 to 2.0 percent to the minimum excess oxygen level found in Step 7, unless the plant is authorized by the District in a permit condition to add a higher percentage to the minimum excess oxygen level of this source, and reset burner controls to operate automatically at this higher stack gas oxygen level. This margin above the minimum oxygen level accounts for fuel variations, variations in atmospheric conditions, load changes, and nonrepeatability or play in automatic controls.

9. If the load of the combustion unit varies significantly during normal operation, repeat Steps 1-8 for firing rates that represent the upper and lower limits of the range of the load. Because control adjustments at one firing rate may affect conditions at other firing rates, it may not be possible to establish the optimum excess oxygen level at all firing rates. If this is the case, choose the burner control settings that give best performance over the range of firing rates. If one firing rate predominates, setting should optimize conditions at that rate.

10. Verify that the new settings can accommodate the sudden load changes that may occur in daily operation without adverse effects. Do this by increasing and decreasing load rapidly while observing the flame and stack. If any of the conditions in Step 5 result, reset the combustion controls to provide a slightly higher level of excess oxygen at the affected firing rates. Next, verify these new settings in a similar fashion. Then make sure that the final control settings are recorded at steady-state operating conditions for future reference.

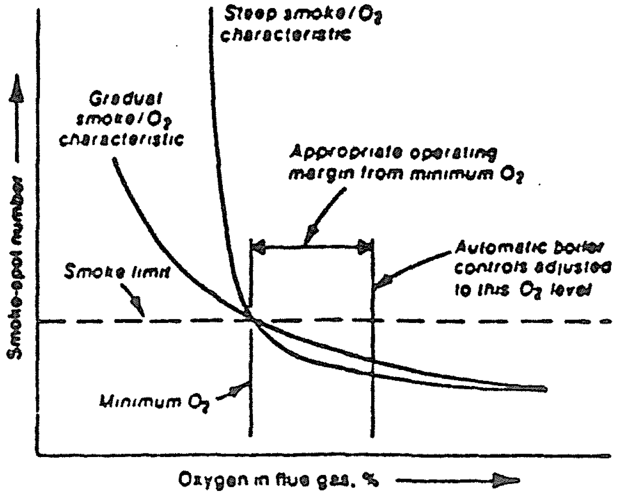
## Figure 1

## Oxygen/CO Characteristic Curve



## Figure 2

## Oxygen/Smoke Characteristic Curve



Source: KVB Inc.

# MANUAL OF PROCEDURES

## VOLUME II

## ENGINEERING PERMITTING PROCEDURES

# MANUAL OF PROCEDURES

## VOLUME II

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# PERMIT REQUIREMENTS

REF: Regs. 2-1-301 to 2-1-306

## 1. INTRODUCTION

The BAAQMD requires permits for any machine, equipment, or other device which may emit any of the major air contaminants (particulate, organic gases, sulfur dioxide, nitrogen dioxide, or carbon monoxide) or any odorous or hazardous pollutants (such as asbestos, beryllium, mercury, sulfuric acid, hydrogen sulfide, hydrogen fluoride, and lead.) Also, any abatement device which may reduce or eliminate air contaminants must have a permit.

## 2. PERMITS APPLICATION, EMISSIONS

A variety of means may be used to estimate the quantity of emissions on the basis of information submitted in a permit application.

The emissions may be estimated from factors taken from AP-42, ("Compilation of Air Pollution Emission Factors," EPA), by material balances using engineering expertise and knowledge of the process, or by any other acceptable documented methodology.

Acceptable estimates may also be obtained from source tests of similar operations, from the technical literature, and from vendor specifications and guarantees.

The District Permit Services Division makes available guidelines for emissions calculations and other pertinent information related to emissions and is available for consultation.

## 3. LISTS AND CRITERIA FOR DETERMINING COMPLETENESS OF PERMIT APPLICATIONS

### 3.1 Objectives

Chapter 4.5, Section 65940 of the Government Code requires that each APCD compile one or more lists which will specify the information required from any applicant for a development project. The ACPD's are also to indicate the criteria which will be applied to determine the completeness of an application.

This document provides the information which an applicant will need to enable him to prepare and file an application with the Bay Area Air Quality Management District (BAAQMD). It will advise him what information is required to ensure a complete application and whom to call if he has problems in preparing the application. Information is also provided on approval schedules, fees and appeals.

In order to make this document more useful to the individual applicant, separate requirement lists and criteria for determining completeness are given for different types of development projects. (See the definition of "development project " attached.)

Applicants who find that the attached material does not fully answer their questions should contact the Permit Services Division at (415) 771-6000, ext. 259.

### 3.2 Procedures for Approval

For some development projects, the California Environmental Quality Act (CEQA) requires the preparation of an Environmental

Impact Report (EIR) including relevant air quality information. EIR requirements are separate from BAAQMD permit requirements. For further information, contact the city or county in which the proposed facility will be located.

Two types of permits are issued, the Authority to Construct (A/C) and the Permit to Operate (P/O). The A/C is an approval by the BAAQMD for construction of equipment described in the A/C. The P/O is issued after construction is complete and operation of the equipment has begun; it certifies that construction was in accordance with the A/C and that there are no apparent emission problems.

Only one application is required for both the A/C and P/O. It will be called the "permit application" and the instructions for information required in the following sections refer to this permit application.

Applications should be mailed to the District (Attention: Permit Services), preferably in duplicate. Within 20 days after the receipt of the application, the District will notify the applicant in writing whether the application is complete or incomplete. If it is incomplete, the information or data needed to make it complete will be listed in the letter. If no such notification is made by the District in 30 calendar days, the application will be deemed to be complete.

When complete, the application will be evaluated to determine whether it meets emission criteria. Further clarification or amplification may be requested during the evaluation. Emission limits are given in a number of documents which you may obtain on request. Call Public Information on (415) 771-6000, ext. 210.

For most applications, the District will complete its evaluation within 60 days of the receipt of the completed application and will notify the applicant of its decision on the application. The decision can be any one of the following:

1. Issue an Authority to Construct
2. Issue an Authority to Construct with Conditions
3. Find part or all of the application Exempt from permit requirements
4. Deny the application

The Authority to Construct is permission for erection of the equipment specified in the application. In the case of denials, the applicant is encouraged to discuss the application with the Permit Services staff; perhaps there is an alternate approach or new and improved abatement equipment whose use could enable the project to be approved. The applicant is encouraged to reapply.

In case an applicant is dissatified with the District's decisions, he may appeal to the Hearing Board. See 3.8, Appeals.

With applications for large projects requiring offsets or other specialized treatment or approvals, the 60-day action time cannot be guaranteed. In these cases, 30 additional days will be allowed for public comment and for review by EPA and the California Air Resources Board. Either of these agencies may ask for extensions.

Once the equipment is constructed and ready to operate, the applicant should notify the District in writing of the date of the expected "startup". The District will inspect the equipment to determine that it was built in accordance with the A/C and to see if there are any obvious emission problems.

As a time delay usually occurs between the time of receipt of the applicant's letter giving date of startup and the time when a District engineer can schedule an inspection, the holder of the A/C may operate without the P/O so long as he has sent the "startup" letter.

In some cases, a source test will be required before the P/O can be issued. If a source test is required, the District will advise the applicant to this effect in the A/C.

The District will issue the Permit to Operate within a few days after the engineering inspection. It is valid for one year and is renewable on the anniversary date of first issuance. (Large plants will be assigned a single anniversary date for the renewal of all P/O's.) Note that when alterations are planned which may affect the emissions from a piece of existing equipment, a new Authority to Construct should be applied for. This application should include the number of the existing Permit to Operate which it is to modify. Any installation of an abatement device on existing equipment, even though it results in a reduction in emissions, requires a new permit.

Again, if you have questions as to whether you require a permit or what the status of your application is, call Permit Services.

### 3.3 Fees

Fee schedules are given in Regulation 3. No permit application will be evaluated until the prescribed fees have been paid.

Note that a fee is paid for each source and one application may have several sources. A source is the operation or equipment which creates or separates the air pollutant. Abatement devices (that is, air pollution control devices) are not "sources" and do not require payment of fees.

### 3.4 Information required for a Permit Application

In order to carry out its statutory responsibilities, the District must obtain sufficient information from each applicant to enable it to determine what the emissions would be and whether the emissions will comply with District regulations. The nature of the information required varies considerably between various types of equipment and processes and between small projects and large projects. The data obtained is used both as the basis for issuing a permit and for obtaining an inventory of source emissions.

For each application, submit a Form P-101 and a quadrant map, with an "X" at the site of emissions. The District will supply this map. If your plant covers a visible area on the map, outline the plant boundaries.

The following paragraphs describe the additional information required for each type of equipment and the application forms to be filled out and submitted for each.

3.4.1 For gasoline tanks under 15,000 gallons, fill out Form P-101G only. Submit with this form a plot plan showing tank locations and a sketch or listing showing the vapor recovery equipment to be installed. (For industrial sources which also have gasoline tanks, fill out a Form T for each tank.)

3.4.2 For other tanks and for gasoline tanks over 15,000 gallons, fill out one Form T for each tank. Submit a plot plan showing the location of tanks and fill and delivery stations. (Note that any fuel with an initial boiling point greater than 300°F., such a diesel fuel or #2 to #6 fuel oil, is exempt from District Permit requirements; however, a Form T should be submitted for information purposes.) If there is an abatement device such as a vapor recovery system connected to the tank, a Form A is required.

3.4.3 For surface coating, printing operations, and other processes involving solvents, fill out one Form S for each surface coating or solvent source operation. Also submit a plot plan showing its location and its relation to other existing operations. If there is an oven or a combustion process connected with the surface coating operation, a Form C is required for each such item. If there are abatement devices planned, submit a Form A for each.

3.4.4 For process operations (such as chemical plants, refineries, can lines, microfilm manufacture, acid plants, metal operations, etc.) several different forms will be necessary to fully describe the operation and enable a good prediction of emissions and compliance to be made. The primary document is a flow chart for the operation, showing materials being handled, flow rates and temperatures. Indicate the relationship between major components and all abatement devices and emission points. (Write a description of the process on a separate sheet.) Submit a Form T for each tank, a Form C for each combustion source, a

Form S for each surface coating or solvent source, and a Form G for any other source which may generate air contaminants. Provide a description of each abatement device on Form A and of each emission point on Form P. If the proposed operation will have more than four sources, summarize the expected emissions on Form P-202. Fugitive emissions should be discussed for new and modified sources.

3.4.5 For combustion processes (including incinerators, boilers, kilns, turbines, and fuel-burning abatement devices) fill out a Form C for each combustion device. List on the Form C the anticipated yearly consumption of each type of fuel and give the sulfur content of all non-gaseous fuels. Give also the maximum ash and fuel nitrogen content, if known. Where the burner itself is designed to minimize the emission of pollutants (as for example a low-$NO_x$ burner or water injection), give details and a drawing of the pollution-reducing features. Also submit a Form P giving stack data.

3.4.6 General Operations. There are many operations which do not fit into any of the above categories. These include (but are not limited to) feed and grain handling, cement operations, sewage treatment plants, landfill operations, animal rendering, asphalt operations, rock and quarry operations, and metallurgical processes. Please submit a flow diagram giving the flow of material and the relation between existing and new sources. In addition to the P-101, submit one Form G for each source. In some cases, these operations will include some sources which burn fuel (for example, a kiln); if so, submit a Form C in addition to the Form G. Form A (abatement devices) and Form P (stack) should be submitted where applicable. Fugitive emissions should be discussed for new sources.

Note: If your facility has emissions of any air contaminant of over 15 lb/hr or 150 lb/day, you will be required to use BACT for any new construction or modifications to existing equipment. (See BACT definition attached.) Call Permit Services at (415) 771-6000, if you wish an interpretation of what BACT is for your application.

### 3.5 Trade Secrets

If you feel that trade secrets are included in the application, you should submit the following information:

3.5.1 A claim that the material is trade secret as defined in Section 6254.7 of the Government Code.

3.5.2 A separate claim identifying each specific type of part of the information which is claimed as trade secret.

3.5.3 A factual statement indicating the basis for considering the information to be trade secret.

All information claimed as trade secret will be subjected to special handling by the District. We will discuss these procedures with you on request.

### 3.6 Criteria to Determine Completeness

A complete application provides sufficient information for the District to estimate what the emissions from the new or modified source will be. The following check list is for your assistance. Not all of the items given below refer to every application. If you have fully answered all of the questions referring to your proposed installation, your application will be complete.

3.6.1 Is the application signed?

3.6.2 Have you included a check for the fee? As the evaluation does not start until the fee is received, you can save time by including a check with the application.

3.6.3 Is the quadrant map included, with the facility location identified?

3.6.4 If you claim any trade secrets, have you justified such a claim in writing and identified the pages with such material?

3.6.5 Note: SIC number on any of the emission forms need not be filled in if you do not have a SIC Manual available.

3.6.6 Have you made a clear statement as to whether the equipment in the application represents a new source, a modification to an existing source, or a replacement for an existing source?

3.6.7 Do you have any offsets for which you are claiming credit? If so, documentation on the offsets should accompany this application. This documentation should be quantitative; vague justifications will not be considered.

3.6.8 Are there any special factors in this application of which we should be aware? For example, if you intend to limit production rate or operating hours, you should so state.

3.6.9 Have you included a plot plan of the facility which shows the relation of the source to other existing sources, and shows all emission points? (If you have already submitted a plot plan, show changes only.)

3.6.10 Have you included a flow diagram showing the flow of process material, with flow rates and temperatures at key points?

3.6.11 For any abatement equipment to be used, have you given the manufacturer, model number and drawing, if available?

3.6.12 Have you given the planned operating schedule (hours/day, days/week and weeks/year)?

3.6.13 Have you given the process throughput?

3.6.14 Have you identified emission points and given stack diameter and height for each? Have you given composition, flow rate and temperature for emitted gases?

3.6.15 Have you submitted the data Forms (C,G,S,T,A and P, as required) and provided all of the data requested?

3.6.16 Gasoline Tanks Under 15,000 Gallons

3.6.16.1 Have you given the throughput in gallons per month?

3.6.16.2 Have you included a sketch or drawing of the vapor recovery equipment?

3.6.16.3 If you claim exemption from vapor recovery, have you stated the basis of such an exemption? (Call the District Permit Services Division at at 771-6000 if you are uncertain as to whether you are exempt.)

3.6.17 Other Tanks (All non-gasoline tanks and all tanks over 15,000 gallons)

3.6.17.1 Have you given the annual throughput?

3.6.17.2 Have you given the maximum fill rate (except for external floating roof tanks)?

3.6.17.3 Have you given the maximum withdrawal rate (for external floating roof tanks)?

3.6.17.4 Have you given the descriptive name of each material stored and its approximate vapor pressure under actual storage conditions? (Code numbers given on the back of Form T will be acceptable in place of descriptive names.)

3.6.17.5 Have you indicated what the loading and unloading techniques are? Have you indicated whether submerged fill is used?

3.6.17.6 In the case of a floating roof, have you provided the design of primary and secondary seals?

3.6.17.7 If a vapor recovery system of any kind is used, have you described the system and provided a drawing?

3.6.17.8 Have you indicated the maximum storage temperature for the liquid being stored?

3.6.18 Surface Coating, Printing Operations and Other Processes Involving Solvents

3.6.18.1 Have you described the coating operation?

3.6.18.2 Have you described the coating material (by name) and given the solvent type and the percent of organic solvent in the material? (Code numbers given on the back of Form S will be acceptable in place of descriptive names.)

3.6.18.3 Have you given the use rate (that is, gallons per day)?

3.6.19 Process Operations (Chemical plants, refineries, can lines, microfilm manufacture, acid plants, metal operations, etc.)

3.6.19.1 Have you provided a process flow chart?

3.6.19.2 Do you have descriptions of all new or modified equipment which may result in the separation of air contaminants from the process materials or in the conversion of the process materials into air contaminants (as in the case of the combustion of fuel)?

3.6.19.3 Have you shown flow rates, temperatures and other relevant parameters on the process flow chart?

3.6.19.4 Have you indicated emission points and marked each one clearly? Have you given stack heights, and diameters? Have you described any abatement equipment used, including manufacturer and design drawings, if available?

3.6.19.5 Have you provided a plot plan which shows transfer of raw materials and products, the relationship between the process line and buildings, and the location of emission points?

3.6.19.6 Have you given the maximum design rate (flow rate, throughput) for the process line? Have you given an operating schedule (hrs/day, days/week, weeks/yr)? Have you given the actual planned process rate or throughput for the first two years of operation ( if it differs from design rate)?

3.6.19.7 Have you discussed the receipt of raw materials, including the emissions from carriers within the District.

3.6.19.8 Have you discussed fugitive emissions?

3.6.19.9 If tanks, combustion or solvent operations are part of the process, have you answered the question in 3.6.17, 3.6.18, and 3.6.20?

3.6.20 Combustion Processes (Incinerators, boilers, kilns, gas turbines, and fuel-burning abatement devices, etc.)

3.6.20.1 Have you described the fuel to be used, including sulfur content and ash and fuel nitrogen content, if known?

3.6.20.2 Have you described the burners, giving manufacturer's name and model, where available? Have you given the firing type and mode of control?

3.6.20.3 If the unit is used to incinerate waste gas or liquid stream, have you described the waste fluid and its method of injection into the burner?

3.6.20.4 If the unit is used to incinerate solid waste, have you characterized the solid waste composition?

3.6.21 General Operations

3.6.21.1 Have you described the equipment, giving manufacturer and model number, where available?

3.6.21.2 Have you given the maximum design rate?

3.6.21.3 Have you given an operating schedule (hrs/day, days/week, weeks/yr)? Have you given the actual planned process rate or throughput for the first two years of operation (if it differs from the design rate)?

3.6.21.4 Have you shown combustion sources and storage tanks (if any)?

3.6.21.5 Have you listed and described all abatement equipment, giving manufacturer and model number, if available?

3.6.21.6 Have you provided a plot plan showing the locations of equipment, transfer of raw materials and products, and all emission points?

3.6.22 Abatement Equipment

3.6.22.1 Have you shown on all sketches, flow diagrams, etc., the abatement equipment to be used, the equipment which feeds it, and the emission point or points which it feeds?

3.6.22.2 Have you described all abatement equipment to be used, giving drawing, manufacturer, size, model number, and efficiency, if available? (Manufacturer's literature may be satisfactory in many cases. If you submit this, have you clearly indicated the specific model and size to be used)?

3.6.23 Emission Points

3.6.23.1 Have you described each emission point on a Form P?

3.6.23.2 Have you shown all emission points on sketches and flow diagrams?

3.7 New Source Review

When a source is subject to New Source Review, certain additional information may be required. This additional information is given below. (For the purposes of this Section, consider that any source which has new or added emissions of over 250 lb/day of particulates, sulfur dioxide and organics, or over 550 lb/day of $NO_x$ is subject to New Source Review.)

3.7.1 Identify all facilities within the District (excluding service stations) which you own or operate and give the compliance status of each.

3.7.2 If you are applying for offsets from other existing sources:

3.7.2.1 Provide sufficient information to determine whether adequate emission reductions will be achieved to offset the air quality impact of your proposed source. This should include the name and location of the offset sources, a description of the emission reductions expected from the offset and a description of how the offsets will be obtained. Source test data on the sources to be reduced are desirable.

3.7.2.2 If any contractual agreements are required to carry out the offset, give evidence that the arrangements have been agreed to by all parties concerned.

3.7.2.3 If the offset involves the shutdown of a facility or a piece of equipment, indicate what assurance there is that the facility or equipment will not be subsequently reused.

3.7.2.4 Give the following data on the emission of cargo carriers: frequency of visits, types and sizes of cargo carriers (other than motor vehicles) and nature of cargo.

3.7.2.5 Give special attention to air pollution control equipment, listing:

3.7.2.5.1 Air pollution control equipment to be used, including type, size, manufacturer, model number and expected control efficiency.

3.7.2.5.2 Changes in processes or operations utilized to reduce emissions.

3.7.2.5.3 Other means of reducing emissions.

3.7.2.6 Discuss fugitive emissons and your plan for controlling them.

3.7.2.7 If you claim an exemption from New Source Review, state the reason for your claim and document it as completely as possible.

### 3.8 Appeals

If you are dissatisfied with the District's decision on your permit application, you may appeal to the Hearing Board within ten (10) days from the day you are notified of the District's decision. In your appeal, you can ask for an order modifying or reversing the District's decision. The Hearing Board is located at 939 Ellis Street, San Francisco 94109; its telephone number is (415) 771-6000.

### 3.9 Definitions

3.9.1 Development Project (For the purposes of air pollution control): Any project which results in the discharge of any air pollutant into the atmosphere. (From Chapter 4.5, Section 65940 of the Goverment Code).

3.9.2 Trade Secrets: Any formula, plan, pattern, process, tool, mechanism, compound procedure, production data, or compilation of information which is not patented, and which gives its user an opportunity to obtain a business advantage over competitors who do not know it.

3.9.3 New Source Review: A procedure for evaluating all proposed new or modified stationary sources which will emit more than 250 lb/day of any particulates, organics or $SO_2$, or over 550 lb/day of $NO_x$.

3.9.4 Source: The equipment used to perform the operations preceding the emission of an air contaminant, which operations result in the creation or separation of the air contaminants, or determine or substantially affect the quantity of air contaminant emitted, but not including air pollution control operations.

3.9.5 Best Available Control Technology (BACT): BACT is that control equipment technology which gives the maximum reduction in emissions of any air contaminant.

3.9.6 Stationary Source: Any building, structure, facility or installation from which air contaminants are emitted. Note that cargo carriers, other than motor vehicles, are considered part of the stationary source for purposes of emission calculations; thus, emissions from the carrier's engines, from purging or venting vapors, and from loading or unloading cargo are considered in computing total emission from a stationary source.

PERMIT SERVICES DIVISION
BAY AREA AIR QUALITY MANAGEMENT DISTRICT
939 ELLIS STREET, SAN FRANCISCO, CA 94109
(415) 771-6000

BAAQMD PLANT NO.______
(IF KNOWN)

# APPLICATION FOR AUTHORITY TO CONSTRUCT AND PERMIT TO OPERATE INDUSTRIAL SOURCES

BUSINESS NAME______________________________________________

MAILING ADDRESS ____________________________________________

PLANT ADDRESS______________________________________________

NAME OF CONTACT_______________________________ PHONE____________

EQUIPMENT DESCRIPTION________________________________________

_______________________________________________________________

NUMBER OF SOURCES ☐ NEW CONSTRUCTION ☐ MODIFICATION ☐ REPLACEMENT ☐

RELOCATION ☐ DEMOLITION OR SHUT DOWN ☐ ABATEMENT EQUIPMENT ONLY ☐

HAS AN ENVIRONMENTAL IMPACT REPORT BEEN PREPARED FOR THIS PROJECT: YES ___ NO ___
IF YES, BY WHOM_____________________________________________

| SOURCES | | EMISSIONS IN LB/HR | | | | | USAGE | | |
|---|---|---|---|---|---|---|---|---|---|
| DESCRIPTION | NO. | TSP | ORGANIC | $SO_X$ | $NO_X$ | CO | HRS/DAY | DAYS/WK | WKS/YR |
| | | | | | | | | | |
| | | | | | | | | | |
| | | | | | | | | | |
| | | | | | | | | | |
| TOTAL | | | | | | | | | |

ARE OFFSETS OR TRADEOFFS INVOLVED IN THIS APPLICATION? ___ IF SO, GIVE DOCUMENTS AND PAGE NUMBER

ON WHICH THIS INFORMATION IS PROVIDED_____________________________

DO YOU CLAIM AN EXEMPTION FROM NEW SOURCE REVIEW FOR SOME OR ALL OF YOUR SOURCES? ________
IF SO, GIVE DOCUMENTS AND PAGE NUMBERS ON WHICH THIS CLAIM IS BASED.

_______________________________________________________________

HAVE YOU PROVIDED AN AIR QUALITY ANALYSIS? ___ IF SO, GIVE DOCUMENTS AND PAGE NUMBERS ON

WHICH THIS INFORMATION IS PROVIDED________________________________

THE FOLLOWING SHOULD ACCOMPANY THIS APPLICATION: TOPOGRAPHICAL MAP SHOWING LOCATION OF FACILITY, PROCESS FLOW DIAGRAM (IF APPLICABLE), AND DESCRIPTION OR MANUFACTURER'S CATALOGUE OF EQUIPMENT AND AIR POLLUTION CONTROL EQUIPMENT. SEE LISTS AND CRITERIA (AB 884) FOR FURTHER DETAILS.

SIGNATURE AND TITLE_________________________________________

NAME (PRINTED)_____________________________ PHONE______________ DATE__________

*IMPORTANT: All information that you submit will be considered as public information unless you indicate that it is considered TRADE SECRET and give the reasons.*

FORM P-101A; REV. 10/79

☐ ACKNOWLEDGEMENT

PERMIT SERVICES DIVISION
BAY AREA AIR QUALITY MANAGEMENT DISTRICT
939 ELLIS STREET, SAN FRANCISCO, CA 94109

## APPLICATION FOR AUTHORITY TO CONSTRUCT AND PERMIT TO OPERATE
## GASOLINE STORAGE AND DISPENSING FACILITIES

BUSINESS NAME ________________________________________

MAILING ADDRESS ________________________________________

EQUIPMENT ADDRESS ________________________________________

CONTACT NAME & TITLE ______________________ PHONE ____________

NATURE OF BUSINESS ________________________________________

NUMBER OF TANKS ☐ NEW CONSTRUCTION ☐ MODIFICATION ☐

DUPLICATE ☐ TRANSFER OF OWNERSHIP ☐ EST. DATE OF INSTALLATION ______

| TYPE OF GASOLINE | TANK SIZE GALLONS | THROUGHPUT, GAL/MO. | NO. OF NOZZLES | SUBMERGED FILL DROP TUBE (YES OR NO) | VAPOR RECOVERY EQUIPMENT (YES OR NO) |
|---|---|---|---|---|---|
| | | | | | |
| | | | | | |
| | | | | | |
| | | | | | |

DESCRIPTION OF VAPOR RECOVERY EQUIPMENT: ______________________________

________________________________________

DO YOU CLAIM AN EXEMPTION FROM VAPOR RECOVERY? ________

IF SO, CHECK THE APPROPRIATE BOX:

TANKS 2000 GALS. OR LESS AND THROUGHPUT LESS THAN 6000 GALS. PER MONTH ☐

AGRICULTURAL USE ONLY ☐

DELIVERY OF GASOLINE FROM EXEMPT BULK DISTRIBUTOR ☐

GIVE NAME OF DISTRIBUTOR: ______________________________

________________________________________

SIGNATURE AND TITLE: ______________________________

NAME (PRINTED) ______________________ PHONE ____________

DATE ____________

ORM P-101G; REV. 6/80

☐ ACKNOWLEDGEMENT

## INSTRUCTIONS

1. Please insure that all applications are complete.

2. Please include the following items with each application:

   a. Topographical or similar map of the area showing location of the facility.

   b. Plot plan of facility drawn to scale, showing location of all gas tanks, pumps, or nozzles and the nearest street intersection.

   c. Cross-section drawing, catalogue number, or make model of certified vapor recovery equipment.

   d. Enclosed postcard, writing your name and mailing address on the front and equipment location on the back. It will be mailed to you in acknowledgement when an application number has been assigned.

3. Before processing can commence, it is necessary that permit fees be included with the application.

## FEES

Standard $100 + $30 per nozzle

Duplicate $20

Transfer of Ownership $100

Modification (Addition of an extra tank with no increase in the number of nozzles) - $100

4. In completing this application, please include all gasoline tanks and nozzles on your site, describing the vapor recovery equipment, if applicable.

5. In a separate cover letter, please describe any details necessary to explain your intentions for this application submittal. Include previous permit numbers if applicable.

BAY AREA
AIR POLLUTION CONTROL DISTRICT
939 Ellis Street, San Francisco, CA 94109 (415) 771-6000

**PLANT DATA FORM P-201**

Plant Identification No.*

Business Name

Other Business Name(s)(if any)

Plant Telephone No.

Name of Parent Company (if any)

PLANT ADDRESS ______________________ Street

City State Zip Code

MAILING ADDRESS ______________________ Street

City State Zip Code

PLANT AREA (Acres) ____________

NUMBER OF EMPLOYEES ____________

PRINCIPAL PRODUCT ______________________

OWNERSHIP:

[ ] Private
[ ] Utility
[ ] Local Government
[ ] State Government
[ ] Federal Government

Please submit a name and address to whom all correspondence regarding air pollution control can be sent.

Contact Name & Title

Street Address

City State Zip Code

*Plant Identification Numbers are assigned by the BAAPCD. Leave blank if number is not known.

Name & Title of person preparing this form.

Date

4-25-77

PERMIT SERVICES SECTION
BAY AREA AIR QUALITY MANAGEMENT DISTRICT
939 Ellis Street, San Francisco, CA 94109
(415) 771-6000

**EMISSIONS SUMMARY**
**P-202**

COMPANY NAME ________________________________ PLANT NO. ______

PROJECT TITLE ________________________________

| SOURCE | | EMISSION IN LB/HR (ACTUAL) | | | | | USAGE | | |
|---|---|---|---|---|---|---|---|---|---|
| Description | No. | Particulate | Organic | $SO_x$ | $NO_x$ | CO | HRS/DAY | DAYS/WK | WKS/YR |
| 1 | | | | | | | | | |
| 2 | | | | | | | | | |
| 3 | | | | | | | | | |
| 4 | | | | | | | | | |
| 5 | | | | | | | | | |
| 6 | | | | | | | | | |
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| 9 | | | | | | | | | |
| 10 | | | | | | | | | |
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| 17 | | | | | | | | | |
| 18 | | | | | | | | | |
| 19 | | | | | | | | | |
| 20 | | | | | | | | | |

New Construction ( ) Demolition ( ) Alteration ( ) Tradeoff ( )

Note: Give description of any trade-offs proposed. Note that BACT is required for any source (or facility) emitting over 15 lb/hr.

PREPARED BY ______________________ Phone No. ____________ Date ________

7/78

# MANUAL OF PROCEDURES

## VOLUME III

## LABORATORY POLICY AND PROCEDURES

# MANUAL OF PROCEDURES

## VOL. III

## LABORATORY POLICY AND PROCEDURES

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2. GENERAL PROVISIONS
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   - 2.3 Accomplishing the Quality Assurance Program
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3. APPLICABILITY TO REGULATIONS

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5. LABORATORY PROCEDURES

   Procedure No. - Analytical Procedure

## 1. INTRODUCTION

This volume of the Manual of Procedure specifies the analytical methods used for the determination of compliance to the Regulations of the Bay Area Air Quality Management District. As new methods are developed and found acceptable, they may replace or be added to the existing methods in this manual.

## 2. GENERAL PROVISIONS

2.1 Laboratory Quality Assurance Program - The goal of these procedures is to provide accurate and precise analyses, and it is essential that a laboratory assurance program be established and maintained.

2.2 Objectives of the laboratory quality assurance program are:

2.2.1 To provide ongoing information for monitoring unsatisfactory performance of personnel, equipment or procedures.

2.2.2 To provide prompt detection and correction of conditions which contribute to the generation of inadequate data.

2.2.3 To collect and supply information necessary to describe the quality of the data.

2.3 Implementation of the following elements will produce data of acceptable precision and accuracy.

2.3.1 Routine monitoring of the known variables which may affect the quality of data.

2.3.2 Routine training and evaluation of analysts.

2.3.2 Corrective action.

2.4 Representative Sampling

2.4.1 Analytical results, regardless of the accuracy and precision of the procedure, can be no better than the representativeness of a submitted sample.

2.5 Sample Submission and Continuity

2.5.1 All samples will be identified and the identification carried forth with the analytical results.

2.6 Reagents

2.6.1 Reagent grade or better chemicals shall be used. Lesser grades may be used provided it is first ascertained that their use will not degrade the accuracy of the determination.

2.6.2 Unless otherwise specified, inorganic reagents used in the preparation of standards shall be dried at 105°C for two hours and kept dessicated until used.

2.7 Distilled water or its equivalent shall be used for reagent preparations.

2.8 Gas Chromatography

2.8.1 Gas chromatographic units used shall have the required systems and sensitivities as specified in the procedure.

2.8.1.1 Each chromatograph will be equipped with a recorder which provides permanent charts for record purposes.

2.8.1.2 All carrier gases, fuel gases and air supplies will be free of interfering substances.

2.8.1.3 Analytical columns are specified in this manual for each procedure. The separation characteristics of an alternate column must be comparable to those specified.

### 2.9 Atomic Absorption

2.9.1 Atomic absorption spectrophotometers utilized should have the following minimum specifications:

- a. Analytical wavelenth coverage of 1937A to 7800A
- b. Less than 0.3% light scatter at 3000A
- c. Less than 1% noise at full gain
- d. Slit system to provide 5A resolution

2.9.2 Acetylene, nitrous oxide, and air supplies used will be those commonly used for best analytical results.

### 2.10 Spectrophotometers

2.10.1 Spectrophotometers employed for colorimetric and turbidimetric procedures should be capable of operation in the 340 to 700 nm range.

2.10.2 Spectrophotometers should have a grating or prism system capable of ±25 nm reproductivity of wavelength settings.

2.10.3 Spectrophotometers should be checked for wavelength accuracy once per year using a didymium filter or comparable system.

### 2.11 Volumetric Glassware

2.11.1 Class A glassware shall be used for all volumetric flasks, pipettes and burets employed in the procedures. Class A specifications are identical to those found in the National Bureau of Standards publication "Circular 602".

## 3. APPLICABILITY

3.1 Each analytical procedure is applicable to a specific regulation, division and section. The designated numbering system applying to the regulation appears on the upper left corner of each procedure.

## 4. METHODOLOGY

4.1 Alternate analytical procedures may be used provided that such procedures have established equivalency to an accepted reference method. Any questions relating to equivalency may be referred to the Chief of Laboratory Services.

4.1.1 Appropriate ASTM and EPA approved methodologies will be deemed equivalent procedures.

## 5. LABORATORY PROCEDURES

| | |
|---|---|
| Lab 1 | Determination of Ammonia in Effluents |
| Lab 2 | Determination of Beryllium in Effluents & Atmospheric Particulate Matter |
| Lab 3 | Determination of Dimethylsulfide in Effluents |
| Lab 4A | Determination of Lead Content in Atmospheric Particulate Matter |
| Lab 4B | Determination of Total Lead in Effluents |
| Lab 5 | Determination of Total Mercaptans in Effluents |
| Lab 6 | Determination of Particulate and Gaseous Mercury Emissions |
| Lab 7A | Determination of Oxides of Nitrogen in Effluents (Alkaline Permanganate Procedure) |
| Lab 7B | Determination of Oxides of Nitrogen in Effluents (Grab Sample Procedure) |

| | |
|---|---|
| Lab 8 | Determination of Phenols in Effluents |
| Lab 9 | Determination of Compliance of Solvents, Coatings, and Related Products |
| Lab 10 | Determination of Sulfur in Fuel Oil |
| Lab 11 | Determination of Sulfur Dioxide in Effluents |
| Lab 12 | Determination of Sulfur Dioxide, Sulfur Trioxide, and Sulfur Acid Mist in Effluents |
| Lab 13 | Determination of the Reid Vapor Pressure of Petroleum Products |
| Lab 14 | Determination of Trimethylamine in Effluents |
| Lab 15 | Standardization of Carbon Dioxide Calibration Gas |
| Lab 16 | Standardization of Carbon Monoxide Calibration Gas |
| Lab 17 | Standardization of Hydrocarbon Calibration Gases |
| Lab 18 | Standardization of Hydrogen Sulfide Calibration Gas |
| Lab 19 | Standardization of Nitric Oxide Calibration Gas |
| Lab 20 | Standardization of Sulfur Dioxide Calibration Gas |
| Lab 21 | Determination of Compliance for Air-Dried Architectural Water Based Coatings |
| Lab 22 | Determination of Compliance for Air-Dried Architectural Oil Based Coatings |
| Lab 23 | Determination of Volatile Weight Loss of Polyester Resins |
| Lab 24 | Determination of Fluoride in Effluents |
| Lab 25 | Determination of Hydrogen Sulfide in Effluents |

REF: Reg. 7-303

## DETERMINATION OF AMMONIA IN EFFLUENTS

### 1. PRINCIPLE

1.1 The ammonia is absorbed in dilute acid solution. The absorbed ammonia is then reacted with Nessler's reagent to produce a yellow-brown color which is proportional to the ammonia content.

### 2. APPARATUS

2.1 Spectrophotometer

2.2 25 ml graduated test tubes

### 3. REAGENTS

3.1 Hydrochloric acid - (0.1 N). Dilute 8.4 ml of concentrated hydrochloric acid to 1 liter with distilled water.

3.2 Nessler's Reagent - may be purchased already prepared, or if desired prepare according to Snell and Snell "Colorimetric Methods of Analysis", page 814, Vol II, 3rd Ed. 6th Printing, D. Van Nostrand Co., 1957.

### 4. ANALYTICAL PROCEDURE

4.1 To 5.0 ml of sample or an aliquot brought to 5.0 ml with 0.1 N hydrochloric acid and containing no more than 80 μgm of ammonia, add 14.0 ml of distilled water.

4.2 Add 1.0 ml of Nessler's reagent and mix well.

4.3 Let stand and read after 10 minutes in a spectrophotometer at 420 nm using 13 mm cuvettes, after setting instrument at 100% transmittance with a reagent blank.

4.4 Determine the μgm of ammonia from the standard curve.

## 5. STANDARD CURVE

5.1 Standard Stock Ammonia Solution - Weigh 0.3144 g of ammonium chloride and dilute to 1 liter with distilled water. This solution contains 100 μgm of ammonia per ml.

5.2 Working Standard Ammonia Solution - Dilute the standard stock solution 1:5 to obtain a working solution of 20 μgm $NH_3$/ml.

5.3 To a series of graduated 25 ml test tubes, add respectively 0, 1.0, 2.0, 4.0, and 5.0 ml of the working standard.

5.4 To each test tube add 5.0 ml of 0.1 N hydrochloric acid solution, and bring the volume of all solutions to 19.0 ml with distilled water.

5.5 Add 1.0 ml of Nessler's reagent, mix and read in spectrophotometer as described under procedure. Prepare a graph of % transmittance vs. concentration on a semi-log graph paper.

## 6. CALCULATION

$$\text{PPM } NH_3 = \frac{\text{Total micrograms ammonia in sample}}{0.695 \times \text{sample volume (liters)}}$$

Where: 0.695 = the μgm in 1 μl of ammonia at 25°C and 760 mm Hg

## 7. REFERENCES

7.1 Goldman, F.H. and Jacobs, M.B., Chemical Methods of Industrial Hygiene. Interscience Publishers Inc., 250 Fifth Ave., New York, N.Y. 1953

7.2 Elkings, H.R., The Chemistry of Industrial Toxicology, 2nd Ed., John Wiley and Son, New York, N.Y. 1959

# LAB 2

REF: Reg. 11-3-301 to 11-3-303

## DETERMINATION OF BERYLLIUM IN EFFLUENT AND ATMOSPHERIC PARTICULATE MATTER

### 1. PRINCIPLE

Samples are collected by passing a known volume of air through an appropriate filter. The filter is decomposed by wet acid oxidation. The aqueous beryllium solution is then analyzed by atomic absorption spectrophotometry.

### 2. APPARATUS

2.1 Atomic absorption spectrophotometer

2.1.1 Acetylene

2.1.2 Nitrous Oxide

2.1.3 Beryllium hollow cathode lamp

2.2 Hot plate

### 3. REAGENTS

3.1 Concentrated Nitric Acid

3.2 Concentrated Sulfuric Acid

3.3 Concentrated Perchloric Acid

3.4 Hydrochloric Acid 25% (v/v). Dilute 250 ml of concentrated hydrochloric acid to 1 liter with distilled water.

3.5 Sulfuric Acid (12 N). Slowly add 33.6 ml concentrated sulfuric acid to 50 ml of distilled water, cool and dilute to 100 ml.

3.6 Beryllium Powder (98% minimum purity)

### 4. ANALYTICAL PROCEDURE

4.1 Place the sample filter in a 150 ml beaker. Add 35 ml concentrated nitric acid. Heat on a hot plate until light brown fumes are evident, thus destroying all the organic matter. Cool to room temperature; add 5 ml of concentrated sulfuric acid and 5 ml of concentrated perchloric acid.

4.2 Replace the beaker on the hot plate and evaporate to dryness in a perchloric acid hood. Cool and dissolve the residue by pipetting 10 ml of 25% v/v hydrochloric acid into the beaker. The sample is now ready for analysis.

4.3 Prepare and analyze a blank filter in the same manner as the samples.

4.4 Set the spectrophotometer parameters to obtain maximum sensitivity at a wave length of 234.8 nm by use of beryllium standards, and manipulation of the acetylene and nitrous oxide gas flows. Use 25% v/v hydrochloric acid to set the instrument at 0% absorption.

4.4.1 Aspirate each sample into the flame and record the percent absorption. Convert the readings to absorbance units.

4.4.2 Samples that have percent absorption values greater that the range of the standard calibration curve of the instrument must be diluted with 25% v/v hydrochloric acid to be within the working range.

4.4.3 Determine the beryllium concentration of the sample from the beryllium standard curve.

4.4.4 Standards should be aspirated after every fourth or fifth sample to insure instrument response has not changed.

## 5. STANDARD <u>AND</u> CALIBRATION CURVE

5.1 Standard Stock Beryllium Solution. Dissolve 0.1000 g of beryllium powder in 80 ml of 12 N sulfuric acid and dilute to 1 liter with 25% v/v hydrochloric acid. This solution contains

100 μgm Be/ml.

5.2 Working Standard Beryllium Solution. Dilute 5.0 ml of the standard stock beryllium solution to 100.0 ml with 25% v/v hydrochloric acid to give a concentration of 5 μgm Be/ml. At least 3 individual standards normally in the range of 0 - 5 μgm Be/ml are freshly prepared by appropriate dilution of the working standard solution. The working standard solution should be freshly prepared prior to use.

5.3 Prepare a standard curve by plotting absorbance vs. concentration of beryllium on linear graph paper.

## 6. CALCULATION

6.1 A blank filter background beryllium value, if any, is subtracted from each sample.

$$^{*}\mu gm\ Be/m^3 = \frac{\mu gm\ Be\ from\ Std\ curve \times 10}{Air\ Sample\ Volume\ (m^3)}$$

*If sample was diluted to be within the standard curve range (4.4.2), the calculation must be multiplied by the appropriate dilution factor.

6.2 Total μgm Be = μgm Be from Standard curve x 10

## 7. REFERENCE

7.1 40 CFR 61 Appendix B, Method 104. "Reference Method for Determination of Beryllium Emissions from Stationary Sources".

## LAB 3

REF: Reg. 7-303

## DETERMINATION OF DIMETHYLSULFIDE IN EFFLUENTS

### 1. PRINCIPLE

1.1 The sample effluent is collected in a 10 liter or larger capacity Tedlar bag. The sample is analyzed for dimethylsulfide by purging a portion of the sample through a gas sampling valve. The sample is then injected into a gas chromatograph containing a poly-m-phenyl ether-phosphoric acid column and flame photometric detector.

### 2. APPARATUS

2.1 Gas Chromatograph. A unit with a flame photometric detector, must be capable of detecting 10 ppb of dimethylsulfide with a peak height of at least 3 times the noise background at the attenuation being used. The instrument must be equipped with a 10 ml gas sampling loop constructed of Teflon or another inert material, to insure no loss of dimethylsulfide during sample transfer.

2.1.1 The analytical column used is a 30' x 1/8" O.D. Teflon tube, packed with 12% poly-m-phenyl ether, 0.5% phosphoric acid on 25 to 40 mesh Fluoropak 80. The column material is prepared, packed and conditioned employing standard techniques. General column parameters are 40 ml/min nitrogen, 150 ml/min hydrogen, 70 ml/min air, 10 ml/min oxygen and maintained at a temperature of 65°C.

2.2 Pump, capable of 1 liter/minute

2.3 Teflon lines

## 3. REAGENTS

3.1 Dimethylsulfide (DMS)

3.2 Charcoal Trap Filter

## 4. ANALYTICAL PROCEDURE

4.1 Connect the Tedlar sample bag to the inlet of the gas sampling valve of the chromatograph. To the outlet side of the sampling valve, connect a small diaphragm pump containing a charcoal trap filter. Pass the sample through the sampling valve, at a rate of about 100 ml/minute for 3 to 4 minutes. Turn off the pump and immediately activate the sampling valve to transfer the sample to the analytical column. Measure the peak height of the dimethylsulfide peak and determine the concentration of the sample by comparison with the standard calibration curve.

## 5. PREPARATION OF STANDARD CALIBRATION CURVE

5.1 Standards are prepared in Tedlar bags by filling with a known volume of purified air. During the filling, introduce into the air stream by means of micro-syringe, a known volume of liquid dimethylsulfide. Calculate ppb by the following equation:

$$\text{PPB DMS} = \frac{\mu\text{l dimethylsulfide} \times 10^3 \times 848\ \mu\text{gm}/\mu\text{l}}{\text{vol. of purified air (liters)} \times 2.54}$$

Where: 2.54 = the μgm in 1 μℓ of dimethylsulfide at 25°C and 760 mm Hg

5.2 Use three different concentrations of standard gas mixtures in the range of 50 to 5000 ppb of dimethylsulfide not including the zero gas, to give responses of 10 to 95% full scale on the recorder. Plot the peak height against the corresponding concentration of DMS on a log-log graph paper to obtain the standard calibration curve.

## 6. CALCULATION

6.1 The concentration of the dimethylsulfide in the sample is determined by referring its peak height to the calibration curve.

## 7. REFERENCES

7.1 Kremer, L. and Spicer, L., "Gas Chromatographic Separation of Hydrogen Sulfide, Carbonyl Sulfide and Higher Sulfur Components with a Single Pass". Anal. Chem., 45, 1963, 1973.

7.2 Stevens, R.K. et al. "Gas Chromatography of Reactive Sulfur Gases in Air at the Part-per-Billion Level". Anal. Chem., 43, 827, 1971.

# LAB 4A

REF: Regs. 11-1-302
11-1-303

## DETERMINATION OF LEAD CONTENT IN ATMOSPHERIC PARTICULATE MATTER

## 1. PRINCIPLE

1.1 Samples are collected by passing a known volume of air through a glass fiber filter. The filter is extracted with hot nitric acid to solubilize the lead and analyzed by atomic absorption spectroscopy.

## 2. APPARATUS

2.1 Glassware - Borosilicate glassware should be used throughout the analysis. The glassware must be cleaned with 10% $HNO_3$ and rinsed with distilled water prior to use.

2.2 Atomic absorption spectrophotometer

2.2.1 Acetylene

2.2.2 Air Supply

2.2.3 Lead hollow cathode lamp

2.3 Hot plate

2.4 500 ml Phillips beakers

## 3. REAGENTS

3.1 Concentrated Nitric Acid (69 to 71%)

3.2 Dilute Nitric Acid. Dilute 10 ml of concentrated nitric acid to 1 liter with distilled water.

3.3 Lead Nitrate ($Pb(NO_3)_2$)

## 4. ANALYTICAL PROCEDURE

4.1 Cut out 1/4 section of the exposed area of the glass fiber filter. Cut into pieces of approximately one inch square and place in a 500 ml Phillips beaker.

4.1.1 Add 50 ml of concentrated nitric acid and cover the beaker with a ribbed watch glass. Place the beaker on a hot plate and heat gently to boiling. Reflux for one hour and cool. Add 50 ml of distilled water to the beaker and mix.

4.1.2 Filter the acid extract through a Whatman No. 1 filter paper, collecting the filtrate in a 400 ml beaker. Transfer the glass filter pads to the filter. Wash the glass fiber filter pads and the filter paper with hot distilled water until approximately 250 ml of filtrate is collected.

4.1.3 Evaporate the filtrate on a hot plate to approximately 5 ml. Cool to room temperature and qualitatively transfer the filtrate to a 50 ml volumetric flask using distilled water. Bring to volume with distilled water.

4.2 Analyze a blank glass fiber filter from each purchased batch of glass fiber filters in the same manner as the samples.

4.3 Set spectrophotometer parameters to obtain maximum sensitivity at a wave length of 283.3 nm by use of lead standards, and manipulation of the acetylene and air flows.

4.4 Aspirate each sample and blank into the flame and record the percent absorption for each. Convert the readings to absorbance units.

4.4.1 Samples that have percent absorption values higher than the range of the standard calibration curve of the instrument, must be diluted with dilute nitric acid to be within the working range.

4.4.2 Determine the lead concentration of the sample from the lead standard curve.

4.4.3 Standards should be aspirated after every fourth or fifth sample to insure instrument response has not changed.

## 5. STANDARD CURVE

5.1 Standard Stock Lead Solution. Weigh and transfer 1.5984 g of lead nitrate to a 1 liter volumetric flask. Dissolve and bring to volume with dilute nitric acid. This solution contains 1000 µgm Pb/ml.

5.2 Working Standard Lead Solution. At least three individual standards, normally in the range of 0 to 20 µgm Pb/ml, are freshly prepared by appropriate dilution of the standard stock lead solution with dilute nitric acid.

5.3 Prepare a standard curve on linear graph paper by plotting absorbance of the individual standards vs. concentration of lead.

## 6. CALCULATION

6.1 A blank filter background lead value, if any, is subtracted from each sample.

$$^{*}\mu gm\ Pb/m^3 = \frac{\mu gm\ Pb/ml\ \text{from Std curve} \times 4 \times 50}{\text{Volume of Air Sample } (m^3)}$$

*If sample was diluted to be within the standard curve range (4.4.1), the calculation must be multiplied by the appropriate dilution factor.

## 7. REFERENCE

7.1 Air and Industrial Hygiene Laboratory, State Dept. of Health, Method No. 54. "Analysis of Lead Content of Atmospheric Particulate Matter Collected on High Volume Glass Fiber Filters".

# LAB 4B

REF: Regs. 10-1-301
11-1-301

# DETERMINATION OF TOTAL LEAD IN EFFLUENTS

## 1. PRINCIPLE

Lead emissions are isokinetically sampled at the source using a glass wool filter, followed by acidic iodine monochloride impingers. The particulate lead content of the filter is removed by acid digestion and analyzed by atomic absorption spectroscopy. The gaseous lead compounds collected by iodine monochloride are determined by atomic absorption spectroscopy after the absorbing solution has been reduced to iodide.

## 2. APPARATUS

2.1 Glassware - Borosilicate glassware should be used throughout the analysis. The glassware must be cleaned with 10% $HNO_3$, and rinsed with distilled water prior to use.

2.2 Atomic absorption spectrophotometer

2.2.1 Acetylene

2.2.2 Air supply

2.2.3 Lead hollow cathode lamp

2.3 Hot plate

2.4 500 ml Phillips beakers

## 3. REAGENTS

3.1 Concentrated Nitric Acid (69 to 71%)

3.2 Dilute Nitric Acid. Dilute 10 ml of concentrated nitric acid to 1 liter with distilled water.

3.3 Lead Nitrate ($Pb(NO_3)_2$)

3.4 Iodine Monochloride Stock Solution (1 M). Dissolve 100 g of potassium iodide in sufficient distilled water to make 400 ml of solution. Add slowly, 400 ml of concentrated hydrochloric acid and cool to room temperature. Add slowly with vigorous stirring, 68 g of potassium iodate. Continue stirring until all the free iodine initially formed has redissolved to yield a clear orange-red solution. Dilute to 1 liter with distilled water and store the solution in a dark bottle.

3.5 Iodine Monochloride Scrubber Solution (0.1 M). Dilute 100 ml of stock iodine monochloride solution to 1 liter with distilled water. This solution should be kept in dark glass bottle to prevent degradation. This reagent should be stable for at least 2 months; however, periodic checks should be performed to insure quality.

3.6 Potassium Iodide Solution (25%). Dissolve 25 g potassium iodide in sufficient distilled water to make 100 ml of solution.

3.7 Sodium Sulfite Solution (10%). Dissolve 10 g of anhydrous sodium sulfite in sufficient distilled water to make 100 ml of solution.

## 4. ANALYTICAL PROCEDURE

### 4.1 Particulate Lead

4.1.1 Transfer the glass wool from the sampling probe to a 500 ml Phillips beaker.

4.1.2 Add 50 ml of concentrated nitric acid or an amount sufficient to cover the glass wool, and cover the beaker with a ribbed watch glass. Place the beaker on a hot plate and heat gently to boiling. Reflux for one hour and cool. Add 50 ml of distilled water to the beaker and mix.

4.1.3 Filter the acid extract through a Whatman No. 1 filter paper, collecting the filtrate in a 400 ml beaker. Wash the glass wool three times with 50 ml portions of hot distilled water. Filter each wash, adding each to the original filtered acid extract.

4.1.4 Evaporate the filtrate on a hot plate to approximately 5 ml. Cool to room temperature and quantitatively transfer the filtrate to a 50 ml volumetric flask using distilled water. Bring to volume with distilled water.

4.2 From each batch of purchased glass wool, analyze a representative portion in the same manner as the sample.

4.3 Set spectrophotometer parameters to obtain maximum sensitivity at wavelength of 283.3 nm by use of lead standards, and manipulation of the acetylene and air flows.

4.4 Aspirate each sample and blank into the flame and record the percent absorption for each. Convert the readings to absorbance units.

4.4.1 Samples that have percent absorption values higher than the range of the standard calibration curve of the instrument must be diluted with dilute nitric acid to be within the working range.

4.4.2 Determine the lead concentration of the sample from the lead standard curve.

4.4.3 Standards should be aspirated after every fourth or fifth sample to insure instrument response has not changed.

4.5 Gaseous Lead

4.5.1 Measure and record the total volume of the iodine monochloride solution remaining in the impingers.

4.5.2 Transfer an aliquot of 20.0 ml to a 25 ml graduated test tube. Add 2.0 ml of 25% potassium iodide to the sample. Mix well to insure that all the iodine is in solution.

4.5.3 Add dropwise, 10% sodium sulfite solution until the solution turns pale yellow. Mix well, and add distilled water to the 25 ml mark.

4.6 Prepare a reagent blank in the same manner as the samples to ascertain the presence of any lead impurities.

4.7 Proceed as in Sections 4.3 and 4.4.

## 5. STANDARD CURVE

5.1 Standard Stock Lead Solution. Weigh and transfer 1.5984 g of lead nitrate to a 1 liter volumetric flask. Dissolve and bring to volume with dilute nitric acid. This solution contains 1000 μgm Pb/ml.

5.2 Working Standard Lead Solution. At least three individual standards, normally in the range of 0 to 20 μgm Pb/ml, are freshly prepared by appropriate dilution of the standard stock lead solution with dilute nitric acid.

5.3 Prepare a standard curve by plotting on linear graph paper the absorbance of the individual standards vs. the concentration of lead.

## 6. CALCULATIONS

### 6.1 Particulate Lead

6.1.1 The blank glass wool value, if any, is subtracted from each sample.

$$^{*}\text{Total mg Pb} = \frac{\mu\text{gm Pb/ml from Std Curve} \times 50}{1000}$$

*If sample was diluted to be within the standard curve range (4.4.1), the calculation must be multiplied by the appropriate dilution factor.

### 6.2 Gaseous Lead

$$\text{*Total mg Pb per impinger} = \frac{\mu\text{gm Pb/ml} \times 25 \times \text{Vol of Impinger (m}\ell}{1000 \times 20}$$

*If sample was diluted to be within the standard curve range (4.4.1), the calculation must be multiplied by the appropriate dilution factor.

Total mg Pb = Total mg Pb in 1st Impinger + 2nd Impinger

## 7. REFERENCES

7.1 Air and Industrial Hygiene Laboratory, State Dept. of Health, Method No. 54. "Analysis of Lead Content of Atmospheric Particulate Matter Collected on High Volume Glass Fiber Filter".

7.2 Purdue, L., Enrione, E. and Thompson, R., "Determination of Organic and Total Lead in the Atmosphere by Atomic Absorption Spectrometry", Anal. Chem. 45, 527-530, 1973.

## LAB 5

REF: Reg. 7-303

## DETERMINATION OF TOTAL MERCAPTANS IN EFFLUENTS

### 1. PRINCIPLE

Mercaptans are absorbed in a mercuric acetate solution forming stable mercaptide salts. The absorbed mercaptides are reacted with N,N,-Dimethyl-P-Phenylenediamine to form a red complex, the amount of which is proportional to the total mercaptides and is measured spectrophotometrically. The total mercaptans are expressed as methyl mercaptan by reference to a calibration curve prepared from known amounts of lead methyl mercaptide.

### 2. APPARATUS

2.1 Spectrophotometer

2.2 25 ml test tubes

### 3. REAGENTS

3.1 Mercuric Acetate Solution, 5%. Dissolve 50 g of mercuric acetate, essentially free of mercurous salts, in approximately 400 ml of water and add 20 ml glacial acetic acid. Mix and dilute the solution to 1 liter with distilled water.

3.2 Amine Solution 0.5%. Dissolve 0.5 g of N,N,-Dimethyl-P-Phenylenediamine dihydrochloride in 100 ml of concentrated hydrochloric acid and transfer to a dark bottle. The solution is stable for at least six months.

3.3 Reissner Solution. Dissolve 6.7 g of ferric chloride hexahydrate in approximately 50 ml distilled water. Add 7.2 ml concentrated nitric acid. Mix and dilute to 100 ml with distilled water. This solution is stable for at least six months.

3.4 Lead Methyl Mercaptide, Eastman Organic Co., No. 8561.

## 4. ANALYTICAL PROCEDURE

4.1 Measure and record the total liquid volume in each of the collection impingers.

4.2 Transfer to a 25 ml graduated test tube 10.0 ml of sample or an aliquot of sample containing no more than 80 μgm of methyl mercaptan equivalent. A blank containing 10.0 ml of 5% mercuric acetate is run with the samples.

4.3 To each sample and blank add 1.5 ml of amine solution and 2 drops of Reissner solution. Mix well, and allow 30 minutes for color development. Remove any turbidity in the sample by centrifuging for 2 minutes at 1000 RPM.

4.4 Read the formed color in a spectrophotometer set at 500 nm using 13 mm cuvettes after setting the instrument at 100% T with the blank. Determine the μgm of methyl mercaptan from the standard curve.

## 5. STANDARD CURVE

5.1 Standard Stock Mercaptan Solution. Weigh and transfer 0.1566 g of crystalline lead methyl mercaptide to a 100 ml volumetric flask. Dissolve and bring to volume with 5% mercuric acetate. This solution contains 500 μgm equivalent of methyl mercaptan per ml, and is stable for at least one year.

5.2 Working Standard Mercaptan Solution. Dilute 2.0 ml of the stock standard solution to 100.0 ml with 5% mercuric acetate. This solution contains 10 μgm per ml methyl mercaptan equivalent.

5.3 To a series of 25 ml graduated tubes, add respectively 0, 1.0, 3.0, 5.0, and 8.0 ml of the working standard.

5.4 Bring each to 10.0 ml with 5% mercuric acetate.

5.5 Develop color as described under the analytical procedure. Prepare a standard curve by plotting μgm methyl mercaptan vs % transmittance using semi-log graph paper.

## 6. CALCULATION

$$\text{PPM Total Mercaptans} = \frac{\mu\text{gm Found in Aliq.} \times \text{Imp. Vol.}}{1.97 \times \text{Aliq. Vol.} \times \text{Sample Vol. (liters)}}$$

Where: 1.97 = the μgm in 1 μℓ of mercaptan at 25°C and 760 mm Hg

Total PPM = PPM in 1st Impinger + PPM in 2nd Impinger

## 7. REFERENCE

7.1 Moore, H., et al, "A Spectrophotometric Method for the Determination of Mercaptan in Air", Amer. Ind. Hyg. Assoc. J. 21, 466, 1960.

# LAB 6

REF: Regs. 11-5-301
11-5-302

## DETERMINATION OF PARTICULATE AND GASEOUS MERCURY EMISSIONS

## 1. PRINCIPLE

Particulate and gaseous mercury emissions are sampled from the source and collected in acidic iodine monochloride solution. The mercury collected in the mercuric form is reduced to elemental mercury in basic solution by hydroxylamine sulfate. Mercury is aerated from the solution and analyzed using spectrophotometry.

## 2. APPARATUS

2.1 Spectrophotometer. To measure absorbance at 253.7 nm, a flameless atomic absorption spectrophotometer is equipped with a gas cell and hollow cathode source. Other suitable mercury analyzers can be used.

2.2 Glassware. Borosilicate glassware should be used throughout the analysis. The glassware must be cleaned with 1:1 v/v nitric acid and rinsed with distilled water prior to use.

2.3 250 ml BOD (Biological Oxygen Demand) sample bottles

2.4 Cylinder Air. Zero grade compressed air is used as an aeration gas.

## 3. REAGENTS

3.1 Potassium Iodide Solution (25%). Dissolve 250 g of potassium iodide in distilled water and dilute to 1 liter.

3.2 Concentrated Hydrochloric Acid

3.3 Potassium Iodate

3.4 Iodine Monochloride Solution (1 M). To 800 ml of 25% potassium iodide, add 800 ml of concentrated hydrochloric acid.

Cool to room temperature. With vigorous stirring, slowly add 135 g of potassium iodate and continue stirring until all free iodine has dissolved to give a clear orange-red solution. Cool to room temperature and dilute to 2 liter with distilled water. Store the solution in amber glass bottles to prevent degradation.

3.5 Absorbing Solution (0.1 M Iodine Monochloride). Dilute 100 ml of 1 M iodine monochloride to 1 liter with distilled water. Store the solution in an amber glass bottle to prevent degradation. The solution is stable for at least 2 months.

3.6 Sodium Hydroxide (10 N). Dissolve 400 g of sodium hydroxide pellets in distilled water and dilute to 1 liter.

3.7 Reducing Agent (12% Hydroxylamine Sulfate, 12% Sodium Chloride). To 60 ml of distilled water, add and dissolve 12 g of hydroxylamine sulfate and 12 g of sodium chloride. Dilute to 100 ml. This quantity is sufficient for 20 analyses and must be prepared daily.

3.8 Hydrochloric Acid (0.3 N). Dilute 25.5 ml of concentrated hydrochloric acid to 1 liter with distilled water.

## 4. ANALYTICAL PROCEDURE

4.1 Transfer the contents of each impinger containing absorbing solution to a graduated cylinder and measure and record the volume to the nearest milliliter. Transfer the sample to a 500 ml Erlenmeyer flask. Rinse the sampling probe and line with two 50 ml portions of absorbing solution and add to the flask. Record the total volume of sample in the flask.

4.2 Adjust the instrument settings according to the instrument manual.

4.3 Transfer a sample of aliquot up to 50 ml to the BOD bottle. Adjust the total volume to 50 ml with 0.1 M absorbing solution, if required.

4.4 Add 5 ml of 10 N sodium hydroxide, cap the bottle with a glass stopper and shake vigorously. Prolonged, vigorous shaking at this point is necessary to obtain an accurate analysis.

4.5 Add 5 ml of the reducing agent and cap the BOD bottle with the bubbler assembly.

4.6 Shake the bottle vigorously and immediately aerate the sample at 1 to 1.3 l/min into the spectrophotometer cell using cylinder compressed air. Continue to aerate until a maximum % absorbance value is reached. Convert the reading to absorbance unit and record the value.

4.7 Determine the mercury concentration of the sample from the mercury standard curve.

4.8 If the aliquot sample is out of the linear range of the spectrophotometer, the sample must be diluted with absorbing solution.

4.9 Prepare a blank from absorbing solution and analyze to determine the reagent blank mercury level.

4.10 Standards should be run after every fourth or fifth sample to insure instrument response has not changed.

## 5. STANDARD CURVE

5.1 Standard Stock Mercury Solution. Weigh and transfer 0.1354 g of mercuric chloride to a 100 ml volumetric flask containing 80 ml of 0.3 N hydrochloric acid. After the mercuric chloride has dissolved, dilute to 100.0 ml with

0.3 N hydrochloric acid. This solution contains 1000 μgm Hg/ml.

5.2 Standard Mercury Working Solution. Dilute 1.0 ml of standard stock mercury solution to 100.0 ml with 0.3 N hydrochloric acid to give a concentration of 10 μgm Hg/ml.

5.3 Prepare at least three 50 ml calibration standards in the linear range of the instrument. Solutions of 0 to 0.6 μgm Hg/ml have been found to be acceptable for most instruments. The working standard solution should be freshly prepared prior to use.

5.4 Prepare a standard curve by plotting absorbance vs. concentration of mercury on linear graph paper.

## 6. CALCULATION

6.1 A blank reagent background mercury value, if any, is subtracted from each sample.

$$^*\text{Total mg Hg} = \frac{\mu\text{gm/ml from Std curve} \times \text{Total Samp. Volume}}{1000}$$

*If sample was diluted to be within the standard curve range (4.3), the calculation must be multiplied by the appropriate dilution factor.

## 7. REFERENCE

7.1 Method 101, "Reference Method for Determination of Particulate and Gaseous Mercury Emissions from Stationary Sources." 40 CFR 60, Appendix B, Revised July 1, 1976.

## LAB 7A

REF: Regs. 9-3-301 to 9-3-304
9-4-301, 9-4-302
10-1-301

# DETERMINATION OF OXIDES OF NITROGEN IN EFFLUENTS (ALKALINE PERMANGANATE PROCEDURE)

## 1. PRINCIPLE

The method is based on the absorption of nitric oxide and nitrogen dioxide in alkaline permanganate bubblers fitted with semi-fine glass frits. The formed nitrite and nitrate ions are determined by first converting the nitrite formed during the collection to nitrate. The total nitrate is then reduced to nitrite, which is determined by a chromatropic acid indicator.

## 2. APPARATUS

2.1 Hot plate

2.2 50 ml graduated Erlenmeyer flasks with screw caps

2.3 Spectrophotometer

2.4 25 ml graduated test tubes

2.5 Burel wrist action shaker

## 3. REAGENTS

3.1 Absorption Solution. Dissolve 40 g of potassium permanganate and 20 g of sodium hydroxide in distilled water and dilute to 1 liter.

3.2 Oxalic Acid Solution. Dissolve 80 g of oxalic acid in 1 liter of distilled water.

3.3 Sulfuric Acid. Add 22.4 ml of concentrated sulfuric acid to 500 ml of distilled water and dilute to 1 liter.

3.4 Reducing and Color Reagent. Nitra Ver III (Cat. #14065) and Nitra Ver VI (Cat. #14119). Hach Chemical Co. Ames, Iowa.

## 4. ANALYTICAL PROCEDURE

4.1 Measure and record the liquid volume of each impinger. Transfer an aliquot, not to exceed 5.0 ml, for analysis containing 0 to 100 µgm of nitrite. The aliquot may require dilution with unreacted absorbing solution or may be used directly. If preferred, all three impingers may be combined to form a composite sample, thereby requiring only a single analysis.

4.2 The aliquot taken is transferred to a 50 ml Erlenmeyer flask fitted with a screw cap. A reagent blank of 2.0 ml is also prepared from the absorbing solution which was used for the sampling. Acidify with 0.8 N sulfuric acid, using 1 ml of acid per ml of aliquot and let stand overnight.

4.3 Add 1 ml of oxalic acid solution per ml of aliquot and let stand until colorless. Heat the sample on a hot plate at 50 to 60°C. Should more oxalic acid solution be required to reduce the permanganate, add dropwise, so as not to have more than 3 drops in excess. Cool to room temperature and dilute to the 30 ml mark with distilled water.

4.4 Add to the sample and the blank, the content of a Nitra Ver VI pillow. Cap the flask and shake for exactly 3 minutes. Allow the sample to stand for 30 seconds and transfer 25 ml to a graduated test tube. Add the content of a Nitra Ver III pillow, cover the test tube with parafilm and mix for one minute. Let stand for 10 minutes and read the formed pink color at 500 nm with a 13 mm cuvette, setting the blank at 100% transmittance. Determine the µgm $NO_2$ in the sample from a standard curve.

## 5. STANDARD CURVE

5.1 Standard Stock Nitrite Solution. Weigh 0.2198 g of potassium nitrate and transfer to a 1 liter volumetric flask containing 100 ml of distilled water. Dissolve and dilute to mark with distilled water. This standard solution contains 100 μgm $NO_2$ equivalent per ml.

5.2 Working Standard Nitrite Solution. Dilute 1:5 to make a working standard containing 20 μgm $NO_2$ equivalent per ml.

5.3 Prepare a series of standards containing 20 to 100 μgm of $NO_2$, add 2 ml of the absorbing solution to each in 50 ml Erlenmeyer flasks. Proceed as in 4.2 to 4.4 to develop color forming reactions.

5.4 Prepare a standard curve plotting μgm $NO_2$ vs. % transmittance on semi-log graph paper.

## 6. CALCULATION

$$\text{PPM } NO_x \text{ as } NO_2 = \frac{(\mu\text{gm } NO_2 \text{ from Standard Curve})\ (\text{Total Vol.})}{(1.88)\ (\text{Aliquot})\ (\text{Sample Vol. in liters})}$$

Where: 1.88 = the μgm in 1 μℓ of nitrogen dioxide at 25°C and 760 mm Hg

## 7. REFERENCE

7.1 Levaggi, D.A. et al, "An Integrated Manual Impinger Method for the Simultaneous Determination of Nitrogen Oxides and Sulfur Oxides in Source Effluents. J. Air Poll. Cont. Assoc., 26, 783, 1976.

# LAB 7B

REF: Regs. 9-3-301 to 9-3-304
9-4-301, 9-4-302
10-1-301

## DETERMINATION OF OXIDES OF NITROGEN IN EFFLUENTS
## (GRAB SAMPLE PROCEDURE)

### 1. PRINCIPLE

A grab sample of the effluent is collected in an evacuated glass flask. Any nitric oxide and nitrogen dioxide present is oxidized to nitrate ion in the flask containing sulfuric acid and hydrogen peroxide. The yellow compound resulting from the reaction of the nitrate ion with phenoldisulfonic acid is measured colorimetrically at 420 nm.

### 2. APPARATUS

2.1 Spectrophotometer

2.2 Mercury manometer, open end

2.3 Hot plate

### 3. REAGENTS

3.1 Phenoldisulfonic Acid (PDSA). In a 500 ml Erlenmeyer flask, dissolve 25 g of pure white phenol in 150 ml of concentrated sulfuric acid on a steam bath. Add 75 ml of fuming sulfuric acid (15-18% free $SO_3$), stir well, cover the flask with a watch glass and heat for two hours at 100°C. Store in a dark, stoppered glass bottle. The PDSA is stable for about 2 years.

3.2 Concentrated Ammonium Hydroxide

3.3 Sodium Carbonate (20%). Dissolve 20 g of sodium carbonate to 100 ml of distilled water.

3.4 pH Paper, 7-14 range

3.5 Litmus paper

## 4. ANALYTICAL PROCEDURE

4.1 The previously calibrated 2 liter glass flask, in which the sample has been collected should remain in contact with the absorbent at least overnight to complete oxidation prior to the analysis.

4.2 Connect the glass flask to an open end mercury manometer, open the stopcock slowly, note and record the manometer reading in millimeters of mercury (samples are normally under a slight vacuum).

4.3 Transfer the absorbing solution (dilute sulfuric acid and hydrogen peroxide) to a 50 ml volumetric flask and bring to volume with distilled water.

4.4 Transfer an aliquot of the sample containing between 40 to 200 μgm of equivalent $NO_2$ to a 50 ml casserole or beaker. Neutralize with 20% sodium carbonate solution until just basic using litmus paper as an indicator.

4.5 Carefully evaporate to complete dryness on a hot plate, avoiding any spattering and loss of sample.

4.6 Add 2 ml of PDSA making sure to "wet" all the residue. Quickly triturate the residue thoroughly with a glass rod for a few minutes. Carefully add 5 ml of distilled water.

4.7 Carefully add 6 to 7 ml of concentrated ammonium hydroxide dropwise with constant swirling until the maximum color is formed. Use pH paper to verify a solution pH of 10 or greater. Transfer the solution to a 25 ml graduated test tube and wash the beaker with small quantities of distilled water. Add the washing to the test tube. Dilute with distilled water to 15 ml.

4.8 Measure the % transmittance of the yellow color complex at 420 nm. Use the reagent blank, which was treated like the samples, to set the spectrophotometer at 100% transmittance. Determine the μgm of nitrite equivalent from the standard curve.

4.9 A standard curve must be prepared with each set of analyses.

## 5. STANDARD CURVE

5.1 Standard Nitrite Stock Solution. Weigh and transfer 0.5495 g of potassium nitrate to a 1 liter volumetric flask containing 100 ml of distilled water. Dissolve and dilute to the mark with distilled water. This standard solution contains 250 μgm $NO_2$ equivalent per ml.

5.2 Working Standard Nitrite Solution. Dilute the standard stock solution 1:10 to obtain a working standard solution containing 25 μgm of $NO_2$ equivalent per ml.

5.3 Prepare standards in 50 ml beakers containing 0, 25, 50, 75 and 100 μgm of $NO_2$. Add 5 ml of the absorbing reagent and process as previously described for the samples in 4.4 to 4.8. Prepare a standard curve plotting μgm $NO_2$ vs. transmittance on a semi-log graph paper.

## 6. CALCULATIONS

$$\text{PPM } NO_x \text{ as } NO_2 = \frac{(\mu\text{gm } NO_2 \text{ from Standard Curve}) \times 50 \times 760 \text{ mm}}{1.88 \times \text{aliquot} \times \text{Sample flask vol} \times \text{flask pressure}}$$

$$\text{Flask pressure} = (760 \text{ mm Hg} - \text{manometer reading in mm Hg})$$

Where: 1.88 = the μgm in 1 μℓ of nitrogen dioxide at 25°C and 760 mm Hg

## 7. REFERENCES

7.1 Beatty, R., et al, "Determination of Oxides of Nitrogen by the Phenoldisulfonic Acid Method," U.S. Bureau of Mines Rept. Invest. 3687, 1943.

7.2 "Methods of Test for Oxides of Nitrogen in Gaseous Combustion Products (PDSA Method)", ASTM designation D 1608-68, Book of ASTM Standards, Part 23, 461-465, 1968.

7.3 Method 7, Reference Method for the "Determination of Nitrogen Oxide Emissions from Stationary Sources." 40 CFR 60, Appendix A, Revised July 1, 1976.

# LAB 8

REF: Reg. 7-303

## DETERMINATION OF PHENOLS IN EFFLUENTS

### 1. PRINCIPLE

1.1 The phenols are absorbed in 0.1 N sodium hydroxide solution to form phenolates. These compounds are hydrolyzed by acid, and the aqueous solution is analyzed for phenols by gas chromatography. Sample clean-up is performed, if necessary, by a carbon tetrachloride extraction.

### 2. APPARATUS

2.1 Gas Chromatograph. This unit is equipped with a flame ionization detector and fitted with a 7' x 1/8" stainless steel column which is packed with 10% Carbowax 20M/Terphthalic acid on acid-washed Chromosorb W(60 to 80 mesh). The gas chromatograph must be capable of detecting 3 ppm of phenol in solution with a peak height of at least 3 times the noise background at the attenuation used.

2.1.1 Injector port fitted with a glass sleeve

2.2 10 µl syringe

### 3. REAGENTS

3.1 Sodium Hydroxide (0.1 N). Dissolve 4 g of sodium hydroxide in 1 liter of distilled water.

3.2 Sulfuric Acid (1.0 N). To about 500 ml of distilled water, slowly add 28.0 ml of concentrated sulfuric acid and dilute to 1 liter with distilled water.

3.3 Copper Sulfate Solution (10%). Dissolve 10 g of copper sulfate in 100 ml of distilled water.

3.4 Carbon Tetrachloride

3.5 Litmus Paper - Blue

## 4. ANALYTICAL PROCEDURE

4.1 All samples are to be refrigerated. If samples are to be analyzed within three days, proceed with 4.2. If samples are to be stored for more than three days, add 1 ml of 10% copper sulfate solution to each impinger.

4.2 If the sample is contaminated with heavy oil, an extraction with carbon tetrachloride is required. If the sample is "clean", no extraction is necessary.

4.3 Measure and record the total liquid volume of each impinger. Transfer a 9.0 ml aliquot to a 25 ml test tube and add 1 ml of 1 N sulfuric acid. Cover the test tube with parafilm, invert and mix well. Check to insure the sample is acidic with litmus paper.

4.4 Inject a 2 μℓ sample into the gas chromatograph injection port. The operating parameters of the chromatograph are: column temperature 180°C; detector temperature 260°C; injection port temperature 250°C; carrier gas 25 ml/min; hydrogen 20 ml/min; and air 250 to 300 ml/min.

4.5 Compare the peak heights of phenols, m-cresol and 3, 4 dimethylphenol with those contained in the standard solution and injected in the same manner. Quantitation of the sample may also be made by integrated area technique.

## 5. PREPARATION OF STANDARD SOLUTION

5.1 Standard Phenol Stock Solution. Weigh 0.1 to 0.11 g (±0.0001 g) of each reagent grade phenol, m-cresol and 3, 4 dimethylphenol. Dissolve in 0.1 N NaOH solution and dilute to 1.0 liter with 0.1 N NaOH. This solution will contain approximately 100 μgm/ml of each phenol. If kept refrigerated this solution is stable for one month.

5.2 Standard Phenol Working Solution. Dilute the stock standard phenol solution 1:10 with o.1 N NaOH to prepare a standard phenol working solution of approximately 10 μgm/ml of each phenol. This working standard solution must be prepared freshly prior to use.

## 6. CALCULATIONS

1) $$\text{Total } \mu\text{gm of Phenol* in sample} = \frac{\text{Tot. Vol of Imp.} \times \text{Pk. ht of Sample}}{\text{Pk. ht of Standard}} \times \text{Conc. of Standard}$$

*Calculate individually for m-cresol and 3, 4 dimethylphenol, if present.

Total μgm of phenol in sample = μgm in 1st Imp. + μgm in 2nd Imp.

Total μgm of m-cresol in sample = μgm in 1st Imp. + μgm in 2nd Imp.

Total μgm of 3, 4 dimethylphenol in sample = μgm in 1st Imp. + μgm in 2nd Imp.

2) $$\text{PPM Phenol} = \frac{\text{Total } \mu\text{gm Phenol in Sample}}{(f^*) \times \text{Sample volume (liters)}}$$

($f^*$) = 3.84 for phenol; 4.42 for m-cresol; 4.99 for 3, 4 dimethylphenol

The values are the μgm in 1 μℓ of each individual phenol at 25°C and 760 mm Hg

3) Total PPM Phenols = PPM Phenol + PPM M-Cresol + PPM 3, 4 Dimethylphenol

## 7. REFERENCES

7.1 Phenols in Water by Gas Chromatography: ASTM Standard Test Method D 2580-68, 1975 Annual Book of ASTM Standards (Water) Part 31.

7.2 Levaggi, D.A., Feldstein, M., "Determination of Phenols and Trimethylamine in Industrial Effluent." AIAA Library No. 71-1115, 750 3rd Ave., New York, N.Y. 10017.

REF: Regs. 8-4-201, 8-4-302, 8-4-303
8-4-310, 8-4-311

## DETERMINATION OF COMPLIANCE OF SOLVENTS, COATINGS, AND RELATED PRODUCTS

### 1. PRINCIPLE

The tests performed in this procedure are designed so that the paraffinic olefinic, aromatic and oxygenated hydrocarbons found in solvents, coatings and related products may be individually identified and determined.

The analysis scheme is outlined in Figures III-1 and III-2 Solvents are treated as is; whereas coatings must be steam distilled to isolate the hydrocarbon fraction for further identification.

Fluorescent Indicator Analysis (FIA) is first performed on the solvent or water immiscible hydrocarbon fraction of the distillate to ascertain the volume percent of the different organic classes. Two FIA procedures are used, one for petroleum related products containing olefins, aromatics and saturates; and the other for solvents which contain oxygenated hydrocarbons in the presence of aromatics and saturates. Compliance may be determined on the basis of the appropriate FIA; if compliance is not defined sufficiently, gas chromatography is necessary for identifying specific compounds in the mixture.

The gas chromatographic procedures are somewhat complex utilizing various analytical columns and subtractive techniques. First, obtain a chromatogram of the solvent diluted with $CS_2$. For the selective removal of oxygenated hydrocarbons, 85% sulfuric acid is used. For the selective removal of olefins, aromatics and oxygenated hydrocarbons, sulfonation acid is utilized.

A second and possibly third chromatogram is then obtained by the selective subtractive techniques applied to the diluted mixture. By comparison of the chromatograms, it is possible to identify the class compounds required for determining compliance with the regulation.

## 2. APPARATUS

2.1 Fluorescent Indicator Analysis apparatus, as shown in Figure III-3

2.2 Pressurized gas manifold (nitrogen or air), equipped with an open end mercury manometer

2.3 Ultra-violet light source

2.4 1 and 5 ml graduated hypodermic syringes

2.5 Steam distillation apparatus, as shown in Figure III-4

2.6 Separatory funnel, 500 ml

2.7 Aluminum foil dish, 58 mm diameter x 10 mm high with flat bottom

2.8 Gas chromatograph. This unit is equipped with a compatible recorder and flame ionization detector

2.9 Vari-whirl mixer

## 3. REAGENTS

3.1 Silica Gel, 100 to 200 mesh, Grade 923. This is available from Davison Chemical, Baltimore, Maryland (Davison Code No. 923-08-08220). Before use, dry the gel at 350°F for 3 hours; transfer and store in a desiccator.

3.2 Fluorescent Indicator Dyed Gel. This is available from U.O.P. Process Division, U.O.P. Inc. Des Plaines, Ill. 60016 (U.O.P. Product No. 675).

3.3 Isopropyl Alcohol

3.4 Pressurized Gas, cylinder nitrogen or air

3.5 Analytical columns used in solvent analyses are:

3.5.1 14' x 1/8" 10% Carbowax 20M/Chromosorb W AW DCMS, 80 to 100 mesh

3.5.2 15' x 1/8" 10% 1,2,3 Tris (2-cyano-ethoxy) propane/ Chromosorb W, 60 to 80 mesh

3.5.3 15' x 1/8" 10% N N Bis 2 cyano-ethyl formamide/ Chromosorb W, 60 to 80 mesh

3.6 Rhodamine B Solution. Rhodamine B base (DuPont Inc.) is prepared by dissolving 400 mg of solid in 10 ml of 200 proof ethyl alcohol.

3.7 N-Butyl Amine

3.8 Carbon Disulfide

3.9 Standards for Fluorescent Indicator Analysis (FIA) and Modified Fluorescent Indicator Analysis

3.9.1 Equal volumes of isooctane, heptene and xylene, or appropriate substitutes. Prepare prior to use.

3.9.2 Equal volumes of isooctane, methyl ethyl ketone and xylene or appropriate substitutes. Prepare prior to use.

3.10 85% Sulfuric Acid. To 12 ml of distilled water, slowly add 88 ml of concentrated sulfuric acid.

3.11 Sulfonation Acid. Add the content of a 1 lb (454 g) bottle of $P_2O_5$ to 575 ±5 ml of fuming sulfuric acid in an Erlenmeyer flask. Stir with a glass rod or mechanical stirrer until only a small amount of residue remains, cover with a watch glass while the mixture cools to room temperature. Decant the acid mixture into ground glass stoppered bottles. Store the acid mixture in a desiccator. Prepare the reagent as rapidly as possible to minimize absorption of moisture from the air during preparation.

## 4. ANALYTICAL PROCEDURES

### 4.1 Determination of Volatile Content of Coatings

4.1.1 Weigh accurately 0.4 to 0.6 g (±0.0001 g) of coating in a pre-weighed aluminum dish. Dry the sample in the oven at 105 ±1°C for three hours. Cool the sample in the desiccator and weigh. Analyze the samples in duplicate. Results should agree to within ±5% of the mean.

### 4.2 Calculations

4.2.1 Wt. Coating = Wt. aluminum dish with paint - Wt. aluminum dish

4.2.2 Wt. Solid = Wt. aluminum dish with solid - Wt. aluminum dish

4.2.3 $\%\text{ Solid in paint} = \frac{\text{Wt. Solid}}{\text{Wt. Coating}} \times 100$

4.2.4 % W/W Volatiles in paint = 100% - % Solid in paint

### 4.3 Steam Distillation of Coatings

4.3.1 Transfer approximately 50 ml of thoroughly mixed coating to a tared 125 ml Erlenmeyer flask, reweigh and determine the weight of coating. Attach the flask to the steam generator and the collection apparatus shown in Figure III-4.

4.3.2 Heat and control the flask temperature with an electric heating mantle at approximately 70 to 80°C and commence delivery of steam to the flask. Collect a minimum of 200 ml of distillate.

4.3.3 Separate the hydrocarbon layer from the water layer by means of a separatory funnel. Record the volumes of both fractions and weight of the hydrocarbon fraction (±0.1 g). When oxygenates are not present, the weight of collected hydrocarbon layer must be within 10% of the expected weight determined by 4.2.4. The water layer is discarded. If oxygenated hydrocarbons are present, the weight of the immiscible hydrocarbon layer is added to the weight of miscible oxygenated hydrocarbons found in the water layer which is determined by gas chromatography, as described in 4.11. The combined weight of the immiscible hydrocarbon layer and the total miscible oxygenates in the water must be within 10% of the expected weight determined by 4.2.4.

4.3.4 For further processing, the immiscible hydrocarbon layer is dried by the addition of a few grams of anhydrous sodium sulfate.

4.4 Fluorescent Indicator Analysis (FIA) for Solvents and Hydrocarbon Fractions of Distillates Not Containing Oxygenated Hydrocarbons

4.4.1 Referring to Figure III-3, freely suspend the column. While vibrating the column along its entire length, add small increments of silica gel through a funnel until the column is 3/4 full. Stop the vibrator and add 3 to 5 mm layer of Fluorescent Indicator Dyed Gel. Start the vibrator and vibrate the column while adding additional silica gel. Continue to add the silica gel until it is tightly packed and extends 75 mm into the charger section.

4.4.2 Attach the filled column to the apparatus assembly. Chill the sample and the hypodermic syringe to 35 to 40°F. Draw 0.75 ml sample into the syringe and inject the sample 30 mm below the surface of the silica gel into the charger section.

4.4.3 Fill the charger section with isopropyl alcohol and connect the column to the gas manifold. Apply 40 to 80 mm Hg pressure for several minutes to move the liquid front down the column. Adjust the pressure to give a transit time of approximately one hour.

4.4.4 Before commencing to read the zone boundaries, carefully wipe the side of the column with a cloth dampened with ethyl alcohol and avoid handling the column with bare hands thereafter.

4.4.5 After the red aromatic boundary has advanced about 50 mm into the analyzer section, make a set of readings by quickly marking the boundary of each hydrocarbon type observed in ultraviolet light in the following sequence. For the non-fluorescent saturate zone, mark the front of the charge and the point where the yellow fluorescence first reaches its maximum intensity; for the upper end of the second or olefin zone, mark the point where the first intense blue fluorescence occurs; finally for the upper third or aromatic zone, mark the upper end of the reddish or brown zone. With colorless distillates, the alcohol-aromatic boundary is clearly defined by a red ring of the dye. When the sample has advanced about an additional 50 mm down the column, make a second set of readings and continue the reading until the zone lengths are constant. On completion, release the gas pressure and disconnect the column.

4.4.6 A standard solution prepared as in 3.9.1 should be run with each set of analyses performed.

4.5 Calculations

For each set of observations, calculate the % v/v of each hydrocarbon type to the nearest 0.1% as follows:

$L_t = L_s + L_o + L_a$

Where: $L_t$ = Total length of the hydrocarbon zone

$L_s$ = Total length of the saturate zone

$L_o$ = Total length of the olefin zone

$L_a$ = Total length of the aromatic zone

$$\% \text{ V/V Saturates} = \frac{L_s}{L_t} \times 100$$

$$\% \text{ V/V Olefins} = \frac{L_o}{L_t} \times 100$$

$$\% \text{ V/V Aromatics} = \frac{L_a}{L_t} \times 100$$

Determine compliance with Regulation 8, Rule 4, Section 201. If definite as to non-compliance, no further analysis is required; if indefinite continue with gas chromatography (4.8) for specific compound identification.

4.6 Modified FIA for Solvents and Hydrocarbon Fractions of Distillates Containing Oxygenated Hydrocarbons

4.6.1 Referring to Figure III-3, freely suspend the column. While vibrating the column along its entire length, add small increments of silica gel through a funnel until the column is 3/4 full. Stop the vibrator and add 3 to 5 mm layer of Fluorescent Indicator Dyed Gel and 3 drops of Rhodamine B solution. Vibrate the column while adding additional silica gel, continuing to add silica gel until it is tightly packed and the gel extends 75 mm into the charger section.

4.6.2 Attach the filled column to the apparatus assembly. Chill the sample and the hypodermic syringe to 35 to 40°F. Inject 0.75 ml of the sample 30 mm below the surface of the silica gel in the charger section.

4.6.3 Fill the charger with n-butyl amine and connect the column to the gas manifold; apply a pressure of 40 to 80 mm Hg. Higher pressure can result in poor boundary definitions. Adjust the pressure to give a transit time of approximately one hour.

4.6.4 Before commencing to read the zone boundaries, carefully wipe the side of the column with a cloth dampened with ethyl alcohol and avoid handling the column with bare hands thereafter.

4.6.5 After the fluorescent orange oxygenated hydrocarbon boundary of the sample has advanced about 50 mm into the analyzer section, make a set of readings by quickly marking the boundary of each hydrocarbon type observed in ultra-violet light in the following sequence. The leading saturate section is colorless; the aromatic section is blue throughout. The aromatic saturate section is taken as the point where the blue fluorescence first reaches its maximum intensity, usually split by a yellow-blue band. The upper aromatic boundary is marked by a red or brown zone which is readily observed in ordinary light and is included in the aromatic portion. The oxygenated compounds are colorless and extend from the brown section at the top of the aromatic section, to the top of the bright orange fluorescence marking the boundary of the oxygenated compounds. When the sample has advanced an additional 50 mm down the column, a second set of readings are made. Continue the readings until the relative zone lengths are constant. On completion, release the gas pressure and disconnect the column.

4.6.6 A standard solution prepared as in 3.9.2 should be run with each set of analyses performed.

### 4.7 Calculations

For each set of observations calculate to the nearest 0.1% of the hydrocarbon type as follows:

$$L_t = L_s + L_a + L_{ox}$$

Where: $L_t$ = Total length of the hydrocarbon zone
$L_s$ = Total length of the saturate zone
$L_a$ = Total length of the aromatic zone
$L_{ox}$ = Total length of the oxygenated zone

$$\text{\% V/V Saturates} = \frac{L_s}{L_t} \times 100$$

$$\text{\% V/V Aromatics} = \frac{L_a}{L_t} \times 100$$

$$\text{\% V/V Oxygenated Hydrocarbon} = \frac{L_{ox}}{L_t} \times 100$$

4.7.1 For solvents, determine compliance with Reg. 5, Rule 1, Section 203. If definite as to non-compliance, no further analysis is required; if indefinite, continue with gas chromatography (4.8) for specific compound identification.

4.7.2 For coating distillates, the modified FIA values calculated in 4.7 must be corrected for the volume of oxygenated hydrocarbons found in the water layer (4.11) as follows:

(1) $$\text{Corrected FIA Saturates} = \frac{V_{hl} \times (L_s/L_t \times 100) -}{V_{hl} + V_{sd}}$$

(2) Corrected FIA Aromatics $= \dfrac{V_{hl} \times (L_a/L_t \times 100)}{V_{hl} + V_{sd}}$

(3) Corrected FIA Oxygenates $= \dfrac{V_{hl} \times (L_{ox}/L_t \times 100) + V_{sd}}{V_{hl} + V_{sd}}$

Where: $V_{hl}$ = Volume of the hydrocarbon layer from the steam distillation

$V_{sd}$ = Volume of water soluble oxygenates as calculated in 4.12.2

Determination is now made for compliance. If definite as to non-compliance, no further analysis is required; if indefinite, continue with gas chromatography (4.8) for specific compound identification.

4.8 Gas Chromatographic Analysis of Solvents and the Hydrocarbon Layer of the Steam Distillation

4.8.1 The selection of the proper analytical column(s) to be used should be based on the FIA using the following criteria:

4.8.1.1 If aromatics and high boiling oxygenates are reported as being present in the sample the Carbowax 20M column is recommended. Columns described in 3.5.2 and 3.5.3 are not recommended where high boilers are present or suspected.

4.8.1.2 If solvent contains only paraffins (olefins are rarely if ever present in solvents) and aromatics all three columns in Section 5 are adequate. All specified columns have the capability of separating $C_9$ to $C_{11}$ paraffins and olefins from toluene.

4.8.2 Prepare a 2 to 5% V/V (±0.01%) solution of the solvent or hydrocarbon distillate in carbon disulfide. Calculate the dilution factor.

4.8.3 Inject 2.0 µℓ of the diluted sample in a gas chromatograph containing one of the specified columns in Section 3.5, using the general criteria outlined in 4.8.1. Due to the complex mixtures used in solvents there will be many cases of overlapping peaks and complete masking of some compounds. Retain the chromatogram.

4.8.4 If oxygenates are present transfer 2 to 3 ml of the diluted sample (4.8.2) to a 10 ml test tube. Add approximately 3 ml of 85% sulfuric acid, cap well and mix thoroughly by use of a Vari-whirl mixer for 30 to 40 seconds. Let the sample settle for a few minutes. All the oxygenated compounds will have been sulfonated and selectively absorbed in the acid layer leaving only the hydrocarbons and aromatics in the carbon disulfide.

4.8.4.1 Inject 2.0 µℓ of the sample now containing only paraffins and aromatics in the gas chromatograph. Retain the chromatogram.

4.8.5 To another 10 ml test tube, repeat steps in Section 4.8.4, substituting sulfonation acid in place of the 85% sulfuric acid. All the aromatics and oxygenated hydrocarbons will have been sulfonated and selectively absorbed in the acid layer.

4.8.5.1 Inject 2.0 µℓ of the sample now containing only paraffins in the gas chromatograph. Retain the chromatogram.

4.8.6 Prepared standards are run with each set of samples. These standards are diluted with carbon disulfide, as are samples, and normally are prepared to contain $C_6$ to $C_{12}$ aliphatics, $C_7$ to $C_{12}$ aromatics, and a variety of commonly encountered ketones, esters and alcohols. The standards are prepared on a v/v basis (μℓ/ml for ready calculation on a volume percent required by the regulation).

4.9 Calculations

Having the retention times and concentrations of specific compounds derived from the prepared standards the comparisons may now be made of the sample chromatograms obtained in 4.8.3, 4.8.4.1, 4.8.5.1 and 4.8.6.

4.9.1 Specific Oxygenates are identified and quantified by comparing the chromatograms derived in 4.8.3 and 4.8.4.1. The "disappearance" of peaks in 4.8.4.1 found in 4.8.3 identifies oxygenated compounds. The retention time is then matched to the oxygenated standards run in 4.8.6 and quantified by the peak height technique as follows:

Total % V/V of each individual oxygenate found =

$$\frac{(\text{Conc. of Std } \mu l/ml)(\text{Peak Height of Samp.})(\text{Dil. Factor}^{*})(100)}{(\text{Peak Height of Std})(1000)}$$

*As found in 4.8.2.

4.9.2 Specific Aromatics are identified and quantified by comparing the chromatograms derived in 4.8.4.1 and 4.8.5.1. Since the aromatics are found in the same retention time frame as many of the oxygenates, comparison of 4.8.4.1 (which has oxygenates selectively removed) and "disappearance" of peaks in 4.8.5.1 (which has both the oxygenates and aromatics remove) will identify the aromatic compounds. The compounds are then quantified and specifically identified by comparing to the standards run in 4.8.6 as follows:

Total % V/V of each individual aromatic found =

$$\frac{(\text{Conc. of Std } \mu\text{l/ml})(\text{Peak Height of Samp.})(\text{Dil. Factor}^{*})(100)}{(\text{Peak Height of Std})(1000)}$$

*As found in 4.8.2.

4.10 Compliance with the regulation is determined by calculation and summation of the volume percent of the applicable compounds found in 4.9.1 and 4.9.2 as described in the regulation.

In the case of coatings, which are steam distilled and contain water soluble oxygenates, these oxygenates (4.11) must be added to the total volume of the sample for calculating the volume percents.

4.11 Gas Chromatographic Analysis of the Oxygenated Hydrocarbons in the Water Layer of Steam Distillation of Coatings

It is necessary to identify and quantify the miscible oxygenated hydrocarbons in the water layer of steam distilled coatings, so that corrections may be made to the FIA (4.7) and gas chromatographic data (4.10) for compliance purposes.

4.11.1 The Carbowax 20M column described in Section 3.5 is the most appropriate when analyzing water mixtures.

4.11.2 Inject 2.0 $\mu\ell$ of the water layer of the distillate from 4.3 in a gas chromatograph, containing a Carbowax 20M analytical column. Retain the chromatogram.

4.11.3 A standard containing the normally encountered oxygenates, is prepared in distilled water ($\mu\ell$/ml). Inject 2.0 $\mu\ell$ of the standard and record the retention times and peak heights. Retain the chromatogram for future reference.

4.12 Calculation

Compare the chromatograms of 4.11.2 and 4.11.3 to identify the specific oxygenates in the water layer of the distillate. Quantitate the individual compounds by the peak height technique.

4.12.1 Total µl of an individual oxygenate found =

$$\frac{(\text{Conc. of Std } \mu l/ml)(\text{Peak Height of Samp.})(\text{Total Vol of Samp.*})}{\text{Peak Height of Std}}$$

*As found in 4.3.3.

4.12.2 Total µl of Oxygenates = Summation of individual oxygenates found

## 5. REFERENCES

5.1 Mac Phee, R., et al, "Recommended Test Methods for Organic Solvents and Vapors (Rule 66)", Technical Services Division Report, April 1968, Los Angeles County Air Pollution Control District.

5.2 Ellis, W.H. and Le Tourneau, R.F., "Analysis of Lacquer Thinner by Fluorescent Indicator Absorption Method" Anal. Chem. 25, 1269-1270, 1953.

5.3 "Hydrocarbon Types in Liquid Petroleum Products" Fluorescent Indicator Absorption (FIA) Method. ASTM Designation D 1319-58. Book of ASTM Standards of Petroleum Products and Lubricants, 761-767, 1959.

5.4 Esposito, G.G., "Application of Gas Chromatography to the Analysis of Organic Coatings", Facts and Methods for Scientific Research, F&M Scientific Corp., 4, 1, 1963.

5.5 Esposito, G.G., et al, "Quantitative Measurements of Photochemically Reactive Aromatic Hydrocarbons in Enamels and Thinners", Journal of Paint Tech., JPTYA, 40, 214, 1968.

ANALYTICAL SCHEME FOR SOLVENTS

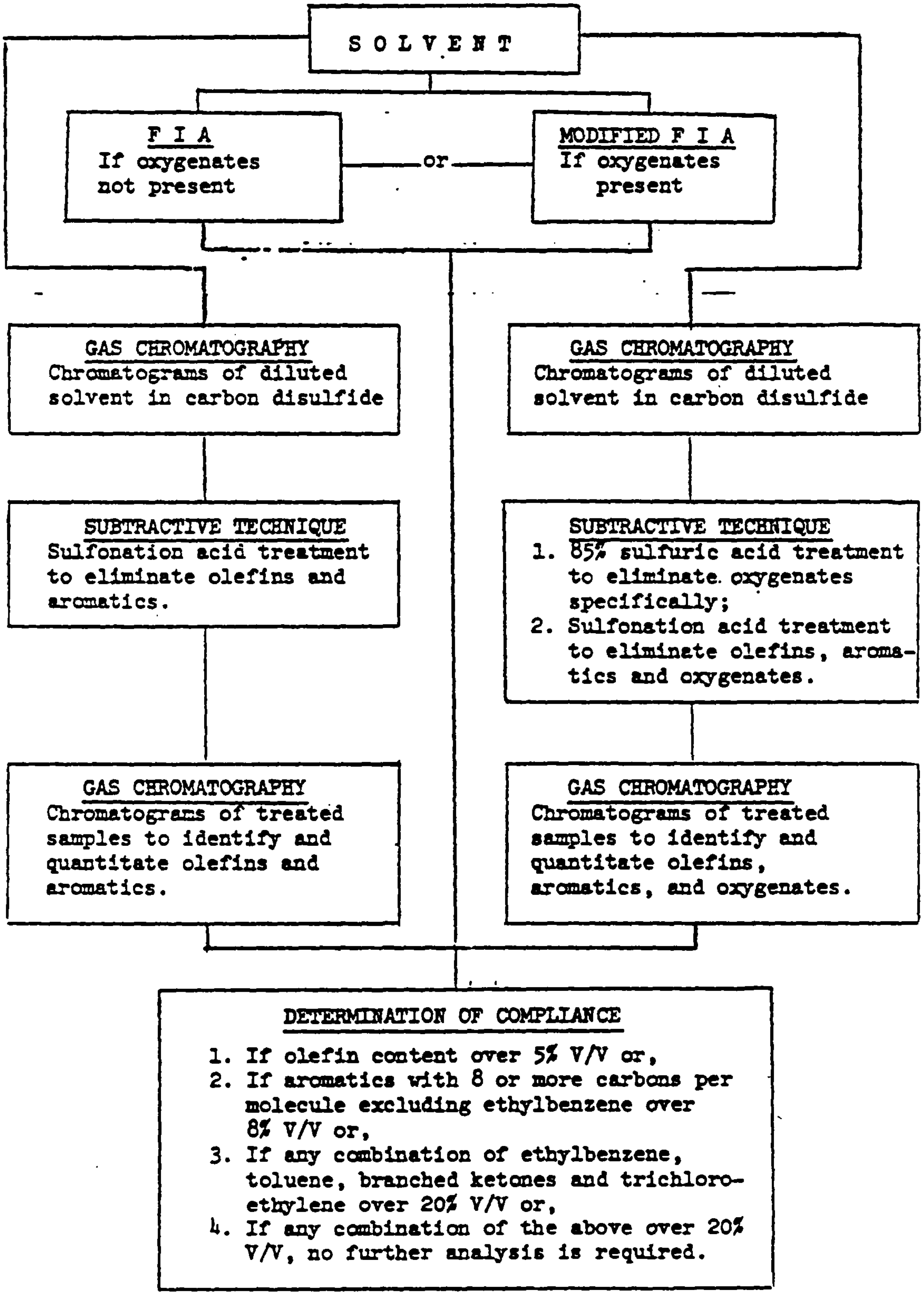


FIG. III-1

ANALYTICAL SCHEME FOR COATINGS

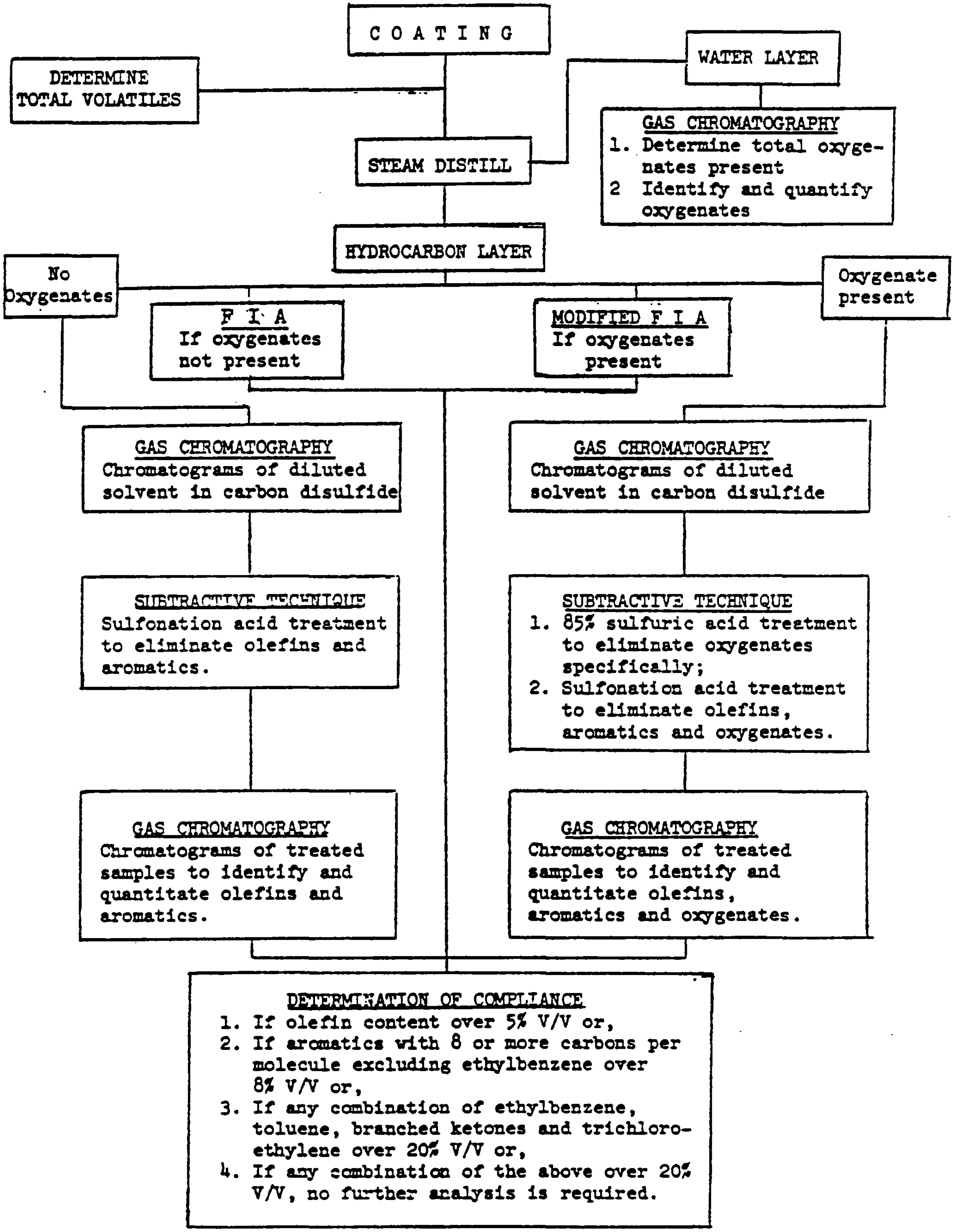


FIG. III-2

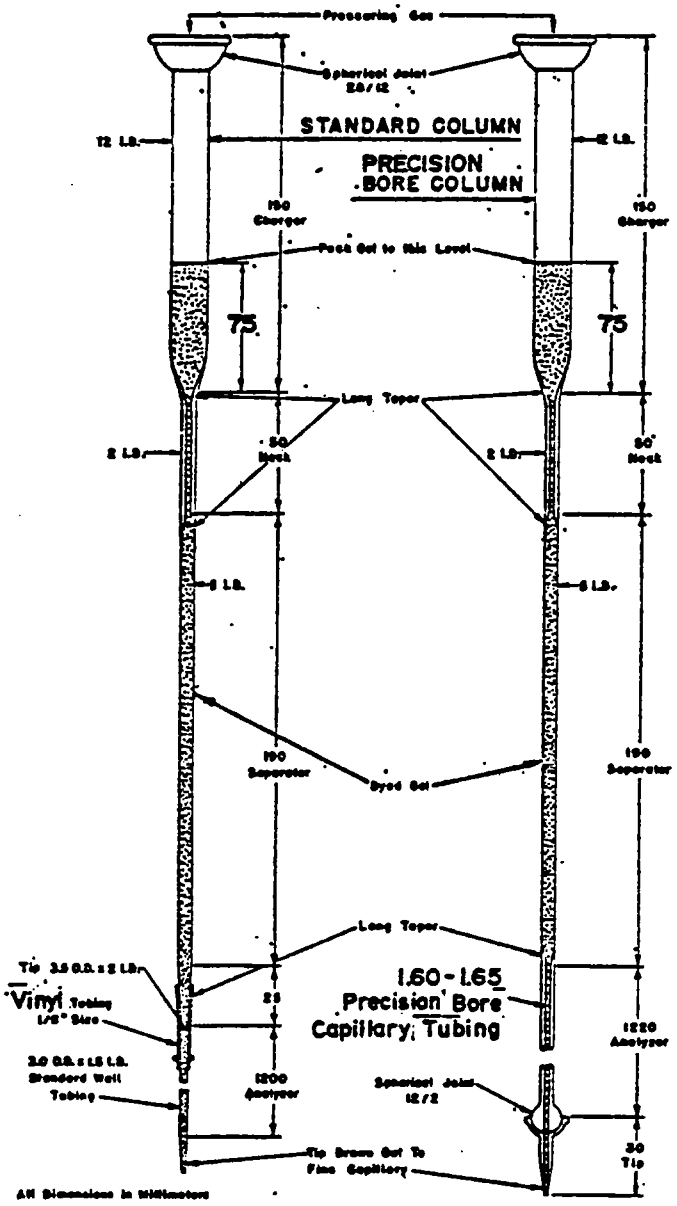


Fig. III-3

FIA APPARATUS

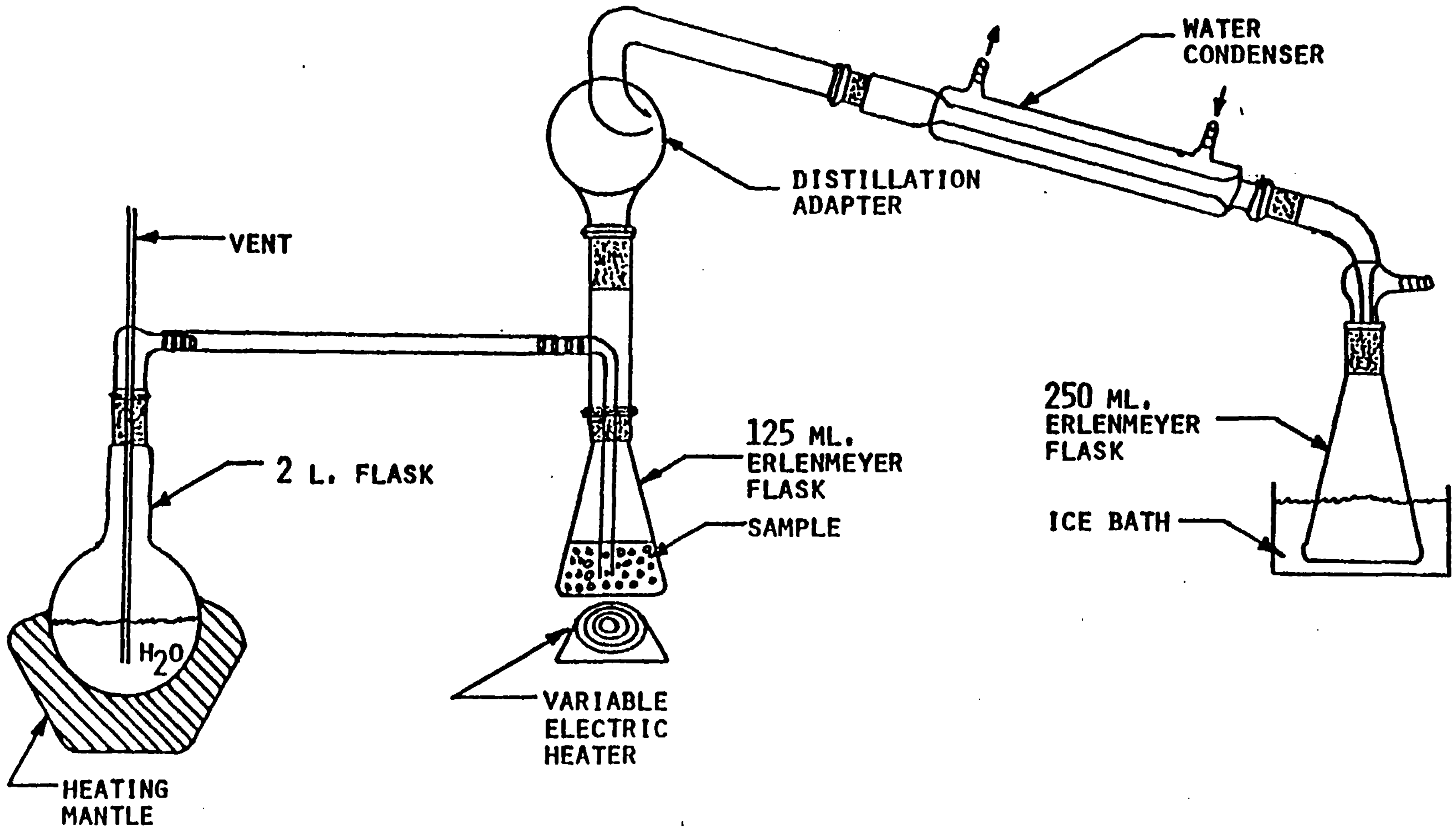


FIG. III-4

STEAM DISTILLATION APPARATUS

# LAB 10

REF: Regs. 9-1-304
10-2-501.2

## DETERMINATION OF SULFUR IN FUEL OIL

## 1. PRINCIPLE

The fuel oil sample is oxidized by combustion in a Schöniger Oxygen Combustion Flask. The sulfur dioxide formed during the combustion is absorbed in a dilute solution of sodium hydroxide containing hydrogen peroxide. The formed sulfate in the sodium hydroxide solution is filtered, if necessary and determined turbidimetrically as barium sulfate.

## 2. APPARATUS

2.1 Schöniger Oxygen Combustion Flask, 1 liter, available from A. Thomas Co., Philadelphia, Pa.

2.2 Filter paper carrier for 2.1, available from A. Thomas Co., Philadelphia, Pa.

2.3 Special Filter paper for 2.2, available from A. Thomas Co., Philadelphia, Pa.

2.4 Special screw clamp to attach 2.2 to 2.1, available rom A. Thomas Co., Philadelphia, Pa.

2.5 Safety Oxygen Flask Ignitor, Thomas-Ogg Model 11, available from A. Thomas Co., Philadelphia, Pa.

2.6 Spectrophotometer

2.7 Analytical balance

2.8 25 ml graduated test tubes

3. REAGENTS

3.1 Cylinder Oxygen, U.S.P. grade

3.2 Sodium Hydroxide (0.05 N). Dissolve 2 g of sodium hydroxide in distilled water and dilute to 1 liter.

3.3 30% Hydrogen Peroxide

3.4 HCl (6 N). Dilute concentrated hydrochloric acid 1:1 with distilled water.

3.5 Sulfa Ver IV Pillows, Cat. No. 12065-00 available from Hach Chemical Co., Ames, Iowa.

4. ANALYTICAL PROCEDURE

4.1 Place 20 ml of 0.05 N NaOH and 5 drops of 30% $H_2O_2$ in the Schöniger Oxygen Combustion Flask.

4.2 Weigh a sample of fuel oil directly onto a tared special filter paper, adding the oil dropwise from a capillary pipet. Record the weight of the oil. The weight of the sample required depends on the sulfur content of the fuel oil. As a general guide, for samples containing 5 to 10% sulfur a 10 to 15 mg sample is taken; for 2 to 5% sulfur 15 to 30 mg; for 0.5 to 2% sulfur 30 to 40 mg; for 0.1 to 0.5% sulfur 40 to 50 mg; for samples containing less than 0.1% 60 to 70 mg. The maximum weight of oil which may be taken is in the 60 to 70 mg range using one liter combustion flask. Larger weights will result in incomplete combustion, evidenced by soot formation during the burning of the sample.

4.3 Fold the filter paper containing the fuel oil sample and attach it to the filter paper carrier (2.2).

4.4 The Schöniger flask is then thoroughly flushed with oxygen.

4.5 Quickly insert the filter paper carrier in the combustion flask and attach the screw clamp and tighten. Place the flask in the safety ignitor and position so that the filter paper will be in line with the infra-red beam. Push ignitor button until the filter paper ignites.

Alternately, the ignition may be performed manually as follows (however, the automatic ignition is preferred) with a match ignite the tip of the filter paper. Quickly insert the filter paper carrier into the combustion flask, holding it securely against the flask as considerable pressure builds up during the combustion. Invert the flask while combustion takes place. After combustion has ceased shake the flask vigorously. After a few moments,the flask pressure will reduce to a partial vacuum; then set the flask aside.

4.6 After combustion is complete, allow the sample to stand 10 to 15 minutes to permit complete absorption of sulfur dioxide and then shake vigorously. If combustion is incomplete (large amount of soot formed) sample must be re-run.

4.7 Filter,if necessary,and pipette a 10 ml aliquot of the filtrate into a 25 ml graduated test tube.

4.8 Make up volume to 19 ml with distilled water. Add 1 ml of 6 N HCl and the contents of a Sulfa Ver IV pillow.

4.9 Cover the test tube with parafilm and invert several times to mix thoroughly and dissolve the reagent.

4.10 Read after 10 minutes at 500 nm using 25 mm cuvettes. Determine the μgm sulfate in the aliquot from the standard curve prepared in Section 5.

4.11 Run a blank and standards with each sample.

## 5. STANDARD CURVE

5.1 Standard Stock Sulfate Solution. Weigh and transfer 0.1480 g of dry sodium sulfate to a 1 liter flask. Dissolve and dilute to mark with distilled water. This solution contains 100 micrograms of sulfate per ml.

5.2 Prepare a standard curve from the 100 µgm/ml standard sulfate solution by pipetting respectively 0, 2, 4, 6, 8, and 10 ml into a series of 25 ml graduated test tubes.

5.3 Make up to 19 ml with distilled water. Add 1 ml 6 N hydrochloric acid and the contents of a Sulfa Ver IV pillow.

5.4 Cover the test tube with parafilm and invert several times to mix.

5.5 Read after 10 minutes at 500 nm using 25 mm cuvettes. Plot % transmittance vs. concentration on semi-log graph paper. The standard curve is non-linear in the 0 to 400 micrograms range.

## 6. CALCULATIONS

$$\text{Total mg sulfur} = \frac{(\mu\text{gm from Standard curve})\ (20\ \text{ml})\ (32)}{(1000)(\text{ml aliquot})\ (96)}$$

Where: 32 = the mol. wt. of sulfur
96 = the mol. wt. of sulfate

$$\%\ \text{Sulfur} = \frac{\text{Total mg Sulfur}}{\text{Wt. of Sample (mg)}} \times 100$$

## 7. REFERENCE

7.1 Levaggi, D.A., Feldstein, M., "A Rapid Method for the Determination of Sulfur in Fuel Oil by the Schöniger Flask Method," J. Air Poll. Cont. Assoc. <u>13</u>, 380, 1963.

## LAB 11

REF: Regs. 9-1-302, 9-1-304.3,
9-1-305 to 9-1-310,
10-1-301

## DETERMINATION OF SULFUR DIOXIDE IN EFFLUENTS

### 1. PRINCIPLE

The sulfur dioxide is absorbed and reacted with a 3% hydrogen peroxide solution forming sulfuric acid. The resultant sulfuric acid is determined by either titration with standard sodium hydroxide or by a barium sulfate turbidimetric procedure. The titration method should not be used if other acidic or basic gases are known to be present in the effluent gas, but may be used when sampling sulfur recovery plants and sulfuric acid plants.

### 2. APPARATUS

2.1 Buret, 0 to 50 ml

2.2 Spectrophotometer with 25 mm cuvettes

2.3 Graduated 25 ml test tubes

### 3. REAGENTS

3.1 Standard Sodium Hydroxide Solution (0.1 N). Dissolve 4.0 g of sodium hydroxide pellets in 150 ml of distilled water and dilute to 1 liter. Determine normality of the solution within ±0.0003 N by standardization against potassium acid phthalate using phenolphthalein indicator (6.1).

3.2 Bromcresol Green Indicator. Mix 0.1 g of bromcresol green in a mortar with 14.3 ml of 0.01 N sodium hydroxide. Dilute to 250 ml with distilled water.

3.3 Precipitating Reagent. Sulfa Ver IV Pillows, Cat. No. 12065-00 obtainable from the Hach Chemical Company, Ames, Iowa.

3.4 Hydrochloric Acid (6 N). Dilute concentrated hydrochloric acid 1:1 with distilled water.

3.5 Phenolphthalein Indicator (0.05%). Dissolve 50 mg phenolphthalein in 50 ml of ethanol and add 50 ml of distilled water.

3.6 Standard Sulfate Solution. Weigh 0.1480 g of anhydrous sodium sulfate and transfer to a 1 liter volumetric flask. Dissolve and bring to volume with distilled water. This solution contains 100 micrograms of sulfate per ml of solution.

## 4. ANALYTICAL PROCEDURE

4.1 Measure and record the total liquid volume of the impingers. Quantitatively transfer a 50.0 ml aliquot to a 250 ml Erlenmeyer flask.

4.2 Bring each flask to a boil, cool to room temperature and add 4 ml of the bromcresol green indicator solution. Titrate to the blue color end point using the standard sodium hydroxide solution.

4.3 Calculations

$$\text{mg } SO_2 = \frac{(\text{Total Imp. Vol}) \times N \times V(NaOH) \times 32}{\text{Aliquot Vol}}$$

Where: 32 = the equivalent weight of sulfur dioxide

$$\text{Total mg } SO_2 = \text{mg } SO_2 \text{ 1st Imp.} + \text{mg } SO_2 \text{ 2nd Imp.}$$

## 5. ALTERNATE ANALYTICAL PROCEDURE (TURBIDIMETRIC METHOD)

5.1 Measure and record the total liquid volume in each impinger.

5.2 Transfer an aliquot of sample containing 200 to 1000 μgm of sulfate to a graduated 25 ml test tube and dilute to the 20 ml mark with distilled water.

5.3 To another series of test tubes add 0, 200, 500 and 1000 micrograms of the sulfate standard (3.6) and dilute to 20 ml with distilled water.

5.2 To the sample and standards add 1.0 ml of 6 N hydrochloric acid and the content of a Sulfa Ver IV pillow. Bring volume to 25.0 ml with distilled water. Stopper and shake sufficiently to dissolve all the Sulfa Ver pillow reagents. Let stand for ten minutes and take readings at 500 nm using the 0 standard to set 100% transmission. Use 25 mm cuvettes. Plot % transmittance vs. concentration, using semi-log graph paper. The standard curve is non-linear in the 0 to 400 μgm range. Use this plot to determine the sulfate concentration in the sample runs.

5.3 Calculation

$$\text{mg } SO_2 = \frac{(\text{Total Imp. Vol})(\text{Micrograms } SO_4^{=} \text{ from Std curve})}{\text{Aliquot Vol} \times 1000} \times \frac{64}{96}$$

Where: 64 = the mol. wt. of sulfur dioxide
96 = the mol. wt. of sulfate

Total mg $SO_2$ = mg $SO_2$ 1st Imp. + mg $SO_2$ 2nd Imp.

## 6. PREPARATION OF STANDARD SODIUM HYDROXIDE SOLUTION

6.1 Standardize the prepared sodium hydroxide solution (3.1) with potassium acid phthalate ($KHC_8H_4O_4$) using phenolphthalein indicator. Run in triplicate.

$$\text{N NaOH} = \frac{\text{Wt of Potassium Acid Phthalate}}{(0.2042) \times (\text{ml NaOH})}$$

Where: 0.2042 = the gms/meqv. of potassium acid phthalate

## 7. REFERENCES

7.1 Jacobs, M.B., "Chemical Analysis of Pollutants," Interscience Publishers Inc, New York, 1960.

7.2 Levaggi, D.A., et al, "An Integrated Manual Impinger Method for the Simultaneous Determination of Nitrogen Oxides and Sulfur Oxides in Source Effluents," J. Air Poll. Cont. Assoc. 26, 783, 1976.

# LAB 12

REF: Regs. 6-320, 6-330,
9-1-302, 9-1-304.3,
9-1-305 to 9-1-310,
10-1-301, 10-6-301,
12-6-301

## DETERMINATION OF SULFUR DIOXIDE, SULFUR TRIOXIDE, AND SULFURIC ACID MIST IN EFFLUENTS

### 1. PRINCIPLE

In a single extractive sampling system, sulfuric acid mist is trapped on a quartz wool probe extracted with distilled water and titrated with a standard sodium hydroxide solution. Sulfur trioxide is absorbed in an impinger containing 80% isopropyl alcohol followed by a backup filter. The formed sulfuric acid is titrated with a standard barium chloride solution using thorin indicator. The sulfur dioxide is absorbed in 3% hydrogen peroxide and the formed sulfuric acid is determined by titration with standard sodium hydroxide solution (applicable to sulfur recovery units and sulfuric acid plants). An alternate turbidimetric barium sulfate procedure can be used when other acids or bases are known or suspected to be present in the effluent gas.

### 2. APPARATUS

2.1 pH meter

2.2 Burets, 0 to 5 ml and 0 to 50 ml

2.3 Spectrophotometer with 25 mm cuvettes

2.4 Graduated 25 ml test tubes

### 3. REAGENTS

3.1 Standard Sodium Hydroxide Solution (0.1 N). Dissolve 4.0 g of sodium hydroxide pellets in distilled water and dilute to 1 liter. Standardize to ±0.0003 N, using an acceptable method.

3.2 Bromcresol Green Indicator. Mix 0.1 g of bromcresol green in a mortar with 14.3 ml of 0.01 N sodium hydroxide. Dilute to 250 ml with distilled water.

3.3 Precipitating Reagent. Sulfa Ver IV Pillows, Cat. No. 12065-00, available from Hach Chemical Company, Ames, Iowa.

3.4 Hydrochloric Acid (6 N). Dilute concentrated hydrochloric acid 1:1 with distilled water.

3.5 80% Isopropyl Alcohol (Peroxide free). Add 200 ml of distilled water to 800 ml of isopropyl alcohol.

3.5.1 Test for peroxide in 80% isopropyl alcohol. Place 50 ml of 80% isopropyl alcohol in a 250 ml Erlenmeyer flask. Add 1 ml of concentrated sulfuric acid, 1 ml of 10% potassium iodide solution and swirl. Any yellow color indicates the present of peroxide.

3.6 Standard Barium Chloride Solution (0.100 N). Dissolve 6.1000 g of barium chloride dihydrate in a 500 ml volumetric flask containing 250 ml of distilled water. Add approximately 200 ml of 100% isopropyl alcohol and bring to volume with distilled water. Store in a tightly capped bottle. One ml of this solution is equivalent to 4.0 mg of sulfur trioxide.

3.7 Thorin Indicator ((0-[2-hydroxy-3, 6 disulfo-1 naphthyl) -azo] benzenearsonic acid disodium salt). Dissolve 0.2 g in 100 ml of distilled water.

3.8 Standard Sulfate Solution. Weigh 0.1480 g of anhydrous sodium sulfate and transfer to a liter volumetric flask. Dissolve and bring to volume with distilled water. This solution contains 100 micrograms of sulfate per ml of solution.

## 4. ANALYTICAL PROCEDURES

### 4.1 Determination of Sulfuric Acid Mist.

4.1.1 Remove the quartz wool from the glass probe and transfer to a 500 ml beaker. Add 200 ml of distilled water, mix well and soak with occasional swirling for at least 2 hours.

4.1.2 Take a 50 ml aliquot, add 4 ml of bromcresol green indicator and titrate to a blue color endpoint using the standard sodium hydroxide solution.

4.1.3 Calculation:

Total mg $H_2SO_4$ = (ml of NaOH) x (N of NaOH) x 49 x 4 ml

Where: 49 = the equivalent wt. of sulfuric acid

### 4.2 Determination of Sulfur Trioxide

4.2.1 The analysis should be performed within four hours after sample collection. If a delay is anticipated, sample should be refrigerated until the analysis can be performed.

4.2.2 The first 80% isopropyl alcohol impinger content is transferred to a 250 beaker. The backup filter is added, mixed, and allowed to soak in the beaker for approximately one hour. The contents are then decanted into a 250 ml volumetric flask. The remaining filter is washed consecutively with 80% isopropyl alcohol and the washings added to the volumetric flask. Make up to the mark with 80% isopropyl alcohol. Take a 25.0 ml aliquot and transfer it to a 125 ml Erlenmeyer flask. Adjust the pH to 3.0 with 1:4 perchloric acid. Add 2 drops of Thorin indicator and titrate using standard barium chloride (using a 0 to 5 ml microburet) to a salmon pink endpoint.

The second 80% isopropyl alcohol impinger is treated the same as in 4.2.2.

4.2.3 Calculation

$$\text{Total mg } SO_3 = \frac{\text{Net Titer (1st Imp. + Filter - 2nd Imp) x 4.0 x 250 ml}}{\text{25 ml aliquot}}$$

Where 4.0 = the mg sulfur trioxide per ml of titrant

4.2.3.1 The second impinger is regarded as a blank since some $SO_2$ may be oxidized to $SO_3$ when sampling sources which have high concentrations of $SO_2$.

4.3 Determination of Sulfur Dioxide

4.3.1 In the absence of other acids or bases in the sample, measure accurately the total liquid volume in each hydrogen peroxide impinger. Transfer a 50.0 ml aliquot from each impinger into a separate 250 ml Erlenmeyer flask and bring to a boil. Cool to room temperature, add 4 ml of bromcresol green indicator and titrate with standard sodium hydroxide solution to blue color endpoint.

4.3.2 Calculations

$$\text{mg } SO_2 = \frac{\text{(Total Imp. Vol) x (N of NaOH) x (ml (NaOH) (32)}}{\text{Aliquot Vol}}$$

Where 32 = the equivalent wt. of sulfur dioxide

Totao mg $SO_2$ = mg $SO_2$ 1st Imp. + mg $SO_2$ 2nd Imp.

4.3.3 Alternative Analytical Procedure (Turbidimetric Method)

4.3.3.1 Measure accurately the total liquid volume in each impinger and transfer an aliquot of the sample containing 200 to 1000 micrograms of sulfate to a graduated 25 ml test tube.

4.3.3.2 To another series of tubes add 0, 200, 500 and 1000 μgm of the sulfate standard (3.8).

4.3.3.3 To the samples and standards add 1 ml of 6 N hydrochloric acid and dilute to 25.0 ml with distilled water.

4.3.3.4 Add the contents of one Sulfa Ver pillow, stopper and shake to dissolve the pillow reagents.

4.3.3.5 Let stand for ten minutes and take readings at 500 nm with 25 mm cuvettes using the 0 μgm standard to set the spectrophotometer at 100% T. The standard curve is non-linear in the - to 400 μgm range.

4.3.3.6 Calculations

$$\text{mg } SO_2 = \frac{(\text{Total Imp. Vol})(\text{Micrograms } SO_4^{=} \text{ from Std Curve})}{\text{Aliquot Vol} \times 1000} \times \frac{64}{96}$$

Where 64 = the mol. wt. of sulfur dioxide
96 = the mol. wt. of sulfate

Total mg $SO_2$ = mg $SO_2$ 1st Imp. + mg $SO_2$ 2nd Imp.

## 5. REFERENCES

5.1 Shell Development Co., Analytical Dept., "Determination of Sulfur Dioxide and Sulfur Trioxide in Stack Gases. Emeryville Method Series 4516/59a.

5.2 Flint, D., "A Method for the Determination of Samll Concentrations of Sulfur Trioxide in the Presence of Higher Concentrations of Sulfur Dioxide", J. Soc. Chem. Inc. (British) 67, 2, 1948.

# LAB 13

REF: Regs. 8-1-206, 8-5-101,
8-6-206, 8-18-111,
10-9-301, 10-9-302

## DETERMINATION OF THE REID VAPOR PRESSURE OF PETROLEUM PRODUCTS

### 1. PRINCIPLE

This method provides for air partial saturation of petroleum products with a Reid vapor pressure below 26 lb using a Reid Vapor Pressure Bomb. The gasoline chamber portion of the vapor pressure apparatus is filled with a chilled sample and connected to the air chamber. The apparatus is immersed in a constant temperature bath (100 ±0.2°F) and shaken periodically, until equilibrium is reached.

### 2. APPARATUS

2.1 Refrigerator or Freezer

2.2 Reid Vapor Pressure Bomb. This unit is equipped with a 4 in., 0 to 15 psig gauge (Fig. III-6).

2.3 Constant temperature water bath (100 ±0.2°F)

### 3. ANALYTICAL PROCEDURE

3.1 Handling of Sample

3.1.1 The size of the sample container used in taking the sample shall not be less than 1 quart nor more than 1 gallon. The container shall be a solvent can, with a 1 3/4 in. lid opening, and filled to approximately 90% capacity.

3.1.2 In all cases after a sample has been taken, the container shall not be opened unless it has been cooled to <32°F.

3.1.3 Samples shall be put in ice as soon as taken, and transferred to the laboratory for immediate storage in the refrigerator, and stored there until the tests have been completed.

Samples in leaky containers shall not be considered for tests but shall be discarded and new samples taken.

3.2 Preparation for Test

3.2.1 Air Saturation of Sample in Sample Container - Remove the sample container from the refrigerator, unseal it examine it for its liquid content, which shall be approximately 90 percent of the container capacity. After the liquid content has been assured, reseal the container, shake vigorously and and return it to the refrigerator.

3.2.2 Preparation of the Gasoline Chamber - Place the open gasoline chamber and the sample transfer connection into the refrigerator for sufficient time to allow the chamber and connection to reach temperature (32°F to 40°F).

3.2.3 Preparation of Air Chamber (100°F Procedure) - After rinsing and purging the air chamber, connect the gauge to the air chamber. Immerse the air chamber to at least 1 in. above its top in the water bath maintained at 100 ±0.2°F for not less than 10 minutes just before coupling it to the gasoline chamber. Do not remove the air chamber from the bath until the gasoline chamber has been filled as described in Section 3.3.

3.3 Sample Transfer - With all in readiness, remove the chilled sample from the refrigerator, uncap it and insert the chilled transfer connection and air tube (Fig. III-5).
Then place the empty chilled gasoline chamber over the sample delivery tube of the transfer connection. Invert the entire system rapidly so that the gasoline chamber is finally in an upright position with the delivery tube extending to within 1/4 in.

of the bottom of the gasoline chamber. Fill the gasoline chamber to overflowing. Lightly tap the gasoline chamber against the work bench to insure that the sample is free of air bubbles. If any sample is displaced, refill the chamber to overflowing.

3.3.1 Assembly of Apparatus - Without delay and as quickly as possible, attach the air chamber to the gasoline chamber.

3.3.2 Introduction of Apparatus to Bath - Turn the assembled vapor pressure apparatus upside down to allow the sample in the gasoline chamber to run into the air chamber and shake vigorously in a direction parallel to the length of the apparatus. Immerse the assembled apparatus into the bath, maintained at 100 ±0.2°F, in an inclined position so that the connection of the gasoline and air chamber is below the water level and may be observed closely for leaks. If no leaks are observed, immerse the apparatus to at least 1 in. above the top of the air chamber. Observe the apparatus for leaks throughout the test. If a leak is detected, discard the test.

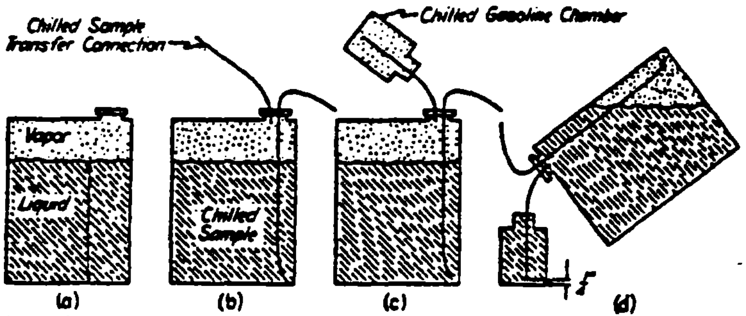
3.3.3 Measurement of Vapor Pressure - After the assembled vapor pressure apparatus has been immersed in the bath for 5 minutes, tap the pressure gauge lightly and record the reading. Withdraw the apparatus from the bath, invert it, shake it vigorously and immediately place back in the bath. At intervals of about 10 minutes, repeat this agitation and gauge observation at least five times, until the last two gauge readings are constant. These operations normally require 60 to 90 minutes. Read the final gauge pressure to the nearest 0.05 psig for gauges with intermediate graduations of 0.1 psig and to the nearest 0.1 psig for gauges with graduation of 0.2 to 0.5 psig. The value obtained is the Reid Vapor Pressure of the sample under test.

4. A nomograph Figs. III-7 and III-8) is used to convert Reid Vapor Pressure to true vapor pressure (See Reference 4.2).

4. REFERENCES

4.1 Vapor Pressure of Petroleum Products (Reid Method) ASTM designation D-323-72, Book 23 ASTM Petroleum Products (1977).

4.2 Nomograph of Petroleum Products Vapor Pressure. Air Pollution Engineering Manual, 2nd Ed., AP40, 635-636.



(a) Sample Container Prior to Transfer of Sample

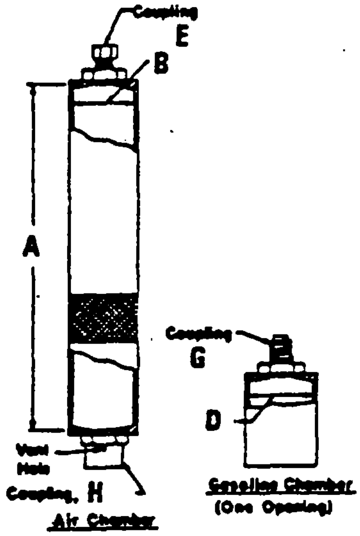
(b) Sealing Closure Replaced by Sample Transfer Connection

(c) Gasoline Chamber Placed Over Liquid Delivery Tube

(d) Position of System for Sample Transfer

Fig. III-5

SAMPLE TRANSFER TO GASOLINE CHAMBER



DIMENSIONS OF VAPOR PRESSURE BOMB

| Key | Description | in. | mm |
|---|---|---|---|
| A | Air chamber, length | 10 ± 1/8 | 254 ± 3 |
| B, D | Air and gasoline chambers, ID | 2 ± 1/8 | 51 ± 3 |
| E | Coupling, ID min | 3/16 | |
| G | Coupling, OD | 1/2 | |
| H | Coupling, ID | 1/2 | |

Fig. III-6

REID VAPOR PRESSURE BOMB

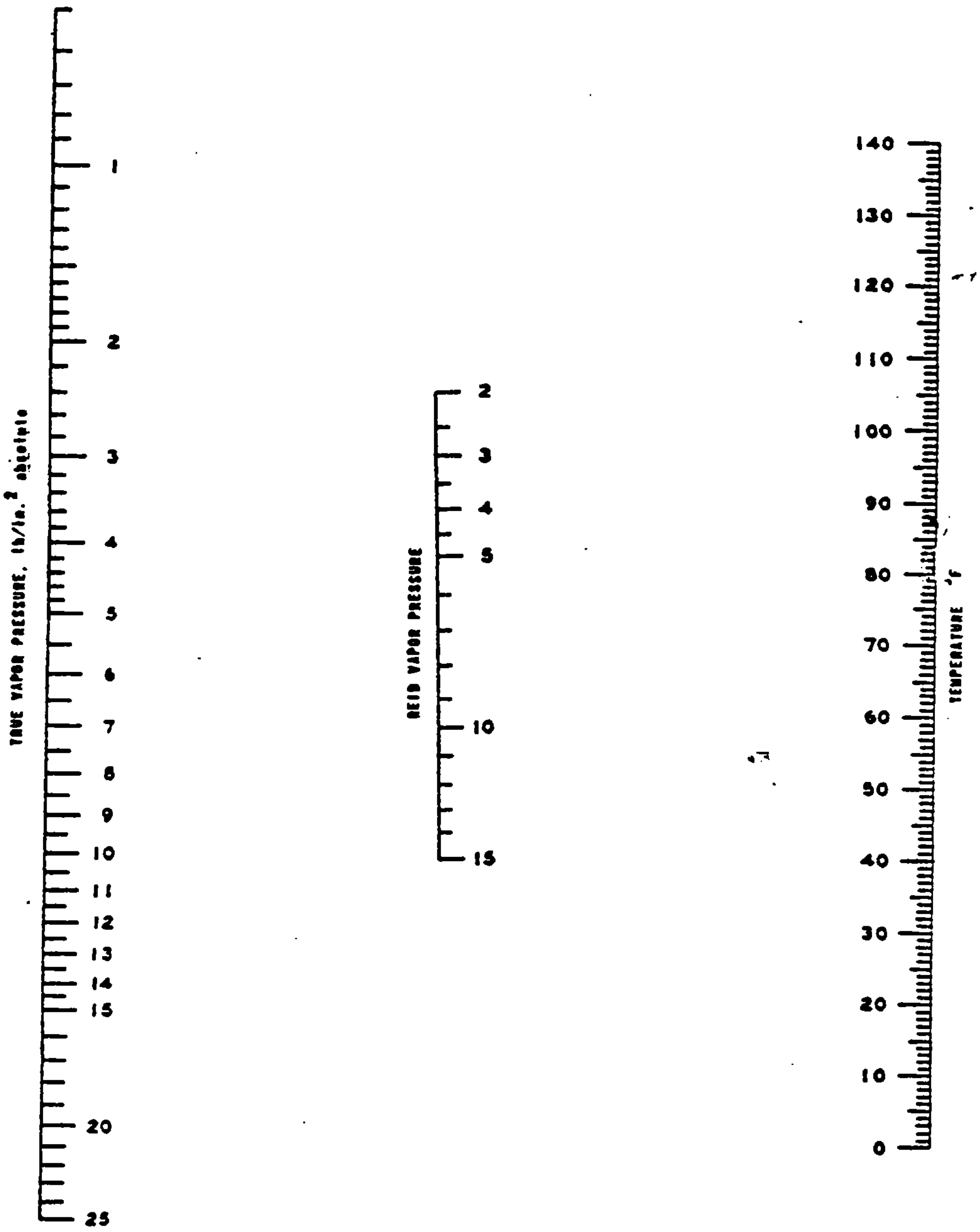
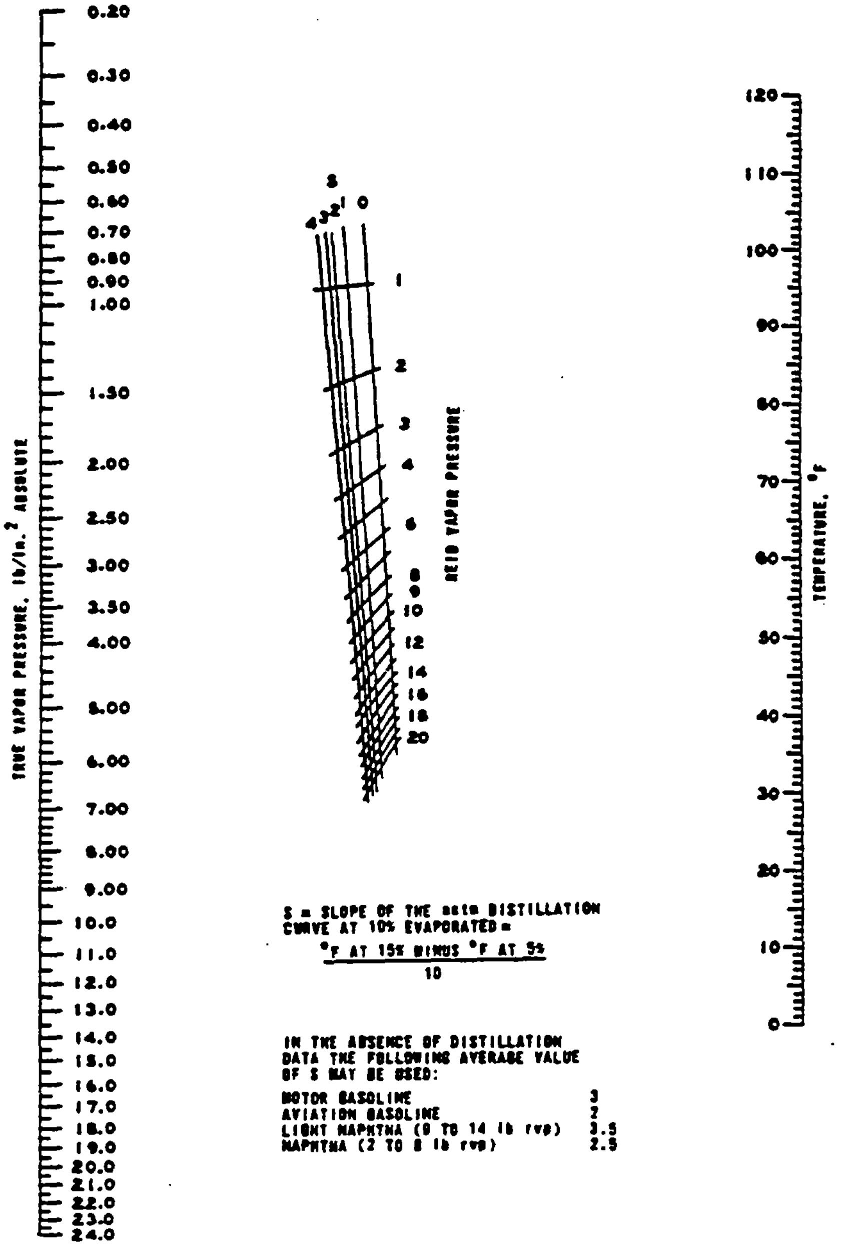


Fig. III-7

VAPOR PRESSURES OF CRUDE OIL



S = SLOPE OF THE ASTM DISTILLATION CURVE AT 10% EVAPORATED =

$$\frac{\text{°F AT 15\% MINUS °F AT 5\%}}{10}$$

IN THE ABSENCE OF DISTILLATION DATA THE FOLLOWING AVERAGE VALUE OF S MAY BE USED:

| | |
|---|---|
| MOTOR GASOLINE | 3 |
| AVIATION GASOLINE | 2 |
| LIGHT NAPHTHA (9 TO 14 lb rvp) | 3.5 |
| NAPHTHA (2 TO 8 lb rvp) | 2.5 |

FIG. III-8

VAPOR PRESSURES OF GASOLINES AND FINISHED PETROLEUM PRODUCTS (1 - 20 lb)

# LAB 14

REF: Reg. 7-303

## DETERMINATION OF TRIMETHYLAMINE IN EFFLUENTS

### 1. PRINCIPLE

The trimethylamine is absorbed and converted to the stable hydrochloride salt in dilute hydrochloric acid solution. The trimethylamine is regenerated by addition of sodium hydroxide and determined by gas chromatography using flame ionization detection.

### 2. APPARATUS

2.1 Gas Chromatograph. This unit equipped with a flame ionization detector, must be capable of detecting 2 µgm/ml of trimethylamine with a peak height of at least 3 times the noise level.

2.1.1 A glass 4' x 1/8" analytical column is used, containing 15% Dowfax 9N9 + 7.5% TEPA on Chromosorb W 60/80 mesh. The material is prepared, packed and conditioned employing standard techniques.

2.2 10 µl syringe

2.3 Injection port fitted with a glass sleeve

### 3. REAGENTS

3.1 Hydrochloric Acid (0.1 N). Add 8.4 ml of concentrated hydrochloric acid to 500 ml distilled water and dilute to 1 liter.

3.2 Sodium Hydroxide Solution (1 N). Dissolve 40 g of sodium hydroxide pellets in 500 ml of distilled water and dilute to 1 liter.

3.3 Litmus Paper - Red

## 4. ANALYTICAL PROCEDURE

4.1 Measure and record the total liquid volume of the impingers. If samples are to be analyzed within 3 days proceed as in 4.2 to 4.4. If analysis is delayed keep samples refrigerated.

4.2 Transfer a 9.0 ml aliquot of the sample to a 25 ml graduated test tube. Add 1 ml of 1 N sodium hydroxide, sufficient to make the solution basic. Cover the test tube with parafilm; invert and mix well. Check to insure the sample is basic with pH paper.

4.3 Inject a 2 µl sample into the gas chromatograph injection port. The operating parameters are: column temperature 75°C; detector temperature 200°C; injection port temperature 160°C; carrier gas 40 ml/min; hydrogen 20 ml/min and air 250 to 300 ml/min.

4.4 Using peak heights, calculate the trimethylamine concentration compared to the peak heights of the standard solutions of trimethylamine.

5.1 Standard Stock Amine Solution. To a 1 liter volumetric flask, add 0.1691 g of trimethylamine hydrochloride salt, dissolve and bring to volume with 0.1 N hydrochloric acid. This standard solution contains 100 µgm trimethylamine/ml.

5.2 Working Standard Solution. Dilute the standard stock solution with 0.1 N hydrochloric acid to make working standards containing 2, 5 and 10 µgm trimethylamine/ml. These standards are processed in the same manner as the samples described in Section 4.1.

## 6. CALCULATION

$$\text{PPM TMA (V/V)} = \frac{(\mu\text{gm in sample})(\text{Total vol of impinger})}{(\text{Aliquot of sample})\ (2.4)\ (\text{Sample vol in liters})}$$

Where 2.4 = the µgm in 1 µℓ of trimethylamine at
25°C and 760 mm Hg

## 7. REFERENCES

7.1 Di Corcia A., et al. "Gas Chromatographic Determination at the Part per Million Level of Aliphatic Amines in Aqueous Solution", Anal. Chem. 46, 977, 1974.

7.2 Levaggi, D.A., Feldstein, M., "Determination of Phenols and Trimethylamine in Industrial Effluents", AIAA Library No. 71-115, 750 3rd Ave., New York, N.Y. 10017.

# LAB 15

## STANDARDIZATION OF CARBON DIOXIDE CALIBRATION GAS

## 1. RATIONALE

Carbon dioxide standards used for calibrating source test instrumentation must be checked periodically for accuracy and quality assurance purposes.

## 2. PRINCIPLE

The carbon dioxide gas is absorbed by Ascarite and the increase in weight of the absorbent is determined gravimetrically. The carbon dioxide gas must first pass through Drierite to remove water vapor, which would otherwise interfere with the determination.

## 3. APPARATUS

3.1 Analytical balance

3.2 Schwartz Absorption Combustion Tubes. These tubes are available from Kontes Glass Co. (Cat. No. K891250). The tubes are filled with the appropriate material and plugged at each end with glass wool.

3.3 Wet Test Meter (readout in liters)

3.4 Rotameter 0 to 1 liter/min range

3.5 Two Stage Regulator, with a controlling valve

## 4. REAGENTS

4.1 Anhydrone

4.2 Ascarite

4.3 Drierite (8 to 14 mesh)

## 5. ANALYTICAL PROCEDURE

5.1 Assemble the sampling train as shown in Figure III-9. The train consists of 2 U-shaped Schwartz Combustion absorption tubes attached to the carbon dioxide standard cylinder equipped with a 2 stage regulator and controlling valve. The first absorption tube contains Drierite to remove water vapor which may be present in the cylinder gas. The inlet of the second absorption tube contains Ascarite and the other half Anhydrone, (separated by a glass wool plug) to remove respectively the carbon dioxide, and any water formed during the collection reaction.

5.2 Prior to the analysis, flush the entire sampling train with approximately 2 liters of the calibration gas.

5.3 Disconnect the Ascarite-Anhydrone tube from the sample train and carefully weigh with an analytical balance. Record the weight ($W_1$). Reconnect the Ascarite-Anhydrone tube to the sampling train.

5.4 Record the wet test meter reading ($M_1$). The cylinder controlling valve is slowly opened, and using the rotometer as a guide, the flow is adjusted as rapidly as possible to 0.5 to 1 liter per minute.

5.5 The volume of sample depends on the concentration of carbon dioxide in the sample. The gain in weight of the Ascarite-Anhydrone tube should be at least 20 mg. As a guide, 1000 ppm carbon dioxide should have a sample size of about 10 liters.

5.6 After sufficient sample has been collected, close the controlling valve. The Ascarite-Anhydrone tube is disconnected and again carefully weighed ($W_2$). The final wet test meter reading is then recorded ($M_2$).

5.7 At least two determinations are to be made and must agree to within ±5% of the mean.

## 6. CALCULATION

1 mg carbon dioxide per liter is equal to 556 ppm

$$\text{PPM } CO_2 = \frac{(W_2 - W_1)(556)}{(M_2 - M_1)}$$

## 7. REFERENCE

7.1 Textbook of Quantitative Inorganic Analysis, Kolthoff and Sandell, 3rd Ed. 1952, MacMillan, N.Y.

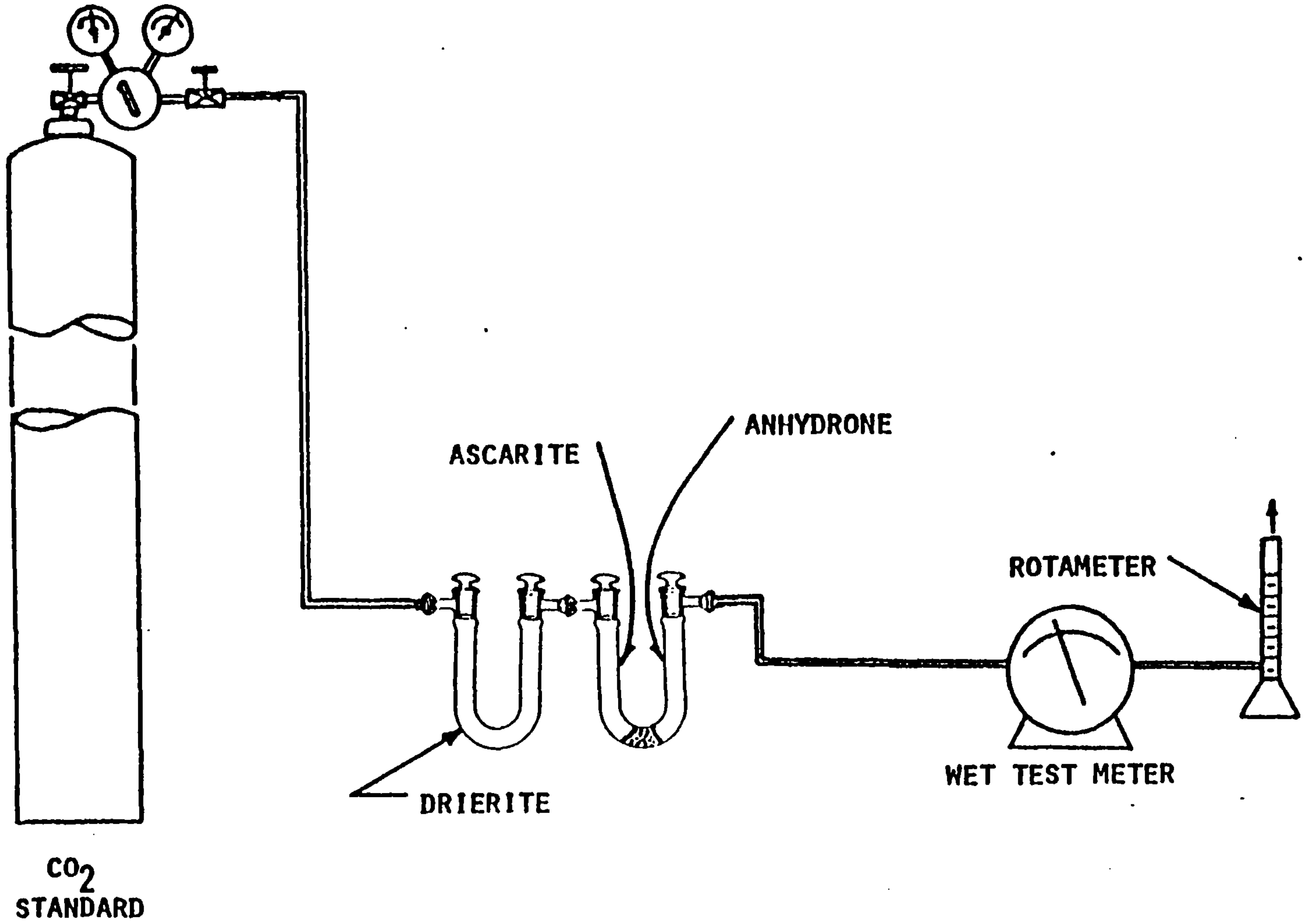


FIG. III-9

GRAVIMETRIC DETERMINATION OF CARBON DIOXIDE

## LAB 16

## STANDARDIZATION OF CARBON MONOXIDE CALIBRATION GAS

### 1. RATIONALE

Carbon monoxide standards used to calibrate source test instrumentation must be checked periodically for accuracy and quality assurance purposes.

### 2. PRINCIPLE

Carbon monoxide calibration gas is oxidized to carbon dioxide by use of Hopcalite catalyst. The formed carbon dioxide is absorbed by the Ascarite and is determined gravimetrically. Any water vapor and carbon dioxide in the sample must be removed prior to the Hopcalite catalyst.

### 3. APPARATUS

3.1 Analytical balance

3.2 Rotameter, 0 to 1 liter range

3.3 Wet Test Meter (readout in liters)

3.4 Two stage regulator, with a controlling valve

3.5 Schwartz Absorption Combustion Tubes. These tubes are available from Kontes Glass Co. (Cat. No. K891250). The tubes are filled with the appropriate material and plugged at each end with glass wool.

3.6 Boiling water bath

3.7 Hopcalite U-trap. This trap is constructed of 7 to 10 mm ID borosilicate glass and is approximately 20 cm in length. The trap is filled with 3 to 6 g of Hopcalite and plugged at each end with glass wool. The trap should be fitted with spherical joints for ease of assembling and disassembling.

## 4. REAGENTS

4.1 Anhydrone

4.2 Ascarite

4.3 Hopcalite, Active (4 to 20 mesh, available from the Mine Safety Appliance Co.)

4.4 Drierite (8 to 14 mesh)

## 5. ANALYTICAL PROCEDURE

5.1 Assemble a sampling train as shown in Figure III-10. The train consists of a Drierite trap to remove moisture; an Ascarite trap to remove carbon dioxide; Hopcalite trap, immersed in boiling water bath, a Drierite trap to remove the generated moisture and a final Ascarite-Anhydrone trap to collect the carbon dioxide formed in the oxidation process. A wet test meter and a rotameter complete the train.

5.2 The Hopcalite catalyst must be conditioned prior to each determination. This is accomplished by disconnecting the sampling train after the Hopcalite trap and allowing approximately 15 liters of the calibration gas to pass through at approximately 0.5 liter/min with the Hopcalite trap immersed in the boiling water bath.

5.3 While conditioning the Hopcalite catalyst, carefully weigh the Ascarite-Anhydrone trap with an analytical balance. Record the weight ($W_1$).

5.4 After conditioning, reconnect the sampling train.

5.5 Record the original wet test meter reading ($M_1$). By means of the controlling valve on the 2 stage regulator, adjust the flow through the sampling train to approximately 0.5 liter per minute as rapidly as possible using the rotameter as an indicator. The gain in weight of the Ascarite-Anhydrone tube should be at least 20 mg. The sample time will depend on the concentration of the carbon monoxide in the sample. As a guide, 200 ppm of carbon monoxide should have a sample size of approximately 60 liters.

5.6 After sufficient sample has been collected, close the controlling valve. The Ascarite-Anhydrone tube is disconnected and again carefully weighed ($W_2$). The final wet test meter reading is then recorded ($M_2$).

5.7 At least two determinations are to be made and must agree to within ±5% of the mean.

## 6. CALCULATIONS

1 mg carbon monoxide per liter is equal to 873 ppm

$$\text{PPM CO in cylinder} = \frac{(W_2 - W_1)\ (873)}{(M_2 - M_1)} \times \frac{28}{44}$$

Where: 28 = the mol. wt. of carbon monoxide
44 = the mol. wt. of carbon dioxide

## 7. REFERENCES

7.1 Feldstein, M., Progress in Chemical Toxicology Vol. 13, 105-106, 1967 Ed. A Stolman, Academic Press, N.Y.

7.2 Methods of Air Sampling and Analysis, 2nd Ed. Katz, M., American Public Health Assn., Washington, D.C. 1977.

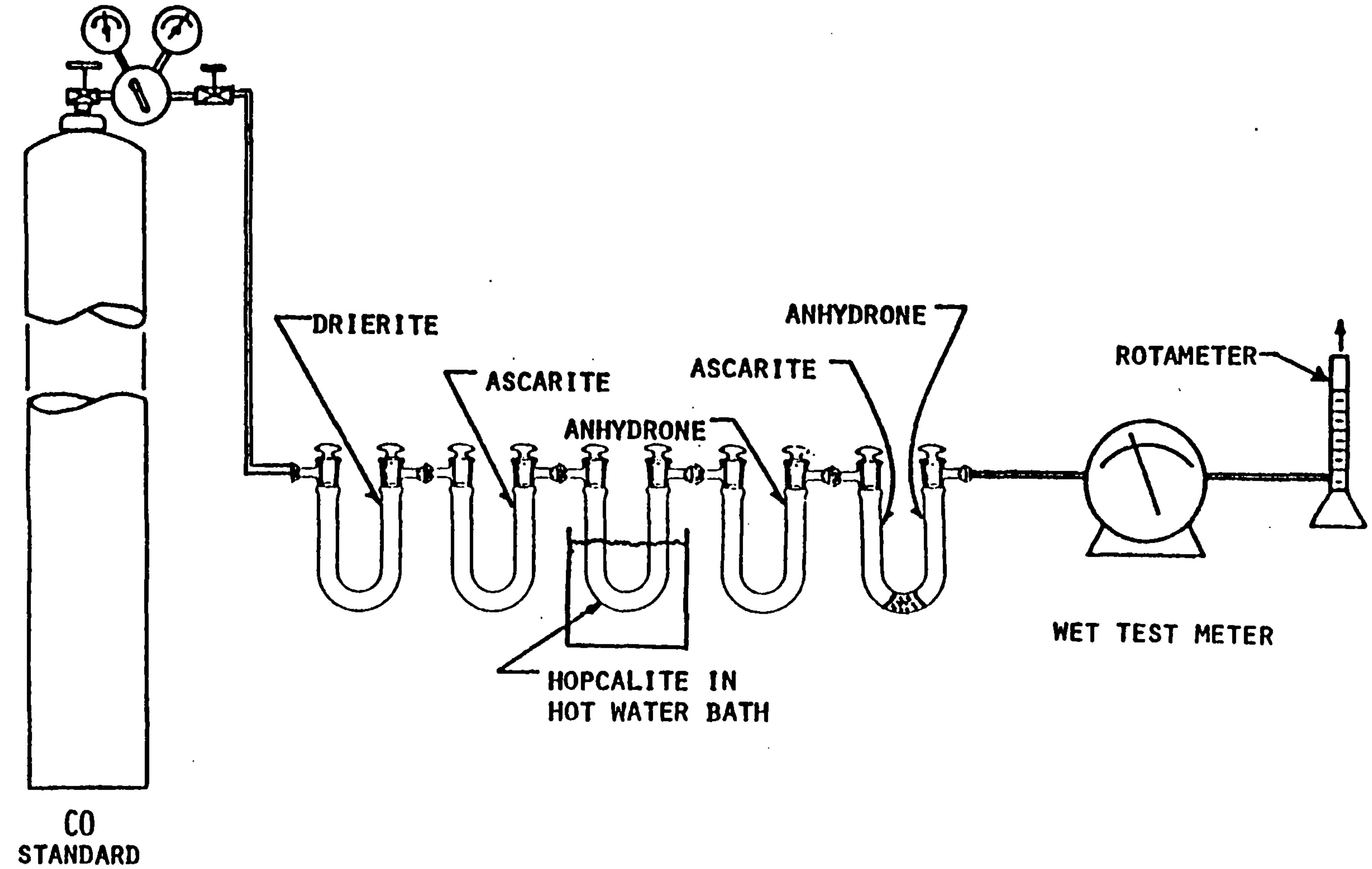


FIG. III-10
GRAVIMETRIC DETERMINATION OF CARBON MONOXIDE

# LAB 17

## STANDARDIZATION OF HYDROCARBON CALIBRATION GASES

## 1. RATIONALE

Hydrocarbon gas standards used for calibrating source test instrumentation must be checked periodically for accuracy and quality assurance purposes. These standards usually consists of a single hydrocarbon normally methane, propane or hexane.

## 2. PRINCIPLE

The hydrocarbon calibration gas concentration is determined by preparing two laboratory standards, one higher and one lower than the expected cylinder concentration. Gas chromatography is then used to determine the cylinder gas concentration by comparison with prepared laboratory standards.

## 3. APPARATUS

3.1 Gas Chromatograph. This unit is equipped with a gas sampling valve, a flame ionization detector and necessary accessory gases.

3.2 Analytical columns. Any column may be used which is capable of resolving the hydrocarbons of interest such as :

3.2.1 For methane, a 6 ft 1/8" Chromosorb 102, 80 to 100 mesh column is normally used.

3.2.2 For propane, a 6 ft 1/8" Chromosorb 102, 80 to 100 mesh column is normally used.

3.2.3 For hexane, a 6 ft 1/4" silicone L-45 on firebrick 60 to 80 mesh is normally used.

3.3 Stainless Steel (SS) Tanks. Use 4 to 34 liter tanks, calibrated for volume which have been previously steam cleaned, to be hydrocarbon free and fitted with a vacuum-pressure gauge, valve and nipple.

3.4 Syringes. Use 5, 10, and 30 ml calibrated syringes.

3.5 Flex Tubing. This tubing must be able to withstand 300 lbs line pressure. The tubing is usually 3 to 4 feet long and adapted with quick connect fittings to easily connect the SS tank to a nitrogen or air cylinder.

3.6 Test gauges (0 to 60 and 0 to 250 psig)

3.7 Two stage regulator with a controlling valve

4. REAGENTS

4.1 Reagent grade lecture bottles of the hydrocarbons of interest (99+% purity)

4.2 Cylinder Nitrogen gas or air (<1 ppm hydrocarbon)

5. PREPARATION OF LABORATORY STANDARDS

5.1 Evacuate two hydrocarbon free SS tanks to at least a vacuum of 100 mm Hg. Introduce the hydrocarbon gas of interest to each evacuated tank by means of a calibrated syringe. The amount of hydrocarbon added is pre-determined in each case to bracket the nominal concentration of the cylinder to be standardized (see 5.4). The addition of the pure hydrocarbon is accomplished by injecting the hydrocarbon from the syringe through a rubber septum placed over the SS tank nipple, and slowly opening the valve of the evacuated SS tank.

5.2 Connect the SS tank to the nitrogen or air cylinder by means of the flex tubing. Pressurize the SS tank to an approximate pre-determined value (see 5.1 and 5.4) using the tank pressure gauge as an indicator.

5.3 Allow the tank to equilibrate for 3 hours. Measure and record the pressure accurately with the appropriate test gauge.

5.4 Calculate the prepared standard concentration with the following formula:

$$\text{PPM HC} = \frac{\text{Vol (cc) of Added Hydrocarbon} \times 1000}{\text{Tank Vol (L)} \times \dfrac{\text{Total Tank Pressure (psig + 14.7)}}{\text{14.7 psi}}}$$

$$\text{PPM Hexane} = \frac{(\mu\text{l Hexane})\ (664\ \mu\text{g}/\mu\text{l})}{\text{Tank Vol (L)} \times \left(\dfrac{\text{Total Tank Pressure (psig + 14.7)}}{\text{14.7 psi}}\right)(3.52)}$$

Where: 3.52 = the µgm in 1 µl of hexane at 25°C
and 760 mm Hg

## 6. STANDARDIZATION OF HYDROCARBON CYLINDER

6.1 By use of the gas chromatograph gas sampling valve, introduce each laboratory hydrocarbon gas standard in the gas chromatograph and record the peak height of the hydrocarbon. This should be repeated a minimum of 5 times for each standard. Obtain the average peak height for each standard (individual peak heights should not vary by more than 5% of the mean). The peak height to concentration ratio of each standard should not exceed 5%.

6.2 As in 6.1 above, determine the peak height of the hydrocarbon calibration gas cylinder.

## 7. CALCULATION

$$\text{PPM HC in cylinder} = \frac{\text{Peak Height Cylinder Gas}}{\text{Peak Height of Standard}} \times \text{Conc. of Standard}$$

7.1 This calculation is performed using both prepared laboratory standards. The cylinder concentration to be reported is the average of the two calculations.

## 8. REFERENCE

8.1 Halzas, I. and Wegner, E.F., Gas Chromatographic Separation of Low Boiling Hydrocarbons. Nature, <u>57</u>, 189, 1961.

# LAB 18

## STANDARDIZATION OF HYDROGEN SULFIDE CALIBRATION GAS

## 1. RATIONALE

Hydrogen sulfide standards used for source test instrumentation must be checked periodically for accuracy and quality assurance purposes.

## 2. PRINCIPLE

Hydrogen sulfide is absorbed from a gas stream by a solution of cadmium sulfate forming a precipitate of cadmium sulfide. The collected sulfide is oxidized by an excess of standard iodine solution which is back titrated with standard sodium thiosulfate.

## 3. APPARATUS

3.1 Greenburg Smith Impingers

3.2 Rotameter, 0 to 10 liter/min range

3.3 Dry Test Meter (readout in cubic feet)

3.4 50 ml burettes

3.5 Two stage regulator with a controlling valve

## 4. REAGENTS

4.1 Cadmium sulfate solution. Add 11.2 g of anhydrous cadmium sulfate to 1 liter of distilled water.

4.2 Hydrochloric Acid, (6 N). Dilute concentrated hydrochloric acid 1:1 with distilled water.

4.3 Standard Sodium Thiosulfate Solution, (0.1 N). Dissolve 15.8 g of anhydrous sodium thiosulfate in 1 liter of distilled water. Add 1 g of sodium carbonate as a preservative. Allow to stand for a day before standardizing.

4.4 Starch Solution - 1% Indicator. Available from any chemical supply house.

4.5 Iodine Solution (0.1 N $KI_3$). Place 12.7 g of reagent grade iodine ($I_2$) in a 500 ml beaker, add 40 g of potassium iodide and 250 ml of distilled water. Stir periodically. When all the iodine is completely dissolved, dilute to approximately 1 liter. Keep the solution in a dark glass stoppered bottle and store in a cool place.

4.6 Arsenic Trioxide

4.7 Sodium Bicarbonate

4.8 Sodium Hydroxide (1 N). Dissolve 40 g of sodium hydroxide pellets in 250 ml of distilled water and dilute to 1 liter.

## 5. SAMPLING PROCEDURE

5.1 Add 100 ml of cadmium sulfate solution to each of the two Greenburg Smith impingers. Connect the impingers in series, the first connected to the standard gas cylinder, the second to a dry test meter, followed by a rotameter. All connections are made with teflon tubing. Fig. III-11 details the sampling train.

5.2 Record the original dry test meter reading ($M_1$). By means of the controlling valve on the 2 stage regulator, on the cylinder, adjust the flow through the sampling train to approximately 10 liters per minute as rapidly as possible, using the rotameter as an indicator. The sampling time will depend on the concentration of the hydrogen sulfide in the cylinder. As a guide, 100 ppm hydrogen sulfide should have a sample size of approximately 300 liters.

5.3 After sufficient sample has been collected, shut off the controlling valve. Record the final dry test meter reading ($M_2$), and remove the impingers from the sampling train.

5.4 A minimum of two determinations are to be made and must agree to within ±5% of the mean.

6. ANALYTICAL PROCEDURE

6.1 Quantitatively transfer the solution and precipitate from the $CdSO_4$ impingers into glass stoppered 500 ml Erlenmeyer flasks.

6.2 From a 50 ml burette, add iodine solution rapidly until an excess is indicated, record the volume added.

6.3 Rapidly add 10 ml of 6 N HCl and back titrate with 0.1 N sodium thiosulfate solution with constant stirring. When the color of the liquid becomes a pale yellow, add 1 ml of starch solution and continue the titration until the color changes from blue to colorless. Record the amount of sodium thiosulfate solution used.

7. CALCULATION

$$\text{PPM } H_2S = \frac{\left[(N \times V)\ KI_3 - (N \times V)\ Na_2S_2O_3\right] \times 17 \times 10^3}{(1.39)\ (M_2 - M_1)\ (27.3 \text{ liters/cubic ft})}$$

Where: 17 = the equivalent wt. of hydrogen sulfide

1.39 = the μgm in 1 μl of hydrogen sulfide at 25°C and 760 mm Hg

Total PPM $H_2S$ = PPM $H_2S$ 1st Imp + PPM $H_2S$ 2nd Imp

8. STANDARDIZATION OF IODINE SOLUTION

8.1 Weigh three portions (0.2 to 0.25 g ±0.0001 g) of arsenic trioxide and transfer them to 250 ml Erlenmeyer flasks. Dissolve each in 10 to 20 ml of 1 N sodium hydroxide, and neutralize trill just acid with 6 N hydrochloric acid. Add 1 g of sodium bicarbonate, and dilute to approximately 100 ml.

8.2 Add 2 ml of starch solution indicator and titrate with the iodine solution to a blue tint. Record volume of $KI_3$ used.

8.3 Calculation (Use average of three determinations)

$$\text{Normality of } KI_3 = \frac{\text{Wt of arsenic trioxide}}{0.4946 \times \text{Vol. of } KI_3}$$

Where: 0.4946 = the gms/meqv. of arsenic trioxide

## 9. STANDARDIZATION OF SODIUM THIOSULFATE

9.1 To two Erlenmeyer flasks containing 50 ml of distilled water add exactly 25.0 ml of standard iodine solution.

9.2 Add 10 ml of 6 N hydrochloric acid and immediately titrate with the sodium thiosuflate solution until a pale yellow color remains. Add 2 ml of starch solution and resume titration until the disappearence of all traces of a blue color. Record the volume.

9.3 Calculation (Use average of two determinations)

$$\begin{array}{l}\text{Normality of}\\ \text{Sodium Thiosulfate}\end{array} = \frac{(N \times V)\ \text{Iodine}}{(V)\ \text{Sodium Thiosulfate}}$$

## 10. REFERENCE

10.1 Jacobs, M., The Chemical Analysis of Air Pollutants, Interscience Publishers Inc., New York, 1960.

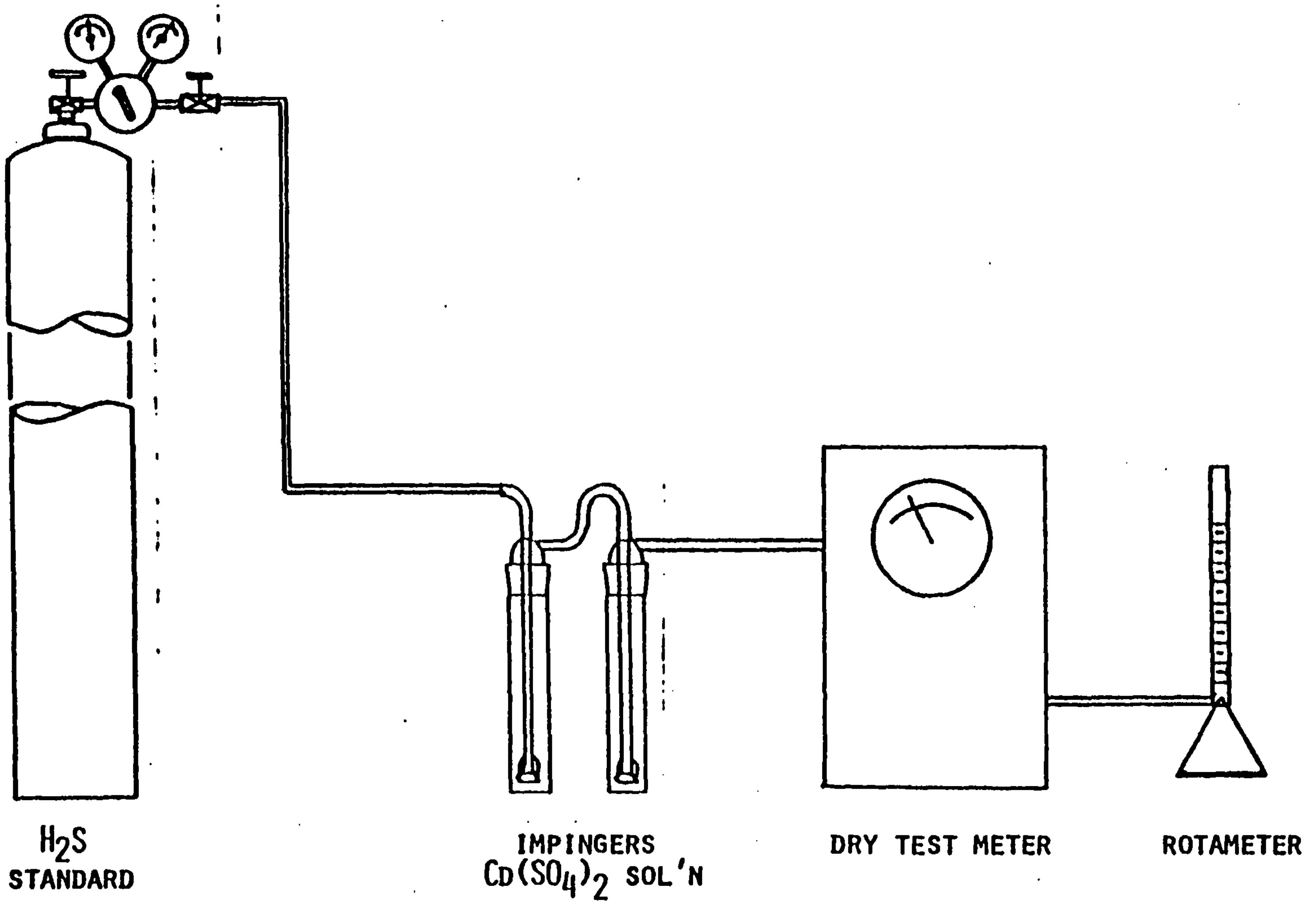


FIG. III-11

HYDROGEN SULFIDE CALIBRATION TRAIN

# LAB 19

## STANDARDIZATION OF NITRIC OXIDE CALIBRATION GAS

## 1. RATIONALE

Nitric oxide standards used for source test instrumentation must be checked periodically for accuracy and quality assurance purposes.

## 2. PRINCIPLE

The nitric oxide is absorbed in alkaline permanganate solution with Greenburg Smith impingers fitted with semi-fine frits. The nitrite and nitrate ions thus formed are determined by first converting the nitrite formed during the collection to nitrate. The total nitrate is then reduced to nitrite, which is determined by a chromatropic acid indicator.

## 3. APPARATUS

3.1 Greenburg Smith Impingers. The impingers are fitted with semi-fine frits (70 porosity), available from Ace Glass Co. (Cat. #7201-04) or equivalent.

3.2 50 ml graduated Erlenmeyer flasks with screw caps

3.3 Two Stage Regulator with a controlling valve

3.4 Wet Test Meter (readout in liters)

3.5 Hot Plate

3.6 Spectrophotometer

3.7 Rotameter 0 to 1 liter/min range

## 4. REAGENTS

4.1 Absorbing Solution. Dissolve 40 g of $KMnO_4$ and 20 g NaOH pellets in 400 ml of distilled water and dilute to 1 liter with distilled water.

4.2 Oxalic Acid Solution. Dissolve 80 g of oxalic acid and dilute to 1 liter with distilled water.

4.3 Sulfuric Acid (1.0 N). Add 27.8 ml of concentrated sulfuric acid to 500 ml of distilled water and dilute to 1 liter.

4.4 Nitrate Reagents. Nitra Ver III (Cat. #14065) and Nitra Ver VI (Cat. #14119) are available from Hach Chemical Co., Ames, Iowa.

## 5. SAMPLING PROCEDURE

5.1 The sampling train consists of 3 Greenburg Smith impingers modified with semi-fine glass frits, each containing 100 ml of absorbing solution as shown in Fig.III-12. The impingers are connected in series followed by a wet test meter and rotameter. The sampling train is connected to the standard gas cylinder by means of teflon tubing.

5.2 Record the original wet test meter reading ($M_1$). By means of the controlling valve on the 2 stage regulator, adjust the flow through the sampling train to approximately 0.5 liter per minute as rapidly as possible, using the rotameter as an indicator. The sample time will depend on the concentration of the nitric oxide in the cylinder. As a guide, 100 ppm of nitric oxide requires a sample size of approximately 20 liters.

5.3 After sufficient sample has been collected shut off the controlling valve. Record the final wet test meter reading ($M_2$), and remove the impingers from the sampling train (Fig. III-12).

5.4 At least 2 determinations are to be made and the results must agree to within ±5% of the mean.

## 6. ANALYTICAL PROCEDURE

6.1 Measure and record the liquid volume of each impinger. Transfer an aliquot, not to exceed 3.0 ml for analysis, containing 0 to 60 μgm of nitrite. The aliquot may require dilution with unreacted absorbing solution or may be used directly. If preferred, all three impingers may be combined to form a composite sample, thereby requiring only a single analysis.

6.2 The aliquot taken is transferred to a 50 ml Erlenmeyer flask fitted with a screw cap. A reagent blank of 2.0 ml is also prepared from the absorbing solution which was used for the sampling. Acidify with 1.0 N sulfuric acid, using 1 ml of acid per ml of aliquot.

6.3 Heat the sample on a hot plate to 50° to 60°C, and add 1 ml of oxalic acid per ml of aliquot, let stand until colorless. Should more oxalic acid be required to reduce the permanganate, add dropwise so as not to have more than 3 drops in excess. Cool to room temperature and dilute to the 30 ml mark with distilled water.

6.4 Add to the sample and the blank, the content of a Nitra Ver VI pillow, cap the flask and shake for exactly 5 minutes. Allow the sample to stand for 30 seconds and transfer to a graduated test tube. Add the content of a Nitra Ver III pillow, cover the test tube with parafilm and mix for one minute. Let stand for 10 minutes and read the formed pink color at 500 nm, using a 13 mm cuvette, setting the blank at 100% transmittance. Obtain μgm $NO_2$ in the sample from a standard curve.

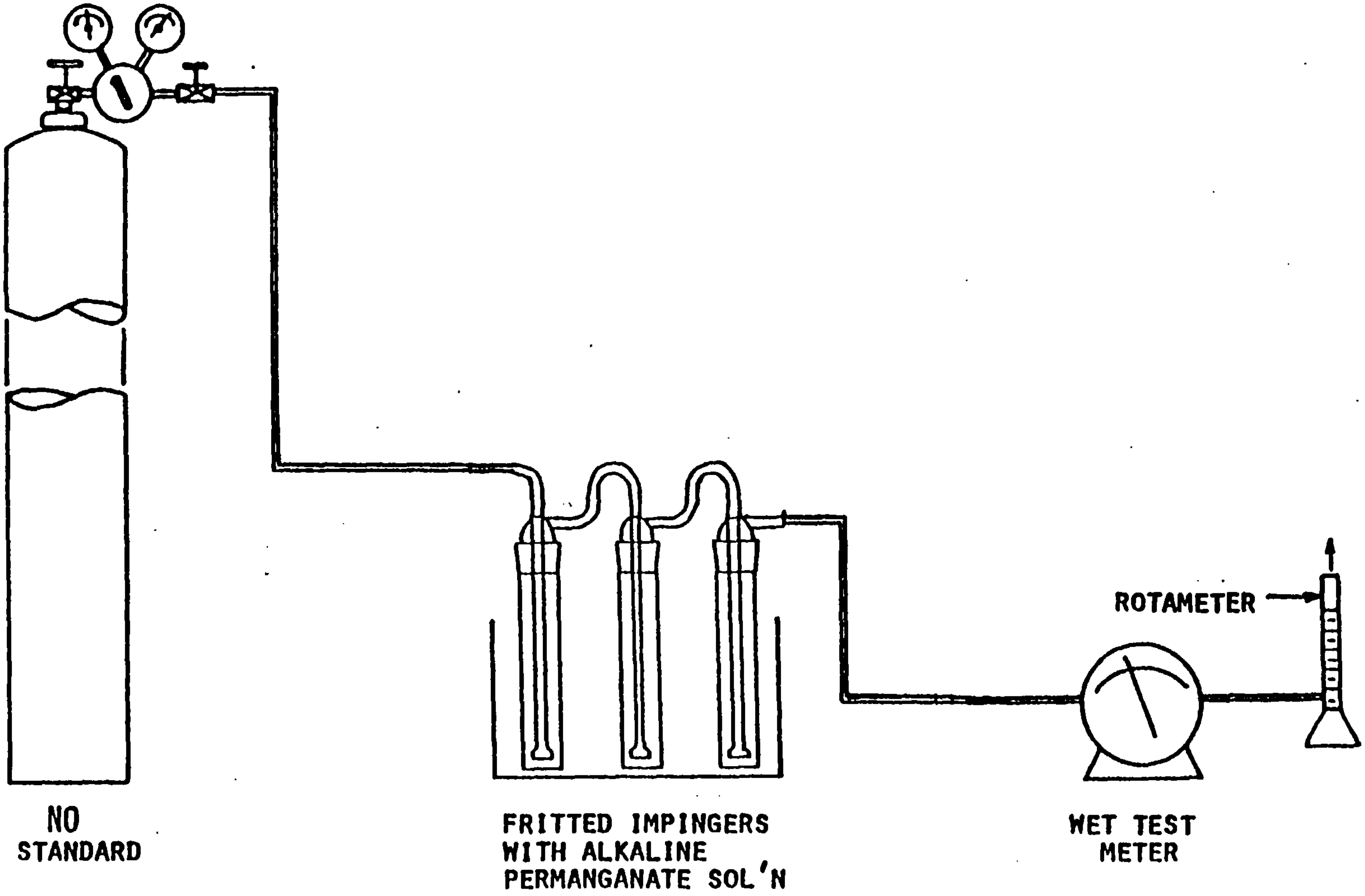


Fig. III-12
NITRIC OXIDE CALIBRATION TRAIN

## 7. STANDARD CURVE

7.1 Standard Stock Nitrite Solution. Weigh and transfer 0.2198 g of potassium nitrate to a 1 liter volumetric flask containing 100 ml of distilled water. Dissolve and dilute to the mark with distilled water. This standard solution contains 100 μgm $NO_2$ equivalent per ml.

7.2 Working Standard Nitrite Solution. Dilute the stock standard 10:1 to make a working standard containing 10 μgm $NO_2$ equivalent per ml.

7.3 Prepare a series of standards containing 10 to 50 μgm of $NO_2$ in 50 ml Erlenmeyer flasks. Proceed as in 6.2 to 6.4 to develop the color forming reaction.

7.4 Prepare a standard curve plotting μgm $NO_2$ vs % transmittance on semi-log graph paper.

## 8. CALCULATION

$$\text{PPM NO as NO}_2 = \frac{\text{Total } \mu\text{gm NO}_2 \text{ in Impingers}}{(M_2 - M_1)\ (1.88)}$$

Where: 1.88 = the μgm in 1 μl of nitrogen dioxide at 25°C and 760 mm Hg

## 9. REFERENCE

9.1 Levaggi, D.A., et al, "An Integrated Manual Impinger Method for Simultaneous Determination of $NO_x$ and $SO_2$ in Source Effluents", J. Air Poll. Cont. Assoc. 26, 783, 1976.

# LAB 20

## STANDARDIZATION OF SULFUR DIOXIDE CALIBRATION GAS

### 1. RATIONALE

Sulfur dioxide standards used for source test instrumentation must be checked periodically for accuracy and quality assurance purposes.

### 2. PRINCIPLE

Sulfur dioxide is absorbed in a solution of hydrogen peroxide to form sulfuric acid. The formed sulfuric acid is determined with a standard sodium hydroxide solution.

### 3. APPARATUS

3.1 Greenburg Smith Impingers

3.2 Dry Test Meter (readout in cubic feet)

3.3 Two Stage Regulator with a controlling valve

3.4 Rotameter, 0 to 10 liter range

3.5 50 ml Buret

3.6 Teflon tubing connections

### 4. REAGENTS

4.1 Bromcresol Green Indicator Solution (0.04%). Mix 0.1 g of dry powder bromcresol green in a mortar with 14.3 ml of 0.01 N NaOH. Dilute to 250 ml with distilled water.

4.2 Hydrogen peroxide 3% (sulfate free). Dilute 50 ml of 30% $H_2O_2$ to 500 ml with distilled water. Prepare fresh prior to use.

4.3 Sodium Hydroxide Solution (0.1 N). Dissolve 4.0 g of sodium hydroxide pellets in 150 ml of distilled water and dilute to 1 liter. Determine normality of the solution within ±0.0005 N by standardization against potassium acid phthalate using phenolphthalein indicator (7.1).

## 5. SAMPLING PROCEDURE

5.1 To each of two Greenburg impingers add 100 ml of 3% hydrogen peroxide solution. Use teflon tubing to connect the gas cylinder to the impingers with the second impinger connected to a dry test meter followed by a rotameter. Fig. III-13 details the sampling train.

5.2 Record the original wet test meter reading ($M_1$). By means of the controlling valve on the 2 stage cylinder regulator, adjust the flow through the sampling train to approximately 5 liters per minute as rapidly as possible, using the rotameter as an indicator. The sample time will depend on the concentration of the sulfur dioxide in the cylinder. As a guide, 200 ppm sulfur dioxide should have a sample size of approximately 7.5 $ft^3$ (200 liters).

5.3 After sufficient sample has been collected, shut the controlling valve. Record the final wet test meter reading ($M_2$) and remove the impingers from the sampling train.

5.4 A minimum of two determinations are to be made and must agree to within ±5% of the mean.

## 6. ANALYTICAL PROCEDURE

6.1 Quantitatively transfer and rinse each impinger into a 500 ml Erlenmeyer flask.

6.2 Bring each to a boil, cool to room temperature and titrate with standard sodium hydroxide solution, using 4 ml of bromcresol green indicator solution. Titrate to the blue color end point, and record the volume used.

## 7. PREPARATION OF STANDARD ALKALI

7.1 Standardize the prepared 0.1 N sodium hydroxide with potassium acid phthalate. Run in triplicate.

$$\text{N NaOH} = \frac{\text{Wt. of Potassium Acid Phthalate (g)}}{(0.2043)\ (\text{ml NaOH})}$$

Where: 0.2043 = the gms/meqv of potassium acid phthalate

## 8. CALCULATION

$$\text{PPM } SO_2 = \frac{\text{Vol NaOH} \times \text{N NaOH} \times 32 \times 10^3}{(M_2 - M_1)\ (28.3 \text{ liters/cubic ft})\ (2.6)}$$

Where: 32 = the equivalent wt. of sulfur dioxide

2.6 = the μgm in 1 μl of sulfur dioxide at 25°C and 769 mm Hg

Total PPM $SO_2$ = PPM $SO_2$ 1st Imp + PPM $SO_2$ 2nd Imp

## 9. REFERENCE

9.1 Jacobs, M.B. "Chemical Analysis of Pollutants." Interscience Publishers Inc., New York, 1960.

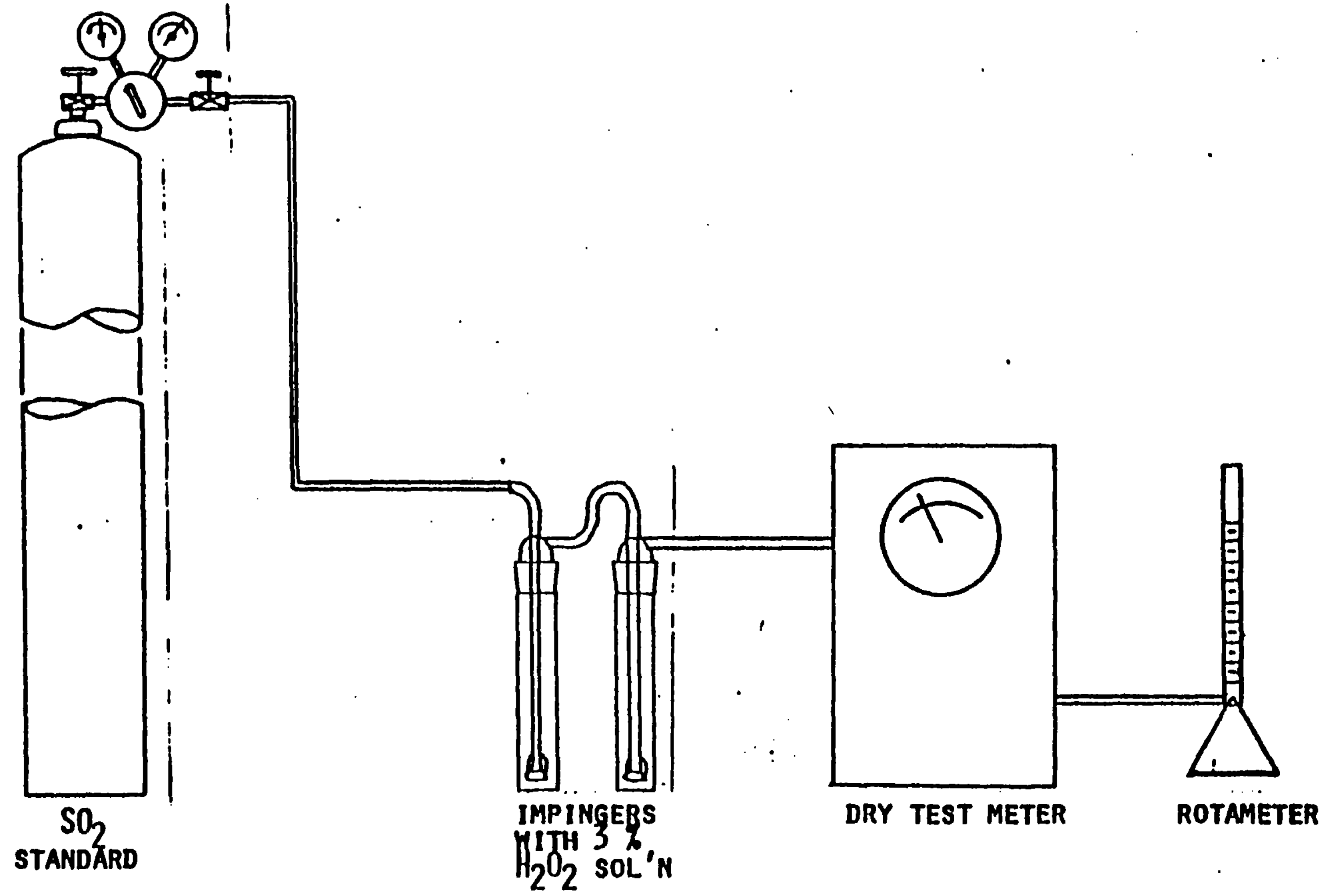


Fig. III-13
SULFUR DIOXIDE CALIBRATION TRAIN

# LAB 21

REF: Regs. 8-3-301, 8-3-302

## DETERMINATION OF COMPLIANCE FOR AIR-DRIED ARCHITECTURAL WATER BASED COATINGS

### 1. PRINCIPLE

A weighed sample of water based architectural coating is distilled to insure complete separation of the water component from the coating. The distillate is then diluted with methanol and the water content determined by a gas chromatograph using a thermal-conductivity detector. The Poropak Q column separates water from any volatile organics present, water being eluted first from the column.

### 2. APPARATUS

2.1 Gas Chromatograph. This unit is equipped with a thermal conductivity detector and a glass sleeve injection port.

2.2 Analytical Column. Use a 6' x 1/4" O.D. column containing Porapak Q, 80/100 mesh.

2.3 10 µℓ syringe

2.4 Simple distillation unit (see Fig. III-14)

2.5 Aluminum Foil Dish. Use a 58 mm diameter x 10 mm high dish with a flat bottom.

2.6 Drying Oven (110°±1°C)

2.7 Glas-col Heater

2.8 Powerstat

2.9 Analytical Balance

2.10 Disposable Beral Pipettes. These are available from Curtin Matheson Co. (Cat. No. 376-970).

## 3. REAGENTS

3.1 Methanol, Anhydrous. This reagent cannot be used for this procedure if it contains >o.1% W/W water. Determine water content by gas chromatography or an equivalent method prior to use.

## 4. ANALYTICAL PROCEDURE

### 4.1 Determination of Total Volatile Content of Paints

4.1.1 Weigh accurately 0.4 to 0.6 g (±0.0001 g) of paint in a pre-weighed aluminum dish. Disperse the paint with 2 ml of distilled water by swirling the dish until the sample is evenly distributed. Dry the sample in an oven at 110°±1°C for 2 hours. Cool the smaple in the desiccator and weigh. Run samples in duplicate. Results should not vary by more than 5%.

### 4.2 Calculations

4.2.1 Wt. paint = Wt. aluminum dish with paint - Wt. aluminum dish

4.2.2 Wt. of Nonvolatile = Wt. aluminum dish with solid - Wt. aluminum dish

4.2.3 Wt. % of Nonvolatile in paint

$$= \frac{\text{Wt. of nonvolatile}}{\text{Wt. of paint}} \times 100$$

4.2.4 Wt. % Total Volatile in paint = 100 - Wt. % of nonvolatile

### 4.3 Sample Preparation by Simple Distillation

4.3.1 Assemble the simple distillation apparatus as shown in Fig. III-14.

4.3.2 Take the Erlenmeyer flask and the 50 ml graduated cylinder out of the assembled apparatus and weigh them accurately.

4.3.3 To a weighed flask, add approximately 50 ml of paint. Accurately weigh the flask and reassemble the apparatus.

4.3.4 Place the Erlenmeyer glask in a Glas-col heater. Wrap the exposed Erlenmeyer flask and the connecting adapter with glass wool, to minimize the condensation of water vapor at the distilling head.

4.3.5 Connect the Glas-col heater to a powerstat. Turn the powerstat on and gradually heat the distilling flask until the head temperature is 110°C. Stopdistillation when the head temperature starts to exceed 110°C. Remove glass wool and the Glas-col heater from the flask and cool to room temperature. Weigh the graduated cylinder containing the distillate. Record the weight and volume of the distillate. Weigh the flask with the nonvolatile.

4.4 Calculations of the Distillation

4.4.1 Wt. of paint = Wt. flask with paint - Wt. of flask

4.4.2 Wt. Distillate = Wt. grad. cyl and distillate - Wt. grad. cyl

4.4.3 $\text{Wt. of 1 cc of distillate} = \dfrac{\text{Wt. distillate}}{\text{Volume of distillate}}$

4.4.4 $\text{Wt. \% distillate in paint} = \dfrac{\text{Wt. distillate}}{\text{Wt. of paint}} \times 100$

4.4.5 Wt. Nonvolatile = Wt. flask and nonvolatile - Wt. flask

4.4.6 $\text{Wt. \% Nonvolatile} = \dfrac{\text{Wt. of nonvolatile}}{\text{Wt. of paint}} \times 100$

4.4.7 Wt. % Recovery = Wt. % distillate in paint + Wt. % nonvolatile

The distillation recovery must be 100 ±5% to be acceptable.

4.5 Determination of Water Content (% W/W) of the Distillate by Gas Chromatography.

4.5.1 General Column and Instrument Parameters:

Column: 6' x 1/4" Porapak Q, 80/100 mesh

| | |
|---|---|
| *Injection temperature | 200°C |
| Detector (T.C) temperature | 240°C |
| Column temperature | 150°C |
| He gas flow | 100 cc/min |
| Filament current | 190 ma |
| Sample size | 2 µℓ |

*glass insert is used in the injector port.

4.5.2 Transfer the distillate from the graduated cylinder into a capped container. Mixed the distillate thoroughly. Pipet 1.0 ml of distillate into a weighed 25 ml volumetric flask. Reweigh the flask containing the distillate. Add to the distillate 10.0 ml of anhydrous methanol and reweigh the flask. Stopper the flask and mix the solution thoroughly.

4.5.3 Using a 10 µℓ syringe, inject 2 µℓ of the distillate/methanol mixture into the gas chromatograph. To determine the percentage of water in the above mixture, compare the peak height of the sample versus a standard curve(Section 6).

4.6 Calculations

4.6.1 Wt. methanol = Wt. flask with distillate and methanol - Wt. flask with distillate

4.6.2 Wt. of distillate/methanol mixture =

Wt. of distillate + Wt. of methanol

4.6.3 Determine Wt. % of water in distillate/methanol mixture from the standard curve (4.5.3).

4.6.4 Wt. of water in mixture = (4.6.2) x (4.6.3)

4.6.5 Wt. % of water in distillate = $\frac{(4.6.4)}{(4.4.3)} \times 100$

4.6.6 Total weight of water in distillate =

$$\frac{\text{Wt. \% Water in distillate}}{100} \times \text{Wt. of distillate}$$

4.6.7 Wt. % of water in paint = $$\frac{\text{Total Wt. of Water in distillate}}{\text{Wt. of paint}} \times 100$$

4.7 Determination of Specific Gravity

4.7.1 Accurately weigh a 25 ml volumetric flask ($W_1$).

4.7.2 By means of a disposable Beral pipette transfer a well mixed sample the foating to the 25 ml volumetric flask. Fill precisely to the 25 ml graduation mark.

4.7.3 Reweigh the test tube ($W_2$).

4.7.4 Samples should be run in duplicate and agree to within ±1%.

4.8 Calculation of Specific Gravity

$$\text{Specific Gravity} = \frac{W_2 - W_1}{25 \text{ cc}} = \text{density (g/cc)}$$

4.9 Alternately, the specific gravity may be determined using reference 7.3.

## 5. COMPLIANCE CALCULATION

5.1 Wt. of volatile organic material per liter of coating without water =

$$\frac{\left[(4.2.1 - 4.2.2) - (4.6.7)(4.2.1)(10^{-2})\right] \times 1000 \text{ cc}}{(4.2.1)\left(\frac{1}{\text{Spec. Grav.}} - (4.6.7)(10^{-2})\right) \times \text{liter}}$$

## 6. PREPARATION OF THE STANDARD CURVE

6.1 Using methanol as the diluent, make up a series of water standards in 25 ml volumetric flasks to contain: 0.5, 1.0, 5.0, 10.0 and 15.0 % W/W water.

6.2 Using a 10 μℓ syringe, inject 2 μℓ of each standard into the gas chromatograph. From the resulting chromatograms construct a standard curve by plotting the average recorder peak height of triplicate analyses versus % water (W/W) on a rectilinear graph paper. The curve is linear to approximately 25% W/W water.

## 7. REFERENCES

7.1 Hollis, O.L., "Separation of Gaseous Mixtures Using Porous Poly Aromatic Polymer Beads", Anal. Chem. 38, 309, 1966.

7.2 "Volatile Content of Paint", ASTM designation D2369-73, Book of ASTM Standards, Part 27, 444-445, 1975.

7.3 "Density of Paint, Varnish, Lacquer and Related Products", ASTM designation ASTM D1475-60, Book of ASTM Standards, Part 27, 233-235, 1975.

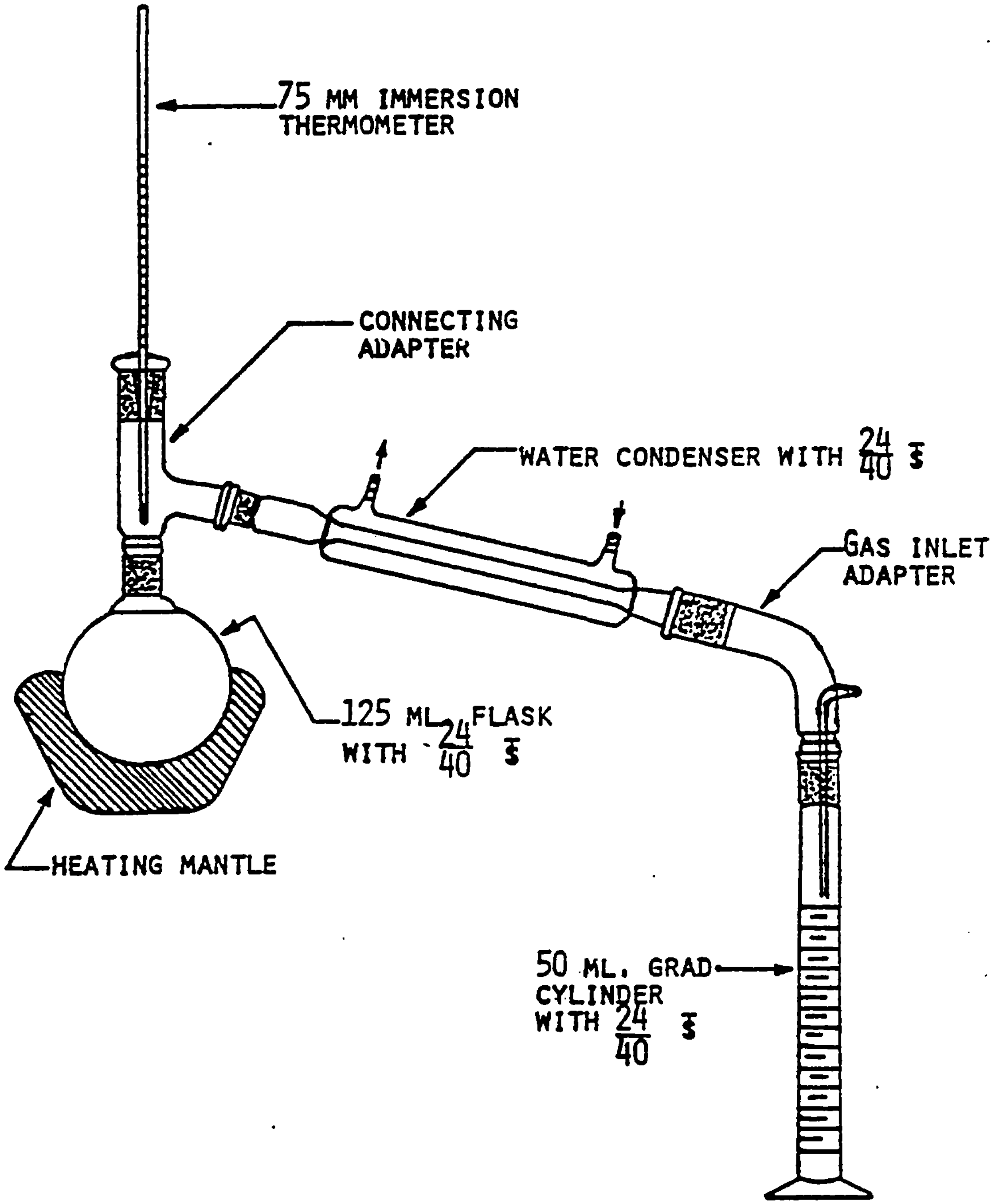


FIG. III-14

SIMPLE DISTILLATION UNIT

# LAB 22

REF: Regs. 8-3-301, 8-3-302

## DETERMINATION OF COMPLIANCE FOR AIR-DRIED ARCHITECTURAL OIL BASED COATINGS

### 1. PRINCIPLE

A weighed sample of paint or related product is refluxed with toluene to determine the water content of the sample. The apparatus consists of a glass flask, heated by suitable means and provided with a reflux condenser discharging into a trap connected to the flask. The trap serves to collect and measure the condensed water. The volatile content of the coating is determined on a separate aliquot of the sample. This method is applicable only to oil based paints containing less than 2% W/W water.

### 2. APPARATUS

2.1 Refluxing unit as shown in Fig. III-15

2.2 Powerstat ( 0 to 110 volts)

2.3 Analytical Balance

2.4 Drying Tube. A glass drying tube of the calcium chloride type.

2.5 Aluminum Foil Dish. Use a 58 mm diameter x 10 mm high dish with a flat bottom. The dish is available from Curtin Matheson Co. (Cat. No. 079-053).

2.6 Drying Oven (110°±1°C)

2.7 Triple Beam Balance, ±0.1 g capability

2.8 Disposable Beral Pipette. These are available from Curtin Matheson Co. (Cat. No. 376-970).

### 3. REAGENTS

3.1 Toluene

3.2 Calcium chloride

## 4. ANALYTICAL PROCEDURE

### 4.1 Determination of Total Volatile Content

4.1.1 Weigh accurately 0.4 to 0.6 g (±0.0001 g) of paint in a weighed aluminum dish. Disperse the paint with 2 ml of toluene by swirling the dish until the sample is even distributed at the bottom of the dish. Dry the sample in the oven at 110±1°C for two hours. Cool the sample in a desiccator and weigh. Run samples in duplicate. Results should not vary by more than 5%.

### 4.2 Calculations

4.2.1 Wt. paint = Wt. Aluminum dish with paint - Wt. Aluminum dish

4.2.2 Wt. of Nonvolatile in paint = Wt. Aluminum dish with solid - Wt. Aluminum dish

4.2.3 Wt. % of Nonvolatile in paint $= \dfrac{\text{Wt. of Nonvolatile in paint}}{\text{Wt. of paint}} \times 100$

4.2.4 Wt. % Total Volatile in paint = 100% - Wt. % of Nonvolatile in paint

### 4.3 Determination of Water Content

4.3.1 Add approximately 100 g of the coating to a weighed 500 ml flask. Record the weight of the sample using a triple beam balance and weigh to the nearest 0.1 g. Add 75 ml of toluene, mix thoroughly by swirling.

4.3.2 Connect the flask, trap and condenser are shown in Fig. III-15. A drying tube of calcium chloride is inserted at the top of the condenser tube to prevent condensation of atmospheric moisture in the condenser tube.

4.3.3 Apply heat to the flask by means of a heating mantle regulated by a powerstat. The condensed distillate should fall from the end of the condenser to the trap at a rate of 2 to 5 drops per second.

4.3.4 Continue the refluxing at the specified rate, until water is no longer visible on any part of the apparatus and the volume of water in the trap remains constant. Read the volume of water in the trap and record.

4.4 Calculation of Water Content

$$\% \text{ W/W water in paint} = \frac{\text{ml of } H_2O \text{ in trap}}{\text{wt. of paint refluxed}} \times 100$$

4.5 Determination of Specific Gravity

4.5.1 Accurately weigh a 25 ml volumetric flask ($W_1$).

4.5.2 By means of a disposable Beral pipette transfer a well mixed sample of the coating to the 25 ml volumetric flask. Fill precisely to the 25 ml graduation mark.

4.5.3 Reweigh the volumetric flask ($W_2$).

4.5.4 Sample should be run in duplicate and agree to within ±1%.

4.6 Calculation of Specific Gravity

$$\text{Specific Gravity} = \frac{W_2 - W_1}{25 \text{ cc}} = \text{density (g/cc)}$$

4.7 Alternately, the specific gavity may be determined using reference 6.3.

## 5. COMPLIANCE CALCULATION

5.1 If no water was found in the coating:

$$\text{Wt. of volatile organic material per liter of coating} = \frac{(\text{Wt. of paint} - \text{Wt. of Nonvolatile in paint})(1000)(\text{Spec. Grav.})}{\text{Wt. of paint}}$$

5.2 If water was found in the coating:

Wt. of volatile organic material per liter of coating without water =

$$\frac{\left[(4.2.1 - 4.2.2) - (4.4)(4.2.1)\ (10^{-2})\right] \text{x } 1000 \text{ cc}}{4.2.1 \left( \dfrac{1}{\text{Spec. Grav.}} - (4.4)\ (10^{-2}) \right) \quad \text{x liter}}$$

## 6. REFERENCES

6.1 "Water in Paint and Paint Related Products" (Reflux Method). Method 4081 of the Federal Test Method Standard 141a.

6.2 "Volatile Content of Paint". ASTM designation D2369-73, Book of ASTM Standards, Part 27, 444-445, 1975.

6.3 "Density of Paint, Varnish, Lacquer and Related Products". ASTM designation ASTM 4175-60. Book of ASTM Standards, Part 27, 233-235, 1975.

# LAB 23

REF: Reg. 8-4-111

## DETERMINATION OF VOLATILE WEIGHT LOSS OF POLYESTER RESINS

### 1. PRINCIPLE

A pour pan method is used, where a weighed amount of polyester resin is reacted with methyl ethyl ketone peroxide (MEKP) catalyst to form a 4" x 1/4" thick casting. The volatility loss is determined at room temperature (75±3°F) over a three hour period, with samples having a gel time between 15 to 20 minutes.

This method is applicable only to polyester resins and does not simulate spray booth operations.

### 2. APPARATUS

2.1 Analytical balance

2.2 4" x 1/2" can lid or equivalent. The lid must be capable of containing about 100 cc volume to which an accurate amount of catalyst can be added.

2.2.1 Stirring rod, glass or metal

2.3 Clock or timer

2.4 8 oz wide mouth bottles

### 3. REAGENT

3.1 Polyester Resin

3.2 Methyl Ethyl Ketone Peroxide (MEKP)

### 4. DETERMINATION OF GEL TIME

4.1 To a tared 8 oz wide mouth bottle (2" in diameter), containing a glass or metal stirring rod, add 100 g (±0.1 g) of polyester resin.

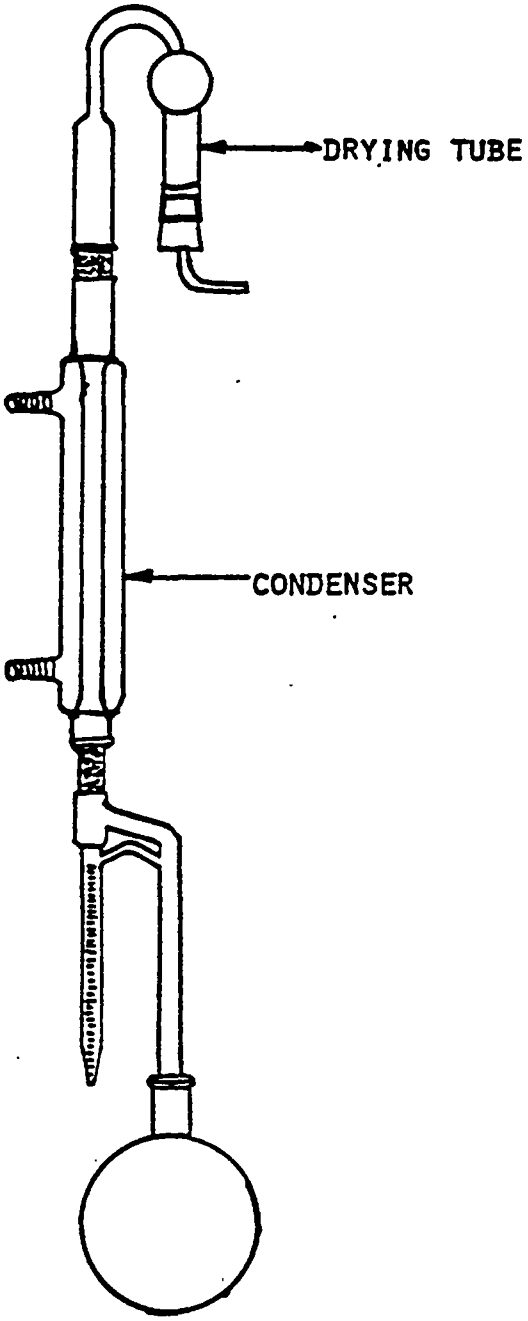


Fig. III-15
REFLUX UNIT

4.2 To the polyester resin, add 1.0 g (±0.1 g) of MEKP. Record the time and thoroughly mix for 30 seconds.

4.3 Periodically mix the contents until it commences to thicken. When the resin thickens, dip and remove the stirrer four times a minute until the resin strings or snaps from the stirrer. This is the gel time. Record the time to the nearest minute. Note: If the gel time does not correspond to 15 to 20 minutes, a catalyst adjustment is necessary for the sample to conform to the required gel time. If the gel time is between 15 to 20 minutes proceed with Section 5.

4.4 Gel Time Adjustment. A catalyst adjustment is necessary whenever the gel time varies from the appropriate 15 to 20 minutes. Additonal catalyst lowers the gel time. Variations in relative gel times with different catalyst additions are listed below and serve as a guide for obtaining the proper gel time.

| % MEKP Catalyst Added | Approximate Gel Time |
|---|---|
| 1.00 | 40 minutes |
| 1.50 | 30 minutes |
| 2.00 | 20 minutes |

If for example a sample using 1% W/W MEKP catalyst has a gel time of 40 minutes, an additional 1.0% MEKP catalyst should reduce the gel time to approximately 20 minutes.

## 5. DETERMINATION OF VOLATILE ORGANICS

5.1 Tare weigh a 4" x 1/2" metal lid or equivalent, containing a stirring rod to ±0.01 g. Record the weight as $W_1$.

5.2 Add approximately 50 ml (50 g) of polyester resin to the metal lid, to form a 1/4" thick casting. Record the weight of the lid plus the polyester resin to ±0.01 g as $W_2$.

5.3 Add 0.5 g ±0.01 g of MEKP catalyst to the polyester resin. Record weight as $W_3$. If a gel time adjustment was necessary, then the MEKP used must be in the same ratio to the polyester resin as was determined in Section 4.4.

5.4 After addition of the catalyst record the time. Thoroughly mix the catalyst into the polyester resin by means of the stirring rod for 30 seconds at room temperature (75±3°F). Note: The mixing and catalyzation volatility loss should be done in a hood or well ventilated area.

5.5 Periodically weigh the polyester resin content to determine the wiehgt loss per unit time. At least three weighings should be made during the first 30 minutes of the test. Record all weight losses with the attendant time lapse as $W_t$.

5.6 Continue the weight loss determinations for 3 hours, taking periodic temperature readings and weighings every 30 minutes. After 3 hours, record the final weight as $W_f$. Note: Periodic weight loss readings are taken to give an indication of the rate loss of the volatile organic compounds.

## 6. CALCULATIONS

6.1 To determine the percent loss of volatile organics after time t.

$$\text{\% Volatile Organics Loss} = \frac{W_3 - W_t}{W_3 - W_1} \times 100$$

6.2 To determine the percent loss of volatile organics for compliance purposes:

$$\% \text{ Volatile Organics Loss} = \frac{W_3 - W_f}{W_3 - W_1} \times 100$$

Where $W_1$ = Tare weight of lid plus stirrer

$W_3$ = Tare weight plus the polyester and MEKP

$W_t$ = The weight of the contents of $W_3$ after t minutes have elapsed in the experiment.

$W_f$ = The weight of the contents of $W_3$ after the required 3 hours have elapsed in the experiment.

## LAB 24

REF: Regs. 10-1-301,
12-5-301

## DETERMINATION OF TOTAL FLUORIDE IN EFFLUENTS

### 1. PRINCIPLE

Gaseous and water soluble particulate fluorides are collected in a dilute akaline solution. The absorved fluorides are quantified by the use of a fluoride specific ion meter. A buffer solution containing a chelating agent is used to prevent possible interferences from aluminum, iron and hydroxyl ions.

### 2. APPARATUS

2.1 Orion Specific Ion Meter (Model 407A)

2.1.1 Sleeve-type Reference Electrode (Orion No. 90-01-00)

2.1.2 Fluoride Ion Electrode (Orion No. 94-09)

2.2 Magnetic stirrer and teflon stirring bar (2.5 cm)

2.3 Polyethylene beakers, 100 ml

2.4 Polyethylene 1 liter volumetric flask

### 3. REAGENTS

3.1 Sodium Fluoride

3.2 Total Ionic Strength Adjustment Buffer (TISAB)

3.2.1 Dissolve 228 ml of glacial acetic acid, 232 g of sodium chloride and 4 g of CYTA (1,2, cyclo-hexylene-dinitrilo) Tetraacetic Acid in a 4 liter beaker containing approximately 2000 ml of distilled water.

3.2.2 Slowly add, with stirring, 160 ml of 50% sodium hydroxide solution while cooling the beaker in an ice bath. Allow the solution to come to room temperature and adjust the pH to between 5.0 and 5.5 using 50% sodium hydroxide solution.

3.2.3 Transfer the solution into a 4 liter bottle and bring to volume with distilled water.

3.3 Sodium Hydroxide Solution (0.1 N). Dissolve 4.0 g of sodium hydroxide pellets in 1 liter of distilled water.

## 4. ANALYTICAL PROCEDURE

4.1 Measure and record the total volumes of each impinger.

4.2 Transfer a 15.0 ml aliquot of sample to a 100 ml polyethylene beaker containing a teflon stirring rod, and add 15.0 ml of the TISAB solution.

4.3 Calibrate the ion meter as described in Section 6.

4.4 Immerse the ion meter electrodes into the prepared sample and stir the solution slowly. Reocrd the μg fluoride reading after a constant reading has been obtained.

4.5 All sample readings must be bracketed between the calibration standards. If the sample reads less than the 1.0 μg F standard, report the result as traces found.

4.5.1 Sample readings greater than 10 μg F must be diluted with a solution containing equal amounts of TISAB and 0.1 N sodium hydroxide to be in the range of the calibration standards. Alternately, a smaller aliquot of the impinger may be taken and brought to 15.0 ml with 0.1 N sodium hydroxide. Add 15.0 ml of TISAB and proceed as in 4.4.

4.6 The ion meter should be recalibrated periodically with the middle range calibration standard. Rechecking after every tenth sample has been found to be adequate.

## 5. STANDARD PREPARATION

### 5.1 Standard Stock Fluoride Solution

Weigh and transfer 0.2210 g of sodium fluoride to a 1 liter volumetric flask. Dissolve in distilled water and bring to volume. This solution contains 100 µg of fluoride ion per ml. This solution is stable for one year when stored in a plastic bottle.

### 5.2 Working Standard Fluoride Solutions

Three standards, respectively 1.0, 5.0 and 10.0 µg F/ml are prepared by the appropriate dilution of the standard stock fluoride solution with distilled water. These standards if stored in plastic bottles are stable for six months.

## 6. CALIBRATION OF THE ION METER

6.1 Prepare three calibration fluoride solutions containing 1.0, 5.0, and 10.0 µg as follows:

6.1.1 The 1.0 µg calibration standard is made by pipetting 1.0 ml of the 1.0 µg F/ml standard (5.2) into a 100 ml polyethylene beaker and adding 14.0 ml of 0.1 N sodium hydroxide.

6.1.2 The 5.0 µg calibration standard is made by pipetting 0.5 ml of the 10.1 µg F/ml standard (5.2) into a 100 ml polyethylene beaker and 14.5 ml of 0.1 N sodium hydroxide.

6.1.3 The 10.0 µg calibration standard is made by pipetting 1.0 ml of the 10.0 µg F/ml standard (5.2) into a 100 ml polyethylene beaker and adding 14.0 ml of 0.1 N sodium hydroxide.

6.2 The Ion meter is calibrated using the three calibration standards (6.1.1 - 6.1.3), each with 15.0 ml of TISAB having been added, as described in the instrument manual. It is important to maintain a constant slow stirring rate when the electrodes are immersed in the calibration solutions. Rinse the electrodes and blot dry with clean tissue between readings to prevent solution carry over.

## 7. CALCULATIONS

7.1 $$\frac{\text{*Total µg F}}{\text{Impinger}} = \frac{(\text{µg F, Meter Reading})\ (\text{Impinger Vol. ml})}{\text{Aliquot (ml)}}$$

*If the sample was diluted to be within the calibration standards, the calculation must be multiplied by the appropriate dilution factor.

7.2 Total µg F = µg F Imp I + µg F Imp II

## 8. REFERENCE

8.1 Orion Analyzer Instruction Manual for Model 407A. Orion Research Inc., Cambridge, Mass.

8.2 40 CFR 60.275 Appendix A, Method 13B. "Determination of Total Fluoride Emissions from Stationary Sources - Specific Ion Electrode Method".

REF: Reg. 10-8-303

## DETERMINATION OF HYDROGEN SULFIDE IN EFFLUENTS

### 1. PRINCIPLE

The hydrogen sulfide is absorbed in an alkaline cadmium hydroxide solution to form cadmium sulfide. The precipitated cadmium sulfide is then dissolved in hydrochloric acid and absorbed in a known volume of iodine solution. The iodine consumed is a measure of the hydrogen sulfide content of the effluent.

### 2. APPARATUS

2.1 Buret, 0 to 50 ml

2.2 Iodine flask, 500 ml

### 3. REAGENTS

3.1 Absorbing Solution. Dissolve 4.3 g cadmium sulfate hydrate $CdSO_4.8H_2O$ and 0.3 g of sodium hydroxide in 1 liter of distilled water. Mix the cadmium hydroxide suspension thoroughly before using the absorbing solution.

3.2 Hydrochloric Acid Solution (10% W/W). Dilute 230 ml of concentrated hydrochloric acid to 1 liter with distilled water.

3.3 Iodine Solution (0.1 N). Dissolve 24 g of potassium iodide in 300 ml of distilled water in a 1 liter graduated cylinder. Weigh 12.7 g of resublimed iodine into a weighing bottle and transfer to the potassium iodide solution. Mix until the iodine is completely dissolved. Slowly dilute the solution to 1 liter with distilled water and transfer to a brown glass stoppered bottle.

3.4 Standard Iodine Soltuion (0.01 N). Dilute 100 ml of the 0.1 N iodine solution (3.3) in a volumetric flask to 1 liter with distilled water. Standardize before using as follows: pipette 25.0 ml of the 0.01 N iodine solution into a 125 ml flask. Titrate with standard 0.01 N thiosulfate solution to a light yellow color. Add a few drops of starch solution, and continue the titration until the blue color just disappears. From the results of this titration, calculate the exact normality of the iodine solution (5.1).

3.5 Standard Thiosulfate Solution (0.1 N). For each liter of solution, dissolve 24.8 g sodium thiosulfate hydrate ($Na_2S_2O_3 \cdot 5H_2O$) and 0.10 g sodium carbonate in distilled water. Standardize the solution as follows: weigh and transfer approximately 2 g of potassium dichromate (to the nearest .0001 g) to a 500 ml volumetric flask. Dissolve and dilute to volume with distilled water. Dissolve approximately 3 g of potassium iodide in 50 ml of distilled water contained in an iodine flask; then add 10 ml of 10% hydrochloric acid solution. Pipette 50.0 ml of the dichromate solution into the same iodine flask, swirl once gently and allow to stand in the dark for 5 minutes. Add approximately 150 ml of distilled water, swirl, and immediately titrate with the thiosulfate solution to a light yellow color. Add 2 ml of starch solution and titrate until the blue color disappears and a pale green color remains. From duplicate titrations, calculate the exact normality of the sodium thiosulfate solution (5.2).

3.6 Sodium Thiosulfate Standard (0.01 N). Pipette 100.0 ml of the standard 0.1 N thiosulfate (Par. 3.5) into a volumetric flask and dilute to 1 liter with distilled water. Calculate the exact normality of this solution by dividing the determined normality of 0.1 N thiosulfate (Par. 3.5) by 10.

3.7 Starch Indicator Solution. This solution is commercially available.

## 4. ANALYTICAL PROCEDURE

4.1 Transfer the contents of each Greenburg-Smith impinger into separate 500 ml iodine flasks. Pipetter 50.0 ml of the 0.01 N iodine solution into the empty impinger. Add 50 ml of 10% hydrochloric acid to the impinger and contact the sides of the impinger thoroughly. Transfer the acidified iodine solution to the iodine flask containing the sample. Give the impinger two additional rinses of 25 ml if distilled water, adding each rinse water to the iodine flask.

4.1.1 Titrate the solution in the iodine flask with 0.01 N thiosuflate to a light yellow color. Add a few drops of starch indicator solution and continue titrating till disappearance of the blue color. Record the volume of thiosulfate used.

4.1.2 Prepare a blank in an iodine flask using 100 ml of absorbing solution, 50.0 ml of 0.01 N iodine solution and 50 ml of 10% hydrochloric acid.

4.1.3 Titrate the blank in the same manner as the sample.

## 5. CALCULATIONS

5.1 Normality of the Iodine Solution

$$N = \frac{\text{(Normality of Thiosulfate) (Volume of Thiosulfate)}}{\text{ml of Iodine}}$$

5.2 Normality of the Standard Thiosulfate

$$N = \frac{2.04\ (W)}{\text{ml of Thiosulfate}}$$

Where W = Weight of potassium dichromate (g)

$$2.04 = \frac{(6\ \text{Eq. } I_2/\text{Mole } K_2Cr_2O_7)\ (1000\ \text{ml/l})}{(294.2\text{g}K_2Cr_2O_7/\text{Mole})(10\ \text{Aliquot factor})}$$

5.3 mg $H_2S$ in each impinger

$$\text{mg } H_2S = 17 \left[ (V_I N_I - V_T N_T)\ \text{Samp.} - (V_I N_I - V_T N_T)\ \text{blank} \right]$$

$$\text{Where } 17 = \frac{(34.07\ \text{g/Mole } H_2S)(1000\ \text{mg/g})}{(1000\ \text{ml/l})\ (2\ H_2S\ \text{Eq./Mole})}$$

Total mg $H_2S$ = mg $H_2S$ 1st Imp. + mg $H_2S$ 2nd Imp. + mg $H_2S$ 3rd Imp.

## 6. REFERENCE

6.1 40 CFR 60.275 Appendix A, Method 11. "Determination of Hydrogen Sulfide Emissions From Stationary Sources".

# MANUAL OF PROCEDURES

## VOLUME IV

## SOURCE TEST POLICY AND PROCEDURES

MANUAL OF PROCEDURES

VOL. IV

SOURCE TEST POLICY AND PROCEDURES

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- 1.5 Tests Conducted by Other Persons
- 1.6 Process Information
- 1.7 Applicability

2. SOURCE TEST PROCEDURES

| Number | Subject |
|---|---|
| ST-1A | Ammonia |
| ST-1B | Ammonia, Continuous Sampling |
| ST-2 | Beryllium Sampling |
| ST-3 | Bulk Gasoline Transfer Plants (500-20, 000 GPD) |
| ST-4 | Bulk Gasoline Loading Terminals |
| ST-5 | Carbon Dioxide, Continuous Sampling |
| ST-6 | Carbon Monoxide, Continuous Sampling |
| ST-7 | Non-Methane Organic Carbon Sampling |
| ST-8 | Dimethylsulfide Sampling |

| | |
|---|---|
| ST-9 | Lead Sampling |
| ST-10 | Mercury Sampling |
| ST-11 | Mercaptans, Integrated Sampling |
| ST-12 | Collection of Odorous Samples |
| ST-13A | Oxides of Nitrogen, Continuous Sampling |
| ST-13B | Oxides of Nitrogen, Integrated Sampling |
| ST-14 | Oxygen, Continuous Sampling |
| ST-15 | Particulates Sampling |
| ST-16 | Phenolic Compounds Sampling |
| ST-17 | Stack Gas Velocity and Volumetric Flowrate |
| ST-18 | Stack Traverse Point Determination |
| ST-19A | Sulfur Dioxide, Continuous Sampling |
| ST-19B | Sulfur Oxides, Integrated Sampling |
| ST-20 | Sulfur Dioxide, Sulfur Trioxide and Sulfuric Acid Mist |
| ST-21 | Total Reduced Sulfur Sampling |
| ST-22 | Trimethylamine Sampling |
| ST-23 | Water Vapor Sampling |
| ST-24 | Evacuated Cylinder Sampling for Orsat Analysis (CO, $CO_2$, $O_2$) |
| ST-25 | Fluoride, Integrated Sampling |
| ST-26 | Coke Burn-Off Rate |
| ST-27 | Pressure Drop, Phase II, Gasoline Vapor Recovery |
| ST-28 | Hydrogen Sulfide, Integrated Sampling |

# 1. SOURCE TEST POLICY

## 1.1 Introduction

The purpose of this volume of the Manual of Procedures is to advise persons subject to the Regulations of the Bay Area Air Quality Management District of the policy of the Air Pollution Control Officer relative to source testing and to promulgate procedures used to determine compliance with the regulations of this District.

Source Test methodology is a state of the art practice and therefore occasional changes will be made to this volume. A form has been provided in the front of this volume for those who wish to receive these periodic changes.

The contents of this Manual, and its subsequent changes, are subject to approval by the Board of Directors of this District, and therefore, become law as provided for in the Health and Safety Code of the State of California.

1.2 Definitions: The definitions used herein are consistent with those used in the regulations of the District. The definitions of type "A" and "B" sample points are expanded for clarification.

1.2.2 Representative Sampling: The over-riding factor for all source tests shall be that every reasonable effort must be made to obtain samples that are truly representative of the source being tested for that given set of process variables. In all cases accepted engineering practice shall be followed for all test procedures.

1.2.3 Sampling Points: The sampling point is the location on a source or its related control equipment where samples are taken. For purposes of determining compliance with District Regulations, samples taken at a sampling point shall be deemed identical to those at the point of emission to the atmosphere. The Regulations address themselves to type "A" and "B" emission points.

The primary consideration for locating a sample port shall be that the sample port location accurately represents the nature, extent, quantity and degree of the contaminant at the emissions point. Ports shall be located, if reasonably possible, at a type "A" sample point.

1.2.3.1 Sampling at type "A" emission points. A type "A" sample point shall be located in a smooth stack at least eight stack diameters downstream of any bends, inlets, constriction, flow altering device or change of area or geometry and two diameters upstream of the stack exit or other flow disturbance. For a non-circular duct, the equivalent diameter will be determined from the following equation:

$$\text{Equivalent Diameter} = 2\,\frac{\text{length} \times \text{width}}{\text{length} \times \text{width}}$$

1.2.3.2.Sampling at type "B" emission Points. A type "B" sample point means any sample point not qualifying as a type "A" emission point.

The quantity of emission from a type "B" emission point shall be the quantity of emission computed by multipying the quantity of emission from a test area by the proportion which the whole area bears to such test area. Such test area may be taken as the cross sectional area of the inlet to a sample probe. The emission from any test area of a type "B" emission point shall be deemed to be representative in every respect of the emissions from the entire area. Emissions from the test area may be measured at the place and by the procedure which result in the highest measurement of air contaminants.

1.2.4 Sampling Facilities: Section 1-410 of Regulation I places the burden of providing proper sampling facilities on the person responsible for the emission. The following are normally considered necessary:

1.2.4.1. Sample Ports: For circular ducts, at least two ports 90 degrees apart on a plane perpendicular to the longitudinal axis of the duct shall be installed at the sample point. For circular ducts, ten feet in diameter or greater, four ports ninety degrees apart on a plane perpendicular to the longitudinal axis shall be installed.

For non circular ducts, access shall be provided to the entire cross-sectional area of the duct.

Each port, where possible, shall be a nominal three inch diameter pipe with external tapered pipe threads.

Ports shall be installed flush with the interior stack wall.

Gate valves should be installed on sample ports only when extreme stack conditions or the presence of hazardous materials require such devices for safety considerations.

Questions concerning locations should be referred to the Chief of Source Test.

1.2.4.2 Sampling Area Clearance: There shall be sufficient clearance in the vicinity of each test port to allow the insertion of a probe equal in length to the stack diameter.

1.2.4.3 Safety: Sampling facilities, access ways and platforms shall meet all applicable OSHA requirements for industrial and personal safety and conform to any other relevant safety guidlines.

1.2.5 Quality Assurance: It is absolutely essential in any testing program that a quality assurance program be established and maintained. The provisions of Air Monitoring Quality Assurance Volume IV, Quality Assurance in the Testing of Stationary Sources, California State Air Resources Board shall apply.

1.2.5.1 Instrumental Methods: Specifications and procedures for zero and span checks on analytical instruments are in each test procedure. Where available, calibration gases shall be traceable to National Bureau of Standards reference materials. Confirmation of their values shall be made by reference procedures at intervals of not more than three months.

1.2.5.2 Recorders: Analog chart recorders must be compatible with instrument output.

1.2.5.3 Manual Methods: Sampling shall be conducted to compensate, where reasonably possible, for significant stratification and non-homogeneity in the gas stream, so that the sample of the gas stream approaches a representative sample.

All sampling lines shall be checked for the presence of condensation. If condensation has occurred, adjustments in procedure shall be made either to prevent it or to compensate for the condensed material in the sample line.

Sufficient test data and notes shall be recorded at the time of the test by the personnel conducting the sampling to permit the determination of emissions and to permit evaluation of results at a later date.

All sampling lines shall be leak-free. The distance between the sample gas inlet and the sample collection or analytical device shall be as short as feasible. The sampling lines shall be composed of inert materials. The sampling lines shall be purged thoroughly with sample gas prior to the taking of the sample.

Sampling equipment which comes in contact with the collected sample shall not alter the composition, and shall be used in such a manner that significant leaks can be detected.

1.3 Alternate Methods: EPA methods may be used alternately without prior approval. Alternate methods may be approved at the discretion of the Chief of Source Test. The burden of proof of equivalency is on the person seeking alternate status. Such alternate status may be granted on a "one-time only" basis. All such requests and supporting documentation shall be made in writing.

1.4 NSPS and NESHAPS Testing: The Bay Area Air Quality Management District has been delegated authority by the U.S. Environmental Protection Agency (EPA) to enforce the New Source Performance Standards (NSPS) and the National Emission Standards for Hazardous Air Pollutants (NESHAPS).

EPA requires that all testing for these standards use its methods unless alternate or equivalent status to it's methods has been granted. The District has been granted alternate status for the instrumental $SO_2$ and $NO_x$ procedures, ST-19A and ST-13A and the integrated sulfer oxide procedure, ST-20. EPA methods are published in Title 40 Code of Federal Regulations, Part 60, and are available from the U.S. Government Printing Office.

1.5 Tests Conducted by Other Persons: Any person who conducts a source test for the purpose of furnishing data to the Air Polluting Officer is Subject to the following conditions:

1.5.1 Notifications: The Chief of Source Test shall be notified at least one week prior to the date the test is to be conducted. Source Test Engineers from the District shall observe any such tests as deemed necessary.

1.5.2 Methodology: The procedures set forth in this volume shall be adhered to in any test except as provided in paragraph 1.3.

1.5.3 Data Presentation: Data shall be collected and presented in the format of the forms shown herein. All calculations shall be included and clearly identified.

1.5.4 Process Information: Where applicable, pertinent process data including rates during the test and maximum capacities shall be included in the data. Confidential information shall be clearly marked as such.

1.5.5 Test Review: Tests furnished the District shall be sent to the attention of the Source Test Section for review and disposition.

1.6 Confidentiality of Process Information:

Process information is a necessary part of any source test in that the test data represents those process conditions at the time of the test.

Source Test records are public information. However, proprietary information is not. Information of a confidential nature should be clearly labeled to insure proper treatment.

1.7 Applicability

Each test procedure is applicable to a specific regulation. The designation appears in the upper left hand corner of the procedure.

# Source Test Procedure ST-1A

# AMMONIA, CONTINUOUS SAMPLING

REF: Reg. 7-303

## 1. Applicability

1.1 This method is used to quantify emissions of ammonia. It determines compliance with Regulation 7-303.

## 2. Principle

2.1 A gas sample is extracted continuously from the sample point and conditioned to remove water and particulate matter. A stainless steel catalyst (at 750C) in a chemiluminescent analyzer converts ammonia ($NH_3$) and nitrogen dixoide ($NO_2$) to the analyzer. By determining the NO and $NO_2$ separately, the $NH_3$ concentration is determined by difference.

## 3. Range and Sensitivity

3.1 The minimum measurable concentration of $NH_3$ is 5% of the total oxides of nitrogen.

3.2 The minimum sensitivity of the analyzer shall be ±2% of full scale.

## 4. Interferences

4.1. Nitrogen bearing compounds (other than NO and $NO_2$) may cause interfeneces.

## 5. Apparatus

5.1 Chemiluminescent analyzer. Use a Thermo Electron Corp. Model 10A analyzer equipped with a stainless steel catalyst or its equivalent.

5.2 Chart recorder. The recorder monitors and records the continuous output from the analyzer.

5.3 Sample conditioning, zero air, and span gas system. The assembly of this system is shown in Fig. IV-1. The sample conditioning system provides a dry, particulate free gas flow to the instrument. The zero air system provides clean dry atmospheric air for instrument calibration. The span gas system provides a known concentration of nitric oxide for use in calibrating the analyzer. Except as specified, all materials which come in contact with either the sample or span gases must be constructed of Teflon or stainless steel.

5.4 Sample probe. Use a borosilicate glass tube of sufficient length to traverse the stack being tested. If the stack temperature exceeds 425C (800F), use a quartz probe. Other probes are acceptable subject to approval by the Source Test Section.

5.5 Condensers. Use modified Greenberg-Smith impingers with the impaction plates removed and the inlet tube shortened to a length of 10cm (4 inches), or equivalent.

5.6 Cooling system. Immerse the impingers in an ice bath during the test.

5.7 Particulate filter. Use a Balston type 95 holder with a grade B filter, or equivalent, in the sample system.

5.8 Pumps. Use leak-free, Teflon-lined, diaphragm pumps in the sample and zero air systems. The pumps must have a capacity of at least 40 liters/min(1.5 CFM) to 28 liters/min (1.0 CFM).

5.9 Back-pressure regulator. Use a back-pressure regulator to maintain the sample and zero gas sample pressures to the instrument at five psig.

5.10 Gas scrubber. Use a bed of silica gel, Ascarite (or soda-lime), and charcoal to remove moisture, carbon dioxide, and hydrocarbons from the zero air system.

5.11 Span gas. Use a high-pressure cylinder containing a known concentration of NO in nitrogen. The span gas concentration must be in the same range as the source being tested.

6. Pre-Test Procedures

6.1 Warm-up the instrument according to manufacturer's instructions.

6.2 Assemble the sampling system and analyzer as shown in Figs IV-1 and IV-2.

6.3 Leak-test the sampling system by starting the pump, plugging the probe, and determining that the pressure to the analyzer falls to zero. Other leak-tests are acceptable subject to the approval of the Source Test Section.

6.4 Introduce zero air, into the analyzer and zero the instrument according to manufacturer's instructions.

6.5 Introduce span gas into the analyzer and calibrate the instrument according to manufacturer's instructions.

6.6 Conduct a preliminary concentration traverse (according to ST-18) to determine if stratification of stack gases exists. If the $NH_3$ concentration at any point differs from the average concentration by more than 10%, traverse the stack during the test. If not, sample at any single point.

6.7 Set-up the chart recorder according to manufacturer's instructions.

7. Sampling

7.1 Each test run shall be of thirty minute duration when testing emissions from continuous operations. Each test run at batch process operations whall be for 90% of the batch time or thirty minutes, whichever is less.

7.2 Introduce sample gas into the analyzer at the same flow rate used to calibrate the analyzer.

7.3 Maintain ice in the cooling system throughout the test.

7.4 Calibrate the analyzer before and after each test run. Record each step of the process clearly on the chart recording.

7.5 Conduct three test runs.

8. Calculations

8.1 From the chart recording determine the time-averaged concentration of $NH_3$ on a dry basis for each run.

9. Reporting

9.1 Report the results indicated on Figure IV-3.

9.2 These values are also.....(see 11.1 of ST-24).

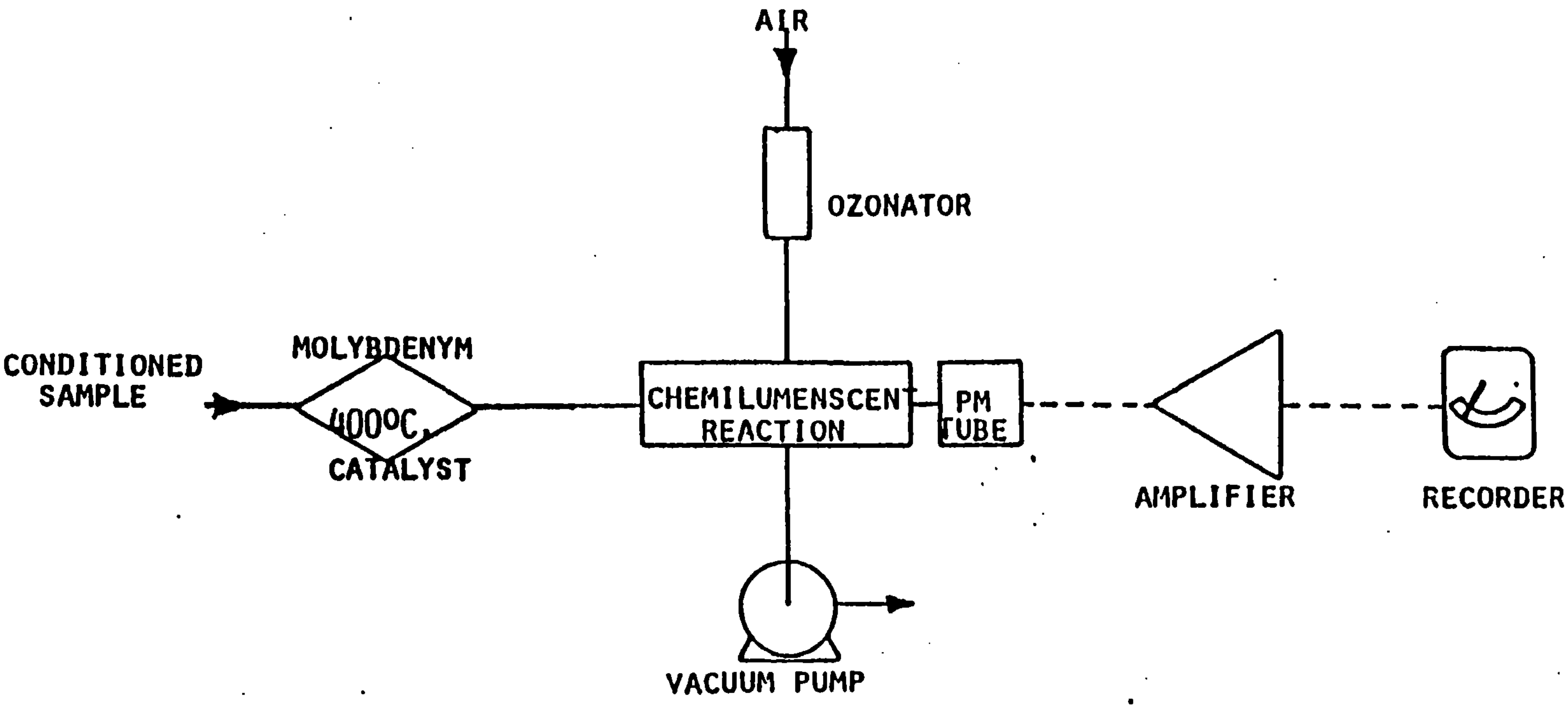

Fig. IV - 2

INSTRUMENTAL ANALYSIS OF AMMONIA

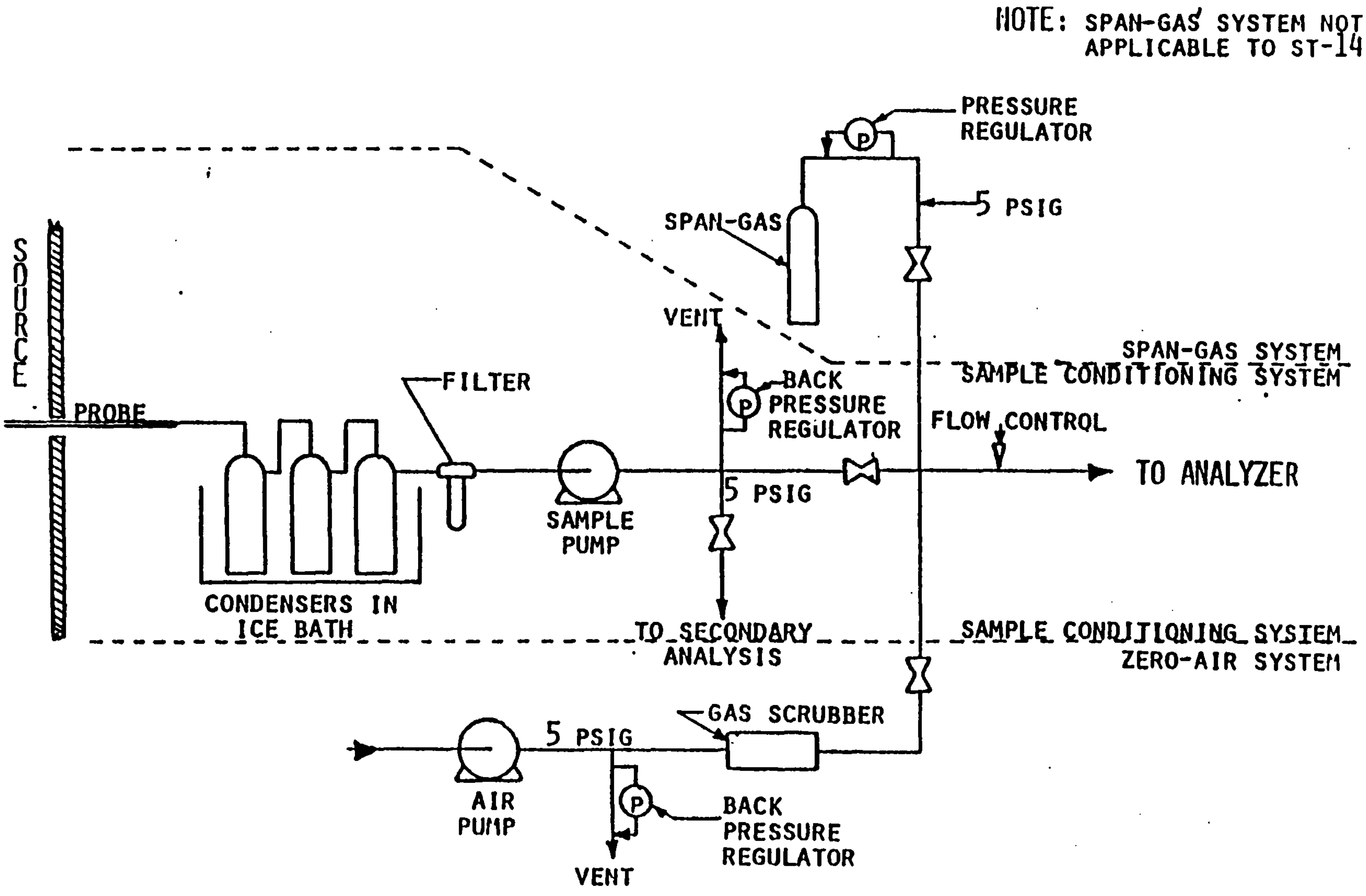

Fig. IV - 1

SAMPLE CONDITIONING, ZERO-AIR AND SPAN-GAS SYSTEMS

# SUMMARY OF SOURCE TEST RESULTS

## SOURCE INFORMATION

**Firm Name and Address**

**Firm Representative and Title**

**Phone No.**

**Source:**

**Conditions During Tests**

**Operates** hr/day & days/yr

**Operating Parameters**

**Report No.** ________________

**Test Date:** ________________

**Test Times:**

**Run A:** ________________

**Run B:** ________________

**Run C:** ________________

**Test Results and Comments**

| METHOD | TEST | RUN A | RUN B | RUN C | AVG. |
|---|---|---|---|---|---|
|  | Run time, minutes |  |  |  |  |
|  | Stack gas Temperature, °F. |  |  |  |  |
| -1A | Ammonia, ppm |  |  |  |  |

FIG IV-3

## Source Test Procedure ST-1B

## AMMONIA, INTEGRATED SAMPLING

REF: Reg. 7-303

### 1. Applicability

1.1 This method is used to quantify emissions of ammonia. It determines compliance with Reg. 7-303.

### 2. Principle

2.1 Sample gas is drawn through a solution of 0.1 normal (0.1N) hydrochloric acid which absorbs the ammonia..The ammonia is then analyzed according to Analytical Prodecure Lab-1.

### 3. Range

3.1 The minimum measurable concentration of ammonia is 1 ppm at the sample volume specified in this procedure.

3.2 Elevated concentrations of ammonia may be determined by increasing the concentration of the absorbing reagent, hydrochloric acid solution. The concentration of reagent to be used may be determined by stoichiometry, allowing a 50% excess.

### 4. Interference

None Known.

### 5. Apparatus

5.1 Probe. The probe is constructed of borosilicate glass tubing fitted with a glass wool filter in the nozzle.

5.2 Condensers. Use three Greenberg-Smith impingers as absorder/condensers. The final impinger has a thermometer attached to the inlet stem.

5.3 Cooling system. Use an ice bath to contain the impingers.

5.4 Sample pump. Use a leak-free vacuum pump capable of maintaining a 14.3 liter/min (0.5 CFM) flow rate at 15 inches of mercury. The pump must have a flow control valve and vacuum gauge attached to the inlet.

5.5 Silica gel tube. Use approximately 500cc of silica gel (with a Drierite indicator) to insure that the gas entering the dry test meter is dry.

5.6 Dry test meter. Use a dry gas test meter accurate within ±2% of the true volume and equipped with a thermometer to measure the outlet temperature.

5.7 Connections. Use Teflon tubing in making all connections that come in contact with the sample. Vinyl tubing is acceptable for all other connections.

5.8 Barometer. Use a barometer that is accurate to within ±0.2 inches of mercury.

5.9 Rotameter. Use a calibrated rotameter to measure the sampling rate.

## 6. Reagents

6.1 Hydrochloric acid, 0.1N. Dissolve 7.30 ml concentrated HCl in sufficient water to make a 1.0 liter solution.

## 7. Pre-Test Procedures

7.1 Add 100 ml of the HCl solution to each of two impingers.

7.2 Stopper the impingers.

7.3 Retain 100 ml of the HCl solution to analyze as a blank.

7.4 Assemble the sampling train as shown in Figure

7.5 Leak-test the sampling train by starting the pump, plugging the probe, and adjusting the pump inlet vacuum to 10 inches Hg. The leak rate must not exceed 0.6 liter/min (0.02 CFM) through the dry test meter. Before stopping the pump, carefully release the plug in the sample probe to avoid backflow of the impinger solution.

7.6 Record the initial dry test meter reading and barometric pressure on the sampling data sheet, Figure

7.7 If there is evidence of concentration stratification, select the sampling traverse points according to ST-18. Otherwise, sample at a single point.

## 8. Sampling

8.1 Each test run shall be of thirty minute duration when testing emissions from continuous operations. Each test run at batch process operation shall be for 90% of the batch time or thirty minutes, whichever is less.

8.2 Position the probe at the sampling point and start the pump.

8.3 Sample at a constant rate of 14.3 liter/min (0.5 CFM) during the test as determined by the rotameter. Use the rotameter only to establish the initial sampling rate. Then remove it from the system.

8.4 Record the following information at five-minute intervals.

Dry test meter temperature
Impinger outlet temperature
Dry test meter volume

8.5 Add ice as necessary to maintain impinger temperatures at 7°C (45°F) or less.

8.6 At the conclusion of each run, stop the pump, remove the probe from the stack, record the final meter reading. Point the probe upward and purge the sample train with ambient air.

8.7 Take three consecutive samplers.

## 9. Post-Test Procedures

9.1 Stopper the impingers until they are analyzed.

9.2 Individually analyze the hydrochloric acid solutions and blank for total ammonia content according to analytical procedure Lab 1.

## 10. Calculations

10.1 Standard sample volume:

$$V_o = \frac{17.71\ V_m P_b}{T_m}$$

Where:

$V_o$ = Corrected sample volume, SDCF at 70°F and 29.92 inches Hg.
$V_m$ = Uncorrected meter volume, $ft^3$
$T_m$ = Average run meter temperature, °R
$P_b$ = Barometric pressure, inches Hg.
17.71 = A constant correcting to 70F and 29.92 inches H

10.2 Ammonia concentration:

$$C = \frac{5.02 \times 10^4 W}{V_o}$$

Where:

C = ammonia concentration, ppm by volume on a dry basis.

W = total weight of ammonia in the impinger catch, for each run, grams.

$5.02 \times 10^4$ = a constant derived from the molecular weight and correcting to 70F and 29.92 inches Hg

## 11. Reporting

11.1 Report the data indicated on Figure IV-6 .

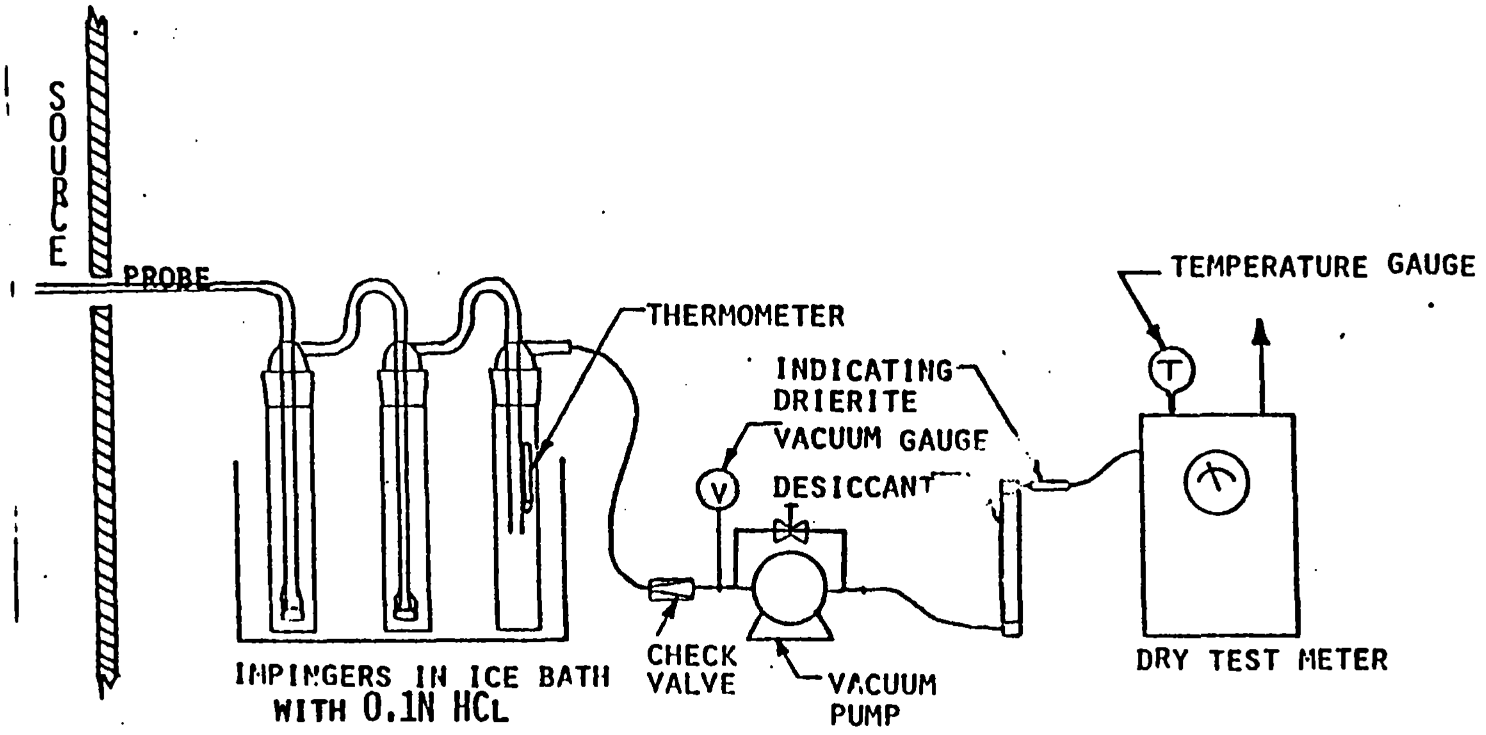

Fig. IV - 4

AMMONIA SAMPLING TRAIN

## Source Test Data Sheet

Source Operation __________
Plant __________
Sample Type __________
Process Cycle __________
Duct Size __________
Duct Pressure __________

Source Test No. __________
Run No. __________
Date: __________

__________ Nozzle Diameter
__________ Pitot Tube
__________ Gas Collector No.
__________ Barometric Pressu
__________ Leak Rate @ 15"Hg

Sampling Train:

| Traverse Point | Dist. From inches | INITIAL TRAVERSE |  |  | SAMPLING |  |  |  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  |  |  |  |  |  | METER |  |  |  |  |  |  |
|  |  | Duct Temp°F | h $H_2O$ | $\sqrt{h}$ | Traverse Point | h $H_2O$ | $V_s$ FPS | Time | Rate CFH | Temp °F | Volume $Ft^3$ | Vac "Hg | Sat'd Gas Temp°F | $T_s$ Duct Temp°F | REMARKS |
|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
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$$D_n = 13.7\left[\frac{T_s + 460}{K_p V_s (100-\%H_2O)}\right]^{1/2}$$

$$Q_m = \left[(2.638 \times 10^{-3}) K_p (100-\%H_2O) D_{mm}^2\right]\frac{V_s}{T_s}$$

Condensate ________ gm.
$V_o$ ________
$\%H_2O$ ________
$\%CO_2$ ________
$\%CO$ ________
$\%O_2$ ________

Source Test Team
__________
__________
__________
__________

FIG. IV-5

# SUMMARY OF SOURCE TEST RESULTS

## SOURCE INFORMATION

| | | |
|---|---|---|
| **Firm Name and Address** | **Firm Representative and Title**<br>**Phone No.** | |
| | **Source:** | **Report No.** |
| **Conditions During Tests** | **Operates hr/day & days/yr** | **Test Date:**<br>**Test Times:**<br>**Run A:** |
| **Operating Parameters** | | **Run B:**<br>**Run C:** |

**Test Results and Comments**

| METHOD | TEST | RUN A | RUN B | RUN C | AVG. |
|---|---|---|---|---|---|
| | Run time, minutes | | | | |
| | Stack gas Temperature, °F. | | | | |
| ST-1B | Ammonia, ppm | | | | |

FIG IV-6

# Source Test Procedure ST-2

## BERYLLIUM

REF:Reg. 11-3-301

### 1. Applicability

1.1 This procedure is used to quantify emissions of beryllium. It determines compliance with Regulation 11-3-301.

### 2. Principle

2.1 Particulate matter (including Beryllium)is withdrawn isokinetically from the stack gas stream and collected on filters in the stack. The weight of the beryllium collected is measured by atomic absorption spectrophotometry according to Analytical Procedure lab 2.

### 3. Range

3.1 The minimum measurable emission of beryllium is .001 gr/SDCF.

### 4. Interferences

None Known

### 5. Apparatus

5.1 Probe nozzle. The sampling train and its components are shown in Figure IV-7. The probe nozzle shall be constructed of borosilicate glass, quartz, or stainless steel.

5.2 Filter medium. Use Millipore Type "A" glass fiber disc type or equivalent.

5.3 Connections. The connection between the filters and the first impinger must be able to withstand stack temperatures. Vinyl tubing is acceptable in making all other connections.

5.4 Pitot tube. Use a Stauscheibe (Type-S), or equivalent, with a known coefficienct which is constant within ±5% over the entire working range, The pitot tube coefficient is determined by placing both the S-type and the standard pitot tube in a gas stream and measuring the pressure head with both over the entire velocity range of interest. Calculate the coefficient of the Type-S pitot tube as follows:

$$C_{P_s} = C_{P_{std}} \left[ \frac{\Delta P_{std}}{\Delta P_s} \right]^{\frac{1}{2}}$$

where:

$C_{P_s}$ = Type-S pitot tube coefficient

$\Delta P_s$ = Pressure head, Type-S pitot tube

$\Delta P_{std}$ = Pressure head, standard pitot tube

$C_{P_{std}}$ = Standard pitot tube coefficient

5.5 Temperature measuring device. Use a Chromel-Alumel thermocouple accurate to ± 15°F., connected to a temperature compensated null type potentiometer, or equivalent, to measure stack temperatures.

5.6 Condensers. Use three Greenberg-Smith impingers. The third impinger shall be modified by removing the impaction plate and attaching a thermometer to the inlet stem.

5.7 Cooling system. Use an ice bath to contain the impingers.

5.8 Sample pump. Use a leak-free vacuum pump capable of maintaining a 1.0 CFM flow rate at 15 inches of mercury. The pump must have a sample rate control valve and a vacuum gauge attached to the inlet.

5.9 Silica gel tube. Use approximately 500cc of silica gel, followed by a Drierite indicator, to insure that the gas entering the dry test meter is free of $H_2O$.

5.10 Dry test meter. Use a 175 CFH dry test meter accurate within ±2% of the true volume and equipped with a thermometer to measure the outlet temperature. The working pressure across the meter shall not exceed a one inch water column.

5.11 Rotameter. Use a calibrated rotameter to measure the sampling rate.

5.12 Pressure gauge. Use a Magnehelic differential pressure guage, or equivalent, in the same range as the velocity and static pressures being measured in the stack.

5.13 Analytical balance. An analytical balance capable of measuring condensate weights to the nearest 0.1 gram is acceptable.

5.14 Barometer. Use a barometer that is accurate to within ±0.2 inches of mercury.

6. Pre-Test Procedures

6.1 Impinger preparation. Fill each of two unmodified Greenberg-Smith impingers with approximately 100ml of distilled water. Weigh and record the weights on the data sheet as shown in figure IV-8.

6.2 Nozzle size determination. (Same as Section 6.3 in ST-15).

6.3 Assemble the sampling train as shown in Figure IV-7

6.4 The entire sampling train must be leak-checked before each test run. Plug the sampling probe, start the pump, and adjust the pump vacuum to 380mm Hg(15" Hg). A leak rate through the meter which exceeds 0.57 lpm (0.02 CFM) is unacceptable.

7. Sampling

7.1 Each test run shall be of 50 minute duration when testing emissions from continuous operations. Each test run at batch process opeㅜtions shall be for 90% of the batch time or 50 minutes, whichever is less.

7.2 When inserting the probe into the stack rotate the nozzle so it points down stream to avoid a particulate collection prior to sampling. Immediately before sampling rotate the probe so the nozzle points upstream.

7.3 Sample at the traverse points determined in accordance with ST-18.

7.4 Record the following information at five-minute intervals or whenever changing sampling locations on a field data sheet as shown in figure IV-9.

tack velocity head
Sample time
Isokinetic sample rate
Cumulative sample volume
Impinger saturation temperature
Stack gas temperature
Impinger vacuum
Dry test meter temperature

7.6 Add ice as necessary to maintain impinger temperatures at 7°C (45°F) or less.

7.7. At the conclusion of each run, stop the pump, remove the probe from the stack and record the final meter reading. Point the probe upward and purge the sample train with ambient air.

7.8 Conduct three consecutive test runs.

8. Post-Test Procedures

8-1 Analyze the filters and any material in the nozzle for beryllium according to Analytical Procedure Lab 2.

## 9. Auxiliary Tests

9.1 Determine the $CO_2$, $O_2$ and CO concentrations simultaneously with each particulate run in accordance with ST-5, ST-14, and ST-6. An Orsat analysis (ST-24) is also acceptable.

## 10. Calculations

### 10.1 I Standard Dry Sample Volume

$$V_o = \frac{17.71\ V_m P_b}{T_m}$$

Where:

$V_o$ = standard dry sample volume, SDCF at 70°F.and 29192 inches Hg.
$V_m$ = actual metered volume, $ft^3$
$P_b$ = barametric pressure, inches Hg.
$T_m$ = Average Meter temperature °R
17.71 = constant correcting to 70°F 29.92 inches $H_2O$.

### 10.2 Water Vapor Content

$$H_2O = \frac{(.0474\ W_c) + \frac{V_o\ P_{sat}}{P_b - P_i - P_{sat}}}{V_o + (.0474\ W_c) + \frac{V_o\ P_{sat}}{P_b - P_i - P_{sat}}} \times 100$$

Where:

$W_c$ = total condensate weight, all impingers, grams

$P_{sat}$ = water saturation pressure, in
$P_b$ = barometric pressure, inches Hg.
$P_i$ = pump inlet vacuum, inches Hg.
$H_2O$ = per cent water vapor
.0474 = cubic feet of vapor resulting from 1 cubic centimeter of liquid $H_2O$.

10.3 Stack Gas Molecular Weight -

$$MW = 0.44\ (\%CO_2) + 0.32(\%O_2) + 0.28(\%N_2{}^{2} + \%100) + 0.18(\%H_2O)$$

MW = molecular weight

$\%CO_2$ = percent carbon dioxide by volume (dry basis)

$\%O_2$ = percent oxygen by volume (dry basis)

%CO = percent carbon monoxide by volume (dry basis)

$\%H_2O$ = percent moisture by volume

$\%N_2$ = percent nitrogen by volume (dry basis - determine by difference)

10.4 Stack Gas Flow Rate - Determine in accordance with ST-17.

10.5 Isokinetic Ratio. Calculate for each traverse point as:

$$R_i = \frac{T_{si}\ Q_{mi}}{60\ (100-H)\ \ AV_{si}t_iT_{mi}} \times 100\%$$

where:

$R_i$ = isokinetic ratio at given point

$t_i$ = time, at point i, minutes

A = nozzle area, $ft^2$

$V_{si}$ = stack velocity, point i, FPS

$T_{mi}$ = meter temperature, point i, °R

$T_{si}$ = stack temperature. point i, °R

$Q_{mi}$ = metered volume, point i

60 = minutes/hr.

overall isokinetic ratio for each run:

$$R = \frac{Q_{mi}}{60(100-H)\ AT_m\ V_{si}t_iT_{si}} \times 100\%$$

10.6 Mass emissions. The emission rate of bervillium shall be calculated as:

$$M = \frac{W \times Q_o \times 60 \times T}{V_o}$$

where: M = mass emission rate, gr/day

W = total weight of BE in filter and nozzle, grams.

$Q_o$ = stack gas flowrate, SDCFM

V = sample volume, SDCF

$T^o$ = plant operation, hr/day

60 = minutes/hor

11. Reporting

11.1 The data and information indicated Figure IV-10 shall be reported.

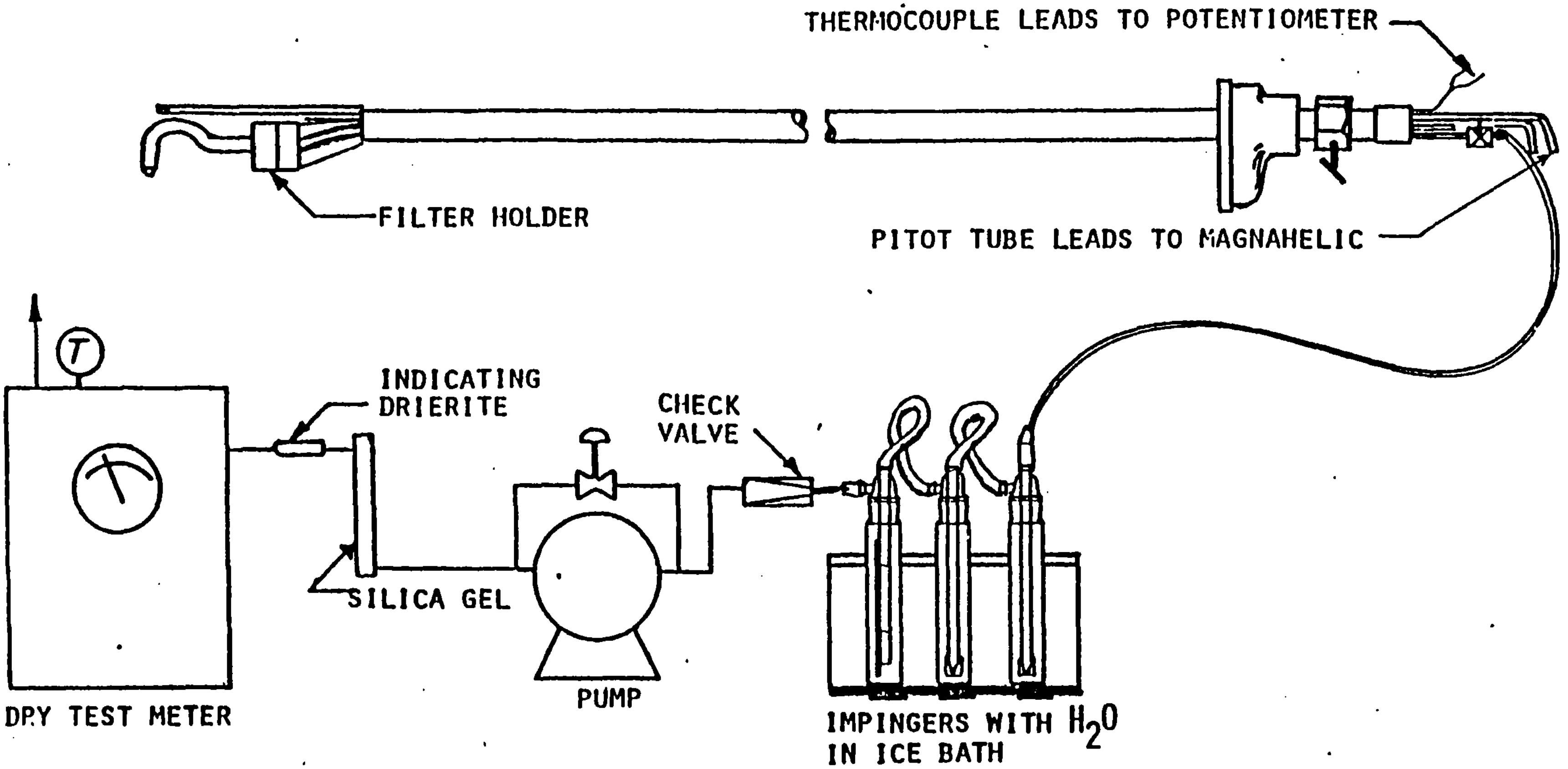

Fig. IV - 7

PARTICULATE SAMPLING TRAIN WITH DISC FILTER

# SOURCE TEST LAB DATA SHEET

PLANT

PAGE OF

SOURCE OPERATION

INITIAL

SOURCE TEST NO.

TEST DATE

FILTER MEDIA

DRYING PROCEDURE: 105°C for 24 hours before and after test, desiccated

STUBBIES

| NO. | TARE | PACKED WT | | | | PARTICULATE |
|---|---|---|---|---|---|---|
| | | | | | | |
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NOZZLES

| NO. | TARE | | | PARTICULATE |
|---|---|---|---|---|
| | | | | |
| | | | | |
| | | | | |
| | | | | |

IMPINGERS

| SOLN. | NO. | a TARE WT | b FILLED WT | c FINAL WT | c-a SAMPLE WT | c-b COND |
|---|---|---|---|---|---|---|
| | | | | | | |
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COMMENTS:

Fig. IV - 8

## Source Test Data Sheet

Source Operation ____________
Plant ____________
Sample Type ____________
Process Cycle ____________
Duct Size ____________
Duct Pressure ____________

Source Test No. ____________
Run No. ____________
Date: ____________

____________ Nozzle Diameter
____________ Pitot Tube
____________ Gas Collector No.
____________ Barometric Pressu
____________ Leak Rate @ 15"Hg

Sampling Train: ____________

| | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Traverse Point | Dist. From Inches | INITIAL TRAVERSE | | | SAMPLING | | | | | | | | | | REMARKS |
| | | | | | | | | | METER | | | | | | |
| | | Duct Temp°F | h $H_2O$ | $\Delta h$ | Traverse Point | h $H_2O$ | $V_s$ FPS | Time | Rate CFH | Temp °F | Volume $Ft^3$ | Vac "Hg | Sat'd Gas Temp°F | $T_s$ Duct Temp°F | |
| | | | | | | | | | | | | | | | |
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$$D_n = 13.7\left[\frac{T_s + 460}{K_p V_s (100-\%H_2O)}\right]^{1/2}$$

$$Q_m = \left[(2.638 \times 10^{-3}) K_p (100-\%H_2O) D_{mm}^2\right]\frac{V_s}{T_s}$$

Condensate ________ gm.
$V_o$ ________
$\%H_2O$ ________
$\%CO_2$ ________
$\%CO$ ________
$\%O_2$ ________

Source Test Team
____________
____________
____________
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FIG. IV

# SUMMARY OF SOURCE TEST RESULTS

## SOURCE INFORMATION

Firm Name and Address

Firm Representative and Title

Phone No.

Source:

Conditions During Tests

Operates hr/day & days/yr

Operating Parameters

Report No.

Test Date:

Test Times:

Run A:

Run B:

Run C:

Test Results and Comments

| METHOD | TEST | RUN A | RUN B | RUN C | AVG. |
|---|---|---|---|---|---|
|  | Run time, minutes |  |  |  |  |
|  | Stack gas Temperature, °F. |  |  |  |  |
| T-17 | Stack flowrate, SDCFM |  |  |  |  |
| ST-14 | $O_2$ conc, dry basis, % |  |  |  |  |
| ST-5 | $CO_2$ conc, dry basis, % |  |  |  |  |
| ST-6 | CO conc, dry basis, % |  |  |  |  |
| ST-23 | $H_2O$ conc, actual, % |  |  |  |  |
|  | Mass emission, gm/day |  |  |  |  |
|  | Isokinetic ratio |  |  |  |  |

FIG IV-10

# Source Test Procedure ST-3

## BULK PLANTS

REF: Regs. 8-6-301
8-7-301

## 1. Applicability

1.1 This procedure is used to determine compliance with Regs. 8-6-301 and 8-7-301.

## 2. Principle

2.1 The efficiency of vapor recovery at bulk plants is determined by comparing the volume of gasoline pumped into the tank with the volume of hydrocarbon vapors emitted from the pressure-vacuum (P-V) relief valve. The vapor volume is measured with a dry test meter.

## 3. Range and Sensitivity

3.1 Not applicable

## 4. Interferences

4.1 The procedure cannot be used if the vapor balance system has any leaks.

## 5. Apparatus

5.1 Combustible gas detector. Use a Johnson-Williams Type SS-P, or equivalent.

5.2 Dry test meter. Use a dry test meter which will operate at the valve leak rate and is fitted with a thermometer in the outlet. The pressure differential across the meter shall be less than 0.1 inch $H_2O$.

5.3 Hose. Use tubing of sufficient length and diameter to connect pressure-vacuum valve and the dry test meter.

## 6. Pre-Test Procedures

6.1 The overall condition of the facilities, especially the absence of leaks, shall be evaluated visually and with the combustible gas detector at the locations listed in 6.2 and 6.3.

6.2 Storage tanks. Check the P-V valve to insure proper operation.

6.2.1 Check piping at all joints.
6.2.2 Check the general storage tank area.
6.2.3 Unintended openings (leaks)

6.3 Loading facilities.

6.3.1 Check the transfer pump packing gland.
6.3.2 Check the hoses and valves.
6.3.3 Check the connection between the tank truck and the loading rack.

**6.4 Any leak over 50 ppm as $C_6$ is unacceptable.**

7. Testing

7.1 Test during a truck-to-tank transfer of fuel.

7.2 Measure the tank truck fuel temperature.

7.3 Connect the dry test meter to the pressure side of the P-V valve.

7.4 During the transfer, check the inspection points in 6.2 adn 6.3 with the combustible gas detector.

7.5 Record the total fuel delivery volume.

7.6 Record the total volume recorded by the dry test meter and the temperature of the meter during the test.

8. Calculations

8.1 The vapor volume from the P-V valve shall be corrected to the truck fuel temperature as:

$$V_T = \frac{(V_M)(T_T)7.48}{T_M}$$

where: $V_T$ = vapor volume at truck temperature, gal.
$T_T$ = truck fuel temperature, °R
$T_M$ = meter temperature, °R
$V_M$ = meter volume, $ft^3$
7.48 = gallons/cubic ft.

8.2 The vapor recovery efficiency shall be calculated as

$$n = \left(1 - \frac{V_T}{V_L}\right)100$$

where: n = efficiency, %
$V_L$ = liquid delivery volume, gal.

9. Reporting

9.1 Results shall be reported as shown in Figure IV-11.

# SUMMARY OF SOURCE TEST RESULTS

## SOURCE INFORMATION

Firm Name and Address

Firm Representative and Title

Phone No.

Source:

Conditions During Tests

Operates hr/day & days/yr

Operating Parameters

Report No.

Test Date:

Test Times:

Run A:

Run B:

Run C:

Test Results and Comments

| THOD | TEST | RUN A | RUN B | RUN C | AVG. |
|---|---|---|---|---|---|
| | Truck tank temperature, °F. | | | | |
| | Delivery volume, gal. | | | | |
| | Vapor volume, gal | | | | |
| | Efficiency, % | | | | |

FIG IV-11

# Source Test Procedure ST-4

## BULK TERMINALS

REF: Reg. 8-6-301

### 1. Applicability

1.1 This procedure is used to quantify hydrocarbon emissions from bulk terminals having a yearly through-put of 6,000,000 gallons or more. It is applicable for determining compliance with Regs. 8-6-301.

### 2. Principle

2.1 The exhaust gas volume and hydrocarbon concentration are measured at the vapor recovery system (VRS) outlet. From these parameters and the total volume of gasoline delivered, the emission factor is calculated.

### 3. Range and Sensitivity

3.1 The minimum and maximum measurable concentrations, as $C_4$, with the NDIR analyzer are 0.5% and 60% respectively.

3.2 The sensitivity of the NDIR analyzer is 1% of full scale.

### 4. Interferences

4.1 The presence of liquid or gas leaks in the delivery or vapor recovery systems preclude the use of this procedure.

### 5. Apparatus

5.1 NDIR Hydrocarbon Analyzer. Use an Infrared Industries Inc. Model 203, or equivalent, to measure hydrocarbon concentrations at the VRS outlet.

5.2 Chart Recorder. The recorder monitors and records the continuous output from the NDIR analyzer.

5.3 Dry test meter. Use a dry test meter capable of operating at the VRS absorber outlet, [illegible]

5.4 Combustible gas detector. Use a Johnson-Williams type SS-P or equivalent.

5.5 Sample conditioning and delivery systems. The assembly of this system is shown in Figure IV-12.

5.6 Zero air system. This system provides clean, dry atmospheric air for analyzer calibration and is assembled as shown in Figure IV-12.

5.7 Span gas system. This system provides a high-pressure mixture of hydorcarbon gas in nitrogen with a concentration in the same range as the concentration being monitored.

5.8 Condensers. Use modified Greenburg-Smith impingers with the impaction plates removed and the inlet tube shortened to 3 or 4 inches. This condenser removes entrained liquid hydrocarbons from the gas sample.

5.9 Particulate filter. Use a Balston type 95 holder, with grade B filter, or equivalent on the sample system.

5.10 Connections. All sample lines shall be Teflon tubing.

5.11 Sample pump. Use a leak free Teflon-lines diaphragm pump with a free-flow rating of 1.5 SCFM.

5.12 Back pressure regulator. A back pressure regulator capable of maintaining sample pressure to the analyzer at 5 psig while venting unused sample.

5.13 Dryer/deodorizer. Use beds of silica gel and activated charcoal to remove moisture and hydrocarbons from the zero air stream.

## 6. Pre-Test Procedures

6.1 Using the combustible gas detector, inspect the gasoline loading racks, holding tank and vapor recovery unit for liquid and gaseous leaks.

6.1.1 If a leak is detected the rest of the test shall be aborted until the leaks have been reparied.

6.2 The test equipment is set up as shown in Figure IV-13

6.3 Zero and span the NDIR hydorcarbon analyzer according to manufacturer's instructions.

## 7. Sampling

7.1 Conduct the test for a minimum of 6 hours during the busiest part of the operating day. The Hydrocarbon content at the VRS shall be measured continuously with the NDIR.

7.2 Start the test when the vapor processing unit is off.

7.3 Record the following:

7.3.1 Initial outlet meter volume.

7.3.2 Holding tank diaphragm height.

7.3.3 Initial readings from gasoline pumps at loading racks from those pumps which are linked to the vapor recovery system.

7.3.4 Outlet temperature each time the unit is operating.

7.4 Check the pressure relief valve on the holding tank with the combustible gas detector every half hour. If the relief valve opens during the test, the test results shall be invalidated.

7.5 The test shall end with the holding tank diaphragm height at the same level as when the test was started.

## 8. Post-Test Procedures

8-1 Record the following:

8:1:1 The final outlet volume meter reading

8:1:2 The final meter readings from gasoline pump meters at the loading rack.

## 9. Calculations

9.1 The mass of hydorcarbons emitted

$$M_o = \frac{(0.796)\ (V_o)\ (C_o)}{T_o}$$

where: $V_o$ = uncorrected meter volume, $ft^3$
$C_o$ = hydorcarbon concentration as $C_4$,%
$M_o$ = lbs, as $C_4$
$T_o$ = average outlet temperature, $^oR$.
0.796 = a constant derived to convert a concentration to a mass, correcting to 70°F.

9.2 The VRS outlet emission factor shall be calculated as:

$$E = \frac{M_o}{G} \times 100$$

where: E = emission factor, lbs of hydorcarbon emissions per 1000 gallons of gasoline delivered

G = Total gallons of gasoline delivered.

## 10. Reporting

10.1 Results shall be reported as in Figure IV-14

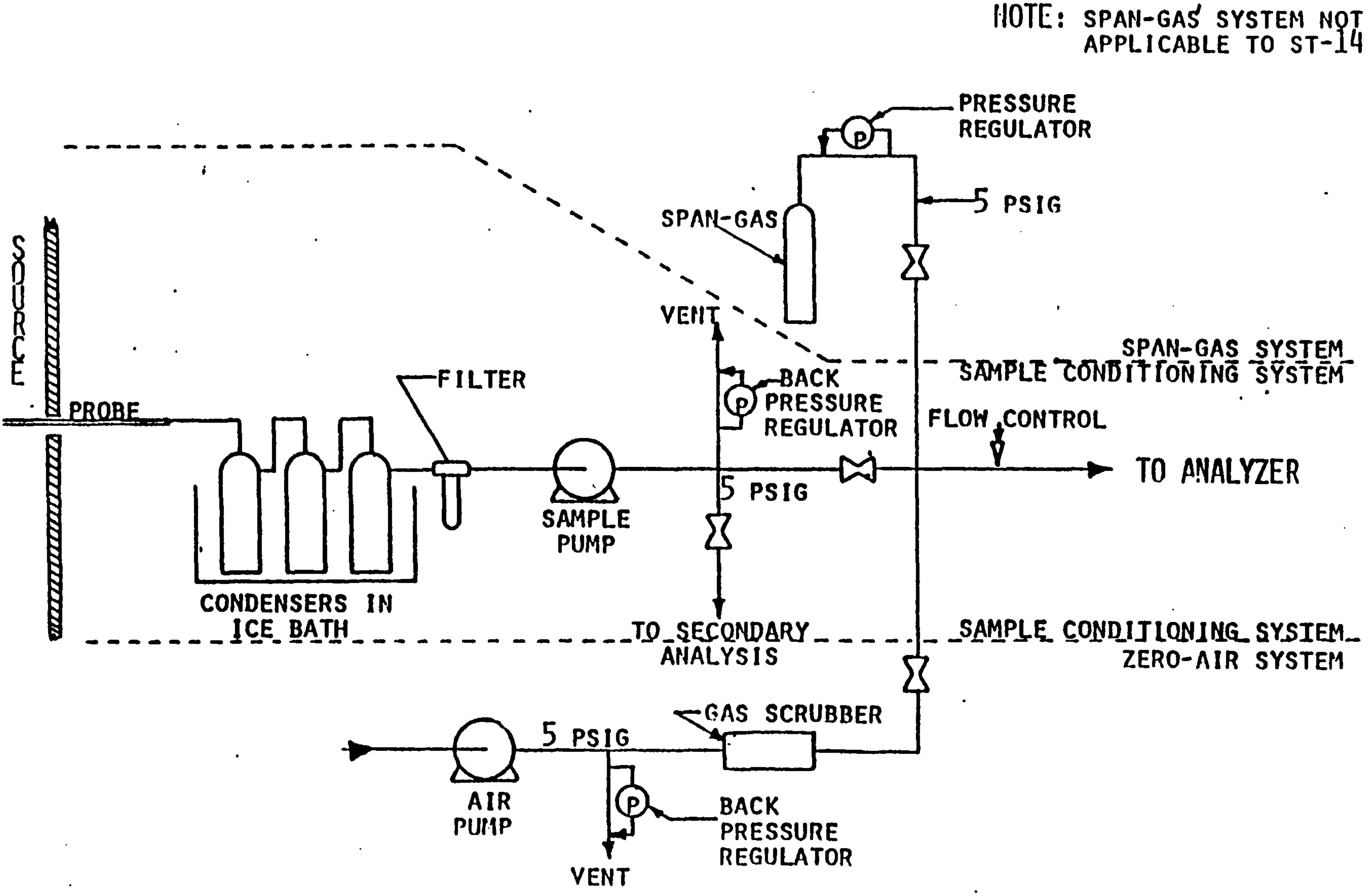


Fig. IV - 12

SAMPLE CONDITIONING, ZERO-AIR AND SPAN-GAS SYSTEMS

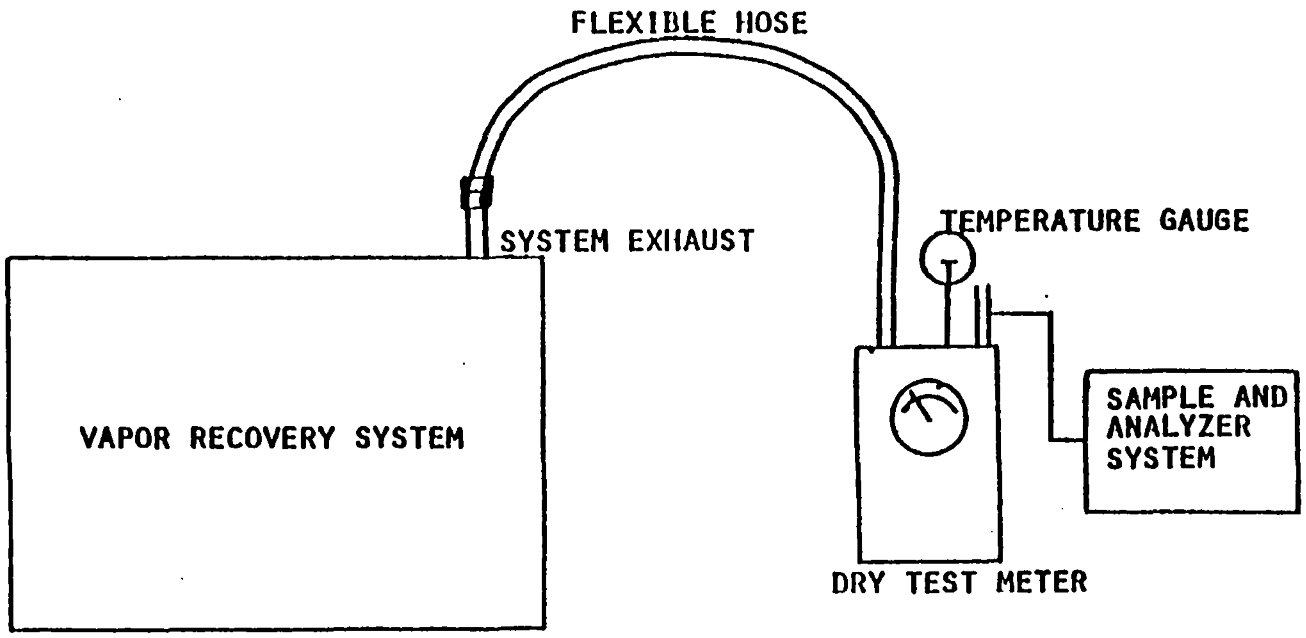


Fig. IV - 13

GASOLINE VAPOR RECOVERY SAMPLING SYSTEM

# SUMMARY OF SOURCE TEST RESULTS

## SOURCE INFORMATION

Firm Name and Address

Firm Representative and Title

Phone No.

Source:

Conditions During Tests

Operates hr/day & days/yr

Operating Parameters

Report No.

Test Date:

Test Times:

Run A:

Run B:

Run C:

Test Results and Comments

Outlet temperature, °F
Delivery volume, gal
Hydrocarbon emissions, lb
Emission factor, %

FIG IV-14

## Source Test Procedure ST-5

## CARBON DIOXIDE, CONTINUOUS SAMPLING

REF: Reg. 6.310.1

### 1. Applicability

1.1 This method is used to quantify emissions of carbon dioxide. It determines compliance with Reg. 6.310.1.

### 2. Principle

2.1 A continuous representative gas sample is extracted from the sampling point and conditioned to remove water and particulate material. The carbon dioxide concentration is determined by passing a small portion of the sample through a non-dispersive infrared analyzer (NDIR) tuned to a frequency at which carbon dioxide absorbs infrared radiation.

### 3. Range and Sensitivity

3.1 The minimum and maximum measurable concentrations of $CO_2$ depend on the sample cell length in the analyzer.

3.2 The minimum sensitivity of the NDIR analyzer shall be ±2% of full scale.

### 4. Interferences

4.1 Possible interferences include methanol, ethanol and water.

### 5. Apparatus

5.1 Carbon dioxide analyzer. Use an Infrared Industries Inc., Model 703 analyzer or its equivalent.

5.2 Chart recorder. The recorder monitors and records the continuous output from the analyzer.

5.3 Sample conditioning, zero air, and span gas system. The assembly of this system is shown in Figure IV-15. The sample conditioning system provides a dry, particulate free gas flow to the instrument. The zero air system provides clean dry atmospheric air for instrument calibration. The span gas system provides a known concentration of $CO_2$ for use in calibrating the analyzer. Except as specified, all meterials which come in contact with either the sample or span gases must be constructed of Teflon or stainless steel.

5.4 Sample probe. Use a borosilicate glass tube of sufficient length to traverse the stack being tested. If the stack temperature exceeds 425C (800F), use a quartz probe. Other probes are acceptable subject to approval by the Source Test Section.

5.5 Condensers. Use modified Greenberg-Smith impingers with the impaction plates removed and the inlet tube shortened to a length of 10cm (4 inches), or equivalent.

5.6 Cooling system. Immerse the impingers in an ice bath during the test.

5.7 Particulate filter. Use a Balston type 95 holder with a grade B filter, or equivalent, in the sample system.

5.8 Pumps. Use leak-free, Teflon-lined, diaphragm pumps in the sample and zero air systems. The pumps must have a capacity of at least 28 liters/min (1.0 CFM).

5.9 Back-pressure regulator. Use a back-pressure regulator to maintain the sample and zero gas sample pressures to the instrument at five psig.

5.10 Gas scrubber. Use a bed of silica gel, Ascarite (or soda-lime), and charcoal to remove moisture, carbon dioxide, and hydrocarbons from the zero air system.

5.11 Span gas. Use a high-pressure cylinder containing a known concentration of $CO_2$ in air or nitrogen. The span gas concentration must be in the same range as the source being tested.

6. Pre-Test Procedures

6.1 Warm-up the instrument according to manufacturer's instructions.

6.2 Assemble the sampling system as shown in Figure IV-15.

6.3 Leak-test the sampling system by starting the pump, plugging the probe, and determining that the pressure to the analyzer falls to zero. Other leak-tests are acceptable subject to the approval of the Source Test Section.

6.4 Introduce zero air, into the analyzer and zero the instrument according to manufacturer's instructions.

6.5 Introduce span gas into the analyzer and calibrate the instrument according to manufacturer's instructions.

6.6 Conduct a preliminary concentration traverse (according to ST-18) to determine if stratification of the stack gases exists.

If the $CO_2$ concentration at any point differs from the average concentration by more than 10%, traverse the stack during the test. If not, sample at any single point.

6.7 Set-up the chart recorder according to manufacturer's instructions.

## 7. Sampling

7.1 Each test run shall be of thirty minute duration when testing emissions from continuous operations. Each test run at a batch process operation shall be for 90% of the batch time or thirty minutes, whichever is less.

7.2 Introduce sample gas into the analyzer at the same flow rate used to calibrate the analyzer.

7.3 Maintain ice in the cooling system throughout the test.

7.4 Calibrate the analyzer before and after each test run. Record each step of the process clearly on the chart recording.

7.5 Conduct three test runs.

## 8. Calculations

8.1 From the chart recording determine the time-averaged concentration of $CO_2$ on a dry basis for each run.

## 9. Reporting

9.1 These values are determined as auxiliary data for other poocedures and shall be reported with those test results.

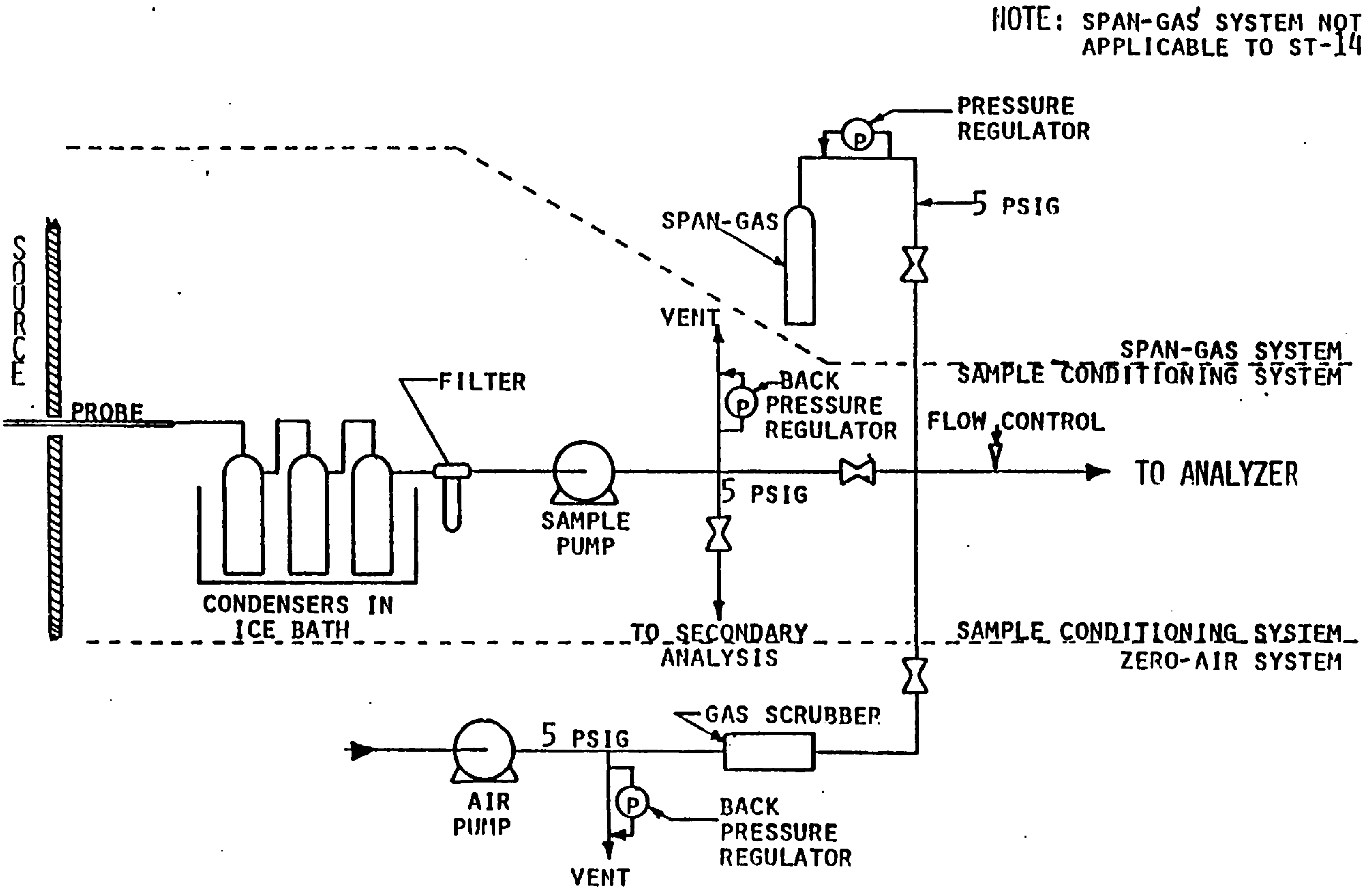


Fig. IV - 15

SAMPLE CONDITIONING, ZERO-AIR AND SPAN-GAS SYSTEMS

## Source Test Procedure ST-6

## CARBON MONOXIDE CONTINUOUS SAMPLING

REF: Reg. 8-1-110.3, 10-8-301.

### 1. Applicability

1.1 This method is used to quantify emissions of carbon monoxide. It determines compliance with Reg. 8-1-110.3.

### 2. Principle

2.1 A continuous representative gas sample is extracted from the sampling point and conditioned to remove water and particulate material. The carbon monoxide concentration is determined by passing a small portion of the sample through a non-dispersive infrared analyzer (NDIR) tuned to a frequency at which carbon monoxide absorbs infrared radiation.

### 3. Range and Sensitivity

3.1 The minimum and maximum measurable concentrations of CO depend on the sample cell length in the analyzer.

3.2 The minimum sensitivity of the NDIR analyzer shall be ±2% of full scale.

### 4. Interferences

4.1 Cyanogen and methyl azide are possible interfering species.

### 5. Apparatus

5.1 Carbon monoxide analyzer. Use a Mine Safety Appliance Co. LIRA Model 202 analyzer or its equivalent.

5.2 Chart recorder. The recorder monitors and records teh continuous output from the analyzer.

5.3 Sample conditioning, zero air, and span gas system. The assembly of this system is shown in Figure IV-16. The sample conditioning system provides a dry, particulate free gas flow to the instrument. The zero air system provides clean dry atmospheric air for instrument calibration. The span gas system provides a known concentration of CO for use in calibrating the analyzer. Except as specified, all materials which come in contact with either the sample or span contacting surfaces must be constructed of Teflon or stainless steel.

5.4 Sample probe. Use a borosilicate glass tube of sufficient length to traverse the stack being tested. If the stack temperature exceeds 425C (800F), use a quartz probe. Other probes are acceptable subject to approval by the Source Test Section.

5.5 Condensers. Use modified Greenberg-Smith impingers with the impaction plates removed and the inlet tube shortened to a length of 10cm (4 inches), or equivalent.

5.6 Cooling system. Immerse the impingers in an ice bath during the test.

5.7 Particulate filter. Use a Balston type 95 holder with grade B filter, or equivalent, in the sample system.

5.8 Pumps. Use leak-free, Teflon-lined, diaphragm pumps in the sample and zero air system. The pumps must have a capacity of at least 28 liters/min (1.0 CFM).

5.9 Back-pressure regulator. Use a back-pressure regulator to maintain the sample and zero gas sample pressures to the instrument at five psig.

5.10 Gas scrubber. Use a bed of silica gel, Ascarite (or soda-lime), and charcoal to remove moisture, carbon dioxide, and hydrocarbons from the zero air system.

5.11 Span gas. Use a high-pressure cylinder containing a known concentration of CO in air or nitrogen. The span gas concentration must be in the same range as the source being tested.

6. Pre-Test Procedures

6.1 Warm-up the instrument according to manufacturer's instructions.

6.2 Assemble the sampling system as shown in Figure 1.

6.3 Leak-test the sampling system by starting the pump, plugging the probe, and determining that the pressure to the analyzer falls to zero. Other leak-tests are acceptable subject to the approval of the Source Test Section.

6.4 Introduce zero air, into the analyzer and zero the instrument according to manufacturer's instructions.

6.5 Introduce span gas into the analyzer and calibrate the instrument according to manufacturer's instructions.

6.6 Conduct a preliminary concentration traverse (according to ST-18) to determine if stratification of the stack gases exists. If the CO concentration at any point differs from the average concentration by more than 10% traverse the stack during the test. If not, sample at any single point.

6.7 Set-up the chart recorder according to manufacturer's instructions.

## 7. Sampling

7.1 Each test run shall be of thirty minute duration when testing emissions from continuous operations. Each test run at a batch process operation shall be for 90% of the batch time or thirty minutes, whichever is less.

7.2 Introduce sample gas into the analyzer at the same flow rate used to calibrate the analyzer.

7.3 Maintain ice in the cooling system throughout the test.

7.4 Calibrate the analyzer before and after each test run. Record each step of the process clearly on the chart recording.

7.5 Conduct three test runs.

## 8. Calculations

8.1 From the chart recording determine the time-averaged concentration of CO on a dry basis for each run.

## 9. Reporting

9.1 Report the results indicated on Figure IV-17.

9.2 These values are also determined as auxiliary data for other procedures and shall be reported with those test results.

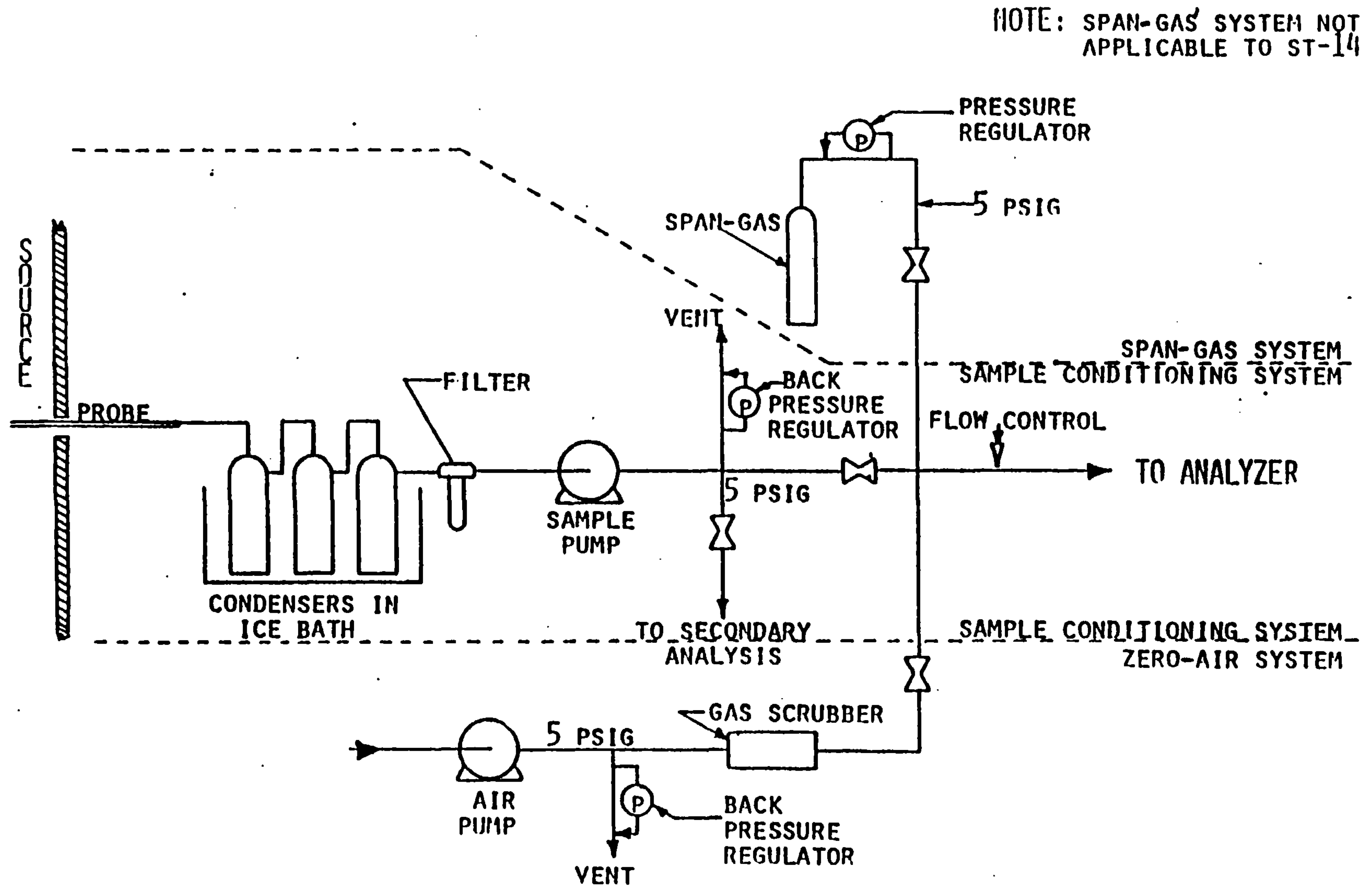


Fig. IV - 16

SAMPLE CONDITIONING, ZERO-AIR AND SPAN-GAS SYSTEMS

# SUMMARY OF SOURCE TEST RESULTS

## SOURCE INFORMATION

| | | |
|---|---|---|
| Firm Name and Address | Firm Representative and Title<br>Phone No. | Report No. |
| Conditions During Tests | Source:<br>Operates hr/day & days/yr | Test Date:<br>Test Times:<br>Run A:<br>Run B:<br>Run C: |
| Operating Parameters | | |

Test Results and Comments

| METHOD | TEST | RUN A | RUN B | RUN C | AVG. |
|---|---|---|---|---|---|
| | Run time, minutes | | | | |
| | Stack gas temperature, °F. | | | | |
| -6 | Carbon monoxide, ppm | | | | |

FIG IV-17

# Source Test Procedure ST-7

# NON-METHANE ORGANIC CARBON

REF: 8-2-301
8-4-301
8-4-302.303

## 1. Applicability

1.1 This method is used to quantify emissions of non-methane organic carbon for determining compliance with Reg. 8-2-301, 8-4-302,303. This method is also used to quantify emissions of total oxidizable carbon (organic carbon plus carbon monoxide ), hereafter referred to as "TOC" for determining compliance of afterburners.

1.2 Use method A (below) when carbon dioxide constitutes over 85%, on a molar basis, of the total carbon (organic plus inorganic, as $C_1$) in the sample; otherwise use Method B.

## 2. Principle

2.1 A continuous sample of effluent is conditioned to remove water and particulate material. A small portion of the conditioned effluent is continuously analyzed by either method A or B.

2.1.1. Method A. The Sample is passed through a bed of soda-lime to remove carbon dioxide. and then through a combustion tube to oxidize all organic carbon and carbon monoxide to carbon dioxide. The carbon dioxide concentration is continuously monitored with a non-dispersive infrared analyzer (NDIR) to indicate the TOC concentration in the sample.

2.1.2 Method B. The sample is divided into two equal volume streams, one of which passes through the combustion tube. The streams are alternately analyzed with the NDIR for carbon dioxide. The difference in analyses between the streams represents the total oxidizable carbon (TOC) concentration of the sample.

2.2 The methane content of the sample is determined either (A) by filling an evacuated cylinder with sample for subsequent gas chromatographic analysis or (B) by directing a portion of the conditioned sample through a bed of activated carbon to remove non-methane organics and then into a flame ionization detector. Subtraction of the methane concentration from TOC yields non-methane TOC.

2.3 If organic carbon alone is measured a separate continuous analysis for carbon monoxide with an NDIR is subtracted from the TOC.

3. Range and Sensitivity

3.1 The minimum measurable concentration of TOC 10 ppm if the appropriate NDIR cell is used.

3.2 The maximum concentration of TOC for which this procedure is applicable is 5% when the appropriate NDIR cell and sample dilution are used.

3.3 Use of this procedure requires a molar concentration ratio of oxygen to TOC of 10.1 or greater. Sample dilution may be used to achieve the 10:1 ratio.

3.4 The sensitivity of the NDIR is ±2% of full scale.

4. Interferences

4.1 Negative bias may occur due to reaction of highly reactive organics (e.g. aldehydes or acids) with internal surfaces or if the condensation point of the sample is above the condenser temperature.

4.2 Additional negative bias may occur in Method A due to absorption of alcohols , acids and aldehydes by the carbon dioxide scrubbing medium.

4.3 High concentrations of carbon monoxide may preclude the use of this procedure for the measurement of only the organic portion of the TOC.

5. Apparatus

5.1 Carbon dioxide analyzer. Use an Infrared Industries Inc. Gas Aanlyzer Model 703, or its equivalent.

5.2 Carbon monoxide analyzer. Use an Mine Safety Appliance Co. LIRA Model 202, or its equivalent.

5.3 Flame ionization detector (only if needed for methane analysis). Use a Beckman Model 400, or equivalent, if necessary for methane analysis.

5.4 Chart recorder. Record the continuous output from the analyzer.

5.5 Sample conditioning, zero air, and span gas system. Assemble this system as shown in Figure IV-18. Sample conditioning system shall provide a dry, particulate-free gas flow to the instrument. The zero-air system shall provide clean dry atmospheric air for instrument calibration. The span-gas system shall provide known concentraions of the appropriate gas for use in calibrating the analyzers. Except as specified, all materials which come in contact with either the sample or span gases must be constructed of Teflon or stainless steel.

5.6 Sample probe. Use a borosilicate glass tube of sufficient length to traverse the stack being tested. If the stack temperature exceeds 425C (800F), use a quartz probe. Other probes are acceptable subject to approval by the Source Test Section.

5.7 Condensers. Use modified Greenberg-Smith impingers with the impaction plates removed and the inlet tubes shortened to a length of 10cm (4 inches). Equivalent condensers may be used.

5.8 Cooling system. Immerse the impingers in an ice bath during the test.

5.9 Particulate filter. Use a Balston type 95 holder with a grade B filter, or equivalent, in the sample system.

5.10 Pumps. Use leak-free, Teflon-lined, diaphragm pumps in the sample and zero air system. The pumps must have a free-flow capacity of at least 28 liters/min (1.0 CFM).

5.11 Back-pressure regulator. Use a back-pressure regulator to maintain the sample and zero gas sample pressures to the instrument at five psig.

5.12 Gas scrubber. Use a bed of silica gel, Ascarite (or soda-lime), and charcoal to remove moisture, carbon dioxide, and hydrocarbons from the zero air system.

5.13. Span gas. Use a high-pressure cylinder containing a known concentration of propane in air or nitrogen. A cylinder containing a known concentration of solvent, where applicable, may also be used. This option may only be used with prior approval of the Source Test Section.

5.14 Soda-lime bed. Use a bed of sufficient capacity to remove carbon dioxide from the sample for at least a thirty minute sampling period.

5.15 Quartz combustor. Use a system to oxidize all organics in the sample including methane. Examples of acceptable combustion tubes found adequate by the BAAPCD are described in Figures IV-19 and 20.

## 6. Pre-Test Procedures

6.1 Warm-up the instrument according to manufacturer's instructions.

6.2 Assemble the sampling system as shown in Fugure IV-21.

6.3 Leak-test the sampling system by starting the pump, plugging the probe, and assuring that the pressure to the analyzer falls to zero.

6.4 Introduce zero-air into the analyzer and calibrate the instrument according to manufacturer's instructions.

6.5 Introduce span-gas into the analyzer and calibrate the instrument according to manufacturer's instructions.

6.6 Conduct a preliminary concentration traverse (in accordance with ST-18) to determine if stratification of the stack gases exists. If the hydrocarbon concentration at any point differs from the average concentration by more than 10% traverse the stack during the test; if not, sample at any single point.

6.7 Prepare the chart recorder according to manufacturer's instructions.

6.8 Figure IV-22 shows an acceptable sample dilution system. Equivalent dilution systems are acceptable.

6.9 Set the voltage to the combustor at least 14 volts A.C. for the combustor in Figure IV-19 & 32 volts A.C. for the combustor in Fig.IV-20. All voltages will be combustor specific and efficiency data will be requested by the Source Test Section.

7. Sampling

7.1 Each test run shall be of 30 minute duration when testing from continuous operations. Each test run of a batch operation shall be for 90% of the batch time or thirty minutes, whichever is less.

7.2 At sources requiring both inlet and outlet tests on a control device (e.g. afterburners), the test times may be adjusted to aid in obtaining representative results.

7.3 Adjust the dilution system (if required) to obtain a known dilution ratio.

7.4 Method A. Introduce sample gas into the Method A analytical system at the same flow rate used to calibrate the analyzer.

7.4.1 Adjust the sample system to achieve flow through the soda-lime scrubber and the combustion tube.

7.4.2 Periodically pass $CO_2$ span gas through the system and ascertain that the NDIR analyzer reads zero; if it does not, replace the scrubber medium.

7.5 Method B. Introduce sample gas into the Method B TOC analytical system at the same flow rate used to calibrate the analyzer.

7.5.1 By-pass the soda-lime scrubber and pass the sample stream through the combustion tube.

7.5.2 (At approximately ten minute intervals). By-pass the combustion tube to measure the background $CO_2$ in the sample stream.

7.6 Maintain ice in the cooling system throughout the test.

7.7 Calibrate the analyzer before and after each test run. Record each step of the process on the chart recording.

7.8 If a sample dilution system is being used, check the dilution ratio before and after each test run.

7.9 Determine the methane concentration by passing a portion of the sample stream through an activated carbon scrubber to remove non-methane hydrocarbon and then through a flame ionization detector.

## 8. Auxiliary Tests

8.1 Stack gas flow rate. Use ST-17 to determine the stack gas flow rate after each test run.

8.2 Moisture content. Use ST-23 to determine the moisture content of the stack gases.

8.3 Carbon monoxide concentration. Simultaneously with each test run, use ST-6 to determine the CO concentration.

## 9. Calculations

9.1 Determine the time-averaged uncorrected TOC concentration (including $CH_4$ and CO).

Method A...... $C_{TOC} = C_{CO_2}$

Method B...... $C_{TOC} = \Delta C_{CO_2}$

where: $C_{TOC}$ = average uncorrected total oxidizable carbon (as $C_1$), ppm

$C_{CO_2}$ = average carbon dioxide concentration, stream 1, ppm

$\Delta C_{CO_2}$ = average difference in concentration, combusted - noncombusted, ppm

9.2 Non-methane TOC concentration:

$$C'_{TOC} = C_{TOC} - C_m$$

where: $C_m$ = methane concentration, ppm

$C'_{TOC}$ = Total oxidizable carbon excluding methane (as $C_1$)ppm

9.3 Non-methane organic concentration of the TOC:

$$C_{ORG} = C'_{TOC} - C_{CO}$$

where: $C_{ORG}$ = organic carbon concentration, as $C_1$, ppm

$C_{CO}$ = average carbon monoxide concentration, ppm

9.4 Mass flow rate of the organic portion of the TOC, as Carbon.

$$M_{ORG} = 1.86 \times 10^{-6} Q_o C_{ORG}$$

where: $M_{ORG}$ = mass flow of organic carbon, as $C_1$, lb/hr.

$Q_o$ = gas flow rate, SDCFM

1.86 = constant derived to convert concentration to mass at 70F and 29.92 inches Hg.

9.5 Mass flow rate of the carbon monoxide:

$$M_{CO} = 4.34 \times 10^{-6} Q_o C_{CO}$$

where: $M_{CO}$ = mass flow rate of CO, lb/hr.
4.34 = constant derived to convert concentration to mass at 70F and 29.92 inches Hg.

9.6 If organic emissions are controlled by incineration, the abatement efficiency of oxidation to carbon dioxide (for determination of exemption) shall be calculated as in Table A. "In" and "out" refer to control device inlet and outlet, respectively.

TABLE A

| Situation | Efficiency |
|---|---|
| $(M_{CO})_{out} \quad (M_{CO})_{in}$ | $N_1 = 100 \times \dfrac{(M_{TOC})_{in} - (M_{TOC})_{out}}{(M_{ORG})_{in}}$ |
| $(M_{CO})_{out} \quad (M_{CO})_{in}$ | $N_2 = 100 \times \dfrac{(M_{ORG})_{in} - (M_{ORG})_{out}}{(M_{ORG})_{in}}$ |

$$M_{TOC} = 1.86 \times 10^{-6} A_o C_{TOC}$$

9.7 If organic emissions are controlled by means other than incineration, the mass efficiency of organics abatement shall be calculated as

$$\text{Efficiency} = \frac{(M_{ORG})_{in} - (M_{ORG})_{out}}{(M_{ORG})_{in}} \times 100$$

10. Reproting

10.1 The data and information indicated in Figure IV-23 shall be reported.

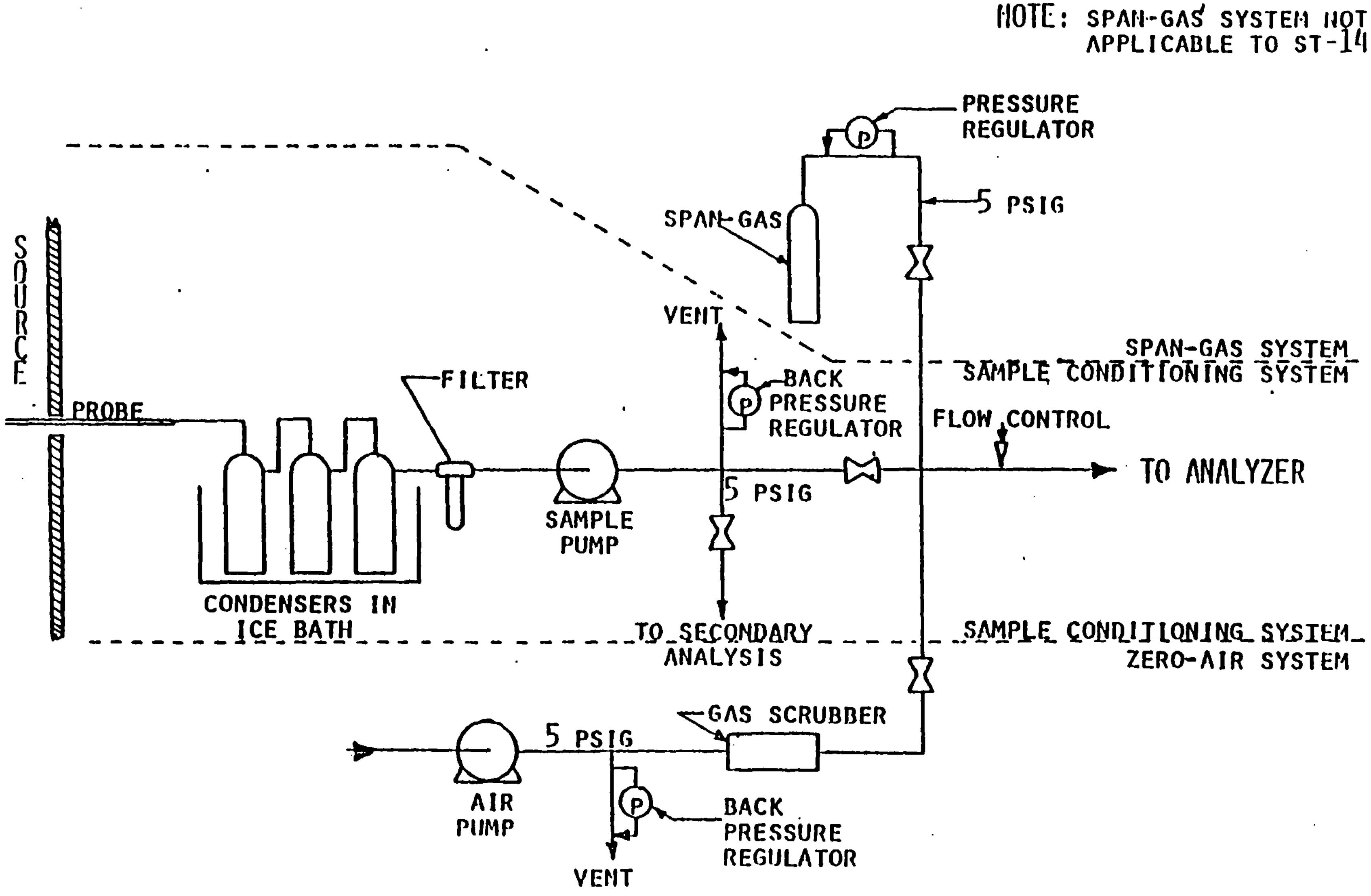


Fig. IV - 18

SAMPLE CONDITIONING, ZERO-AIR AND SPAN-GAS SYSTEMS

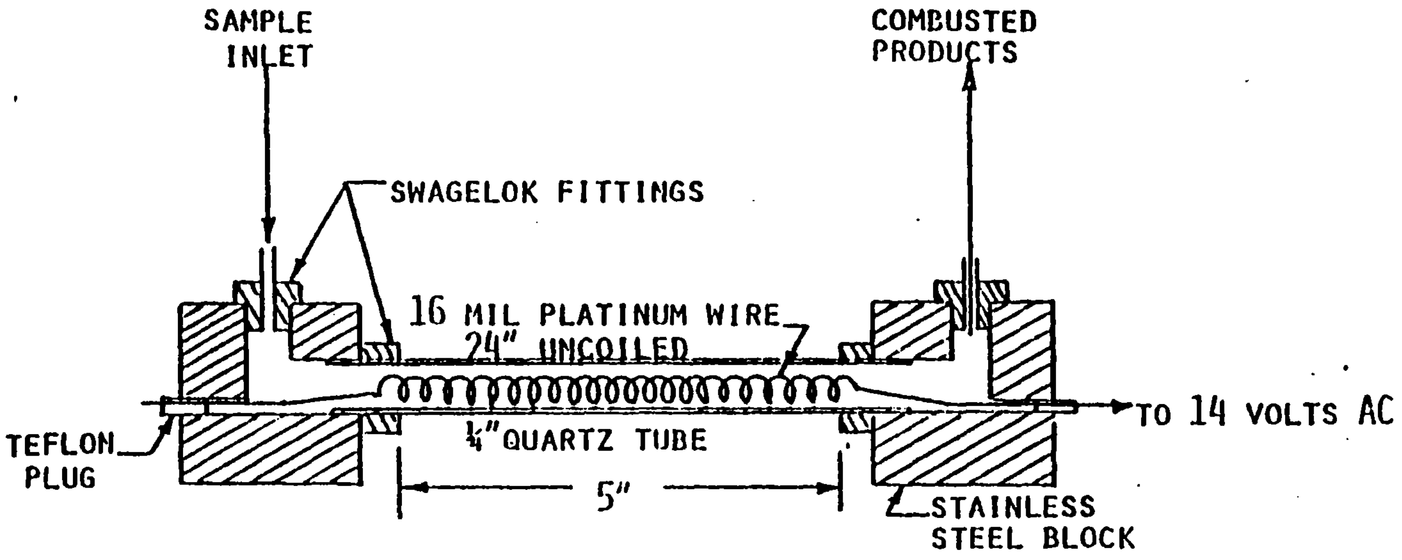
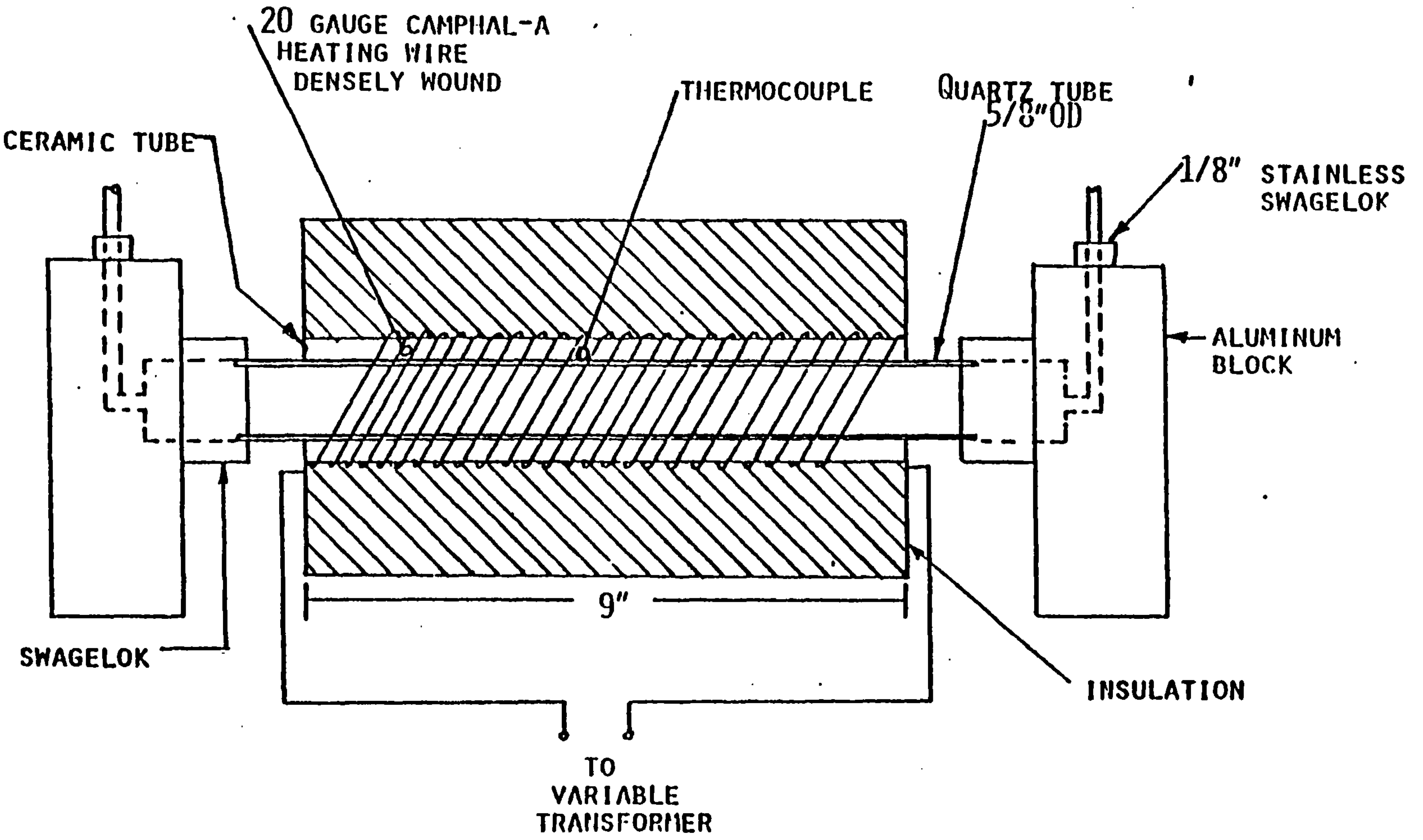


Fig. IV - 19

INTERNALLY HEATED COMBUSTION TUBE



NOTE: FURNACE OPERABLE TO 1100C

Fig. IV - 20

EXTERNALLY HEATED COMBUSTION TUBE

## Spource Test Method ST-8

## DIMETHYLSULFIDE

REF: Reg. 7-303

### 1. Applicability

1.1 This method is used to determine emissions of dimethylsulfide (DMS). It is applicable to the determination of compliance with Reulation 7-303

### 2. Principle

2.1 A sample is collected in a clean Tedlar bag. The sample is analyzed for DMS by chromatography with flame photometric detection.

### 3. Range and Sensitivity

3.1 The minimum measurable concentration of DMS is 15 ppb.

3.2 Non-linear response by the flame photometric detector occurs for DMS concentrations over 10ppm. However, appropriate dilution of the sample will allow concentrations up to 50 ppm to be analyzed.

### 4. Interferences - none known

### 5. Apparatus

5.1 Sampling probe. Use a borosilicate glass tube fitted at the downstream end with an appropriate tubing connector.

5.2 Sample bag. Use a Tedlar bag equipped with a capacity of at least 10 liters and equipped with two stainless steel valves.

5.3 Sampling pump. Use a leak-free Teflon-lined diaphragm pump, or equivalent, capable of at least 0.5CFM.

5.4 Sample lines, Use Teflon.

5.5. Drier/deodorizer. Use three glass cartridges fitted with ball joints. The first contains Drierite (calcium chloride); the others contain activated carbon and shall be followed by a Pyrex wool filter.

### 6. Pre-Test Procedures

6.1 Before going to the test site, assemble the train as shown in Figure IV-24. Purge the entire train, including the Tedlar bag, until the discharge is clean. The Tedlar bag is considered clean when the laboratory analysis determines the DMS concentration to be undetectable.

# SUMMARY OF SOURCE TEST RESULTS

## SOURCE INFORMATION

**Firm Name and Address**

**Firm Representative and Title**

**Phone No.**

**Source:**

**Conditions During Tests**

**Operates** hr/day & days/yr

**Operating Parameters**

**Report No.**

**Test Date:**

**Test Times:**

**Run A:**

**Run B:**

**Run C:**

**Test Results and Comments**

| METHOD | TEST | RUN A | | RUN B | | RUN C | | AVG. | |
|---|---|---|---|---|---|---|---|---|---|
| | | IN* | OUT** | IN | OUT | IN | OUT | IN | OUT |
| | Run time, minutes | | | | | | | | |
| | sample point temp., °F. | | | | | | | | |
| ST-17 | Flow rate, SDCFM | | | | | | | | |
| ST-14 | $O_2$, dry basis, % | | | | | | | | |
| ST-5 | $CO_2$, dry basis, % | | | | | | | | |
| ST-6 | CO, dry basis, % | | | | | | | | |
| ST-23 | $H_2O$, actual basis, % | | | | | | | | |
| ST-7 | Non-methane organic carbon, as $C_1$ | | | | | | | | |
| | a) ppm (dry) | | | | | | | | |
| | b) lb/hr | | | | | | | | |
| ST-6 | Carbon monoxide | | | | | | | | |
| | a) ppm (dry) | | | | | | | | |
| | b) lb/hr. | | | | | | | | |
| | Abatement efficiency, % | | | | | | | | |

FIG. IV-23

* control device inlet

** control device outlet

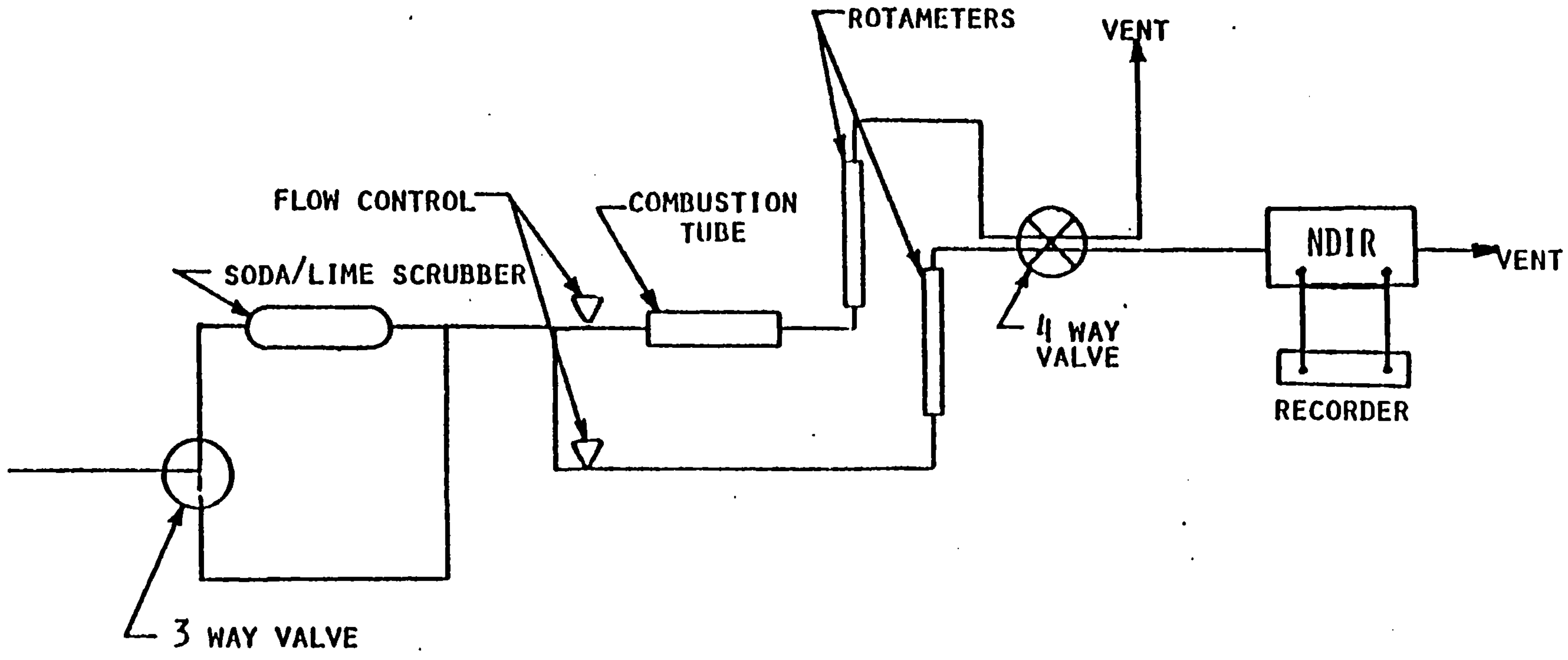


Fig. IV - 21

TOC ANALYTIC SYSTEM

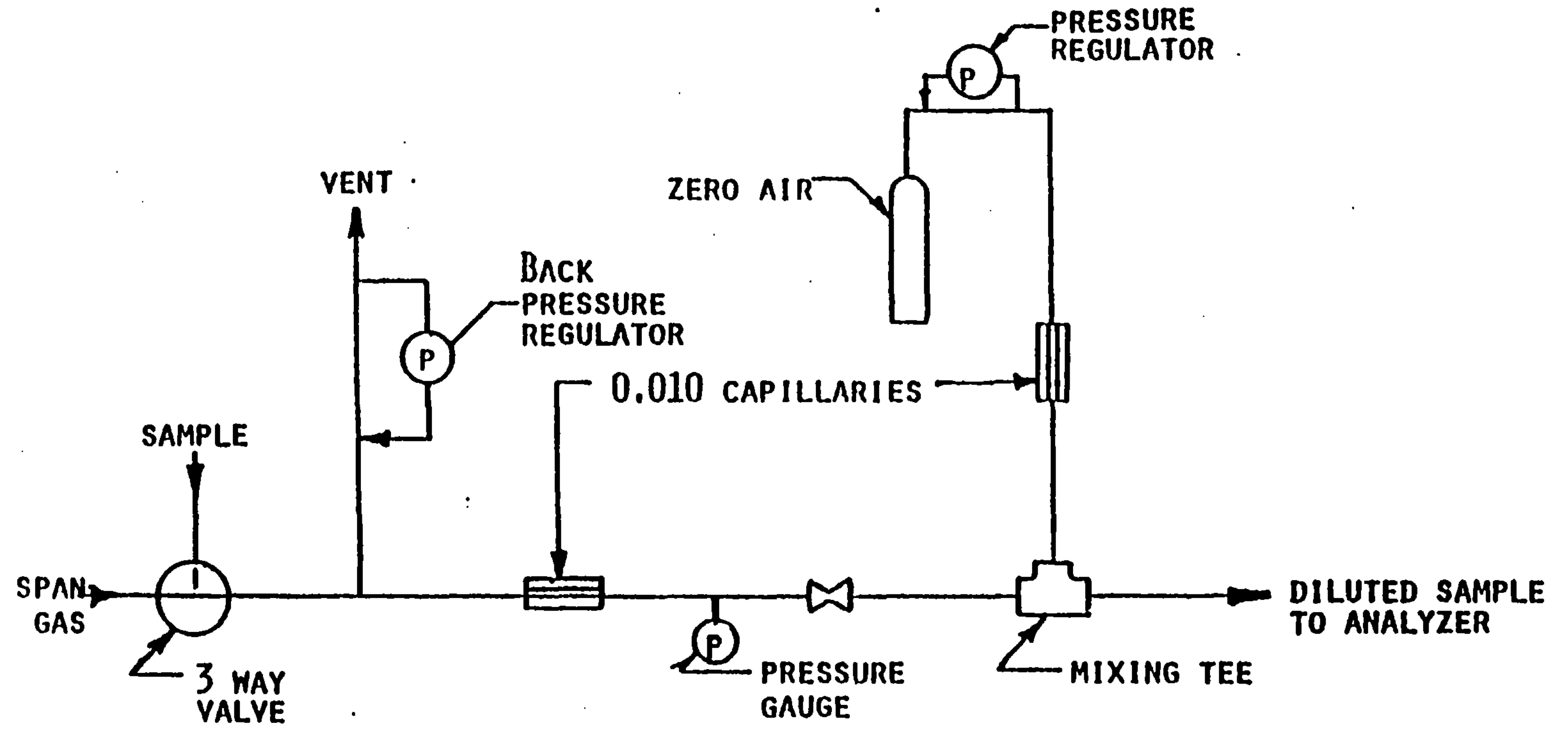


Fig. IV - 22

DILUTION SYSTEM

6.2 Evacuate the Tedlar bag.

6.3 At the sampling site, assemble the train as shown in Figure IV-24 leaving out the drier-deodorizer.

7. Sampling

7.1 For stack sources, insert the probe into the stack.

7.2 For ambient sample, sample where the odor appears to be strongest.

7.3 Start the pump and purge the gas to be sampled through the pump and bag for five minutes.

7.4 Then close the outlet valve on the Tedlar bag and fill the bag over a period of not less than three minutes.

7.5 Three bags filled as in 7.3 and 7.4 shall constitute a test.

8. Post-Test Procedures

8.1 The bags must be analyzed for DMS within four hours of collection. Refer to Analytical Procedure Lab-3.

9. Reporting

9.1 The result of each test is reported as shown in Figure IV-25.

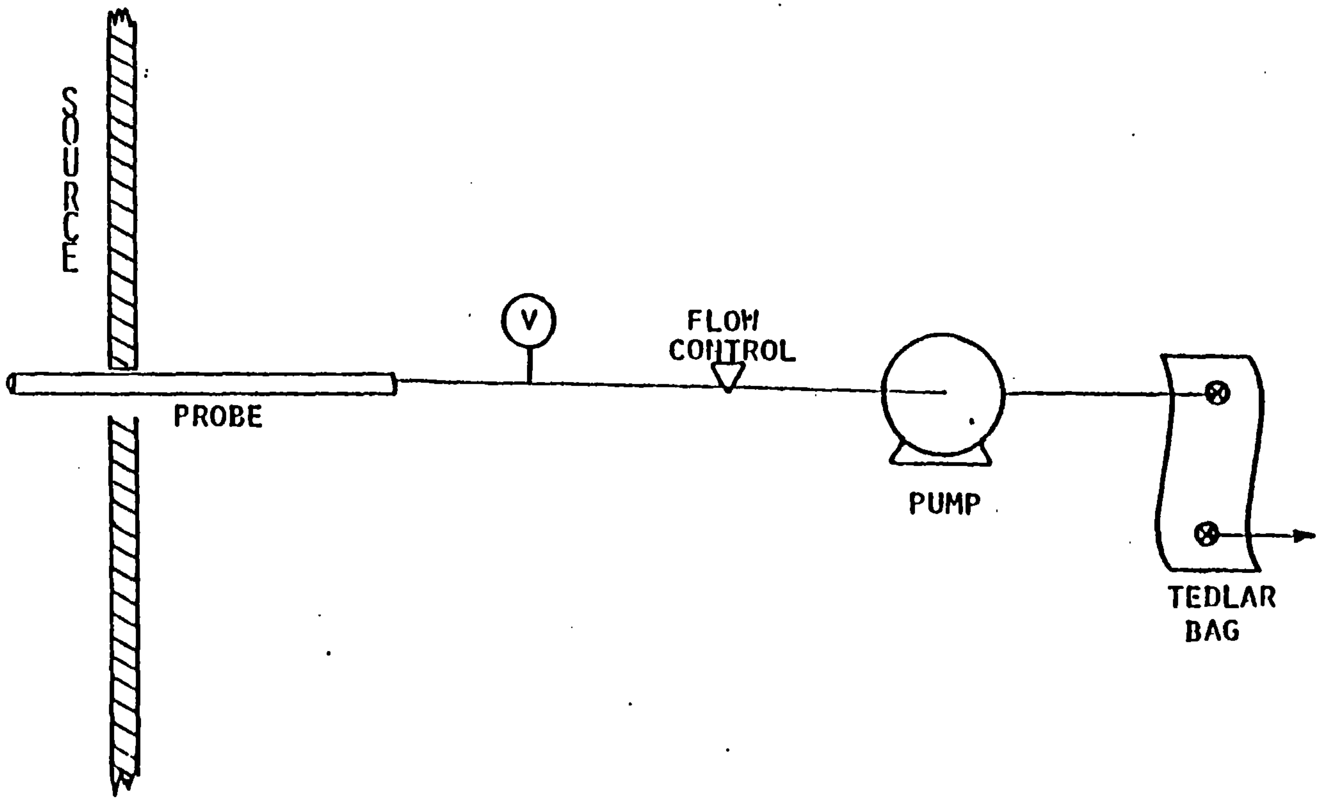


Fig. IV - 24

COLLECTION OF ORGANIC SULFIDE SAMPLES

## Source Test Procedure ST-9
## LEAD

REF Regs. 10-1-301, 11-1-301

### 1. Applicability

1.1 This procedure is used to quantify emissions of Lead. It determines compliance with Regs. 10-1-301 and 11-1-301.

### 2. Principle

2.1 The stack gases are withdrawn isokinetically and passed through a glass fiber filter and impingers containing iodine monochloride. The filter and impinger catches are then measured for lead content according to Analytical Procedure Lab 4b.

### 3. Range

3.1 The minimum measurable emission of particulate lead is $7 \times 10^{-5}$ grain/SDCF and gaseous lead is $2 \times 10^{-5}$ gr/SDCF.

### 4. Interferences. None known.

### 5. Aoparatus

5.1 Probe nozzle. The sampling train and its components are shown in Figure IV-26. The probe nozzle shall be constructed of borosilicate glass, quartz, or stainless steel.

5.2 Filter medium. Use a Gelman, Type "A" glass fiber disc type filter or equivalent.

5.3 Connection. The connection between the filter and the first impinger must be able to withstand stack temperatures. Vinyl tubing is acceptable in making all other connections.

5.4 Pitot tube. Use a Stauscheibe (Type-S), or equivalent, with a known coefficient which is constant within ±5% over the entire working range. The pitot tube coefficient is determined by placing both the S-type and the standard pitot tube in a gas stream and measuring the pressure head with both over the entire velocity range of interest. Calculate the coefficient of the Type-S pitot tube as follows:

$$C_{p_s} = C_{p_{std}} \left[\frac{\Delta P_{std}}{\Delta P_s}\right]^{\frac{1}{2}}$$

where: $C_{p_s}$ = Type-S pitot tube coefficient
$\Delta P_s$ = Pressure head, Type-S pitot tube
$\Delta P_{std}$ = Pressure head, standard pitot tube
$C_{p_{std}}$ = Standard pitot tube coefficient.

# SUMMARY OF SOURCE TEST RESULTS

## SOURCE INFORMATION

Firm Name and Address

Firm Representative and Title

Phone No.

Source:

Conditions During Tests

Operates hr/day & days/yr

Operating Parameters

Report No.

Test Date:

Test Times:

Run A:

Run B:

Run C:

Test Results and Comments

| METHOD | TEST | RUN A | RUN B | RUN C | AVG. |
|---|---|---|---|---|---|
| ST-8 | Dimethylsulfide, ppm | | | | |

FIG. IV-25

5.5 Temperature measuring device. Use a Chromel-Alumel thermocouple accurate to ±15°F., connected to a temperature compensated null type potentiometer, or equivalent, to measure stack temperatures.

5.6 Absorbers. Use three Greenberg-Smith impingers. The third impinger shall be modified by removing the impaction plate and attaching a thermometer to the inlet stem.

5.7 Cooling system. Use an ice bath to contain the impingers.

5.8 Sample pump. Use a leak-free vacuum pump capable of maintaining a 1.0 CFM flow rate at 15 inches of mercury. The pump must have a sample rate control valve and a vacuum gauge attached to the inlet.

5.9 Silica gel tube. Use approximately 500cc of silica gel followed by Drierite indicator to insure that the gas entering the dry test meter is free of $H_2O$.

5.10 Dry test meter. Use a 175 CFH dry test meter accurate within ±2% of the true volume and equipped with a thermometer to measure the outlet temperature. The working pressure across the meter shall not exceed a one inch water column.

5.11 Rotameter. Use a calibrated rotameter to measure the sampling rate.

5.12 Pressure gauge. Use a Magnehelic differential pressure gauge, or equivalent, in the same range as the velocity and static pressures being measured in the stack.

5.13 Analytical Balance. An analytical balance capable of measuring condensate weights to the nearest 0.1 gram is acceptable.

5.14 Barometer. Use a barometer that is accurate to within ±0.2 inches of mercury.

6. Reagents

6.1 0.1M Iodine Monochloride - Refer to Analytical procedure Lab-6.

7. Pre-Test Procedures

7.1 Impinger preparation. Fill each of two unmodified Greenberg-Smith impingers with approximately 100ml of iodine monochloride. Weigh and record the weights on the data as shown in Figure IV-27.

7.2 Nozzle size determination. Do the preliminary tests outlined below to determine the correct nozzle size to aid in isokinetic sampling.

7.2.1 Determine the number and location of the stack traverse points in accordance with ST-18.

7.2.2 Conduct a velocity traverse in accordance with ST-17 and measure the stack gas temperature.

7.2.3 Determine the moisture content of the stack gases in accoradnce with ST-23.

7.2.4 Nozzle diameter.

$$D_n = 13.7 \left[ \frac{T_s}{V_s(100-\%\ H_2O)} \right]^{\frac{1}{2}}$$

$D_n$ = nozzle diameter, mm
$T_s$ = stack gas temperature, °R
$H_2O$ = stack gas moisture concentration, %
13.7 = a constant based on an assumed meter rate of 0.5 CFM, meter temperature of 70F, and a molecular weight of 28.8.
$V_s$ = stack gas velocity fps as calculated in Section 8.2 of ST-17.

7.3 Assemble the sampling train as shown in Figure IV-26.

7.4 The entire sampling train must be leak-checked before each test run. Plug the sampling probe, start the pump, and adjust the pump vacuum to 380mm Hg (15"hg). A leak rate through the meter which exceeds 0.57 lpm (0.02 CFM) is unacceptable.

8. Sampling

8.1 Each test run shall be of 50 minute duration when testing emissions from continuous operations. Each test run at batch process operations shall be for 90% of the batch time or 50 minutes, whichever is less.

8.2 Sample at the traverse points determined in accordance with ST-18.

8.3 The sampling rate at each traverse point must be isokinetic. Measure the stack velocity and stack temperature at each sample point and adjust the meter flow rate according to the following equation:

$$Q_m = \frac{2.638 \times 10^{-3}(100-H_2O)\ D_n^2 V_s}{T_s}$$

where:
$Q_m$ = isokinetic sampling rate, ACFM
$T_s$ = meter temperature, °R
$H_2O$ = stack gas moisture content (from 6.3.3)
$2.638 \times 10^{-3}$ = constant derived from 60 sec/min, 70°F, 29.92 in. Hg and molecular weight.

8.4 When inserting the probe into the stack rotate the nozzle so it points down stream to avoid particulate collection prior to sampling. Immediately before sampling rotate the probe so the nozzle points upstream.

8.5 Record the following information at five-minute intervals or whenever changing sampling locations on a field data sheet as shown in Figure IV-28.

Stack velocity head
Sample time
Sample rate
Cumulative sample volume
Impinger saturation temperature
Stack gas temperature
Impinger vacuum
Dry test meter temperature.

8.6 Add ice as necessary to maintain impinger temperatures at 70°C (45°F) or less.

8.7 At the conclusion of each run, stop the pump, remove the probe from the stack and record the final meter reading. Point the probe upward and purge the sample train with ambient air.

8.8 Take three consecutive samples.

## 9. Post-Test Procedures

9.1 Rinse the nozzles with approximately 50ml of 6 normal nitric acid.

9.2 Analyze the filter, any material in the nozzle and the ICl solutions for lead according to Analytical Procedure Lab 4b.

## 10. Auxiliary Tests

10.1 Determine the $CO_2$, $O_2$ and CO concentrations simultaneous with each particulate run in accordance with ST-5, ST-14, and ST-6. An Orsat analysis (ST-2) is also acceptable.

## 11. Calculations

### 11.1 Standard Dry Sample Volume

$$V_o = \frac{17.71 V_m P_b}{T_m}$$

where: $V_o$ = standard dry sample volume, SDCF @ 70°F and 29.92 inches Hg.
$V_m$ = actual metered volume, $ft^3$
$P_b$ = barometric pressure, inches Hg.
$T_m$ = Average meter temperature, °R
17.71 = constant correcting to 70°F and 29.92 inches Hg.

## 11.2 Water Vapor Content

$$H_2O = \frac{(.0474\ W_c) + \dfrac{V_o P_{sat}}{P_b - P_I - P_{sat}}}{V_o + (.0474\ W_c) + \dfrac{V_o\ P_{sat}}{P_b - P_I - P_{sat}}} \times 100$$

where: $W_c$ = total condensate weight, all impingers, grams
$P_{sat}$ = water saturation pressure in impingers, inches
$P_b$ = barometric pressure, inches Hg.
$P_I$ = pump inlet vacuum, inches Hg.
$H_2O$ = percent water vapor
.0474 = cubic ft of vapor resulting from l cubic centimeter of liquid $H_2O$.

## 11.3 Stack Gas Molecular Weight.

$$MW = 0.44(\%\ CO_2) + 0.32(\%O_2) + 0.28(\%N_2 + \%CO) + 0.18(\%H_2O)$$

MW = molecular weight
$\%CO_2$ = percent carbon dioxide by volume (dry basis)
$\%O_2$ = percent oxygen by volume (dry basis)
$\%CO$ = percent carbon monoxide by volume (dry basis)
$\%H_2O$ = percent moisture by volume
$\%N_2$ = percent nitrogen by volume (dry basis - determine by difference)

## 11.4 Stack Gas Flow Rate - Determine in accordance with ST-17

## 11.5 Mass Emission Rate

$$M = \frac{W \times 60 \times Q_o}{454 \times 10^{-6} \times V_o} \times T$$

where: M = mass emission rate, lbs/day
W = total wt. of lead collected in filter and impingers, μgrams
$Q_o$ = stack gas lfowrate, SDCFM
$V_o$ = sample volume, SDCF
T = plant operation, hr/day
60 = minutes/hour
.454 = grams/pound

11.6 Isokinetic Ratio. Calculate for each traverse point as:

$$R_i = \frac{T_{si}\ Q_{mi}}{60\ (100-H)\ AV_{si} t_i T_{mi}} \times 100\%$$

where:

$R_i$ = Isokinetic ratio at given point
$t_i$ = time, at point i, minutes
$A$ = nozzle area, $ft^2$
$V_{si}$ = stack velocity, point i, FOS
$T_{mi}$ = meter temperature, point i, °R
$T_{si}$ = stack temperature, point i, °R
$Q_{mi}$ = metered volume, point i
60 = seconds/minute

overall isokinetic ratio for each run:

$$R = \frac{Q_{mi}}{0.6(100-H)\ AT_m\ V_{si} t_i T_{si}}$$

## 12. Reporting

11.1 The data and information indicated in Figure IV-29 shall be reported.

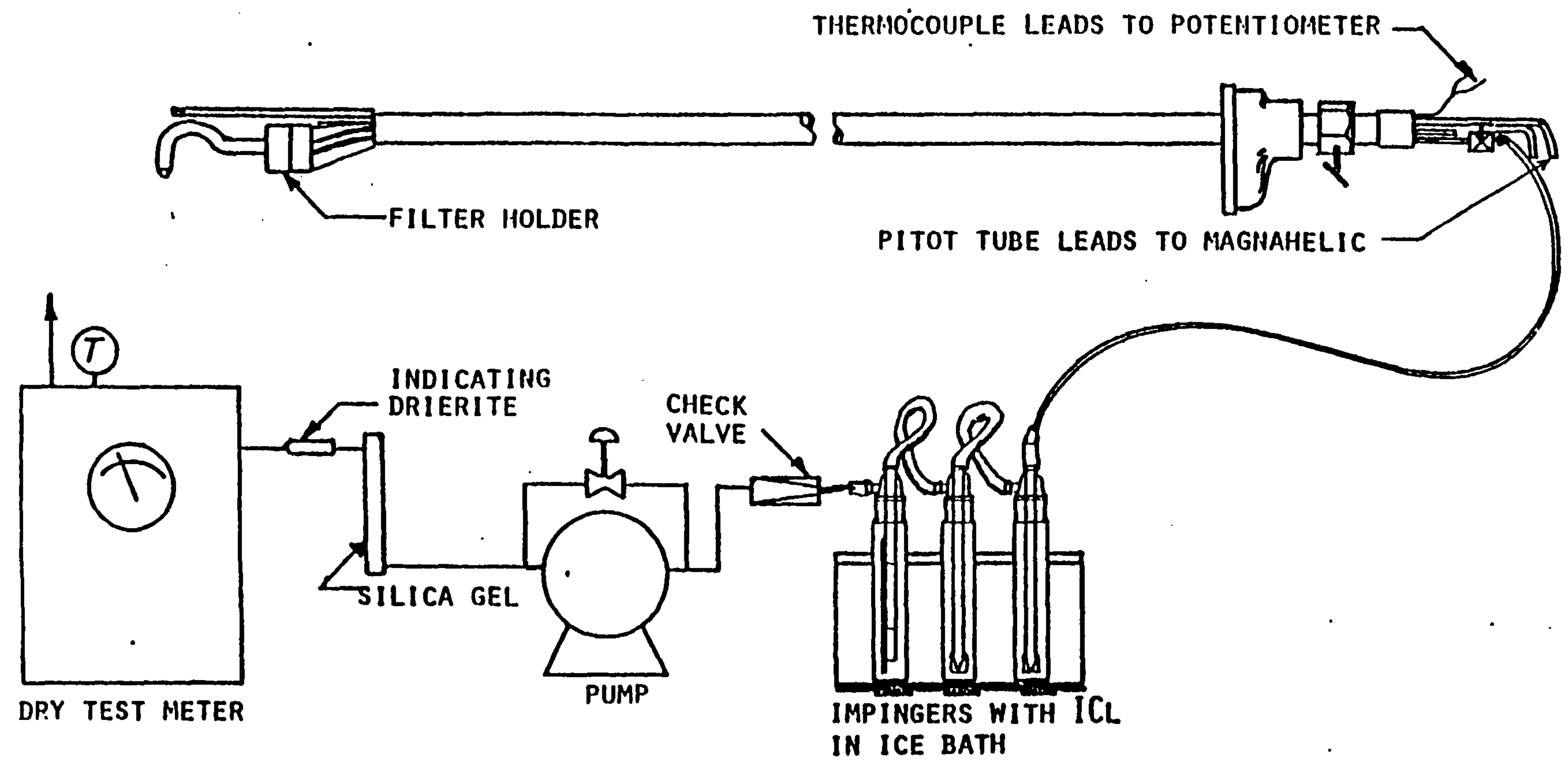


Fig. IV - 26

PARTICULATE SAMPLING TRAIN WITH DISC FILTER

# SOURCE TEST LAB DATA SHEET

PLANT ______________________ PAGE ________ OF ________
SOURCE OPERATION ______________________ INITIAL ______________
SOURCE TEST NO. ______________________ TEST DATE ______________
FILTER MEDIA ______________________
DRYING PROCEDURE: 105°C for 24 hours before and after test, desicated

STUBBIES

| NO. | TARE | PACKED WT | | | | PARTICULATE |
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NOZZLES

| NO. | TARE | | | PARTICULATE |
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IMPINGERS

| SOLN. | NO. | a TARE WT | b FILLED WT | c FINAL WT | c-a SAMPLE WT | c-b COND |
|---|---|---|---|---|---|---|
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COMMENTS:

Fig. IV - 27

## Source Test Data Sheet

Source Operation ____________
Plant ____________
Sample Type ____________
Process Cycle ____________
Duct Size ____________
Duct Pressure ____________

Source Test No. ____________
Run No. ____________
Date: ____________

____________ Nozzle Diameter
____________ Pitot Tube
____________ Gas Collector No.
____________ Barometric Pressure
____________ Leak Rate @ 15"Hg

Sampling Train:

| Traverse Point | Dist. From Inches | INITIAL TRAVERSE | | | SAMPLING | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | METER | | | | | | |
| | | Duct Temp°F | h $H_2O$ | $\sqrt{h}$ | Traverse Point | h $H_2O$ | $V_s$ FPS | Time | Rate CFH | Temp °F | Volume $Ft^3$ | Vac "Hg | Sat'd Gas Temp°F | $T_s$ Duct Temp°F | REMARKS |
| | | | | | | | | | | | | | | | |
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$$D_n = 13.7\left[\frac{T_s + 460}{K_p V_s (100-\%H_2O)}\right]^{1/2}$$

$$Q_m = \left[(2.638 \times 10^{-3}) K_p (100-\%H_2O) D_{nn}^{2}\right]\frac{V_s}{T_s}$$

Condensate ________ gm.
$V_o$ ________
$\%H_2O$ ________
$\%CO_2$ ________
$\%CO$ ________
$\%O_2$ ________

Source Test Team
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FIG. II 1

# SUMMARY OF SOURCE TEST RESULTS

## SOURCE INFORMATION

Firm Name and Address

Firm Representative and Title

Phone No.

Source:

Conditions During Tests

Operates hr/day & days/yr

Operating Parameters

Report No.

Test Date:

Test Times:

Run A:

Run B:

Run C:

Test Results and Comments

| METHOD | TEST | RUN A | RUN B | RUN C | AVG. |
|---|---|---|---|---|---|
| | Run time, minutes | | | | |
| | Stack gas temp., °F. | | | | |
| ST-17 | Stack flowrate, SDCFM | | | | |
| -14 | $O_2$ conc, dry basis, % | | | | |
| -5 | $CO_2$ conc, dry basis, % | | | | |
| ST-6 | CO conc, dry basis, % | | | | |
| ST-23 | $H_2O$ conc, actual, % | | | | |
| | Mass emission, lb/day | | | | |
| | Isokinetic ratio | | | | |

FIG. IV-29

# Source Test Procedure ST-10

## MERCURY

Ref: Reg. 11-5-301

## 1. Applicability

1.1 This method is used to quantify emissions of gaseous and particulate mercury. It determines compliance with Regulation 11-5-301

## 2. Principle

2.1 The sample stream is drawn through a solution of iodine monochloride which collects the mercury in the gas stream. The mercury compounds in the iodine monochloride (ICL) are reduced to elemental mercury and analyzed according to Analytical Procedure Lab-6. If high concentrations of particulate are expected, use particulate filters as prescribed in ST-15.

## 3. Range

3.1 The minimum measurable emission of mercury is $2 \times 10^{-5}$ grains/SDCF.

3.2 Elevated concentrations of mercury may be determined by increasing the concentration of the iodine monochloride in the absorbing reagent. The concentration of reagent to be used may be tetermined by stoichiometry, allowing a 50% excess.

## 4. Interferences - None known.

## 5. Apparatus

5.1 Probe nozzle. The probe nozzle shall be euqivalent to the nozzle shown in Figure IV-30. The probe nozzle shall be constructed of borosilicate glass, quartz, or stainless steel.

5.2 Filter holder. Use filter tubes equivalent to the one shown in Figure IV-30.and constructed of borosilicate glass or quartz.

5.3 Filter tube holder. Use a filter tube holder which will contain three filter tubes and the probe nozzle in a leak-free manner. Firuge IV-31 shows an acceptable filter tube holder configuration.

5.4 Filter medium. Use borosilicate glass wool, or equivalent. Corning Glass Works, Catalogue#3950 is acceptable.

5.5. Connections. The connection between the filters and the first impinger must be able to withstand stack temperatures. Vinyl tubing is acceptable in making all other connections.

5.6 Pitot tube. Use a Stauschelbe (Type-S), or equivalent, with a known coefficient which is constant within ±5% over the entire working range. The pitot type coefficient is determined by placing both the S-type and the standard pitot tube in a gas stream and measuring the pressure head with both over the entire velocity range of interest. Calculate the coefficient of the Type-S pitot tube as follows:

$$Cp_s = Cp_{std} \left[ \frac{\Delta P_{std}}{\Delta P_s} \right]^{\frac{1}{2}}$$

where: $Cp_s$ = Type-S pitot tube coefficient
$\Delta P_s$ = Pressure head, Type-S pitot tube
$\Delta P_{std}$ = Pressure head, standard pitot tube
$Cp_{std}$ = Standard pitot tube coefficient

5.7 Temperature measuring device. Use a Chromel-Alumel thermocouple accurate to ±15°F., connected to a temperature compensated null type potentiometer, or equivalent, to measure stack temperatures.

5.8 Encasement tube. Assemble the items in 5.5, 5.6 and 5.7 in a pipe as shown in Figure IV-32 to facilitate handling. To prevent the pitot tube from interfering with the gas flow stream-lines approaching the sample nozzle, position the pitot tube and sample nozzle not closer together than 0.75 inches.

5.9 Absorber. Use four Greenberg-Smith impingers. The fourth impinger shall be modified by removing the impaction plate and attaching a thermometer to the inlet stem.

5.10 Cooling system. Use an ice bath to contain the impingers.

5.11 Sample pump. Use a leak-free vacuum pump capable of maintaining a 1.0 CFM flow rate at 15 inches of mercury. The pump must have a sample rate control valve and a vacuum gauge attached to the inlet.

5.12 Silica gel tube. Use approximately 500cc of silica gel followed by a Drierite indicator to insure that the gas entering the dry test meter is free of $H_2O$.

5.13 Dry test meter. Use a 175 CFH dry test meter accurate within ±2% of the true volume and equipped with a thermometer to measure the outlet temperature. The working pressure across the meter shall not exceed one inch water column.

5.14 Rotameter. Use a calibrated rotameter to measure the sampling rate.

5.15 Pressure gauge. Use a Magnehelic differential pressure gauge, or equivalent, in the same range as the velocity and static pressures being measured in the stack.

5.16 Analytical balance. An analytical balance capable of measuring condensate weights to the nearest 0.1 gram is acceptable.

5.17 Barometer. Use a barometer that is accurate to within ±0.2 inches of mercury.

## 6. Reagents

6.1 0.1M Iodine Monochloride - Refer to Analytical Procedure Lab-6.

## 7. Pre-Test Procedures

7.1 Impinger preparation. 100 ml of the 0.1 M ICL shall be placed in the first three impingers which shall then be weighed. Record the data on the data sheet shown in Figure IV-33.

7.2 Nozzle size determination. Do the preliminary tests outlined below to determine the correct nozzle size to aid in isokinetic sampling.

7.2.1 Determine the number and location ofthe stack traverse points in accordance with ST-18.

7.2.2 Conduct a velocity traverse in accordance with ST-17 and measure the stack gas temperature.

7.2.3 Determine the moisture content of the stack gases in accordance with ST-23.

7.2.4 Nozzle diameter

$$D_n = 13.7 \left[ \frac{T_s}{V_s \ (100-\%H_2O)} \right]^{\frac{1}{2}}$$

$D_n$ = nozzle diameter, mm
$T_s$ = stack gas temperature, °R
$H_2O$ = Stack gas moisture concentration, %
13.7 = A constant based on an assumed meter rate of 0.5 CFM, meter temperature of 70F, and a molecular weight of 28.8
$V_s$ = stack gas velocity fps as calculated in Section 8.2 of ST-17.

7.3 Assemble the sampling train as shown in Figures IV-31 and 34.

7.4 The entire sampling train must be leak-checked before each test run. Plug the sampling probe, start the pump, and adjust the pump vacuum to 380mm Hg (15" Hg). A leak rate through the meter which exceeds 0.57 ipm (0.02 CFM) is unacceptable.

## 8. Sampling

8.1 Each test run shall be of 50 minute duration when testing emissions from continuous operations. Each test run at batch process operations shall be for 90% of the batch time or 50 minates, whichever is less.

8.2 Sample at the traverse points determined in accordance with ST-18.

8.3 The sampling rate at each traverse point must be isokinetic. Measure the stack velocity and stack temperature at each sample point and adjust the meter flow rate according to the following equation:

$$Q_m = \frac{2.638 \times 10^{-3}(100-\%H_2O)D_n{}^2V_s}{T_s}$$

where: $Q_m$ = isokinetic sampling rate, ACFM
$T_m$ = meter temperature, $^{o}R$
$H_2O$ = stack gas moisture content (from 6.3.3)
$2.638 \times 10^{-3}$ = constant derived from 60 sec/min, 70°F, 29.92 in. Hg and the molecular weight

8.4 When inserting the probe into the stack rotate the nozzle so it points down stream to avoid particulate collection prior to sampling. Immediately before sampling rotate the probe so that the nozzle points upstream.

8.5 Record the following information at five-minute intervals or whenever changing sampling locations on a field data form as shown in Figure IV-35.

Stack velocity head
Sample time
Sample rate
Cumulative sample volume
Impinger saturation temperature
Stack gas temperature
Impinger vacuum
Dry test meter temperature.

8.6 See ST-1B Section 8.5

8.7 See ST-1B Section 8.6

8.8 See ST-1B Section 8.7

## 9. Post-Test Procedures

9.1 Stopper the impingers to minimize sample losses.

9.2 Weigh each impinger to the nearest 0.1g

## 10. Auxiliary Tests

10.1 Determine the $CO_2$, $O_2$, and CO concentrations simultaneously with each run in accordance with ST-5, ST-14 and ST-16. An Orsat analysis (ST-2) is also acceptable.

## 11. Calculations

### 11.1 Standard Dry Sample Volume

$$V_o = \frac{17.71 V_m P_b}{T_m}$$

where $V_o$ = standard dry sample volume, SDCF @ 70°F and 29.92 inches Hg.
$V_m$ = actual metered volume, $ft^3$
$P_b$ = barometric pressure, inches Hg.
$T_m$ = Average meter temperature, °R
17.71 = constant correcting to 70°F & 29.92 inches Hg.

### 11.2 Water Vapor Content

$$H_2O = \frac{(.0474\ W_c) + \dfrac{V_o\ P_{sat}}{P_b - P_i - P_{sat}}}{V_o + (.0474\ W_c) + \dfrac{V_o\ P_{sat}}{P_b - P_i - P_{sat}}} \times 100$$

where: $W_c$ = total condensate weight, all impingers, grams
$P_{sat}$ = water saturation pressure in the impingers, inches Hg.
$P_b$ = barometric pressure, inches Hg.
$P_i$ = pump inlet vacuum, inches Hg.
$H_2O$ = per cent water vapor
.0474 = cubic ft of vapor resulting from 1 cubic centimeter of liquid $H_2O$.

### 11.3 Stack Gas Molecular Weight -

$$MW = 0.44\ (\%CO_2) + 0.32(\%O_2) + 0.28(\%N_2 + \%CO) + 0.18(\%H_2O)$$

MW = molecular weight
$\%CO_2$ = percent carbon dioxide by volume (dry basis)
$\%O_2$ = percent oxygen by volume (dry basis)
$\%CO$ = percent carbon monoxide by volume (dry basis)
$\%H_2O$ = percent moisture by volume
$\%N_2$ = percent nitrogen by volume (dry basis - determine by difference)

11.4 Stack Gas Flow Rate - Determine in accordance with ST-17.

11.5 Total mercury emissions. The emission rate of mercury shall be calculated as

$$M = \frac{W \times 10^6 \times Q_o \times 60 \times T}{V_o}$$

where:
$M$ = mass emission rate, gr/day
$W$ = total weight of mercury collected, u grams.
$Q_o$ = stack gas flowrate, SDCFM
$V_o$ = sample volume, SDCF
$T$ = plant operation, hr/day

11.6 Isokinetic Ratio. Calculate for each traverse point as:

$$R_i = \frac{T_{si}\ Q_{mi}}{60(100-H)\ AV_{si}t_iT_{mi}} \times 100\%$$

where:
$R_i$ = isokinetic ratio at given point
$t_i$ = time, at point i, minutes
$A$ = nozzle area, ft$^2$
$V_{si}$ = stack velocity, point i, FPS
$T_{mi}$ = meter temperature, point i, °R
$T_{si}$ = stack temperature, point i, °R
$Q_{mi}$ = metered volume, point i
60 = seconds/minute

overall isokinetic ratio for each run:

$$R = \frac{Q_{mi}}{60\ (100-H)\ AT_m\ V_{si}t_iT_{si}} \times 100\%$$

## 12. Reporting

12.1 The data and information indicated in Figure IV-35 shall be reported.

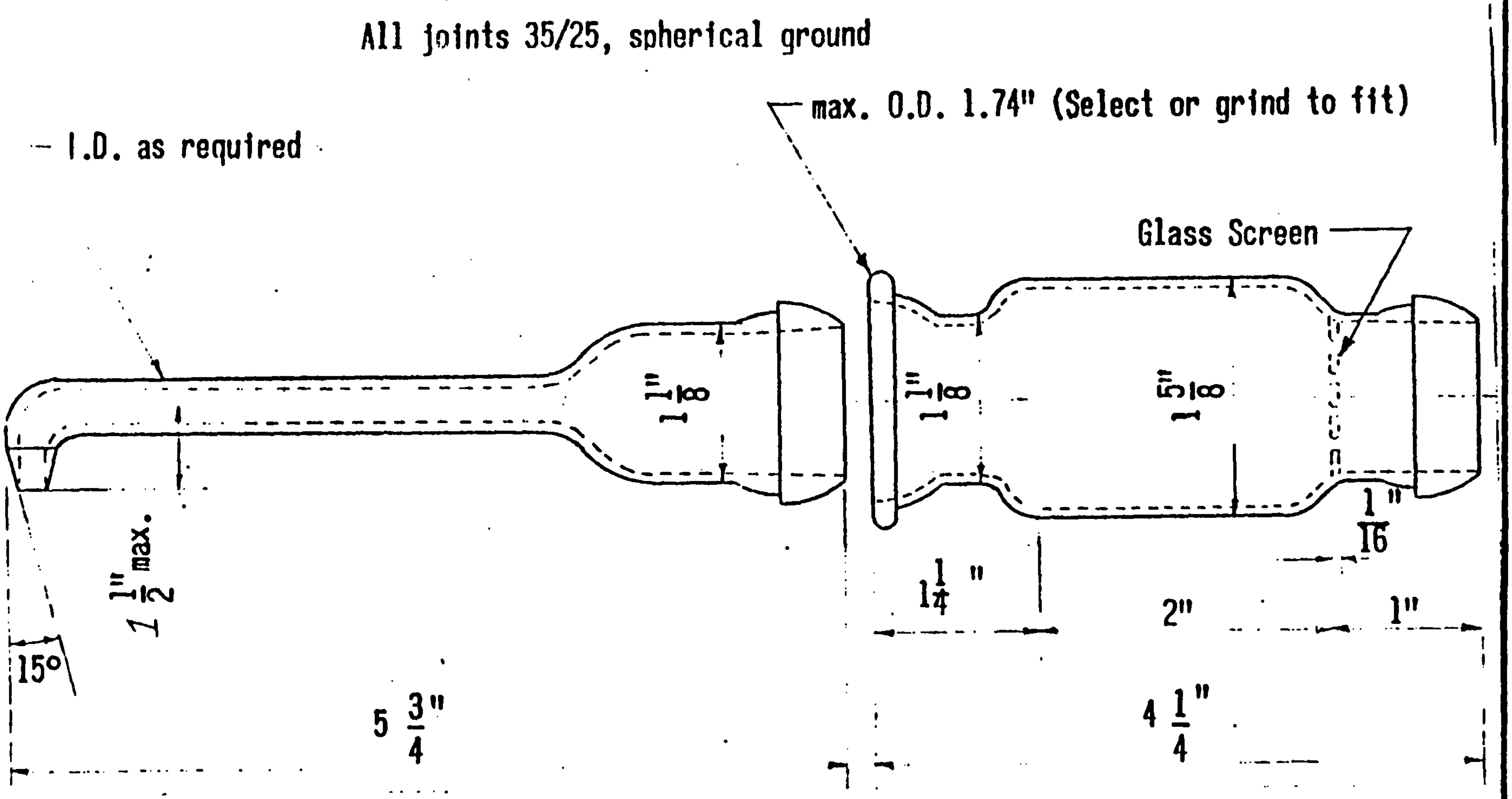

Fig. IV - 30

NOZZLE AND FILTER TUBE DETAILS

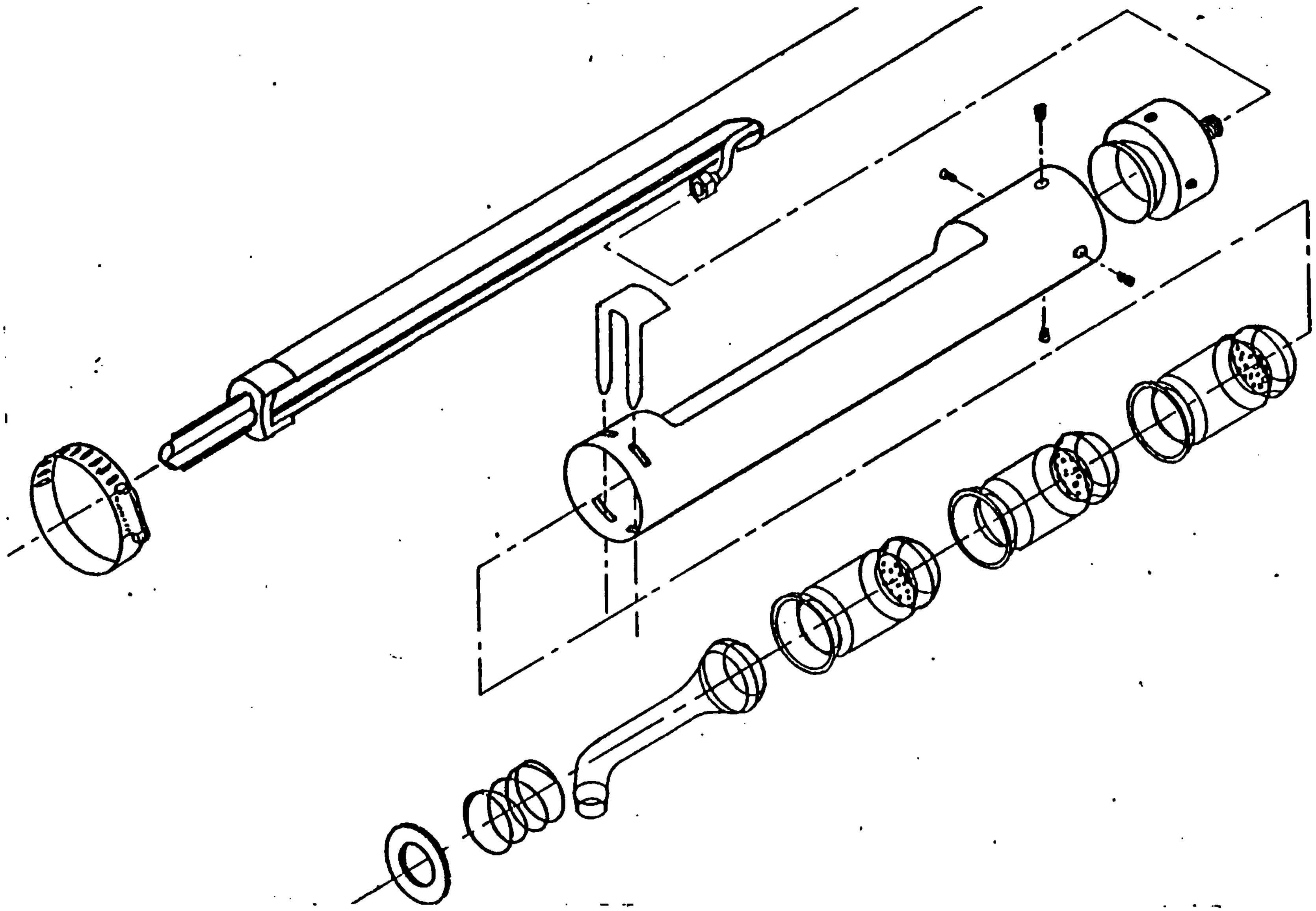

Fig. IV - 31

PROBEHOLDER ASSEMBLY

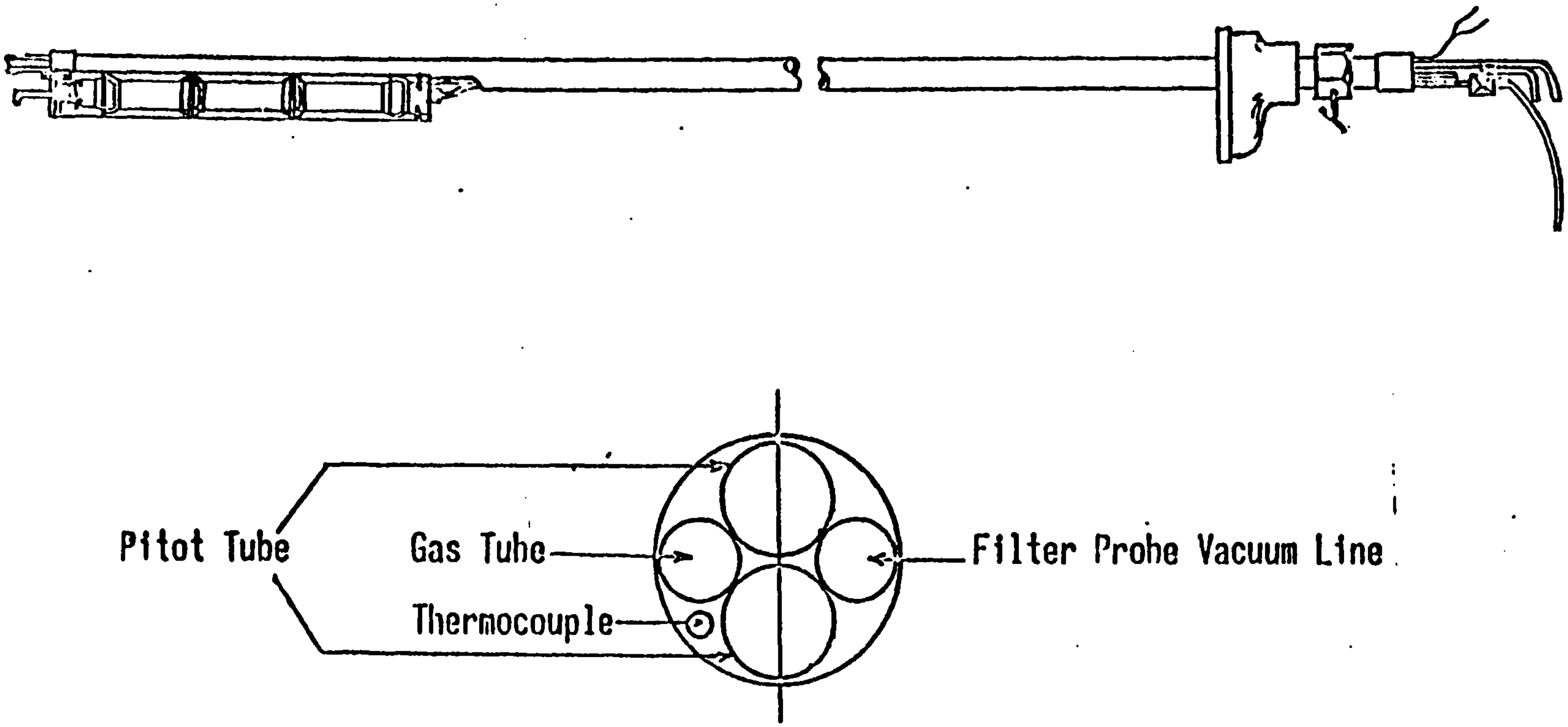

Fig. IV - 32

PROBE ENCASEMENT TUBE

# SOURCE TEST LAB DATA SHEET

PLANT ____________________ PAGE ________ OF ________
SOURCE OPERATION ____________________ INITIAL
SOURCE TEST NO. ____________________ TEST DATE ____________________
FILTER MEDIA ____________________
DRYING PROCEDURE: 105°C for 24 hours before and after test, desicated

STUBBIES

| NO. | TARE | PACKED WT |  |  |  | PARTICULATE |
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NOZZLES

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IMPINGERS

| SOLN. | NO. | a TARE WT | b FILLED WT | c FINAL WT | c-a SAMPLE WT | c-b COND WT |
|---|---|---|---|---|---|---|
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COMMENTS:

Fig. IV - 33

NOTE: FILTERS REQUIRED ONLY IF HIGH CONCENTRATIONS OF PARTICULATE MATTER IS PRESENT

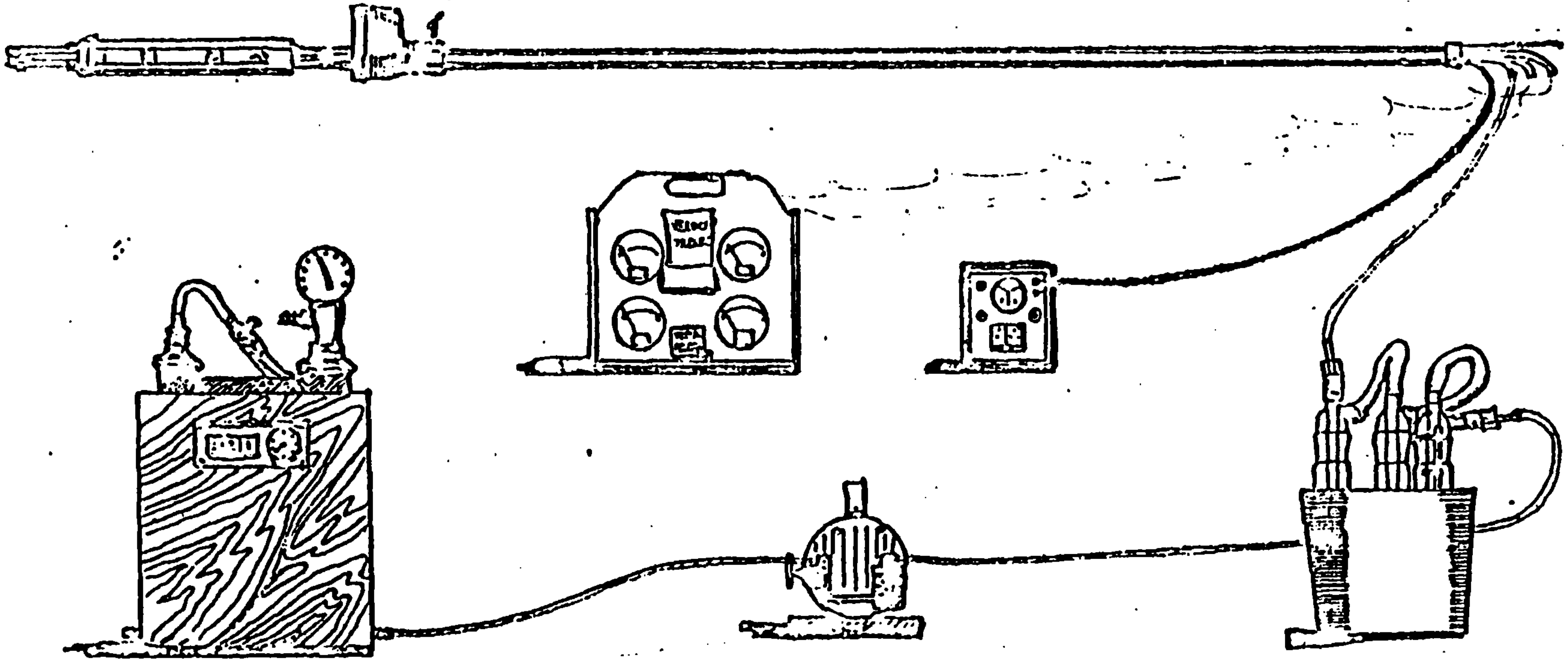

Fig. IV - 34

PARTICULATE SAMPLING TRAIN

## BAY AREA AIR POLL[illegible]ON CONTROL DISTRICT

### Source Test Data Sheet

Source Operation ____________
Plant ____________
Sample Type ____________
Process Cycle ____________
Duct Size ____________
Duct Pressure ____________

Source Test No. ____________
Run No. ____________
Date: ____________

____________ Nozzle Diameter
____________ Pitot Tube
____________ Gas Collector No.
____________ Barometric Pressure
____________ Leak Rate @ 15"Hg

Sampling Train:

| Traverse Point | Dist. From Inches | INITIAL TRAVERSE | | | SAMPLING | | | | | | | | | | REMARKS |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | METER | | | | | | |
| | | Duct Temp°F | h $H_2O$ | $\sqrt{h}$ | Traverse Point | h $H_2O$ | $V_s$ FPS | Time | Rate CFH | Temp °F | Volume $Ft^3$ | Vac "Hg | Sat'd Gas Temp°F | $T_s$ Duct Temp°F | |
| | | | | | | | | | | | | | | | |
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$$D_n = 13.7\left[\frac{T_s + 460}{K_p V_s (100-\%H_2O)}\right]^{1/2}$$

$$Q_m = \left[(2.638 \times 10^{-3}) K_p (100-\%H_2O) D_{mm}^2\right]\frac{V_s}{T_s}$$

Condensate ________ gm.
$V_o$ ________
$\%H_2O$ ________
$\%CO_2$ ________
$\%CO$ ________
$\%O_2$ ________

Source Test Team
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________________
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FIG IV-35

# SUMMARY OF SOURCE TEST RESULTS

## SOURCE INFORMATION

Firm Name and Address

Firm Representative and Title

Phone No.

Source:

Conditions During Tests

Operates hr/day & days/yr

Operating Parameters

Report No.

Test Date:

Test Times:

Run A:

Run B:

Run C:

Test Results and Comments

| METHOD | TEST | RUN A | RUN B | RUN C | AVG. |
|---|---|---|---|---|---|
| | Run time, minutes | | | | |
| | Stack gas temp., °F. | | | | |
| ST-17 | Stack flowrate, SDCFM | | | | |
| ST-14 | $O_2$ conc, dry basis, % | | | | |
| ST-5 | $CO_2$ conc, dry basis, % | | | | |
| ST-6 | CO conc, dry basis, % | | | | |
| ST-23 | $H_2O$ conc, actual, % | | | | |
| | Mass emission, gr/day | | | | |
| | Isokinetic ratio | | | | |

FIG. IV-36

# Source Test Procedure ST-11

## MERCAPTANS

REF: Reg. 7-303

## 1. Applicability

1.1.This method is used to determine emissions of mercaptans. It is applicable to the determination of compliance with Reg. 7-303

## 2. Principle

2.1 A sample is collected in a clean Tedlar bag. The sample is analyzed for mercaptans by chromatography with flame photometric detection.

## 3. Range and Sensitivity

3.1 The minimum measurable concentration of mercaptans is 20 ppb.

3.2 Non-linear response by the flame photometric detector occurs for mercaptans concentrations over 10ppm. However, appropriate dilution of the sample will allow concentrations up to 50 ppm to be analyzed.

## 4. Interferences

None Known

## 5. Apparatus

5.1 Sampling probe. Use a borosilicate glass tube fitted at the downstream end with an appropriate tubing connector.

5.2 Sampling bag. Use a Tedlar bag with a capacity of at least 10 liters and equipped with two stainless steel valves.

5.3 Sampling pump. Use a leak-free Teflon-lined diaphragm pump, or equivalent, capable of at least 0.5 CFM.

5.4 Sample lines. Use Teflon because of its non-reactive properties.

5.5 Drier/deodorizer. Use three glass cartridges fitted with ball joints. The first contains Drierite (calcium chloride); the others contain activated carbon and shall be followed by a Pyrex wool filter.

## 6. Pre-Test Procedures

6-1 Before going to the test site, assemble the train as shown in Figure IV-37. Purge the entire train, including the Tedlar bag, until the discharge is clean. The tedlar bag is considered clean when the lab determines the mercaptan concentration to be undectable.

6.2 Evacuate the Tedlar bag.

6.3 At the sampling site, assemble the train as shown in Figure 1, leaving out the drier-deodorizer.

7. Sampling

7.1 For stack sources, insert the probe into the stack.

7.2 For ambient sample, sample where the odor appears to be the strongest.

7.3 Start the pump and purge the gas to be sampled through the pump and bag for five minutes.

7.4 Then close the outlet valve on the Tedlar bag and fill the bag over a period of not less than three minutes.

7.5 Three bags filled as in 7.3 and 7.4 shall constitute a test.

8. Post-Test Procedures

8.1 The bags must be analyzed for mercaptans within four hours of collection. Refer to Analytical Procedure Lab-3.

9. Reporting

9.1 The mercaptan concentration of each bag is reported as in Figure IV-38.

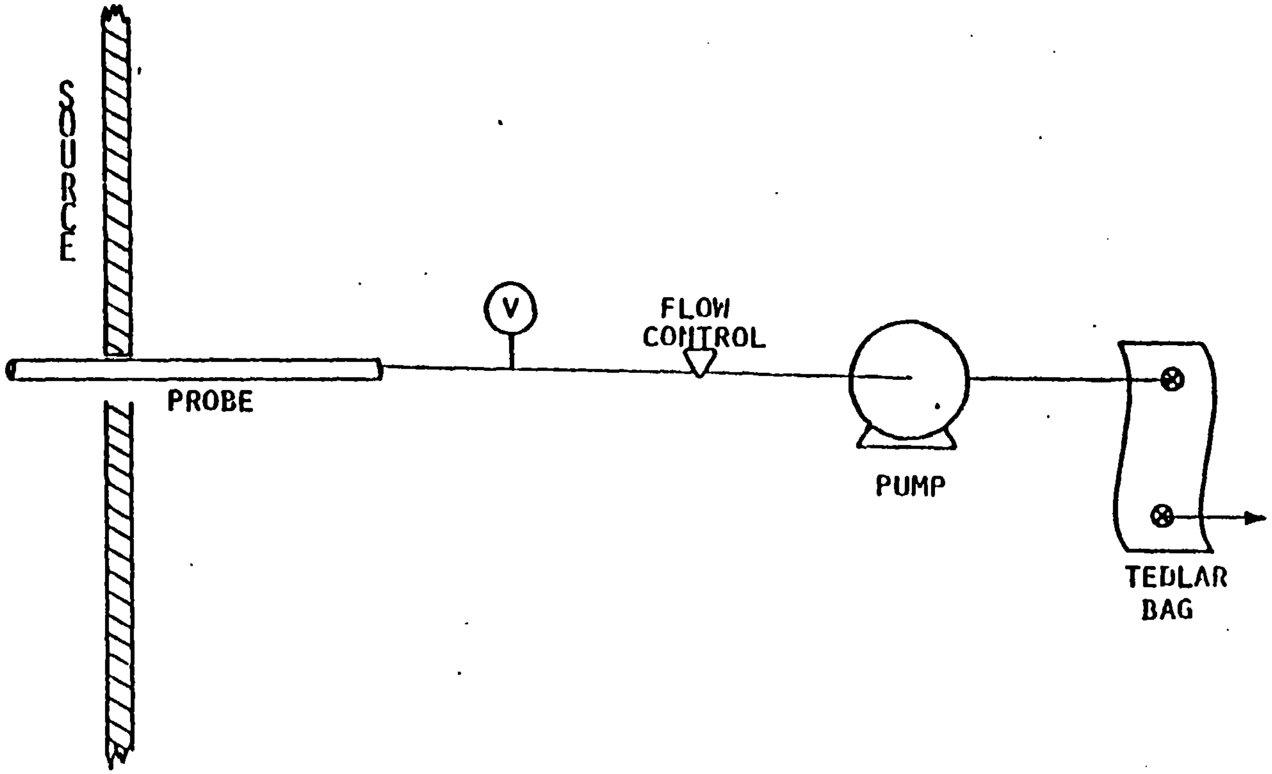

Fig. IV - 37

COLLECTION OF MERCAPTAN SAMPLES

# SUMMARY OF SOURCE TEST RESULTS

## SOURCE INFORMATION

**Firm Name and Address**

**Firm Representative and Title**

**Phone No.**

**Source:**

**Conditions During Tests**

**Operates** hr/day & days/yr

**Operating Parameters**

**Report No.**

**Test Date:**

**Test Times:**

**Run A:**

**Run B:**

**Run C:**

**Test Results and Comments**

| METHOD | TEST | RUN A | RUN B | RUN C | AVG. |
|---|---|---|---|---|---|
| ST-11 | Mercaptans, as $CH_3SH$, ppm | | | | |

FIG. IV-38

## Source Test Procedure ST-12

## COLLECTION OF ODOROUS SAMPLES

REF: Reg. 7-401

### 1. Applicability

1.1. This procedure is used for the collection of odorous samples to be evaluated according to Regulation 7-401.

### 2. Principle

2.1 Sample gas is drawn into a clean Tedlar bag at stack temperature. When condensation is expected the sample is diluted with clean dry air at stack temperature. If condensation is not expected the gas sample is drawn directly into a Tedlar bag.

2.2 The sample probe uses critical orifices for both the dilution air and the gas sample. The two are mixed at the same temperature to assure a constant dilution.

### 3. Range and Sensitivity - not applicable

### 4. Interferences

4.1 Particulate material will plug the critical orifice in the dilution probe.

4.2 Sample dilution must be sufficient to prevent condensation in the bag or probe.

### 5. Apparatus

5.1 Dilution probe. The dilution probe is constructed as shown in Figure IV-39.

5.1.1. All surfaces which contact the sample shall be Teflon, borosilicate glass or type 316 stainless steel.

5.1.2 The critical orifices shall be sized to provide a dilution sufficient to prevent condensation in the sample gas. The dilution shall be at least 10:1.

5.2 Pump. Use a Teflon-lined diaphragm pump or equivalent capable of at least 20 inches Hg vacuum. The pump shall be fitted with an inlet vacuum gauge and an inlet flow control valve.

5.3 Sample bag. A Tedlar bag with two stainless steel valves and a 10 liter capacity.

5.4 Drier/deordorizer. Use three glass cartridges fitted with ball joints. The first contains Drierite; the others contain activated carbon and shall be followed by a Pyrex wool filter.

5.5 Sampling lines. All sample contacting tubing shall be Teflon.

5.6 Rotameter. Use a calibrated rotameter capable of measuring the total (diluted) and undiluted sample.

6. Pre-Sampling Procedures

6.1 Purge the sample pump and Tedlar bag with clean, dry air for a minimum of 12 hours prior to sample collection.

6.2 Use the pump to be used for the test and fill the Tedlar sample bag with clean dry air and close both valves.

6.2.1 Evaluate the bag according to Section 7-400 of Regulation 7 within three hours prior to testing.

6.2.2 Two or more positive responses will disqualify the bag from being used.

6.3 Assemble the train as shown in Figure IV-40.

6.4 Start the pump, block the sample and air inlets and check that the flow out of the pump falls to zero.

6.5 Start the pump and purge the stack gas through the pump for at least three minutes.

6.6 Dilution measurement.

6.6.1 This step may be performed simultaneously with 6.5 or it may be done "out-of-stack".

6.6.2 Start the pump and adjust the inlet vacuum to at least 20 inches Hg and measure the total (diluted) sample flow.

6.6.3 Block the air line and adjust the pump vacuum to 20 inches Hg, and measure the undiluted sample flow.

6.6.4 Calculate the dilution ratio as:

$$R = \frac{Q_d - Q_u}{Q_u}$$

where: $R$ = dilution ration, air to sample
$Q_d$ = flow rate of diluted sample
$Q_u$ = flow rate of undiluted sample

7. Sampling

7.1 Start the pump and adjust inlet vacuum to at least 20 in. Hg

7.2 Attach the Tedlar bag to the pump outlet and purge for three minutes or longer.

7.3 Close the bag outlet and fill the bag.

## 8. Post-Sampling Procedures

8.1 The dilution ratio shall be checked as in 6.4

8.2 The bag shall be returned and evaluated within three hours.

## 9. Reporting

9.1 The data and information shown in Figure IV-41 shall be reported.

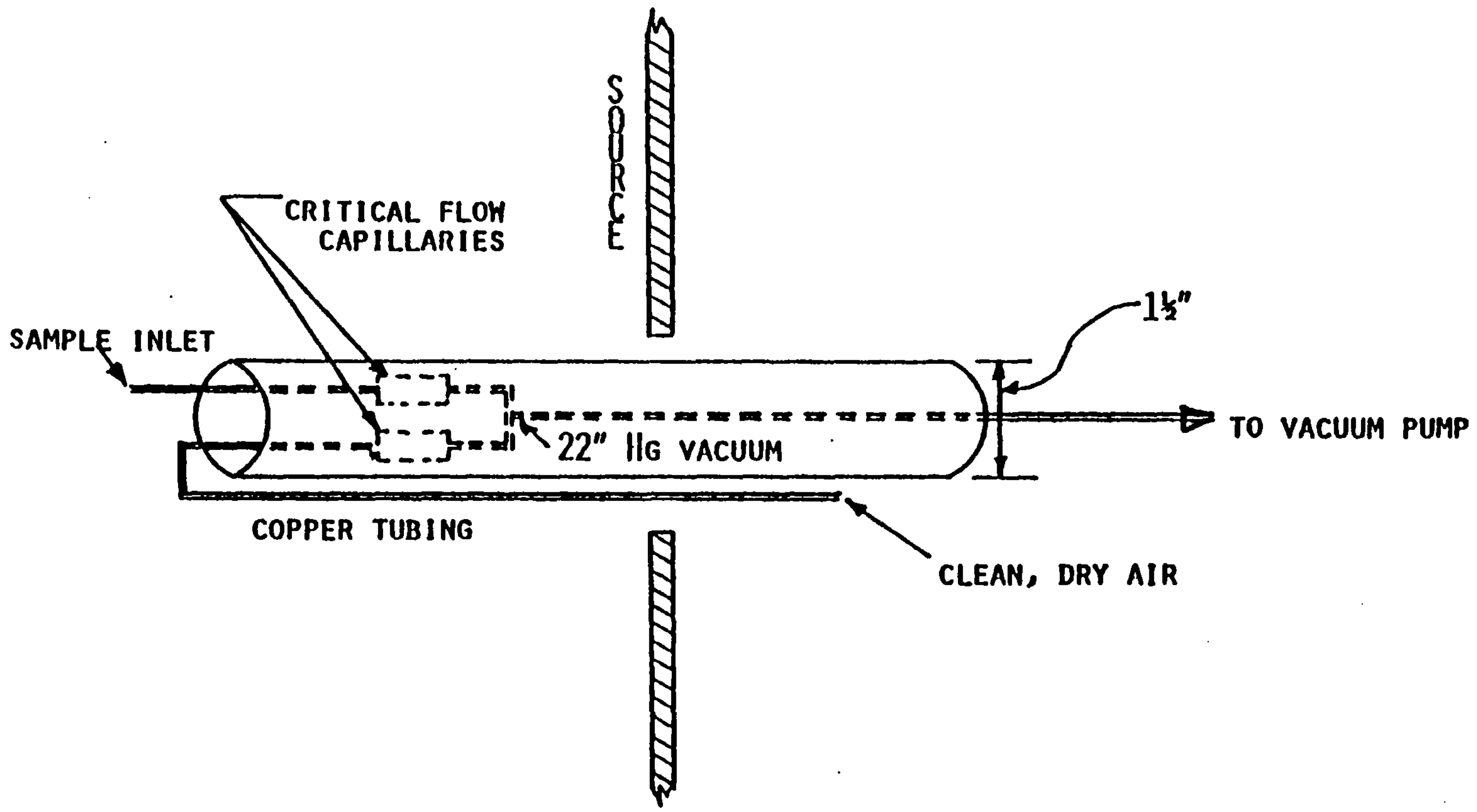

Fig. IV - 39

DILUTION PROBE

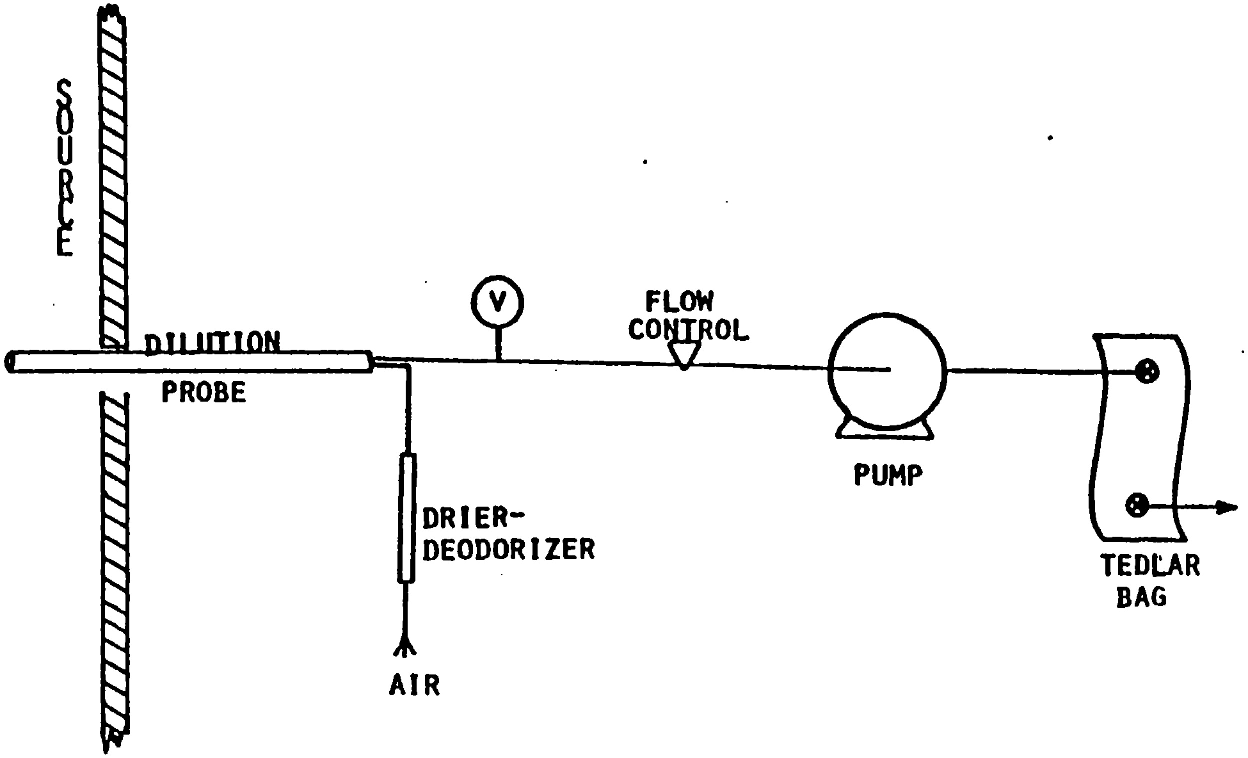

Fig. IV - 40

COLLECTION OF ODOROUS SAMPLES

# SUMMARY OF SOURCE TEST RESULTS

## SOURCE INFORMATION

Firm Name and Address

Firm Representative and Title

Phone No.

Source:

Conditions During Tests

Operates hr/day & days/yr

Operating Parameters

Report No.

Test Date:

Test Times:

Run A:

Run B:

Run C:

Test Results and Comments

Source Test Method 12

Location of Sample Point

Elevation of sample point, ft.

Dilution rate

This sample was deemed (ODOROUS or NON-ODOROUS) according to Section 7-404 of Regulation 7.

FIG. 19-41

# Source Test Procedure ST-13A

## OXIDES OF NITROGEN, CONTINUOUS SAMPLING

REF: Regs. 9-3-301
9-3-302
10-1-301

### 1. Applicability

1.1 This method is used to quantify emissions of oxides of nitrogen. It determines compliance with Regs. 9-3-301, 9-3-302 and 10-1-301.

### 2. Principle

2.1 A gas sample is extracted continuously from the sampling point and conditioned to remove water and particulate matter. Nitric oxide (NO) emissions are determined by passing a small portion of the sample through a chemiluminescent analyzer. The chemiluminescent processes is based on the light given off when nitric oxide and ozone react. Nitrogen dioxide ($NO_2$) concentrations are determined by passing the sample through a catalyst which reduces the $NO_2$ to NO. The total oxides of nitrogen concentration ($NO_2$ + NO) is then determined by chemiluminescence.

### 3. Range and Sensitivity

3.1 The minimum and maximum measurable concentrations of $NO_x$ depends on the specific chemiluminescent analyzer.

3.2 The minimum sensitivity of the analyzer shall be ±2% of full scale.

### 4. Interferences

4.1 If the molybdenum catalyst is used, compounds containing nitrogen (other than ammonia) may cause interference.

### 5. Apparatus

5.1 Oxides of nitrogen analyzer. Use a Thermo Electron Corp. Model 10A analyzer or its equivalent.

5.2 Chart recorder. The recorder monitors and records the continuous output from the analyzer.

5.3 Sample conditioning, zero air, and span gas system. The assembly of this system is shown in Figure IV-42. The sample conditioning system provides a dry, particulate free gas flow to the instrument. The zero air system provides clean dry atmospheric air for instrument calibration. The span gas system provides a known concentration of NO for use in calibrating the analyzer. Except as specified, all materials which come in contact with either the sample or span gas must be constructed of Teflon or stainless steel.

5.4 Sample probe. Use a borosilicate glass tube of sufficient length to traverse the stack being tested. If the stack temperature exceeds 425C (800F), use a quartz probe. Other probes are acceptable subject to prior approval by the Source Test Section.

5.5 Condensers. Use modified Greenberg-smith impingers with the impaction plates removed and the inlet tube shortened to a length of 10cm (4 inches), or equivalent.

5.6 Cooling system. Immerse the impingers in an ice bath during the test.

5.7 Particulate filter. Use a Balston type 95 holder with a grade B filter, or equivalent, in the sample system.

5.8 Pumps. Use leak-free, Teflon -lined, diaphragm pumps in the sample and zero air systems. The pumps must have a capacity of at least 28 liters/min (1.0 CFM).

5.9 Back-pressure regulator. Use a back-pressure regulator to maintain the sample and zero gas sample pressures to the instrument at five psig.

5.10 Gas scrubber. Use a bed of silica gel, Ascarite (or soda-lime), and charcoal to remove moisture, carbon dioxide, and hydrocarbons from the zero air system.

5.11 Span gas. Use a high-pressure cylinder containing a known concentration of NO in Nitrogen. The span gas concentration must be in the same range as the source being tested.

6. Pre-Test Procedures

6.1 Warm-up the instrument according to manufacturer's instructions.

6.2 Assemble the sampling system and analyzer as shown in Figs. IV-42 and IV-43.

6.3 Leak-test the sampling system by starting the pump, plugging the probe, and determining that the pressure to the analyzer falls to zero. Other leak-tests are acceptable subject to the approval of the Source Test Section.

6.4 Introduce zero air, into the analyzer and zero the instrument according to manufacturer's instructions.

6.5 Introduce span gas into the analyzer and calibrate teh instrument according to manufacturer's instructions.

6.6 Conduct a preliminary concentration traverse to determine if strafification of the stack gases exists. If the $NO_x$ concentration at any point differs from the average concentration by more than 10%, traverse the stack during the test. If not, sample at any single point.

6.7 Set-up the chart recorder according to manufacturer's instructions.

7. Sampling

7.1 Sample at continuous operations for a period of thirty minutes for each test run. Sample at batch operations for thirty minutes or 90% of the batch process time, whichever is less.

7.2 Introduce sample gas into the analyzer at the same flow rate used to calibrate the analyzer.

7.3 Maintain ice in the cooling system throughout the test.

7.4 Calibrate the analyzer before and after each test run. Record each step of the process clearly on the chart recording

7.5 Conduct three test runs.

8. Auxiliary Tests

8.1 Oxygen concentration. Determine the oxygen concentration simultaneously with each $NO_x$ run in accordance with ST-14.

9. Calculations

9.1 Determine the time-averaged concentration of NO on a dry basis for each run from the chart recording.

9.2 Concentration of nitrogen oxides corrected to 3% oxygen.

$$C_{NO,3\%} = C_{NO_x} \frac{17.95}{20.95 - C_{O_2}}$$

where: $C_{NO,3\%}$ = Total concentration of $NO_x$ on a dry basis at 3% $O_2$.

$C_{NO_x}$ = Total concentration of $NO_x$ (from 9.1)

$C_{O_2}$ = Concentration of oxygen on a dry basis (from 8.1).

17.95 = Ambient $O_2$ less 3%

9.3 When necessary to calculate the mass emission rate of $NO_x$, the molecular weight of $NO_2$ shall be used.

10. Reporting

The data and information shown in Fig. IV-44 shall be reported.

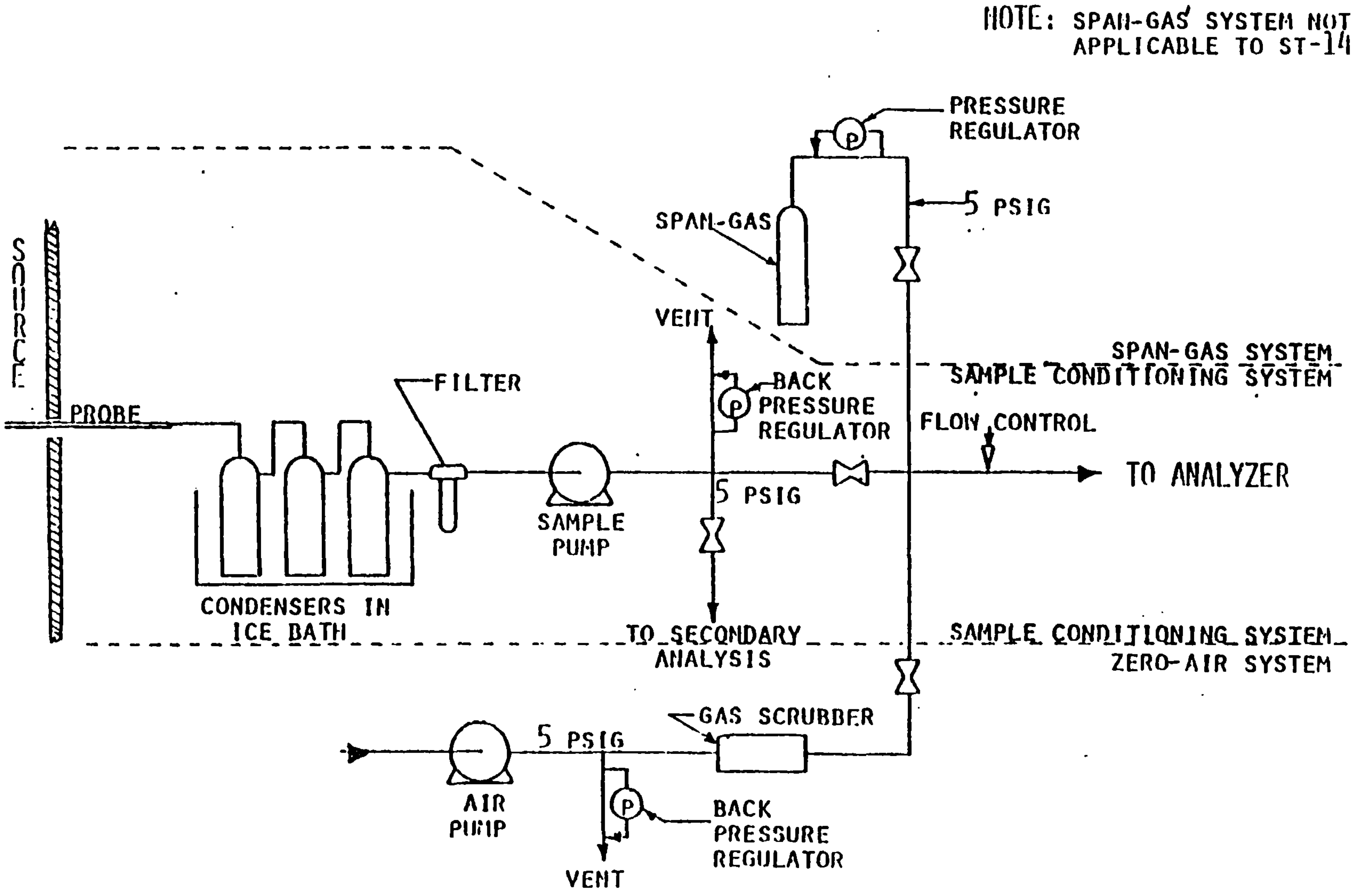

Fig. IV - 42

SAMPLE CONDITIONING, ZERO-AIR AND SPAN-GAS SYSTEMS

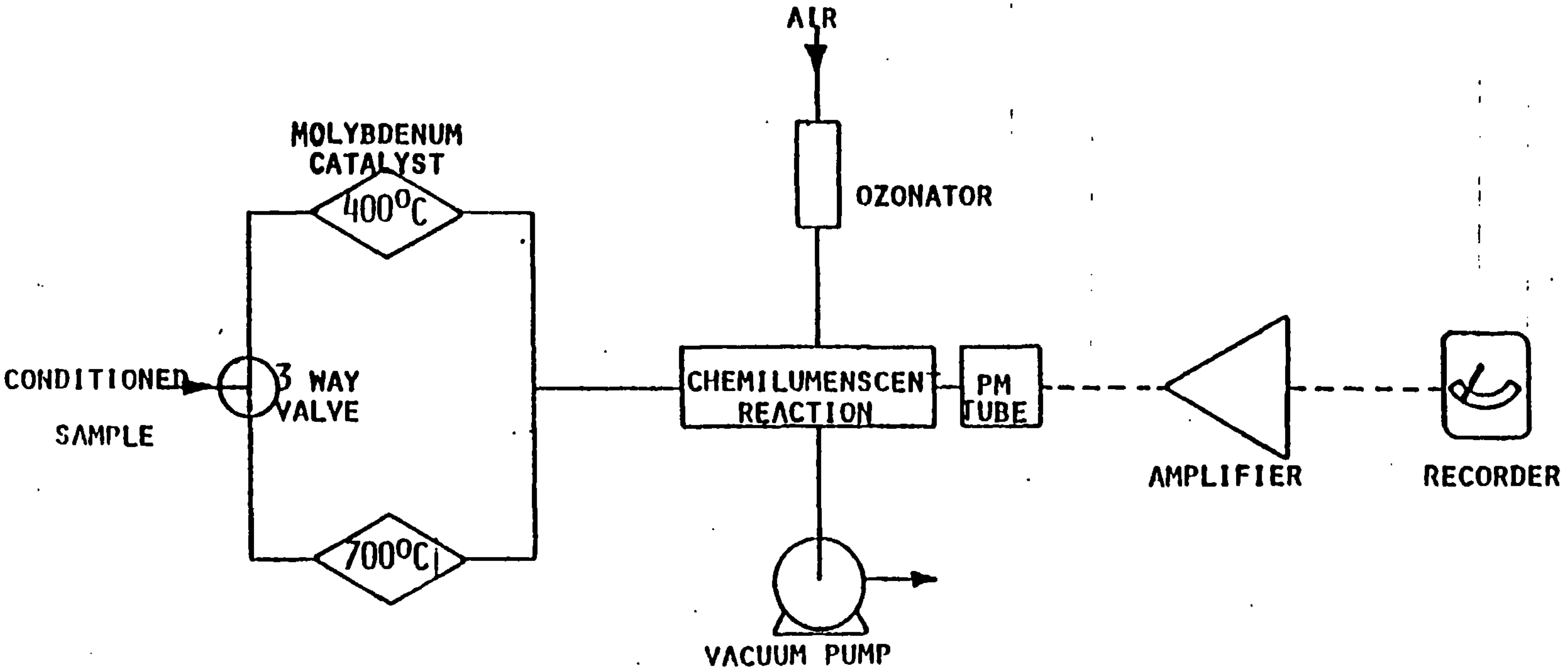

Fig. IV - 43

INSTRUMENTAL ANALYSIS OF NITROGEN OXIDES

## Source Test Procedure ST-13B

## OXIDES OF NITROGEN, INTERATED SAMPLE

| REF: REGS. | | | |
|---|---|---|---|
| | 9-3-301 | 9-3-304 | 10-1-301 |
| | 9-3-302 | 9-4-301 | |
| | 9-3-303 | 9-4-302 | |

### 1. Applicability

1.1 This method is used to quantify emissions of oxides of nitrogen. It determines compliance with Regs. 9-3-301, 9-3-302, 9-3-303, 9-3-304, 9-4-301, 9-4-302, 10-1-301 and is an acceptable alternate method to ST-13A.

### 2. Principle

2.1 Sample gas is drawn through an alkaline permanganate which absorbs the oxides of nitrogen. The oxides of nitrogen are subsequently analyzed for nitrite ($NO_2$) as specified in Analytical Procedure Lab-7A.

### 3. Range and Sensitivity

3.1 The minimum measurable concentration of oxides of nitrogen is 6 ppm at the sample volume specified in this procedure.

3.2 The maximum concentration for which this procedure has been proven is 1800 ppm.

### 4. Interference

None.

### 5. Apparatus

5.1 Probe. The probe is constructed of borosilicate glass tubing.

5.2 Absorbers. Use three Greenberg-Smith impingers modified by replacing the orifice and impaction plates with semi-fine frits of approximately 70 porosity. The third impinger has a thermometer attached to the inlet.

5.3 Cooling system. An ice bath is used to contain the impingers.

5.4 Sample pump. Use a leak-free vacuum pump capable of maintaining a 0.5 CFM flow rate at 15 inches of mercury-vacuum. The pump has a flow control valve and vacuum gauge attached to the inlet.

5.5. Silica gel tube. Approximately 500cc of silica gel with Drierite indicator are used to insure that the gas entering the dry gas meter is dry.

5.6 Dry test meter. Use a dry gas test meter accurate within ±2% of the true volume and equipped with a thermometer to measure the outlet temperature.

# SUMMARY OF SOURCE TEST RESULTS

## SOURCE INFORMATION

Firm Name and Address

Firm Representative and Title

Phone No.

Source:

Conditions During Tests

Operates hr/day & days/yr

Operating Parameters

Report No.

Test Date:

Test Times:

Run A:

Run B:

Run C:

Test Results and Comments

| METHOD | TEST | RUN A | RUN B | RUN C | AVG. |
|---|---|---|---|---|---|
| | Run time, minutes | | | | |
| | Stack gas temp., °F. | | | | |
| ST-13A | Total oxides of nitrogen, uncorrected, ppm | | | | |
| ST-14 | $O_2$, conc., % | | | | |
| ST-13A | Total oxides of nitrogen, corrected, ppm | | | | |

FIG. IV-44

5.7 connections. Use Teflon tubing in making all connections that come in contact with the sample. Vinyl tubing is acceptable for all other connections.

5.8 barometer. Use a mercury, aneroid, or other barometer that is accurate to within ± 0.2 inches of mercury.

5.9 Rotameter. Use a calibrated Rotameter to measure the sampling rate.

6. Reagents

6.1 absorption solution. Dissolve 40 grams of potassium permanganate and 20 grams of sodium hydroxide in distilled water and dilute to 1 liter with distilled water.

7. Pre-Test Procedures

7.1 Add 100 ml of alkaline permanganate solution to each of the three impingers.

7.2 Stopper the impingers.

7.3 Assemble the sampling train as shown in Figure .IV-45 Record the equipment identification on the test data sheet.

7.4 Leak-test the sampling train by turning on the pump, plugging the probe, and adjusting the pump inlet vacuum to 10 inches Hg. The leak rate must not exceed 0.6 lpm (0.02 CFM) through the dry test meter. Before turning off the pump, carefully release the plug in the sample probe to avoid backflow of the impinger solution.

7.5 Record the initial dry test meter reading and barometric pressure on a data sheet as shown in Figure IV-26.

8. Sampling

8.1 Sample at continuous operations for a period of thirty minutes for each test run. Sample at batch processes for a period of thirty minutes or 90% of the batch process time, whichever is less.

8.2 Position the probe at the sampling point and start the pump.

8.3 Sample at a constant rate of 6.0 liter/Hr (0.2 CFH) during the test as determined by the Rotameter.

8.4 Record the following information at five-minute intervals:

Dry test meter temperature
Impinger outlet temperature
Dry test meter volume
Rotameter flow.

8.5 Add ice as necessary to maintain impinger temperatures at 7°C (45°F) or less.

8.6 At the conclusion of each run, stop the pump, remove the probe from the stack, and record the final meter volume.

8.7 Take three consecutive samples.

## 9. Post-Test Procedures

9.1 Stopper the impingers until they are analyzed.

9.2 Individually analyze the alkaline permanganate solutions for total oxides of nitrogen as $NO_2$.

## 10. Auxiliary Tests

10.1 Oxygen. Determine the oxygen content of the stack gases simultaneously with each oxides of nitrogen run using ST-14.

## 11. Calculations

11.1 Standard sample volume:

$$V_o = \frac{17.71\ V_m P_b}{T_m}$$

where:

$V_o$ = corrected sample volume, SDCF at 70°F and 29.92 inches Hg.
$V_m$ = uncorrected meter volume, $ft^3$
$T_m$ = average run meter temperature, °R
$P_b$ = barometric pressure, inches Hg.
17.71 = a constant correcting to 70F and 29.92 inches Hg.

11.2 Uncorrected oxides of nitrogen concentration:

$$C_{NO} = \frac{19.3 \times 10^3 W}{V_o}$$

where:

$C_{NO}$ = oxides of nitrogen concentration, (as $NO_2$) ppm by volume on a dry basis.
$W$ = total weight of nitrite in the impinger catch, for each run, grams.
$19.3 \times 10^3$ = constant derived from molecular weight and molar volume to convert concentration to standard conditions.

11.3 concentration of oxides of nitrogen corrected to 3% oxygen:

$$C_{NO_2}, 3\% = C_{NO} \frac{17.95}{20.95-\%O_2}$$

where:
$\%O_2$ = percent oxygen by volume (dry basis).
17.95 = ambient $O_2$ less 3%

12. Reporting

The data and information shown in Fig. IV-47 shall be reported.

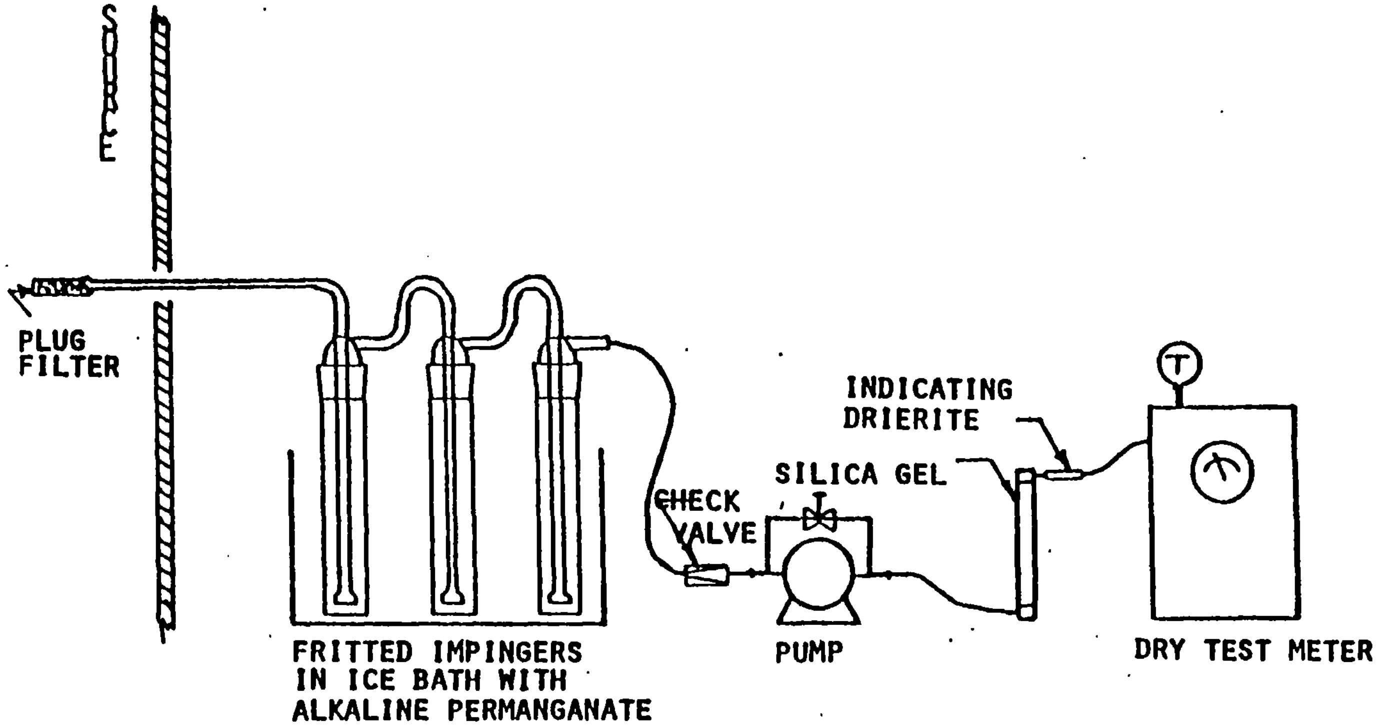

Fig. IV - 45

NITROGEN OXIDE SAMPLING TRAIN

BAY AREA AIR POLLUTION CONTROL DISTRICT

Source Test Data Sheet

Source Operation ____________
Plant ____________
Sample Type ____________
Process Cycle ____________
Duct Size ____________
Duct Pressure ____________

Source Test No. ____________
Run No. ____________
Date: ____________

____________ Nozzle Diameter
____________ Pitot Tube
____________ Gas Collector No.
____________ Barometric Pressur
____________ Leak Rate @ 15"Hg

Sampling Train:

| Traverse Point | Dist. From | INITIAL TRAVERSE | | | SAMPLING | | | | | | | | | | REMARKS |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | METER | | | | | | |
| | inches | Duct Temp°F | h $H_2O$ | $\sqrt{h}$ | Traverse Point | h $H_2O$ | $V_s$ FPS | Time | Rate CFH | Temp °F | Volume $Ft^3$ | Vac "Hg | Sat'd Gas Temp°F | $T_s$ Duct Temp°F | |
| | | | | | | | | | | | | | | | |
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$$D_n = 13.7\left[\frac{T_s + 460}{K_p V_s (100-\%H_2O)}\right]^{1/2}$$

$$Q_m = \left[(2.638 \times 10^{-3}) K_p (100-\%H_2O) D_{mm}^2\right]\frac{V_s}{T_s}$$

Condensate ________ gm.
$V_o$ ________
$\%H_2O$ ________
$\%CO_2$ ________
$\%CO$ ________
$\%O_2$ ________

Source Test Team
____________
____________
____________
____________

FIG. IV-46

# SUMMARY OF SOURCE TEST RESULTS

## SOURCE INFORMATION

Firm Name and Address

Firm Representative and Title

Phone No.

Source:

Conditions During Tests

Operates hr/day & days/yr

Operating Parameters

Report No.

Test Date:

Test Times:

Run A:

Run B:

Run C:

Test Results and Comments

| METHOD | TEST | RUN A | RUN B | RUN C | AVG. |
|---|---|---|---|---|---|
| | Run time, minutes | | | | |
| | Stack gas temp., °F. | | | | |
| ST-13B | Total oxides of nitrogen uncorrected, ppm | | | | |
| ST-14 | $O_2$ conc., % | | | | |
| ST-13B | Total oxides of nitrogen, corrected, ppm | | | | |

FIG. IV-47

## Source Test Procedure ST-14

## OXYGEN, CONTINUOUS SAMPLING

REF: Regs. 9-3-301
9-3-302

### 1. Applicability

1.1 This method is used to quantify emissions of oxygen. It determines compliance with Regs. 9-3-301 and 9-3-302.

### 2. Principle

2.1 A continuous representative gas sample is extracted from the sampling point and conditioned to remove water and particulate material. A small portion of the smaple is passed through a fuel cell type oxygen analyzer which measures the electrical current generated by the oxidation reaction at the gas/fuel cell interface.

### 3. Range and Sensitivity

3.1 The minimum measurable concentration of oxygen is 0.1%.

3.2 The upper limit depends on the range of the instrument.

3.3 The sensitivity of the $O_2$ analyzer shall be ±2% of full scale.

### 4. Interferences

4.1 Halogens and halogenated compounds will cause a positive interference. Acid gases will consume the fuel cell and cause a slow calibration drift.

### 5. Apparatus

5.1 Oxygen analyzer. Use a Teledyne Analytical Instruments Inc., Model 326 analyzer or its equivalent.

5.2 Chart recorder. The recorder monitors and records the continuous output from the analyzer.

5.3 Sample conditioning, zero air, and span gas system. The assembly of this system is shown in Fig. IV-48. The sample conditioning system provides a dry, particulate free gas flow to the instrument. The zero air system provides clean dry atmospheric air for instrument calibration. Except as specified, all materials which come in contact with either the sample or span should be constructed of Teflon or stainless steel.

5.4 Sample probe. Use a borosilicate glass tube of sufficient length to traverse the stack being tested. If the stack temperature exceeds 425C (800F), use a quartz probe. Other probes are acceptable subject to prior approval by the Source Test Section.

5.5 Condensers. Use modified Greenberg-Smith impingers with the impaction plates removed and the inlet tube shortened to a length of 10cm (4 inches), or equivalent.

5.6 Cooling system. Immerse the impingers in an ice bath during the test.

5.7 particulate filter. Use a Balston type 95 holder with a grade B filter, or equivalent, in the sample system.

5.8 pumps. Use leak-free, Teflon-lined, diaphragm pumps in the sample and zero air systems. The pumps must have a capacity of at least 28 liters/min (1.0 CFM).

5.9 Back-pressure regulator. Use a back-pressure regulator to maintain the sample and zero gas sample pressures to the instrument at five psig.

5.10 Gas scrubber. Use a bed of silica gel, Ascarite (or soda-lime), and charcoal to remove moisture, carbon dioxide, and hydrocarbons from the zero air system.

5.11 Span gas. The analyzer is spanned using dry air from the zero-gas system.

6. Pre-Test Procedures

6.1 Warm-up the instrument according to manufacturer's instructions.

6.2 Assemble the sampling system as shown in Figure IV-28.

6.3 Leak-test the sampling system by starting the pump, plugging the probe, and determining that the pressure to the analyzer falls to zero. Other leak-tests are acceptable subject to the approval of the Source Test Section.

6.4 Introduce zero air, into the analyzer and zero the instrument according to manufacturer's instructions.

6.5 Introduce span gas into the analyzer and calibrate the instrument according to manufacturer's instructions.

6.6 Conduct a preliminary concentration traverse (according to ST-18) to determine if stratification of the stack gases exists. If the $O_2$ concentration at any point differs from the average concentration by more than 10%, traverse the stack during the test. If not, sample at any single point.

6.7 Set-up the chart recorder according to manufacturer's recommendations.

## 7. Sampling

7.1 Each test run shall be of thirty minute duration when testing emissions from continuous operations. Each test run at a batch process operation shall be for 90% of the batch time or thirty minutes, whichever is less.

7.2 Introduce sample gas into the anlayzer at the same flow rate used to span the analyzer.

7.3 Maintain ice in the cooling system throughout the test.

7.4 Check the zero and span before and after each test run. Record each step of the process clearly on the chart recording.

7.5 Do three test runs.

## 8. Calculations

8.1 Determine the time-averaged concentration of $O_2$ on a dry basis for each run from the chart recording.

## 9. Reporting

9.1 These values are determined as auxiliary data for other procedures and shall be reported with those test results.

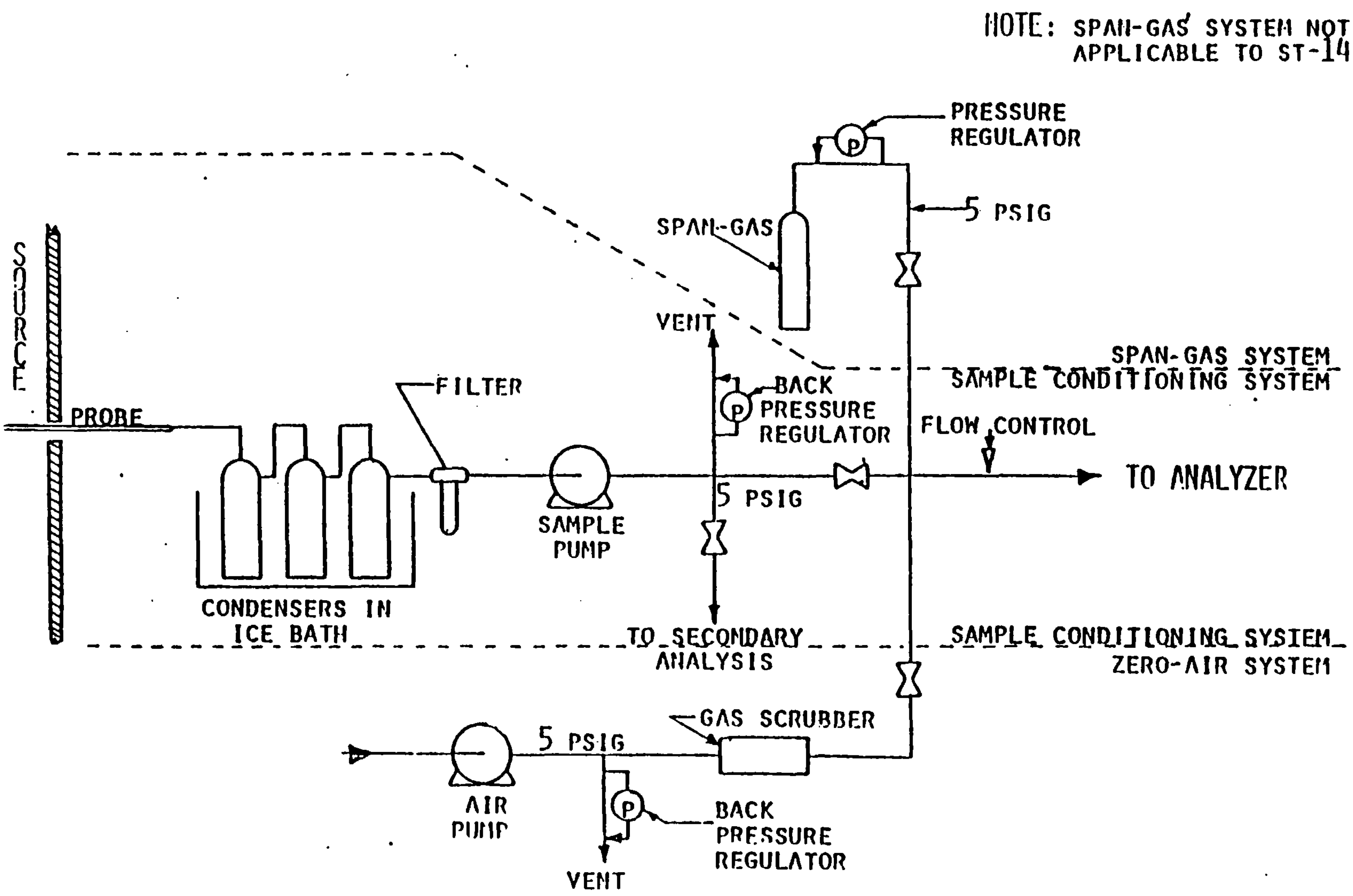

Fig. IV - 48

SAMPLE CONDITIONING, ZERO-AIR AND SPAN-GAS SYSTEMS

## Source Test Procedure ST-15

## PARTICULATE

REF: Regs. 6-310 10-1-301
6-311

### 1. Applicability

1.1 This method is used to quantify particulate emissions. It determines compliance with Regulations 6-310, 6-311 and 10-1-301.

### 2. Principle

2.1 Stack gases are drawn isokinetically through glass fiber filters at stack conditions. The weight of particulate matter, including any material that condenses at or above the stack temperature, is determined gravimetrically after the removal of uncombed water.

### 3. Range

3.1 The minimum particulate emissions measurable by this procedure is .001 gr/SDCF.

### 4. Interferences

4.1 Sulfer oxides, sulfates and some other species which are not particulate at stack conditions may react with the filter medium so as to produce a spurious weight gain. This phenomona is minimized by use of a back-up filter as a blank.

### 5. Apparatus

5.1 Probe nozzle. The probe nozzle shall be equivalent to the nozzle shown in Fig IV-49. The probe nozzle shall be constructed of borosilicate glass, quartz, or stainless steel.

5.2 Filter holder. Use filter tubes equivalent to the one shown in Fig. IV-49 and constructed of borosilicate glass or quartz.

5.3 Filter tube holder. Use a filter tube holder which will contain threefilter tubes and the probe nozzle in a leak-free manner. Fig IV-50 shows an acceptable filter tube holder configuration.

5.4 Filter medium. Use borosilicate glass wool, or equivalent. Corning Glass Works Glass, Catalogue #3950 is acceptable.

5.5 Connections. The connection between the filters and the first impinger must be able to withstand stack temperatures. Vinyl tubing is acceptable in making all other connections.

5.6 Pitot tube. Use a Stauscheibe (Type-S), or equivalent, with a known coefficient which is constant within ±5% over the entire working range. The pitot tube coefficient is determined by placing both the S-type and the standard pitot tube in a gas stream and measuring the pressure head with both over the entire velocity range of interest. Calculate the coefficient of the Type-S pitot tube as follows:

$$C_{P_s} = C_{P_{std}} \left[ \frac{\Delta P_{std}}{\Delta P_s} \right]^{1/2}$$

where:

$C_{P_s}$ = Type-S pitot tube coefficient

$\Delta P_s$ = Pressure head, Type-S pitot tube

$\Delta P_{std}$ = Pressure head, standard pitot tube

$C_{P_{std}}$ = Standard pitot tube coefficient

5.7 Temperature measuring device. Use a Chromel-Alumel thermocouple accurate to ±15°F., connected to a temperature compensated null type potentiometer, or equivalent, to measure stack temperautres.

5.8 Encasement tube. Assemble the items in 5.5, 5.6 and 5.7 in a pipe as shown in Fig. IV-51 to facilitate handling. To prevent the pitot tube from interfering with the gas flow stream-lines approaching the sample nozzle, position the pitot tube and sample nozzle not closer together than 0.75 inches.

5.9 Condensers. Use three Greenberg-Smith impingers. The third impinger shall be modified by removing the impaction plate and attaching a thermometer to the inlet stem.

5.10 Cooling system. Use an ice bath to contain the impingers.

5.11 Sample pump. Use a leak-free vacuum pump capable of maintaining a 1.0 CFM flow rate at 15 inches of mercury. The pump must have a flow control valve and vacuum gauge attached to the inlet.

5.12 Silica gel tube. Use approximately 500cc of silica gel (with a Drierite indicator) to insure that the gas entering the dry test meter is free of $H_2O$.

5.13 Dry test meter. Use a 175 CFH dry test meter accurate within ±2% of the true volume and equipped with a thermometer to measure the outlet temperautre. The working pressure across the meter shall not exceed one inch water column.

5.14 Rotameter. Use a calibrated rotameter to measure the sampling rate.

5.15 Pressure gauge. Use a Magnehelic differential pressure gauge, or equivalent, in the same range as the velocity and static pressures being measured in the stack.

5.16 Analytical balance. Use an analytical balance accurate to within ±0.5mg to measure filter weights. An analytical balance capable of measuring condensate weights to the nearest 0.1 gram is acceptable.

5.17 Barometer. Use a barometer that is accurate to within ± 0.2 inches of mercury.

6. Pre-Test Procedures

6.1 Filter preparation. Pack three labeled filter tubes for each run with borosilicate glass wool so as to produce a 10 inch $H_2O$ pressure drop across each filter tube at 0.5 CFM flow. Dry the filter tubes in an oven at 105C for 24 hours cool them in a desiccator. Weigh each filter tube on an analytical balance to the nearest 0.5 mg. Record each weight on the lab data sheet shown in Figure IV-52.

6.2 Impinger preparation. Fill each of two unmodified Greenberg-Smith impingers with approximately 100 ml of distilled water. Weigh and record the weights on the data sheet as shown in Figure IV-52.

6.3 Nozzle size determination. Do the preliminary tests outlined below to determine the correct nozzle size to aid in isokinetic sampling.

6.3.1 Determine the number and location of the stack traverse points in accordance with ST-18.

6.3.2 Conduct a velocity traverse in accordance with ST-17 and measure the stack gas temperature.

6.3.3 Determine the moisture content of the stack gases in accordance with ST-23.

6.3.4 Nozzle diameter.

$$D_n = 13.7 \left[\frac{T_s}{V_s(100 - H_2O)}\right]^{1/2}$$

$D_n$ = Nozzle diameter, mm
$T_s$ = Stack gas temperature, °R
$H_2O$ = Stack gas moisture concentration, %
13.7 = A constant based on an assumed meter rate of 0.5 CFM, meter temperature of 70F, and a molecular weight of 28.8.
$V_s$ = stack gas velocity fps

6.4 Assemble the sampling train as shown in Figs. IV-50 and IV-53.

6.5 The entire sampling train must be leak-checked before each test run. Plug the sampling probe, start the pump, and adjust the pump vacuum to 380mm Hg (15"Hg). A leak rate through the meter which exceeds 0.57 lpm (0.02 CFM) is unacceptable.

7. Sampling

7.1 Each test run shall be of 50 minute duration when testing emissions from continuous operations. Each test run at batch process operations shall be for 90% of the batch time or 50 minutes, whichever is less.

7.2 Sample at the traverse points determined in accordance with ST-18.

7.3 The sampling rate at each traverse point must be isokinetic. Measure the stack velocity and stack temperature at each point and adjust the meter flow rate according to the following equation:

$$Q_m = \frac{2.638 \times 10^{-3} (100-\%H_2O) D_n^2 V_s}{T_s}$$

where: $Q_m$ = isokinetic sampling rate, ACFM
$T_m$ = meter temperature, °R
$H_2O$ = stack gas moisture content (from 6.3.3)

7.4 When inserting the probe into the stack rotate the nozzle so it points down stream to avoid particulate collection prior to sampling. Immediately before sampling, rotate the probe so the nozzle points upstream.

7.5 Record the following information at five-minute intervals or whenever changing sampling locations on a field data sheet as shown in Figure IV-54.

Stack velocity head
Sample time
Sample rate
Cumulative sample volume
Impinger saturation temperature
Stack gas temperature
Impinger vacuum
Dry test meter temperature

7.6 At the conclusion of each run, stop the pump, remove the probe from the stack and record the final meter reading. Point the probe upward and purge the sample train with ambient air.

7.7 Conduct three consecutive test runs.

8. Post-Test Procedures

8.1 Remove the nozzle and filters as a unit and seal both ends. This must be done in a clean dry location to avoid sample contamination.

8.2 Stopper the impingers to minimize sample losses.

8.3 Clean the exterior of the nozzle and filter tubes and dry them in an oven for 24 hours at 105C. Allow to cool in a desiccator and weigh to the nearest 0.5 mg. Repeat the desiccation and weighing process daily until constant weights are recorded.

8.4 After weighing the nozzle containing particulate matter, clean, dry and weigh the nozzle to obtain its tare weight.

8.5 Weigh each impinger to the nearest 0.1 g.

9. Auxiliary Tests

9.1 Determine the $CO_2$, $O_2$ and CO concentrations simultaneously with each particulate run in accordance with ST -5, ST-14, & ST-6. An Orsat analysis (ST-24) is also acceptable.

10. Calculations

10.1 Standard Dry Sample Volume

$$V_o = \frac{17.71 V_m P_b}{T_m}$$

where: $V_o$ = standard dry sample volume, SDCF @ 70F and 29.92 inches Hg.
$V_m$ = actual metered volume, $ft^3$
$P_b$ = barometric pressure, inches Hg.
$T_m$ = Average meter temperature, $^{o}R$
17.71 = constant correcting to 70F and 29.92 inches Hg.

10.2 Water Vapor Content

$$H2O = \frac{(.0474\ W_c) + \frac{V_o\ P_{sat}}{P_b - P_i - P_{sat}}}{V_0 + (.0474\ W_c) + \frac{V_o\ P_{sat}}{P_b - P_i - P_{sat}}} \times 100$$

where: $W_c$ = total condensate weight, all impingers, grams
$P_{sat}$ = water saturation pressure in the impingers, inches Hg.
$P_b$ = barometric pressure, inches Hg.
$P_i$ = pump inlet vacuum, inches Hg.
$H_2O$ = per cent water vapor
.0474 = cubic feet of vapor resulting from 1 cubic centimeter of liquid $H_2O$.

10.3 Stack Gas Molecular Weight -

$$MW = 0.44\ (\%CO_2) + 0.32(\%O_2) + 0.28(\%N_2 + \%CO) + 0.18(\%H_2O)$$

$MW$ = molecular weight
$\%CO_2$ = percent carbon dioxide by volume (dry basis)
$\%O_2$ = percent oxygen by volume (dry basis)
$\%CO$ = percent carbon monoxide by volume (dry basis)
$\%H_2O$ = percent moisture by volume
$\%N_2$ = percent nitrogen by volume (dry basis - determine by difference)

10.4 Stack Gas Flow Rate - Determine in accordance with ST-17.

10.5 Corrected Particulate Weight - Calculate using the third filter net weight as blank:

$$W_p = (W_1 + W_2) - \frac{W_o}{F_3}(F_1 + F_2)$$

$W_p$ = Corrected weight of particulate catch, grams
$W_1$ = Weight gain in 1st filter, grams
$W_2$ = Weight gain in 2nd filter, grams
$W_3$ = Weight gain in 3rd filter, grams
$F_1$ = Weight of wool in 1st filter, grams
$F_2$ = Weight of wool in 2nd filter, grams
$F_3$ = Weight of wool in 3rd filter, grams

10.6 Particulate Weight Concentration -

$$G = 15.43\ \frac{W_p}{V_o}$$

where:
$G$ = Particulate concentration, grains/SDCF
$W_p$ = Weight of particulate catch, grams
$V_o$ = Standard dry sample volume, SDCF
15.43 = grains/gram

10.7 Particulate Mass Emission Rate

$$M = \frac{GQ_o}{116.7}$$

where:
$M$ = Particulate mass emission rate, lbs/hr.
$Q_e$ = Standard dry stack flow rate, SDCFM
116.7 = Conversion factor for grains to pounds and minutes to hours.

10.8 Correction to 12% Carbon Dioxide

$$M' = \frac{12.0M}{C_{CO_2}}$$

where:

$M'$ = Mass emissions, lb/hr at 12% $CO_2$

$C_{CO_2}$ = Percent carbon dioxide in stack gas (dry basis).

10.9 Auxiliary Fuel Correction Factor. If the test results are applied to Regulation 6-310.1 and if auxiliary fuel is used, a correction for the carbon dioxide shall be calculated as

$$M'' = \frac{0.12(Q_o+1.04Q_g)M}{Q_oC_{co_2}/100+1.04Q_g}$$

where:

$Q_o$ = Dry stack flowrate, SDCFM

$Q_g$ = Natural gas flowrate, SCFM

$C_{CO_2}$ = Percent carbon dioxide in stack gas (dry basis)

10.10 Isokinetic Ratio. Calculate for each traverse point as:

$$R_i = \frac{T_{si}\ Q_{mi}}{60(100-H)\ AV_{si}t_iT_{mi}}$$

where:

$R_I$ = isokinetic ratio at given point

$t_i$ = time, at point i, minutes

$A$ = nozzle area, ft2

$V_{si}$ = stack velocity, point i, FPS

$T_{mi}$ = meter temperature, point i, °R

$T_{si}$ = stack temperautre, point i, °R

$Q_{mi}$ = metered volume, point i

60 = minutes/hour.

$$R = \frac{Q_{mI}}{60(100-H)\ AT_m\ V_{si}t_iT_{si}}$$

## 11. Reporting

11.1 The data and information indicated in Fig. IV-55 shall be reported.

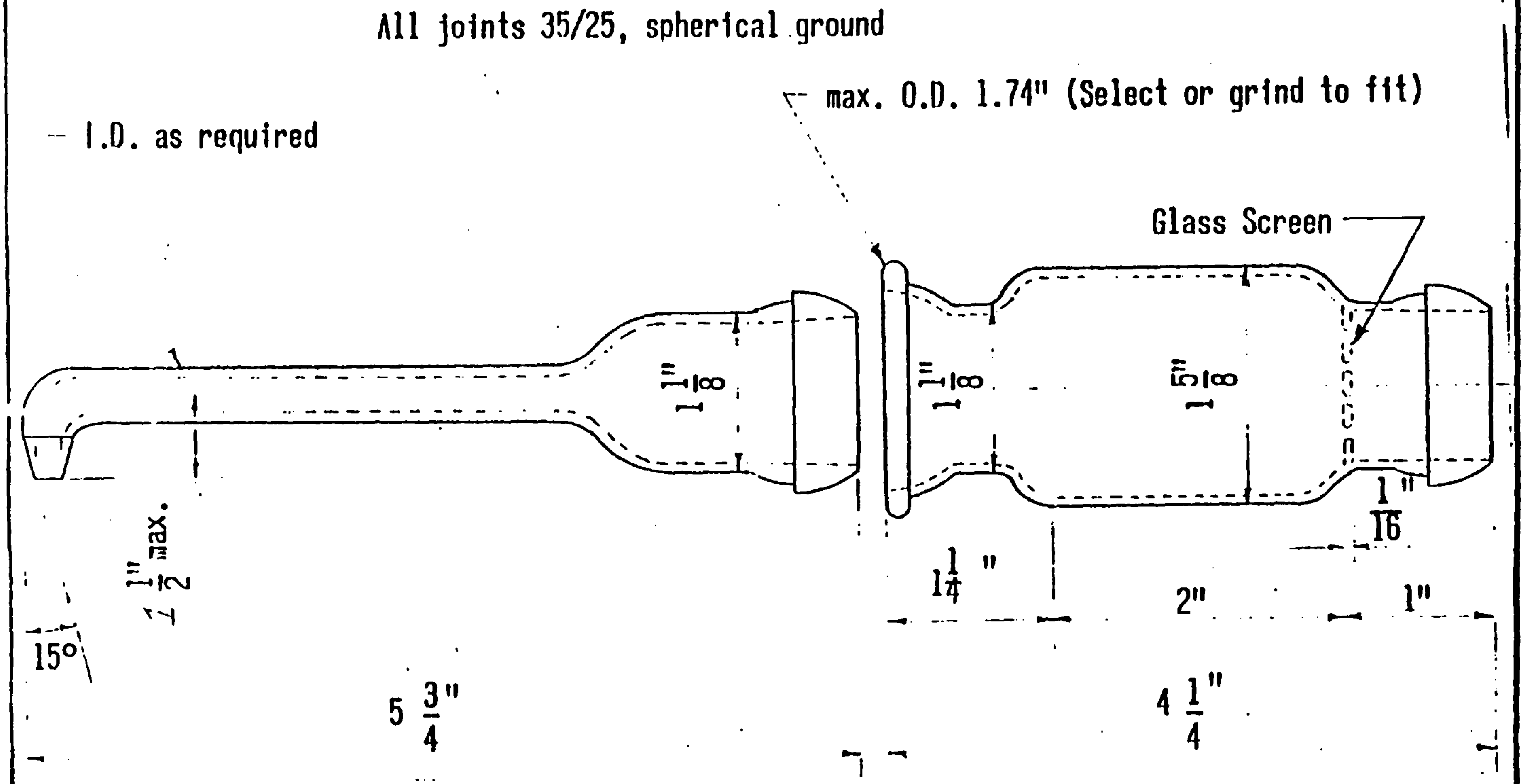

Fig. IV - 49

NOZZLE AND FILTER TUBE DETAILS

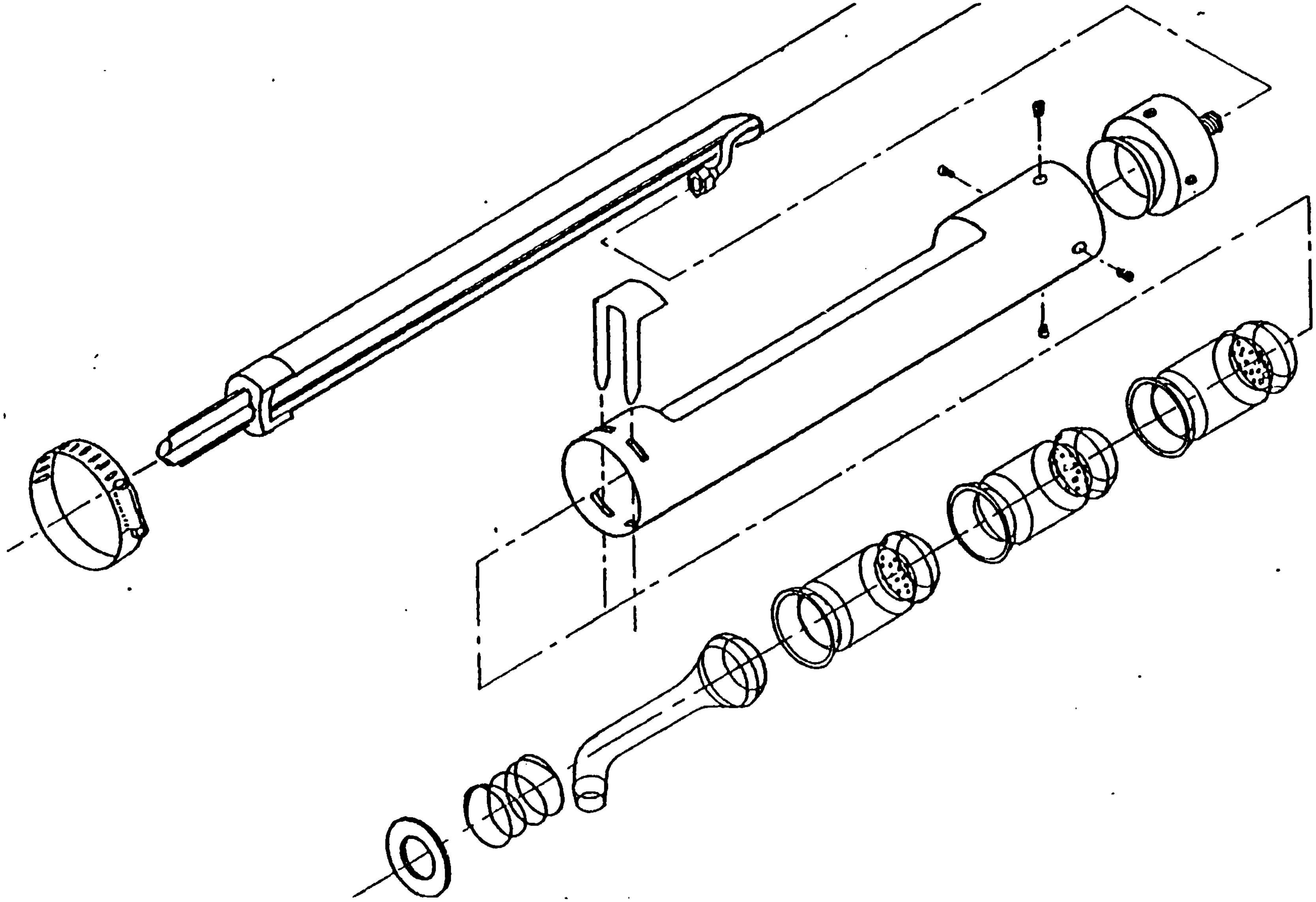

Fig. IV - 50

PROBEHOLDER ASSEMBLY

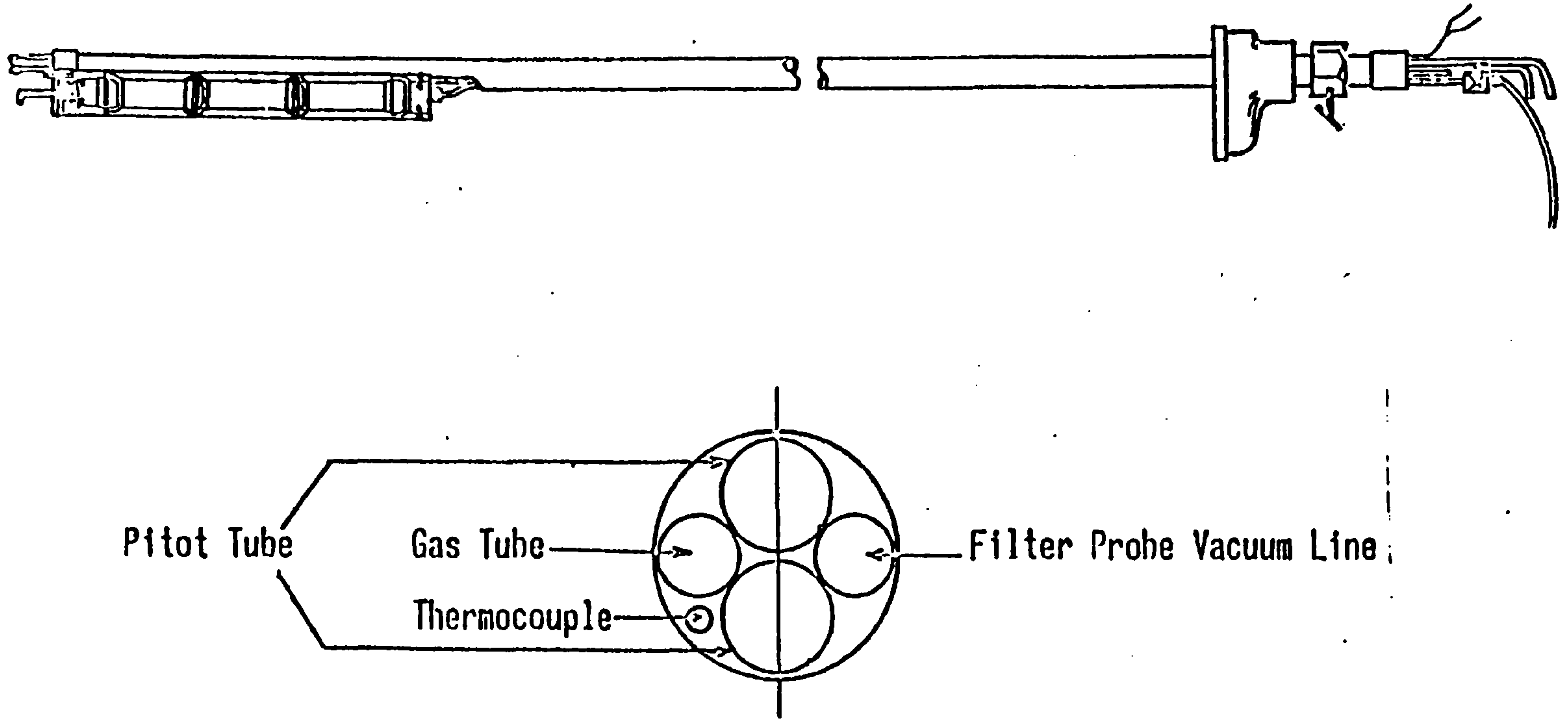

Fig. IV - 51

PROBE ENCASEMENT TUBE

# SOURCE TEST LAB DATA SHEET

PLANT ______________________ PAGE ________ OF ________
SOURCE OPERATION ______________________ INITIAL ________
SOURCE TEST NO. ______________________ TEST DATE ________
FILTER MEDIA ______________________
DRYING PROCEDURE: 105°C for 24 hours before and after test, desicated

STUBBIES

| NO. | TARE | PACKED WT | | | | PARTICULATE |
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NOZZLES

| NO. | TARE | | | PARTICULATE |
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IMPINGERS

| SOLN. | NO. | a TARE WT | b FILLED WT | c FINAL WT | c-a SAMPLE WT | c-b COND |
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COMMENTS:

Fig. IV - 52

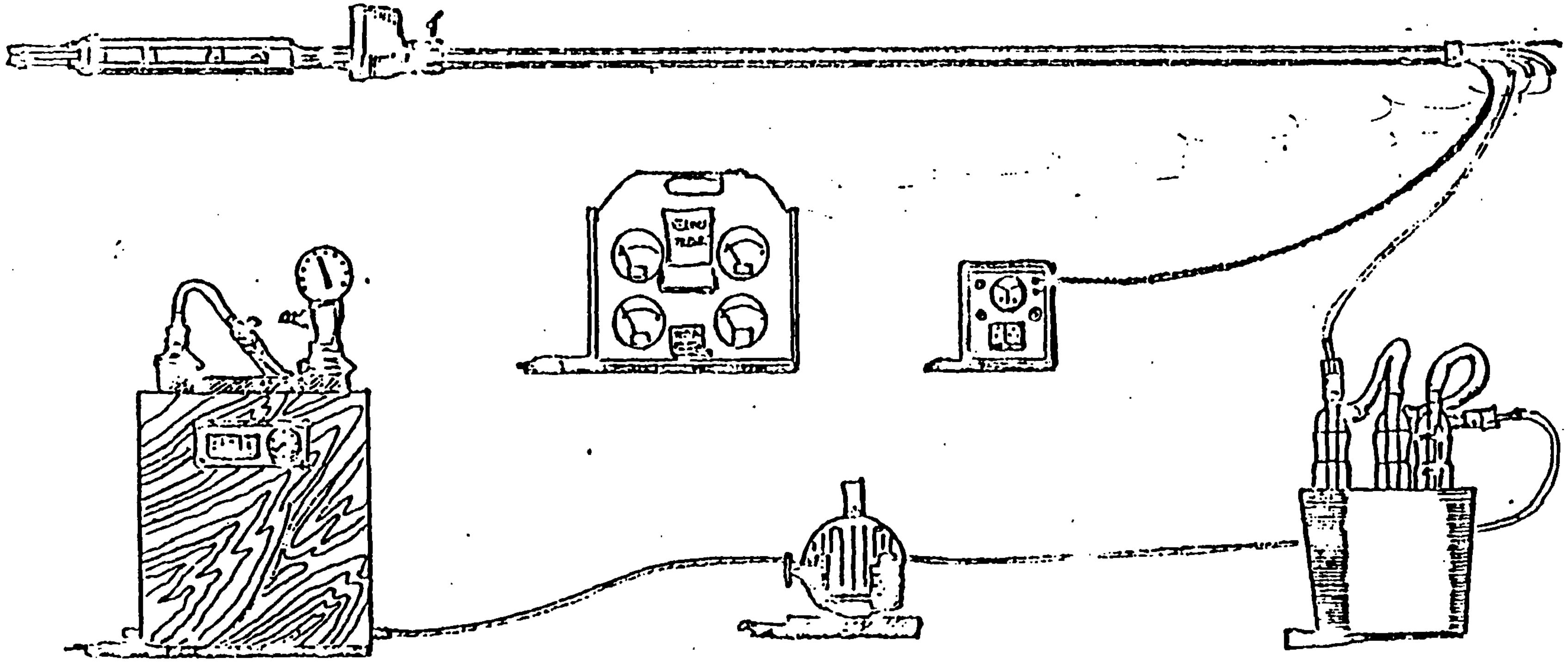

Fig. IV - 53

PARTICULATE SAMPLING TRAIN

## BAY AREA AIR POL ION CONTROL DISTRICT

### Source Test Data Sheet

Source Operation ____________
Plant ____________
Sample Type ____________
Process Cycle ____________
Duct Size ____________
Duct Pressure ____________

Source Test No. ____________
Run No. ____________
Date: ____________

____________ Nozzle Diameter
____________ Pitot Tube
____________ Gas Collector No.
____________ Barometric Pressu
____________ Leak Rate @ 15"Hg

Sampling Train:

| Traverse Point | Dist. From inches | INITIAL TRAVERSE | | | SAMPLING | | | | METER | | | | | | REMARKS |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Duct Temp°F | h $H_2O$ | $\sqrt{h}$ | Traverse Point | h $H_2O$ | $V_s$ FPS | Time | Rate CFH | Temp °F | Volume $Ft^3$ | Vac "Hg | Sat'd Gas Temp°F | $T_s$ Duct Temp°F | |
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$$D_n = 13.7\left[\frac{T_s + 460}{K_p V_s (100 - \%H_2O)}\right]^{1/2}$$

$$Q_m = \left[(2.638 \times 10^{-3}) K_p (100 - \%H_2O) D_{mun}^2\right]\frac{V_s}{T_s}$$

Condensate ________ gm.
$V_o$ ________
$\%H_2O$ ________
$\%CO_2$ ________
$\%CO$ ________
$\%O_2$ ________

Source Test Team
________________
________________
________________
________________

FIG. IV-54

# SUMMARY OF SOURCE TEST RESULTS

## SOURCE INFORMATION

Firm Name and Address

Firm Representative and Title

Phone No.

Source:

Conditions During Tests

Operates hr/day & days/yr

Operating Parameters

Report No.

Test Date:

Test Times:

Run A:

Run B:

Run C:

Test Results and Comments

| METHOD | TEST | RUN A | RUN B | RUN C | AVG. |
|---|---|---|---|---|---|
| | Run time, minutes | | | | |
| | Stack gas temp., °F. | | | | |
| ST-17 | Stack flowrate, SDCFM | | | | |
| ST-14 | $O_2$ conc., dry basis, % | | | | |
| ST-5 | $CO_2$ conc., dry basis, % | | | | |
| ST-6 | CO conc., dry basis, % | | | | |
| ST-23 | $H_2O$ conc, actual, % | | | | |
| ST-15 | Particulate, Gr/SDCF | | | | |
| | Particulate, lbs/hr. | | | | |
| | Isokinetic ration | | | | |

FIG. IV-55

# Source Test Procedure ST-16

# PHENOLIC COMPOUNDS

REF: Reg. 7-303

## 1. Applicability

1.1 This method is used to quantify emissions of phenolic compounds as phenol. It is applicable to the determination of compliance with Regulation 7-303.

## 2. Principle

2.1 Sample gas is drawn through a solution of 0.1 normal (0.1N) sodium hydroxide which absorbs the phenolic compounds. The phenolic compounds are then analyzed by gas chromatography as specified in Analytical Procedure Lab-8.

## 3. Range and Sensitivity

3.1 The minimum measurable concentration of phenolic compounds is 200 ppb at the sample volume specified in this procedure.

3.2 Elevated concentrations of phenolic compounds may be determined by increasing the concentration of the absorbing reagent, sodium hydroxide solution. The concentration of reagent to be used may be determined by stoichiometry, allowing a 50% excess.

## 4. Interference

None. known.

## 5. Apparatus

5.1 probe. The probe is constructed of borosilicate glass tubing fitted with glass wool in the nozzle.

5.2 Absorbers. Use three Greenberg-Smith impingers. The third impinger has a thermometer attached to the inlet stem.

5.3 cooling system. An ice is used to contain the impingers.

5.4 sample pump. Use a leak-free vacuum pump capable of maintaining a 0.5 CFM flow rate at 15 inches of mercury-vacuum. The pump has a flow control valve and vacuum gauge attached to the inlet.

5.5 silica gel tube. Approximately 500cc of silica gel with a Drierite indicator are used to insure that the gas entering the dry gas meter is dry.

5.6 dry test meter. Use a 375 CFH dry gas test meter accurate within ± 2% of the true volume and equipped with a thermometer to measure the outlet temperature.

5.7 connections. Use Teflon tubing in making all connections that come in contact with the sample. Vinyl tubing is acceptable for all other connections.

5.8 barometer. Use a mercury, aneroid, or other barometer that is accurate to within ± 0.2 inches of mercury.

5.9 Rotameter. Use a calibrated Rotameter to measure the sampling rate.

6. Reagents

6.1 0.1N sodium hydroxide acid. Dissolve 4.0grams of NaOH in sufficient distilled water to make a 1.0 liter solution.

7. Pre-Test Procedures

7.1 Add 100 ml of the 0.1N NaOH solution to each of the two impingers.

7.2 Stopper the impingers.

7.3 Retain 100 ml of the solution to later analyze as a blank for phenol compounds.

7.4 Assemble the sampling train as shown in Figure IV-56. Record the equipment identification on the test data sheet.

7.5 Leak-test the sampling train by turning on the pump, plugging the probe, and adjusting the pump inlet vacuum to 10 inches Hg. The leak rate must not exceed 0.02 CFM through the dry test meter. Before turning off the pump, carefully release the plug in the sample probe to avoid backflow of the impinger solution.

7.5 Record the initial dry test meter reading and barometric pressure using IV-57.

8. Sampling

8.1 Sample at continuous operations for a period of thirty minutes for each test run. Sample at batch processes for a period of thirty minutes or 90% of the batch process time, whichever is less.

8.2 Position the probe at the sampling point and start the pump.

8.3 Sample at a constant rate of 14.3 liter/min (0.5 CFM) during the test as determined by the rotometer.

8.4 Record the following information at five-minute intervals:

dry test meter temperature
impinger outlet temperature
dry test meter volume
Rotometer flow.

8.5 Add ice as necessary to maintain impinger temperatures at 7°C (45°F) or less.

8.6 At the conclusion of each run, stop the pump, remove the probe from the stack, and record the final meter volume.

8.7 Take three consecutive samples.

## 9. Post-Test Procedures

9.1 Stopper the impingers until they are analyzed.

9.2 Individually analyze the sodium hydroxide solutions and blank for total content of phenolic compounds, as phenols, according to analytical procedure Lab 8.

## 10. Calculations

10.1 Standard sample volume:

$$V_o = \frac{17.71\, V_m P_b}{T_m}$$

where:

$V_o$ = corrected sample volume, SDCF at 70°F and 29.92 inches Hg.
$V_m$ = uncorrected meter volume, ft.$^3$
$T_m$ = average run meter temperature, °R
$P_b$ = barometric pressure, inches Hg.
17.71 = a constant correcting to 70F and 29.92 inches Hg.

10.2 phenolic compound, as phenol concentration:

$$C = \frac{9.07 \times 10^{3} W}{V_o}$$

where:

C = phenolic compound, as phenol concentration, ppm by volume on a dry basis.
W = total weight of phenolic compounds, as phenol in the impinger catch, for each run, grams.
$9.07 \times 10^{-3}$ = constant derived from molar volume, 453.6 grams/ll and molecular weight of phenol.

## 11. Reporting

11.1 Report the data indicated on Figure IV-58.

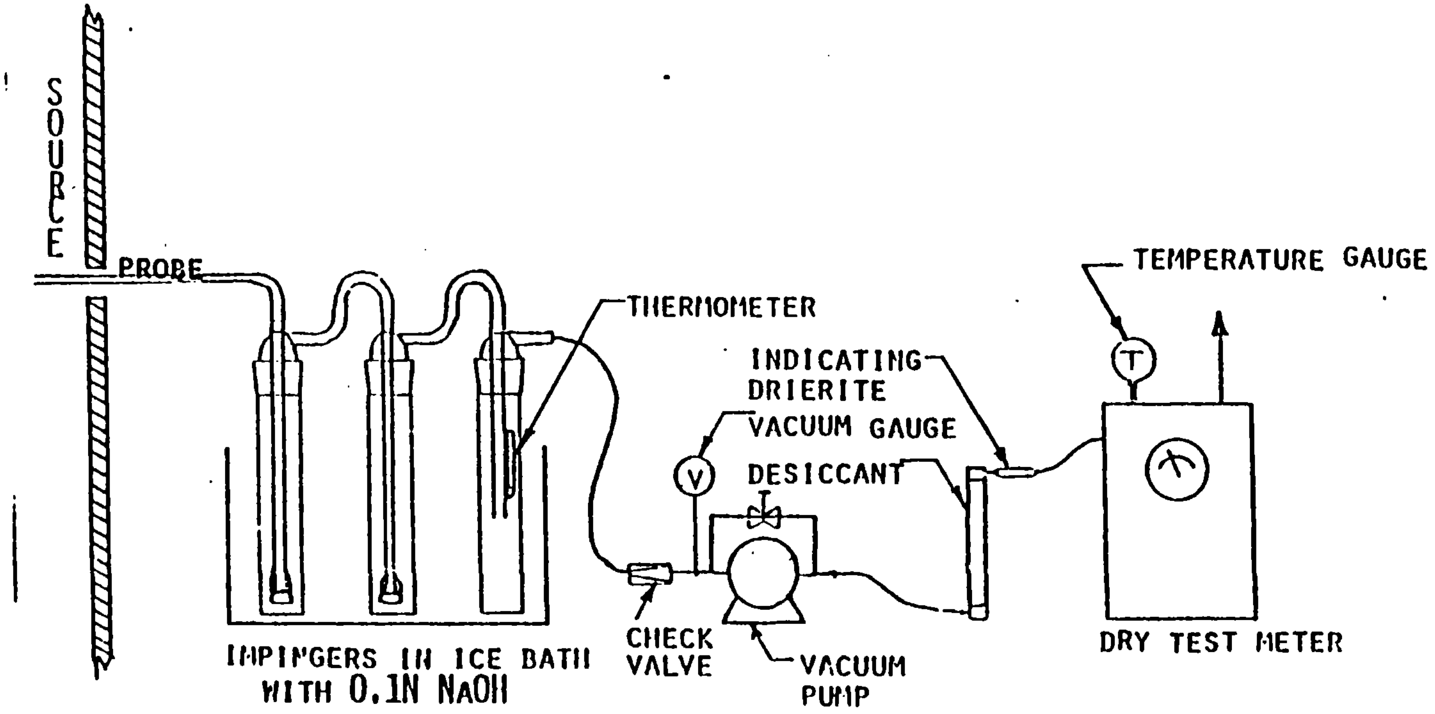

Fig. IV - 56

PHENOLIC COMPOUND SAMPLING TRAIN

# BAY AREA AIR POLLUTION CONTROL DISTRICT

## Source Test Data Sheet

Source Operation ____________
Plant ____________
Sample Type ____________
Process Cycle ____________
Duct Size ____________
Duct Pressure ____________

Source Test No. ____________
Run No. ____________
Date: ____________

____________ Nozzle Diameter
____________ Pitot Tube
____________ Gas Collector No.
____________ Barometric Pressur
____________ Leak Rate @ 15"Hg

Sampling Train:

| Traverse Point | Dist. From | INITIAL TRAVERSE | | | SAMPLING | | | | | | | | | | REMARKS |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | METER | | | | | | |
| | inches | Duct Temp°F | h $H_2O$ | $\sqrt{h}$ | Traverse Point | h $H_2O$ | $V_s$ FPS | Time | Rate CFH | Temp °F | Volume $Ft^3$ | Vac "Hg | Sat'd Gas Temp°F | $T_s$ Duct Temp°F | |
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$$D_n = 13.7\left[\frac{T_s + 460}{K_p V_s (100-\%H_2O)}\right]^{1/2}$$

$$Q_m = \left[(2.638 \times 10^{-3}) K_p (100-\%H_2O) D_{mm}^2\right]\frac{V_s}{T_s}$$

Condensate ________ gm.
$V_o$ ________
$\%H_2O$ ________
$\%CO_2$ ________
$\%CO$ ________
$\%O_2$ ________

Source Test Team
____________
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____________
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FIG. IV-57

# SUMMARY OF SOURCE TEST RESULTS

## SOURCE INFORMATION

Firm Name and Address

Firm Representative and Title

Phone No.

Source:

Conditions During Tests

Operates hr/day & days/yr

Operating Parameters

Report No.

Test Date:

Test Times:

Run A:

Run B:

Run C:

Test Results and Comments

| METHOD | TEST | RUN A | RUN B | RUN C | AVG. |
|---|---|---|---|---|---|
| | Run time, minutes | | | | |
| | Stack gas temp., °F. | | | | |
| ST-16 | Total phenols, as $C_6H_5OH$, ppm | | | | |

FIG. IV-58

# Source Test Procedure ST-17

## STACK GAS VELOCITY AND VOLUMETRIC FLOW RATE

### 1. Applicability

1.1 This procedure is used to determine stack gas velocity and to quantify volumetric flow rate. It is applicable for use in determining compliance with any regulation of the BAAQMD wherein stack gas velocity or flow rate is required.

### 2. Principle

2.1 The stack gas velocity is determined by using a pitot tube to measure the velocity heads at pre-determined traverse points (ST-18) across the stack. The stack gas temperature, static pressure, and molecular weight and moisture content are also measured. The volumetric flow rate can then be determined from knowledge of the duct geometry. Velocity measurements should be made from a Type "A" sampling point whenever possible. If sampling facilities permit, velocity traverses are conducted from two ports which are in radii of 90°.

### 3. Range and Repeatability

3.1 The minimum measurable stack gas velocity is 8 feet per second. The maximum measurable velocity is limited only by available equipment.

3.2 The repeatability of the stack gas velocity method is ±7%.

### 4. Interferences

4.1 Not applicable.

### 5. Apparatus

5.1 Pitot tube. Use a Stauscheibe (type S) or equivalent, with a known coefficient which is constant within ±5% over the entire working range. The pitot tube coefficient is determined by placing both the S-type and a standard pitot tube in a gas stream and measuring the pressure head with both over the entire velocity range of interest. The coefficient of the type-S pitot tube shall be calculated as:

$$C_{p_s} = C_{p_{std}} \left[\frac{\Delta P_{std}}{\Delta P_s}\right]^{1/2}$$

where:

$C_{p_s}$ = type S pitot tube coefficient

$\Delta P_s$ = pressure head, type S

$\Delta P_{std}$ = pressure head, standard

$C_{p_{std}}$ = standard pitot tube coefficient

5.2 Differential Pressure gauge. Use a Magnehelic differential pressure gauge, or equivalent, capable of measuring the velocity head with ±5% accuracy.

5.3 Temperature gauge. Use a Chromel-alumel thermocouple to measure stack temperature within ±15° of the stack absolute temperature (°F).

5.4 Barometer. Use a mercury, aneroid, or other capable of measuring atmospheric pressure to within ±0.2 inches of mercury.

5.5 Connections. All flexible tubing connections must be leak free.

## 6. Pre-Test Procedures

6.1 Set up the apparatus.

6.2 The pitot tube shall be pressurized so as to create a reading on the differential pressure gauge and then blocked at both ports. The pressure should remain constant.

6.3 Determine the location of the traverse point according to ST-18.

6.4 Calculate the molecular weight of the gas stream. The following stack gas concentrations shall be measured by the procedures indicated. An orsat analysis as outlined in ST-24 may be substituted for ST-5, ST-6 and ST-14.

% carbon dioxide, dry basis(ST-5)
% carbon monoxide, dry basis (ST-6)
% oxygen, dry basis (ST-14)
% water vapor. (ST-23)

Record the stack gas composition on the test data sheet, Figure IV-59.

## 7. Test Procedures

7.1 The velocity head and the temperature at each traverse point is measured and recorded along with the point location on the source test data sheet.

7.2 Measure the static pressure in the stack and record on the data sheet.

## 8. Calculations

8.1 Average Molecular Weight

$$\overline{MW} = 0.44\ (\%CO_2) + 0.32(\%O_2) + 0.28(\%N_2+CO) + 0.18(\%H_2O)$$

where: MW = average molecular weight
$\%CO_2$ = percent carbon dioxide by volume (dry basis)
$\%O_2$ = percent oxygen by volume (dry basis)
$\%CO$ = percent carbon monoxide by volume (dry basis)
$\%N_2$ = percent nitrogen by volume(dry basis- determined by difference)

8.2 Stack Gas Velocity.

$$V_s = 85.49\ C_{ps} \left[(\Delta P)^{1/2}\right]_{avg} \left[\frac{T_s}{(P_b + P_d)MW}\right]^{1/2}$$

where: $V_s$ = average stack velocity, FPS
$C_{ps}$ = Pitot tube coefficient
$T_s$ = Stack gas temperature, °R
$P_b$ = Barometric pressure, inches Hg (absolute)
$P_d$ = Stack gas static pressure, inches Hg (absolute)
85.49 = A constant derived from molecular weight standard conditions, and Bernoulli's equation.
$\left[(\Delta P)^{1/2}\right]_{avg}$ = Arithemtic average of square roots of the velocity heads in inches or water.

8.3 Stack gas Flowrate

$$Q_o = \frac{(10.6) V_s A (P_b + P_d)(100 - CH_2O)}{T_s}$$

where: $Q_o$ = volumetric flowrate, SDCFM
A = stack cross-sectional area, ft$^2$
$C_{H_2O}$ = % water vapor
10.6 = A constant derived from correction to 70°F, 29.92 in Hg, and 60 sec/ min.

## 9. Reporting

9.1 These valves are determinedas.auxilllary data for other other procedures and shall be reported with those test results.

BAY AREA AIR POLLUTION CONTROL DISTRICT

## Source Test Data Sheet

Source Operation ____________
Plant ____________
Sample Type ____________
Process Cycle ____________
Duct Size ____________
Duct Pressure ____________

Source Test No. ____________
Run No. ____________
Date: ____________

____________ Nozzle Diameter
____________ Pitot Tube
____________ Gas Collector No.
____________ Barometric Pressur
____________ Leak Rate @ 15"Hg

Sampling Train: .

| Traverse Point | Dist. From Inches | INITIAL TRAVERSE | | | SAMPLING | | | | | | | | | | REMARKS |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | METER | | | | | | |
| | | Duct Temp°F | h $H_2O$ | √h | Traverse Point | h $H_2O$ | $V_s$ FPS | Time | Rate CFM | Temp °F | Volume $Ft^3$ | Vac "Hg | Sat'd Gas Temp°F | $T_s$ Duct Temp°F | |
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| | | | | | | | | | | | | | | | |

$$D_n = 13.7\left[\frac{T_s + 460}{K_p V_s (100-\%H_2O)}\right]^{1/2}$$

$$Q_m = \left[(2.638 \times 10^{-3}) K_p (100-\%H_2O) D_{nn}^2\right]\frac{V_s}{T_s}$$

Condensate ________ gm.
$V_o$ ________
$\%H_2O$ ________
$\%CO_2$ ________
$\%CO$ ________
$\%O_2$ ________

Source Test Team
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FIG. IV-59

# Source Test Procedure ST-18

## STACK TRAVERSE POINT DETERMINATION

### 1. Applicability

1.1 This procedure is used to determine the number and location of traverse points required when determining stack gas velocity or extracting a sample from a type "A" sample point.

### 2. Principle

2.1 Depending on the stack geometry, a cross-section of the stack perpendicular to the gas flow is divided into a specified number of equal areas. Each traverse point is then located at pre-determined points in each area.

### 3. Calculations

3.1 For circular ducts, the following guidelines for the number of traverse points shall be followed:

TABLE 18-1

| Duct Diameter, Inches | Number of Traverse Points |
|---|---|
| $D < 12$ | 4 |
| $13 < D < 20$ | 6 |
| $21 < D < 30$ | 8 |
| $31 < D < 48$ | 10 |
| $D > 48$ | 12 |

3.2 For circular ducts, the following formula shall be used to determine the location of each traverse point:

$$r_i = \sqrt{\frac{(i - 0.5) \times R^2}{a}}$$

where: $r_i$ = distance to ith traverse point on radius from the center

$i$ = ith traverse point on a radius

$a$ = total number of traverse points on a radius

$R$ = inside radius of the duct

3.3 For rectangular ducts, the following formula shall be used to determine the equivalent diameter of the stack:

$$\text{equivalent diameter} = \frac{2(\text{length})(\text{width})}{(\text{length}) + (\text{width})}$$

The number of traverse points is then determined from Table 18-1 using the equivalent diameter.

3.4 For rectangular ducts, divide the cross section into elemental areas such that the ratio of the length to width of the elemental areas is between one and two. Locate the traverse points at the centroid of each elemental area.

3.5 No traverse point shall be located within one inch of the stack wall.

# Source Test Procedure ST-19A

# SULFUR DIOXIDE, CONTINUOUS SAMPLING

REF: Regs. 9-1-302 10-1-301
9-1-304 thru 310

## 1. Applicability

1.1 This method is used to quantify emissions of sulfur dioxide ($SO_2$). It determines compliance with Regulations 9-1-302, 9-1-304 thru 310 and 10-1-301.

1.2 The EPA has granted alternate status to EPA Method 6 for this method. It determines compliance with sulfur dioxide emissions covered under Regulation 7 (New Source Performance Standards).

## 2. Principle

2.1 A continuous representative gas sample is extracted from the sampling point and conditioned to remove water and particulate material. The sulfur dioxide concentration is determined by passing a small portion of the sample through an ultraviolet analyzer.

## 3. Range and Sensitivity

3.1 The minimum and maximum measurable concentrations of $SO_2$ depends on the sample cell length in the analyzer.

3.2 The minimum sensitivity of the UV anlayzer shall be ±2% of full scale.

## 4. Interferences

4.1 Elemental sulfur, sulfur trioxide, and carbon disulfide will cause interferences.

## 5. Apparatus

5.1 Sulfur dioxide analyzer. Use an E.I. DuPont de Nemours and Co. Model 400 photometric analyzer or its equivalent.

5.2 Chart recorder. The recorder monitors and records the continuous output from the analyzer.

5.3 Sample conditioning, zero air, and span gas system. The assembly of this system is shown in Fig. IV-60. The sample conditioning system provides a dry, particulate free gas flow to the instrument. The zero air system provides clean dry atmospheric air for instrument calibration. The span gas system provides a known concentration of $SO_2$ for use in calibrating the analyzer. Except as specified, all materials, which come in contact with either the sample or span gasses must be constructed of Teflon or stainless steel.

5.4 Sample probe. Use a borosilicate glass tube of sufficient length to traverse the stack being tested. If the stack temperature exceeds 425C (800F), use a quartz probe. Other probes are acceptable with approval of Source Test

5.5 Condensers. Use modified Greenberg-Smith impingers with the impaction plates removed and the inlet tube shortened to a length of 10cm (4 inches), or equivalent.

5.6 Cooling system. Immerse the impingers in an ice bath during the test.

5.7 Particulate filter. Use a Balston type 95 holder with a grade B filter, or equivalent, in the sample system.

5.8 Pumps. Use leak-free, Teflon-lined, diaphragm pumps in the sample and zero air system. The pumps must have a capacity of at least 28 liters/min (1.0 CFM).

5.9 Back-pressure regulator. Use a back-pressure regulator to maintain the sample and zero gas sample pressures to the instrument at five psig.

5.10 Gas scrubber. Use a bed of silica gel, Ascarite (or soda-lime), and charcoal to remove moisture, carbon dioxide, and hydrocarbons from the zero air system.

5.11 Span gas. A high-pressure cylinder containing a known concentration of $SO_2$ in nitrogen. The span gas concentration must be in the same range as the source being tested.

6. Pre-Test Procedures

6.1 Warm-up the instrument according to manufacturer's instructions

6.2 Assemble the sampling system as shown in Figure IV-60.

6.3 Leak-test the sampling system by starting the pump, plugging the probe, and determining that the pressure to the analyzer falls to zero.

6.4 Introduce zero air into the analyzer and zero the instrument according to manufacturer's instructions

6.5 Introduce span gas into the analyzer and calibrate the instrument according to manufacturer's instructions.

6.6 Conduct a preliminary concentration traverse according to ST-18 to determine if stratification of the stack gases exists. If the $SO_2$ concentration at any point differs from the average concentration by more than 10%, traverse the stack during the test. If not, sample at any single point.

6.7 Set-up the chart recorder according to manufacturer's recommendations.

## 7. Sampling

7.1 Each test run shall be of thirty minute duration when testing emissions from continuous operations. Each test run at batch process operations shall be for 90% of the batch time or thirty minutes, whichever is less.

7.2 Introduce sample gas into the analyzer at the same flow rate used to calibrate the analyzer.

7.3 Maintain ice in the cooling system throughout the test.

7.4 Calibrate the analyzer before and after each test run. Record each step of the calibration process clearly on the chart recording.

7.5 Conduct three test runs.

## 8. Auxiliary Tests

8.1 Stack flow rate. Use ST-17 to determine the stack gas flow rate after each test run.

8.2 Moisture content. Use ST-23 to determine the moisture content of the stack gases.

8.3 Production rate. Determine the sulfuric acid or sulfur production from plant data based on a 24 hour, daily production rate in tons per day, if the test is being conducted on a sulfur recovery unit or a sulfuric acid plant.

8.4 Oxygen concentration. Use ST-14 to determine the oxygen concentration of the stack gas.

## 9. Calculations

9.1 From the chart recording determine the time-averaged concentration of $SO_2$ on a dry basis for each run.

9.2 Mass emission rate of $SO_2$: $M_{SO_2} = KC_{SO_2}Q_o$

where:

$M_{SO_2}$ = mass emission rate of $SO_2$ Kg/hr (lb/hr)

$C_{SO_2}$ = concentration of $SO_2$, dry basis, ppm

$Q_o$ = stack gas flow rate, $\frac{SDM^3}{min} \left(\frac{SDFT^3}{min}\right)$

$K = (9.93 \times 10^{-6}) \frac{LB}{(ppm)Ft^3Hr.}$ for English units

$= (1.59 \times 10^{-4}) \frac{Kg}{ppm\ M^3\ hr}$ for metric units

9.3 Mass emissions based on production rate:

$$M_{tp} = \frac{M_{SO_2}}{M_d}$$

where:

$M_{tp}$ = Mass emissions per ton of product, $\frac{Kg}{\text{metric ton}} \left(\frac{lbs}{\text{short ton}}\right)$

$M_{SO_2}$ = Mass emission rate of $SO_2$, $\frac{Kg}{hr.} \left(\frac{lbs}{hr.}\right)$

$M_d$ = Production rate per hour. (based on up to 48 hour average.)

9.4 Oxygen Correction factor:

$$F = \frac{21.95 - X_{O_2}}{21.95 \times P_{O_2}}$$

where:

F = Oxygen correction factor

$X_{O_2}$ = Oxygen concentration to be corrected to; 0% for Sulfur Recovery plants and 12% for Sulfuric Acid Plants.

$P_{O_2}$ = Oxygen content present in stack gas.

9.5 $SO_2$ concentration corrected for oxygen content.

$$C_{SO_2F} = F \times C_{SO_2}$$

where:

$C_{SO_2F}$ = $SO_2$ concentration corrected for oxygen content.

## 10. Reporting

10.1 The results of each test is reported as shown in Figure IV-61.

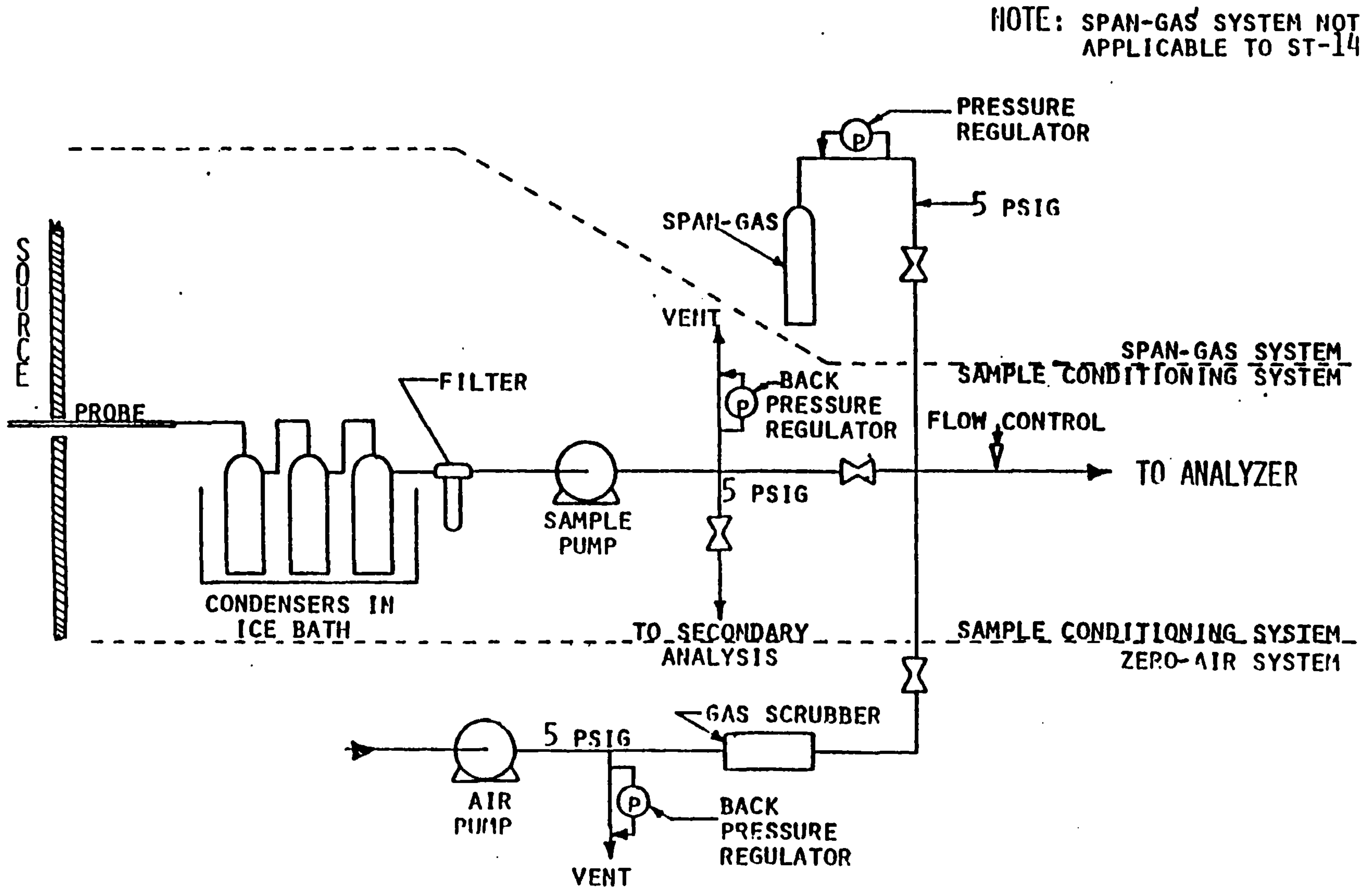

Fig. IV - 60

SAMPLE CONDITIONING, ZERO-AIR AND SPAN-GAS SYSTEMS

# SUMMARY OF SOURCE TEST RESULTS

## SOURCE INFORMATION

Firm Name and Address

Firm Representative and Title

Phone No.

Source:

Conditions During Tests

Operates hr/day & days/yr

Operating Parameters

Report No.

Test Date:

Test Times:

Run A:

Run B:

Run C:

Test Results and Comments

| METHOD | TEST | RUN A | RUN B | RUN C | AVG. |
|---|---|---|---|---|---|
| | Run time, minutes | | | | |
| | Stack gas temp., °F. | | | | |
| ST-17 | Stack flowrate, SDCFM | | | | |
| ST-14 | $O_2$ conc., dry basis, % | | | | |
| ST-5 | $CO_2$ conc., dry basis, % | | | | |
| ST-6 | CO conc., dry basis, % | | | | |
| ST-23 | $H_2O$ conc., real basis, % | | | | |
| ST-19A | Sulfur Dioxide, ppm | | | | |
| | Sulfur Dioxide, lb/hr. | | | | |
| | $SO_2$, lbs/ton product | | | | |

FIG. IV-61

## Source Test Procedure ST-19B

## TOTAL SULFUR OXIDES INTEGRATED SAMPLE

REF: Regs. 9-1-302 10-1-301
9-1-304 thru 310

### 1. Applicability

1.1 This method is used to quantify emissions of total sulfur oxides. It determines compliance with Regulation 9-1-302, 9-1-304 thru 310 and 10-1-301, it is an acceptable alternate method to ST-19A.

### 2. Principle

2.1 Sample gas is drawn through 3% hydrogen peroxide solution which absorbs the sulfur oxides. The peroxide solution is then analyzed according to Analytical Procedure.Lab-11.

### 3. Range

3.1 The minimum measurable concentration of sulfur oxides is 7ppm at the sample volume specified in this procedure.

3.2 The maximum measurable concentration of sulfur oxides is 2.5%.

### 4. Interference

4.1 The presence of strong acids, such as hydrochloric acid or sodium bisulfite give erroneously high results. The presence of alkaline gases or reactive basic solids, such as ammonia or calcium oxide give erroneously low results.

### 5. Apparatus

5.1 Probe. The probe is constructed of borosilicate glass tubing.

5.2 Absorbers. Use three Greenberg-Smith Impingers. The final impinger has a thermometer attached to the inlet stem.

5.3 Filter. Use a glass filter tube of the same type as is used in ST-15.

5.4 Cooling system. An ice bath is used to contain the impingers.

5.5 Sample pump. Use a leak-free vacuum pump capable of maintaining a 0.5 CFM flow rate at 15 inches of mercury. The pump must have a flow control valve and vacuum gauge attached to the inlet.

5.6 Silica gel tube. Use approximately 500cc of silica gel (with a Drierite indicator) to insure that the gas entering the dry test meter is dry.

5.7 Dry test meter. Use a dry test meter accurate within ±2% of the true volume and equipped with a thermometer to measure the outlet temperature.

5.8 Connections. Use Teflon tubing in making all connections that come in contact with the sample. Vinyl tubing is acceptable for all other connections.

5.9 Barometer. Use a barometer that is accurate to within ±0.2 inches of mercury.

5.10 Rotameter. Use a calibrated rotameter to measure the sampling rate.

6. Reagents

6.1 Hydrogen peroxide solution, 3%. Prepare a solution of 3%, by volume, hydrogen peroxide in distilled water.

7. Pre-Test Procedures

7.1 Add 100 ml of 3% $H_2O_2$ to each of two impingers.

7.2 Stopper the impingers.

7.3 Retain 100 ml of the hydrogen peroxide solution to analyze as a blank.

7.4 Assemble the sampling train as shown in Figure IV-62.

7.5 Leak-test the sampling train by starting the pump, plugging the probe, and adjusting the pump inlet vacuum to 10 inches Hg. The leak rate must not exceed 0.02 CFM through the dry test meter. Before stopping the pump, carefully release the plug in the sample probe to avoid backflow of the impinger solution.

7.6 Record the initial dry test meter reading and barometric pressure as shown in Figure IV-63.

8. Sampling

8.1 Each test run shall be of thirty minute duration when testing emissions from continuous operations. Each test run at batch process operations shall be for 90% of the batch time or thirty minutes, whichever is less.

8.2 Position the probe at the sampling point and start the pump.

8.3 Sample at a constant rate of 14.3 liter/min (0.5 CFM) during the test as determined by the rotameter. Use the rotameter only to establish the initial sampling rate. Then remove it from the system.

8.4 Record the following information at five-minute intervals:

dry test meter temperature
impinger outlet temperature
dry test meter reading

8.5 Add ice as necessary to maintain impinger temperatures at $7^{o}C$ or less.

8.6 At the conclusion of each run, stop the pump, remove the probe from the stack, and record the final meter reading.

8.7 Take three consecutive samples.

## 9. Post-Test Procedures

9.1 Immediately after each test run, stopper the impingers to minimize sample losses.

9.2 Individually analyze the hydrogen peroxide solutions for total sulfur oxide content according to analytical procedure Lab 11.

## 10. Auxiliary Tests

10.1 Stack flowrate. Determine the stack gas flowrate after each test run in accordance with ST-17.

10.2 Moisture. Determine the stack gas moisture content in accordance with ST-23.

10.3 Production rate. Determine the sulfuric acid or sulfur production from plant data based on a 24 hour, daily production rate in tons per day, if the test is being conducted on a sulfur recovery unit or a sulfuric acid plant.

10.4 Oxygen concentration. Use ST-14 to determine the oxygen concentration of the stack gas.

## 11. Calculations

11.1 Standard sample volume:

$$V_o = \frac{17.71\ V_m P_b}{T_m}$$

where: $V_o$ = corrected sample volume, SDCF at $70^{o}F$ and 29.92 inches Hg.
$V_m$ = uncorrected meter volume, $ft^3$
$T_m$ = average run meter temperature, $^{o}R$
$P_b$ = barometric pressure, inches Hg.
17.71 = a constant correcting to 70F and 29.92 inches Hg.

11.2 Sulfur oxide concentration:

$$C_{SO} = \frac{1.33 \times 10^4 W}{V_o}$$

where: $C_{SO}$ = sulfur oxides concentration, as $SO_2$ ppm by volume on a dry basis.

$W$ = total weight of sulfur oxides in the impinger catch, for each run, grams

1.33 = constant derived from molar volume, 454 grams/lb, and molecular weight of $SO_2$.

11.3 Mass emission rate of $SO_x$:

$$M_{SO_x} = K D_{SO_x} Q_o$$

where: $M_{SO_x}$ = mass emission rate of $SO_x$ (as $SO_2$) kg/hr (lb/hr.)

$Q_o$ = stack gas flow rate $\frac{SDM^3}{min}$ $\left(\frac{SDFT^3}{min}\right)$

$K$ = $9.93 \times 10^{-6}$ $\frac{lb}{ppm\text{-}ft^3\text{-}hr}$ for English units.

= $1.59 \times 10^{-4}$ $\frac{kg}{ppm\text{-}m^3\text{-}hr.}$ for SL units.

11.4 Mass emissions based on production rate:

$$M_{tp} = \frac{M_{SO_2}}{M_d}$$

where:

$M_{tp}$ = mass emissions per ton or product, $\frac{Kg}{metric\ ton}$ $\left(\frac{lbs}{short\ ton}\right)$

$M_{SO_2}$ = mass emission rate of $SO_2$, $\frac{kg}{hr.}$ $\left(\frac{lbs.}{hr.}\right)$

$M_d$ = production rate per hour. (based on a 48 hour average).

11.5 Oxygen Correction factor:

$$F = \frac{21.95 \times X_{O2}}{21.95 \times P_{O2}}$$

where:

$F$ = oxygen correction factor

$X_{O2}$ = Oxygen concentration to be corrected to 0% for Sulfur Recovery plants and 12% for Sulfuric Acid plants.

$P_{O2}$ = Oxygen content present in stack gas.

11.6 $SO_2$ concentration corrected for oxygen content.

$$C_{SO2}F = F \times C_{SO2}$$

where:

$C_{SO2}F$ = $SO_2$ concentration corrected for oxygen content.

## 12. Reporting

12.1 Report the data indicated on Figure IV-64.

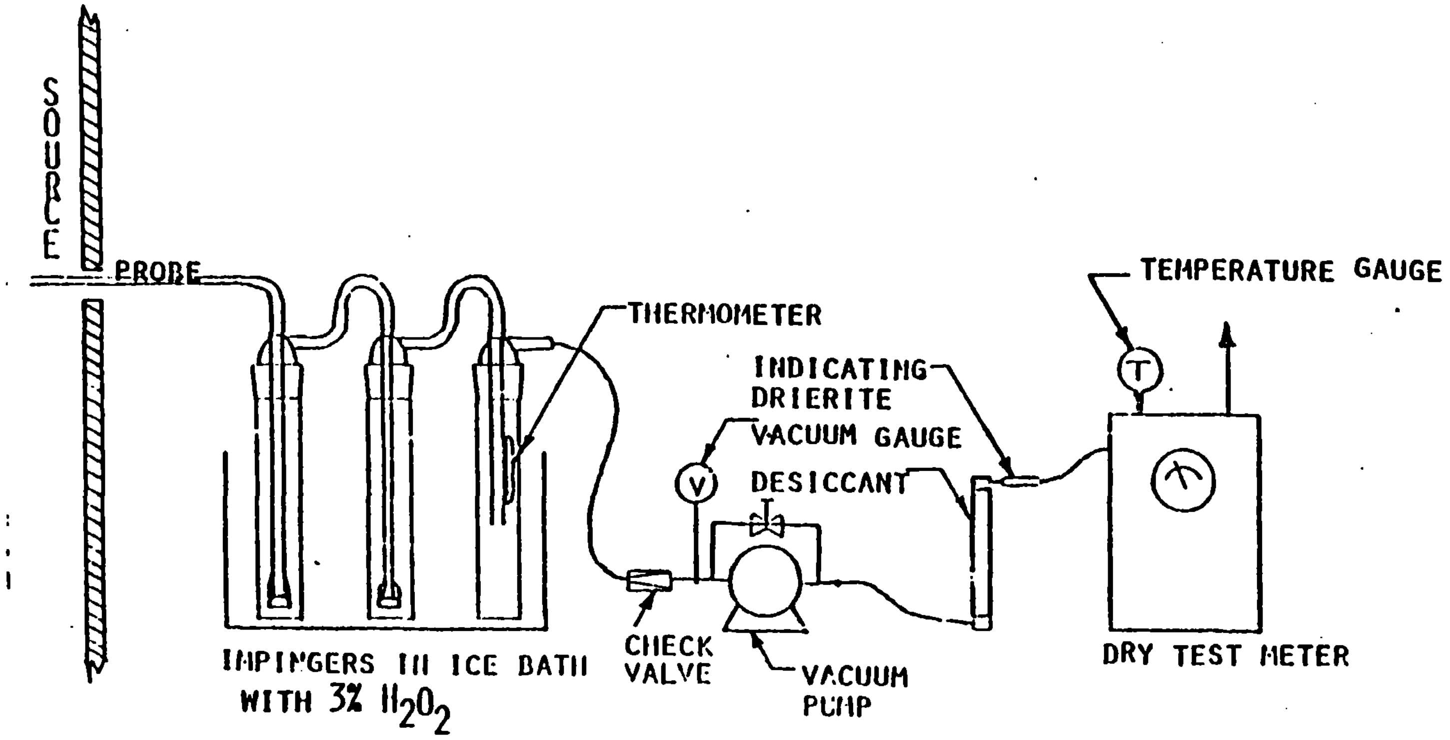

Fig. IV - 62

SULFUR DIOXIDE SAMPLING TRAIN

## BAY AREA AIR POLLUTION CONTROL DISTRICT

### Source Test Data Sheet

Source Operation ____________
Plant ____________
Sample Type ____________
Process Cycle ____________
Duct Size ____________
Duct Pressure ____________

Source Test No. ____________
Run No. ____________
Date: ____________

____________ Nozzle Diameter
____________ Pitot Tube
____________ Gas Collector No.
____________ Barometric Pressur
____________ Leak Rate @ 15"Hg

Sampling Train: .

| Traverse Point | Dist. From inches | INITIAL TRAVERSE | | | SAMPLING | | | | | | | | | | | REMARKS |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | METER | | | | | | | |
| | | Duct Temp°F | h $H_2O$ | $\sqrt{h}$ | Traverse Point | h $H_2O$ | $V_s$ FPS | Time | Rate CFH | Temp °F | Volume $Ft^3$ | Vac "Hg | Sat'd Gas Temp°F | $T_s$ Duct Temp°F | | |
| | | | | | | | | | | | | | | | | |
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$$D_n = 13.7\left[\frac{T_s + 460}{K_p V_s (100-\%H_2O)}\right]^{1/2}$$

$$Q_m = \left[(2.638 \times 10^{-3}) K_p (100-\%H_2O) D_{mm}^2\right]\frac{V_s}{T_s}$$

Condensate ________ gm.
$V_o$ ________
$\%H_2O$ ________
$\%CO_2$ ________
$\%CO$ ________
$\%O_2$ ________

Source Test Team
________________
________________
________________
________________

FIG. IV-63

# SUMMARY OF SOURCE TEST RESULTS

## SOURCE INFORMATION

Firm Name and Address

Firm Representative and Title

Phone No.

Source:

Report No.

Conditions During Tests

Test Date:

Test Times:

Run A:

Operates hr/day & days/yr

Operating Parameters

Run B:

Run C:

Test Results and Comments

| METHOD | TEST | RUN A | RUN B | RUN C | AVG. |
|---|---|---|---|---|---|
|  | Run time, minutes |  |  |  |  |
|  | Stack gas Temp., °G |  |  |  |  |
| ST-17 | Stack flowrate, SDCFM |  |  |  |  |
| ST-19B | Sulfur Dioxide, ppm |  |  |  |  |
|  | Sulfur Dioxide, lb/hr |  |  |  |  |
|  | $SO_2$, lbs/ton product |  |  |  |  |

FIG. IV-64

# SOURCE TEST PROCEDURE ST-20

## SULFUR DIOXIDE, SULFUR TRIOXIDE, SULFURIC ACID MIST

REF: Regs. 6-320, 6-330,
9-1-302, 9-1-304 thru 310
10-1-301, 12-6-301

### 1. Applicability

1.1 This method is used to quantify emissions of sulfur dioxide, sulfur trioxide and sulfuric acid mist. It determines compliance with Regulations 6-320 and 6-330 for SULFUR TRIOXIDE and SULFURIC ACID MIST, and 9-1-302, 9-1-304 thru 310 and 10-1-301 and 12-61301 for SULFUR DIOXIDE.

1.2 This method, modified with a glass fiber disc filter as the back-up $SO_3$ filter, has been given alternate status by the EPA to EPA Method 8. It may be used to determine compliance with oxides of sulfur regulations under Regulation 9.

### 2. Principle

2.1 Sulfuric acid mist, sulfur trioxide and sulfur dioxide are collected in a single extractive sampling train. Acid mist is trapped in a quartz wool plug in the sample probe and is subsequently analyzed with an acid-base titration. Sulfur trioxide is absorbed in an 80% isopropyl alcohol (IPA)/water solution with a quartz wool back-up filter and is analyzed using analytical procedure LAB 12. Sulfur dioxide is absorbed in a aqueous hydrogen peroxide solution and is analyzed using analytical procedure LAB 12.

### 3. Range

3.1 The minimum measurable concentrations using this method listed below are:

3.1.1 Acid mist - .0002 $gr/ft^3$ as $H_2SO_4$
3.1.2 Sulfur trioxide - 7ppm
3.1.3 Sulfur dioxide - 7ppm

3.2 The maximum measurable concentrations using this method listed below are:

3.2.1 Acid mist - undetermined
3.2.2 Sulfur trioxide - 350ppm
3.2.3 Sulfur dioxide - 2.5%

### 4. Interferences

4.1 Acid mist and sulfur dioxide. The presence of strong acids or salts such as hydrochloric acid or sodium bisulfite give erroneously high results. The presence of alkaline gases or reactive basic solids such as ammonia or calcium oxide give erroneously low results.

4.2 Sulfur Trioxide. Sulfur dioxide at 2000 ppm or over may oxidize to sulfur trioxide in the IPA/$H_2O$ solution. For this reason, two IPA/$H_2O$ impingers are used in series. The sample concentration of $SO_3$ as indicated by the second impinger is regarded as a blank analysis and is subtracted from the analysis of the first impinger.

## 5. Apparatus

5.1 Probe. Use a borosilicate glass probe long enough to extend across the stack diameter. If stack temperatures exceed 800°F, use a quartz probe. The probe entrance shall be enlarged to approximately 20mm I.D. for a length of 10cm. The downstream end should be fitted with a 90° elbow and a ball joint. The probe shall be heat-traced and insulated if necessary to prevent sample condensation.

5.2 Acid mist filter. Insert approximately 3 grams of quartz wool in the probe entrance.

5.3 Absorbers. Use four Greenberg-Smith impingers, one with the inlet fitted with a ball joint to receive the probe.

5.4 Filter. Approximately 10 grams of quartz or quartz wool are packed into a glass holder of the same specifications as the filter holders used in ST-15.

5.5 Cooling system. An ice bath is used to contain the impingers.

5.6 Sample pump. Use a leak-free vacuum pump capable of maintaining a 0.5 CFM flow rate at 15 inches of mercury-vacuum. The pump has a flow control valve and vacuum gauge attached to the inlet.

5.7 Silica gel tube. Use approximately 500cc of silica gel (with a Drierite indicator) to insure that the gas entering the dry test meter is dry.

5.8 Dry test meter. Use a dry gas test meter accurate within ±2% of the true volume and equipped with a thermometer to measure the outlet temperature.

5.9 Connections. Use Teflon tubing in making all connections that come in contact with the sample. Vinyl tubing is acceptable for all other connections.

5.10 Barometer. Use a barometer that is accurate to within ±0.2 inches of mercury.

5.11 Rotameter. Use a calibrated rotameter to measure the sampling rate.

6. Reagents

6.1 Isopropanol, 80%. Prepare an 80% by volume solution of isopropanol (IPA) in distilled water. Check the solution for contamination using Analytical Procedure Lab-10.

6.2 Hydrogen peroxide, 3%. Prepare a 3% by volume solution of hydrogen peroxide in distilled water.

7. Pre-Test Procedures

7.1 Add 100 ml of the 80% IPA to each of the impingers.

7.2 Add 100 ml of the hydrogen peroxide solution to each of the two impingers.

7.3 Stopper the impingers.

7.4 Retain 100 ml of each solution to analyze as a blank.

7.5 Assemble the sampling train as shown in Figure IV-65.

7.6 If condensation is expected, heat trace the sample line.

7.7 Leak-test the sampling train by starting the pump, plugging the probe, and adjusting the pump inlet vacuum to 10 inches Hg. The leak rate must not exceed 0.02 CFM through the dry test meter. Before stopping the pump, carefully release the plug in the sample probe to avoid backflow of the impinger solution.

7.8. Record the initial dry test meter reading and barometric pressure on a data sheet as shown in Figure IV-66.

8. Sampling

8.1 Sample at continuous operations for a period of thirty minutes for each test run. Sample at batch processes for a period of thirty minutes or 90% of batch process time, whichever is less.

8.2 Position the probe at the sampling point and start the pump.

8.3 Sample at a constant rate of 14.3 liter/min (0.5 CFM) during the test as determined by the rotameter.

8.4 Record the following information at five-minute intervals:

dry test meter temperature
impinger outlet temperature
dry test meter reading

8.5 Check the sample probe periodically for condensate. If condensation occurs, stop the test until the problem is rectified.

8.6 Add ice as necessary to maintain the temperature exiting the last impinger at 7°C(45°F) or less.

8.7 At the conclusion of each run, stop the pump, remove the probe from the stack, and record the final meter volume.

8.8 Take three consecutive samples.

## 9. Post-Test Procedures

9.1 Immediately after sampling, purge the impinger train with ten cubic feet of $SO_2$-free ambient air at a rate of 0.5 CFM.

9.2 Keep the two IPA solutions on ice and stoppered until they are analyzed.

9.3 Analyze the IPA solution within 24 hours after sampling.

9.4 Individually analyze each train for acid mist, sulfur trioxide, and sulfur dioxide using Analytical Procedure Lab-12.

## 10. Auxiliary Tests

10.1 Stack velocity. Determine the stack gas velocity after each run in accordance with ST-17.

10.2 Moisture content. Determine the moisture in the stack gases in accordance with ST-23.

10.3 Production rate. Determine the sulfuric acid or sulfur production from plant data based on a 24 hour, daily production rate in tons per day, if the test is being conducted on a sulfur recovery acid plant.

10.4 Oxygen concentration. Use ST-14 to determine the oxygen concentration of the stack gas.

## 11. Calculations

11.1 The standard sample volume:

$$V_o = \frac{17.71\ V_m P_b}{T_m}$$

where:

$V_o$ = corrected sample volume, SDCF @70°F and 29.92 inches Hg
$V_m$ = sample volume as recorded by dry test meter, SCF
$T_m$ = average meter temperature, °R
$P_b$ = barometric pressure, inches Hg.
17.71 = a constant correcting to 70°F and 29.92 inches Hg.

11.2 Acid mist concentration:

$$C_{H_2SO_4} = \frac{15.4W}{V_o}$$

where:

$C_{H_2SO_4}$ = concentration of acid mist, grains/SDCF
W = weight of acid on the probe filter, grams.
15.4 = correction from grams to grains

11.3 Sulfur trioxide concentration, as sulfuric acid:

$$C_{SO_3} \text{ (impinger \#1)} = \frac{15.4W_1}{V_o}$$

$$C_{SO_3} \text{ (impinger \#2)} = \frac{15.4\ W_2}{V_o}$$

$$C_{SO_3} \text{ (filter)} = \frac{15.4\ W_F}{V_o}$$

where:

$W_1$ = weight of $SO_3$ (as $H_2SO_4$) in impinger #1.
$W_2$ = weight of $SO_3$(as $H_2SO_4$) in impinger #2
$W_F$ = weight of $SO_3$(as $H_2SO_4$) in the filter.

11.4 Total sulfur trioxide content of the sample:

$$C_{SO_3} = C_{SO_3}\text{(impinger \#1)} - C_{SO_3}\text{(impinger \#2)} + C_{SO_3}\text{ (filter)}$$

where:

$C_{SO_3}$ = concentration of $SO_3$, as $H_2SO_4$, grains/SDCF.

11.5 Total of acid mist and sulfur trioxide concentration:

$$C_{H_2SO_4}\text{ (total)} = C_{H_2SO_4} + C_{SO_3}$$

11.6 The concentration of sulfur dioxide:

$$C_{SO_2} = \frac{1.33 \times 10^4 W}{V_o}$$

where:

$C_{SO2}$ = concentration of $SO_2$, ppm (dry)
$W^{SO2}$ = total impinger catch of $SO_2$ for each run, grams.
$1.33 \times 10^4$ = a constant derived from the molar volume and molecular weight of $SO_2$

11.7 The total sample concentration of sulfur dioxide:

$$C_{SO_2} = C_{SO_2}\text{ (impingers\#3)} + C_{SO_2}\text{(impinger \#4)}$$

11.8 Mass emission rate of $SO_2$:

$$M_{SO_2} = KC_{SO_2}Q_o$$

where:

$M_{SO_2}$ = mass emission rate of $SO_2$ kg/hr(lb/hr)

$Q_o$ = stack gas flow rate $SDM^3$/min($SDFT^3$)/min)

$K = 9.92 \times 10^{-6} \dfrac{lb}{ppm\text{-}ft^3\text{-}hr}$ for English units.

$= 1.59 \times 10^{-4} \dfrac{kg}{ppm\text{-}M^3\text{-}hr}$ for SL units.

11.9 Mass emissions based on production rate:

$$M_{tp} = \frac{M_{SO_2}}{M_d}$$

where:

$M_{tp}$ = mass emissions per ton of product, $\dfrac{Kg}{\text{metric ton}}$ $\left(\dfrac{lbs}{\text{short ton}}\right)$

$M_{SO_2}$ = mass emission rate of SO2, $\dfrac{Kg}{hr.}$ $\left(\dfrac{lbs}{hr.}\right)$

$M_d$ = Production rate per hour. (based on up to 48 hour average.)

11.10 Oxygen Correction factor:

$$F = \frac{21.95 - X_{O_2}}{21.95 \times P_{O_2}}$$

where:

$F$ = Oxygen correction factor

$X_{O_2}$ = Oxygen concentration to be corrected to 0% for Sulfur Recovery plants and 12% for Sulfuric Acid Plants.

$P_{O_2}$ = Oxygen content present in stack gas.

11.11 $SO_2$ concentration corrected for oxygen content.

$$C_{SO_2}F = F \times C_{SO_2}$$

where:

$C_{SO_2}F$ = $SO_2$ concentration corrected for oxygen content.

12. Reporting

12.1 Report the data indicated in Figure IV-67.

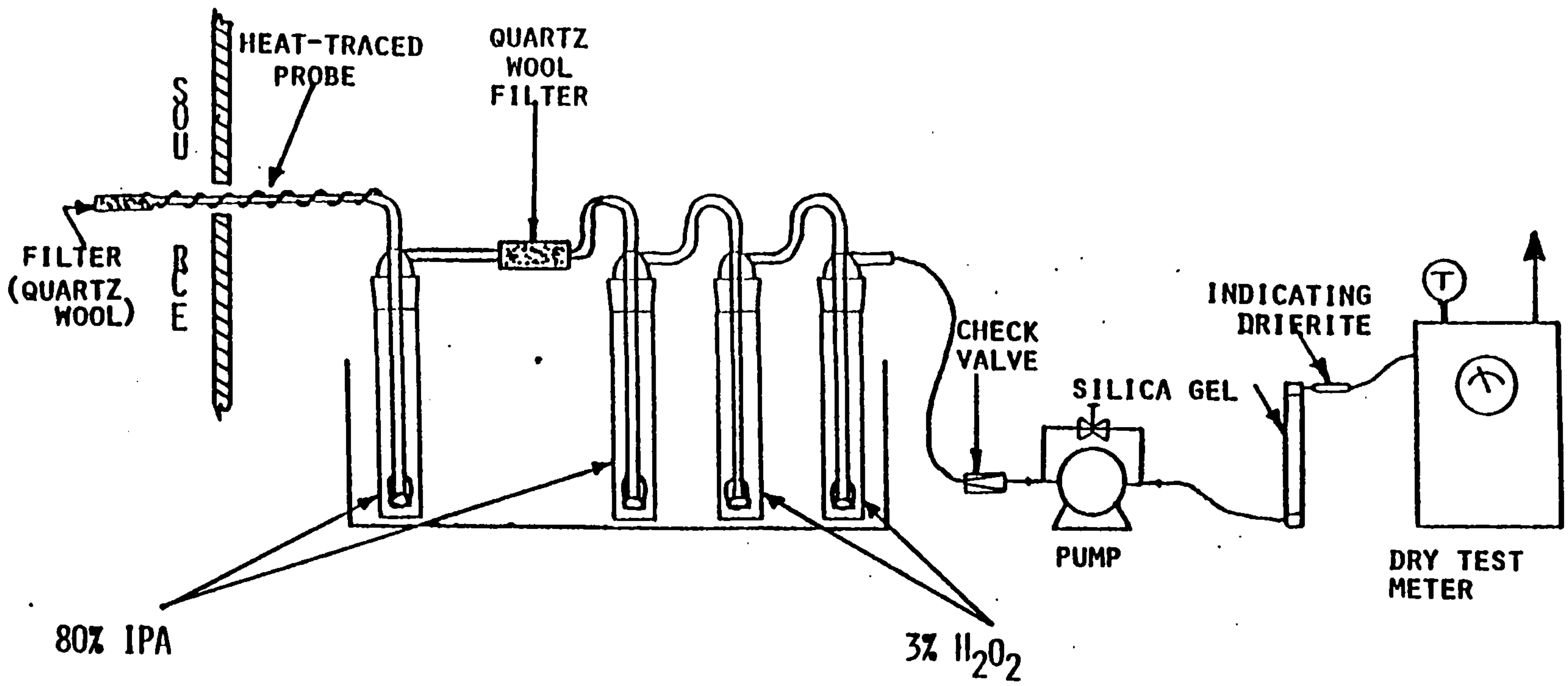

Fig. IV - 65

SULFUR OXIDES SAMPLING TRAIN

# SUMMARY OF SOURCE TEST RESULTS

## SOURCE INFORMATION

Firm Name and Address

Firm Representative and Title

Phone No.

Source:

Conditions During Tests

Operates hr/day & days/yr

Operating Parameters

Report No.

Test Date:

Test Times:

Run A:

Run B:

Run C:

Test Results and Comments

| METHOD | TEST | RUN A | RUN B | RUN C | AVG. |
|---|---|---|---|---|---|
| | Run time, minutes | | | | |
| | Stack gas temp., °F. | | | | |
| ST-17 | Stack flowrate, SDCFM | | | | |
| ST-14 | $O_2$ conc., dry basis, % | | | | |
| ST-5 | $CO_2$ conc., dry basis, % | | | | |
| ST-6 | CO conc., dry basis, % | | | | |
| ST-23 | $H_2O$ conc., actual basis, % | | | | |
| ST-19A | Sulfur dioxide, ppm | | | | |
| | Sulfur dioxide, lb/hr | | | | |
| | Sulfur trioxide, as acid grains/SDCF | | | | |
| | Sulfuric acid mist, grains/SDCF | | | | |
| | Total acid, grains/SDCF | | | | |
| | $SO_2$, lbs/ton product | | | | |

FIG. IV-67

## BAY AREA AIR POLLUTION CONTROL DISTRICT

### Source Test Data Sheet

Source Operation ______
Plant ______
Sample Type ______
Process Cycle ______
Duct Size ______
Duct Pressure ______

Source Test No. ______
Run No. ______
Date: ______

______ Nozzle Diameter
______ Pitot Tube
______ Gas Collector No.
______ Barometric Pressur
______ Leak Rate @ 15"Hg

Sampling Train:

| Traverse Point | Dist. From | INITIAL TRAVERSE | | | SAMPLING | | | | | | | | | | REMARKS |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | METER | | | | | | |
| | Inches | Duct Temp°F | h $H_2O$ | $\sqrt{h}$ | Traverse Point | h $H_2O$ | $V_s$ FPS | Time | Rate CFH | Temp °F | Volume $Ft^3$ | Vac "Hg | Sat'd Gas Temp°F | $T_s$ Duct Temp°F | |
| | | | | | | | | | | | | | | | |
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$$D_n = 13.7\left[\frac{T_s + 460}{K_p V_s (100-\%H_2O)}\right]^{1/2}$$

$$Q_m = \left[(2.638 \times 10^{-3}) K_p (100-\%H_2O) D_{mm}^2\right]\frac{V_s}{T_s}$$

Condensate ______ gm.
$V_o$ ______
$\%H_2O$ ______
$\%CO_2$ ______
$\%CO$ ______
$\%O_2$ ______

Source Test Team
______
______
______
______

FIG. IV-66

# Source Test Procedure ST-21

## TOTAL REDUCED SULFUR

REF: Regs. 12-1-301 thru 303

### 1. Applicability

1.1 This method is used to quantify emissions of total reduced (TRS compounds as $H_2S$, in the presence of sulfur dioxide. It determines compliance with Regulations 12-301, 12-302 and 12-303.

### 2. Principle

2.1 A continuous representative gas sample is extracted from the sampling point and conditioned to remove water and particulate material. A small portion of the conditioned sample is passed through a potassium citrate/citric acid buffer solution to remove sulfur dioxide and then through a combustion tube to oxidize all reduced sulfur to sulfur dioxide. The sulfur dioxide is measured with an ultraviolet analyzer.

### 3. Range and Sensitivity

3.1 The minimum measurable concentration of reduced sulfur, as $H_2S$, is 5 ppm with this method.

3.2 The maximum concentration of reduced sulfur is 5000 ppm.

3.3 The method has been proven in the presence of up to 3500 ppm sulfur dioxide.

3.4 The analyzer sensitivity is ± 2% of instrument scale.

### 4. Interferences

4.1 None are known.

### 5. Apparatus

5.1 Analyzer. Use an E.I. DuPont de Nemours Photometric analyzer Model 400 equipped with a stainless steel sample cell or its equivalent to determine $SO_2$ concentrations.

5.2 Chart recorder. The recorder monitors and records the continuous output from the analyzer.

5.3 Sample conditioning, zero air, and span gas system. The assembly of this system is shown in Fig. IV-68. The sample conditioning system provides a dry, particulate free gas flow to the instrument. The zero air system provides clean dry atmospheric air for instrument calibration. The span gas system provides a known concentration of $SO_2$ for use in calibrating the analyzer. Except as specified, all materials which come in contact with either the sample or span gases must be constructed of Teflon or stainless steel.

5.4 Sample probe. Use a borosilicate glass tube long enough to traverse the stack being tested. If the stack temperature exceeds 425C (800F), use a quartz probe. Other probes are acceptable subject to prior approval by the Source Test Section.

5.5 Condensers. Use modified Greenberg-Smith impingers with the impaction plates removed and the inlet tube shortened to a length of 10cm (4 inches), or equivalent.

5.6 Cooling system. Immerse the impingers in an ice bath during the test.

5.7 Particulate filter. Use a Balston type 95 holder with a grade B filter, or equivalent, in the sample system.

5.8 Pumps. Use leak-free, Teflon-lined, diaphragm pumps in the sample and zero air system. The pumps must have a free-flow capacity of at least 40 liters/min (1.5 CFM).

5.9 Back-pressure regulator. Use a back-pressure regulator to maintain the sample and zero-gas sample pressures to the instrument at five psig.

5.10 Gas scrubber. Use a bed of silica gel, Ascarite (or soda-lime), and charcoal to remove moisture, carbon dioxide, and hydrocarbons from the zero-air system.

5.11 Span gas. Use high-pressure cylinder containing a known concentration of $SO_2$ in nitrogen. The span gas concentration must be in the same range as the source being tested.

5.12 Combustor. Use a system to oxidize all reduced sulfur compounds in the sample stream to $SO_2$. An example of an acceptable combustion tube found adequate by the BAAQMD is shown in Figures IV-69 and IV-70.

5.13 Sulfur dioxide scrubber. Use three midget impingers containing the scrubbing reagent.

5.14 Filter. Use a Balston type 95 holder with a grade B filter following the combustion tube to remove $SO_3$ and particulate from the effluent.

## 6. Reagents

6.1 Potassium Citrate/Citric Acid Buffer. Add 300 grams of potassium citrate and 41.0 grams of citric acid to one liter of distilled water. Check the ph of the solution and adjust as necessary to 5.6 with the appropriate reagents.

## 7. Pre-Test Procedures

7.1 Warm-up the instrument according to manufacturer's instructions.

7.2 Assemble the sampling system as shown in Figure IV-71.

7.3 Leak-test the sampling system by starting the pump, plugging the probe, and checking that the pressure to the analyzer falls to zero.

7.4 Introduce zero-air, into the analyzer and zero the instrument according to manufacturer's instructions.

7.5 Introduce span gas into the analyzer and calibrate the instrument according to manufacturer's instructions.

7.6 Conduct a preliminary concentration traverse (in accordance with ST-18) to determine if stratification of the stack gases exists. If the concentration of reduced sulfur compounds at any point differs from the average concentration by more than 10%, traverse the stack during the test. If not, sample at any single point.

7.7 Prepare the chart recorder according to manufacturer's instructions.

7.8 Add approximately 25ml of the citrate buffer reagent to each of two midget impingers.

7.9 Check the scrubber efficiency when the stack $SO_2$ concentration exceeds 300 ppm. Pass $SO_2$ span gas in the range expected through the sample system at a flow rate of 2 CFH. Break-through should not occur in less than 20 minutes. If breakthrough occurs, add 25 ml more of the citrate buffer reagent.

## 8. Sampling

8.1 Each test run shall be of thirty minute duration when testing emissions from continuous operations. Each test run at a batch operation shall be for 90% of the batch time or thirty minutes, whichever is less.

8.2 Introduce sample gas into the analyzer at the same flow rate used to calibrate the analyzer.

8.3 Maintain ice in the cooling system throughout the test.

3.4 Calibrate the analyzer before and after each test run. Record each step of the process clearly on the chart recording.

8.5 Conduct three test runs.

8.6 Periodically pass $SO_2$ span gas through the scrubber and ascertain that the analyzer reads zero. If it doesn't,replace the buffer reagent.

## 9. Auxiliary Tests

9.1 Stack flow rate. Determine the stack gas flow rate after each test run in accordance with ST-17.

9.2 Moisture. Determine the stack gas moisture content in accordance with ST-23.

## 10. Calculations

10.1 From the chart recording determine the time-averaged concentration of TRS on a dry basis for each run.

10.2 The mass emission rate of TRS, as $H_2S$, at kraft pulp mills:

$$W = \frac{5.27 \times 10^{-6} C_{R_s} Q_o t}{T}$$

where: $W$ = mass emission of reduced sulfur, as $H_2S$, in lbs, per ton of pulp produced.

$C_{R_s}$ = time-averaged concentration of reduced sulfur, as $H_2S$, ppm

$Q_o$ = stack flow rate, SDCFM

$t$ = time of pulp production/day, hrs/day

$T$ = tons of pulp produced/day.

$5.27 \times 10^{-6}$ = a constant based on the above units, standard conditions and molecular weight.

## 11. Reporting

11.1 The results are reported as shown in Figure IV-72.

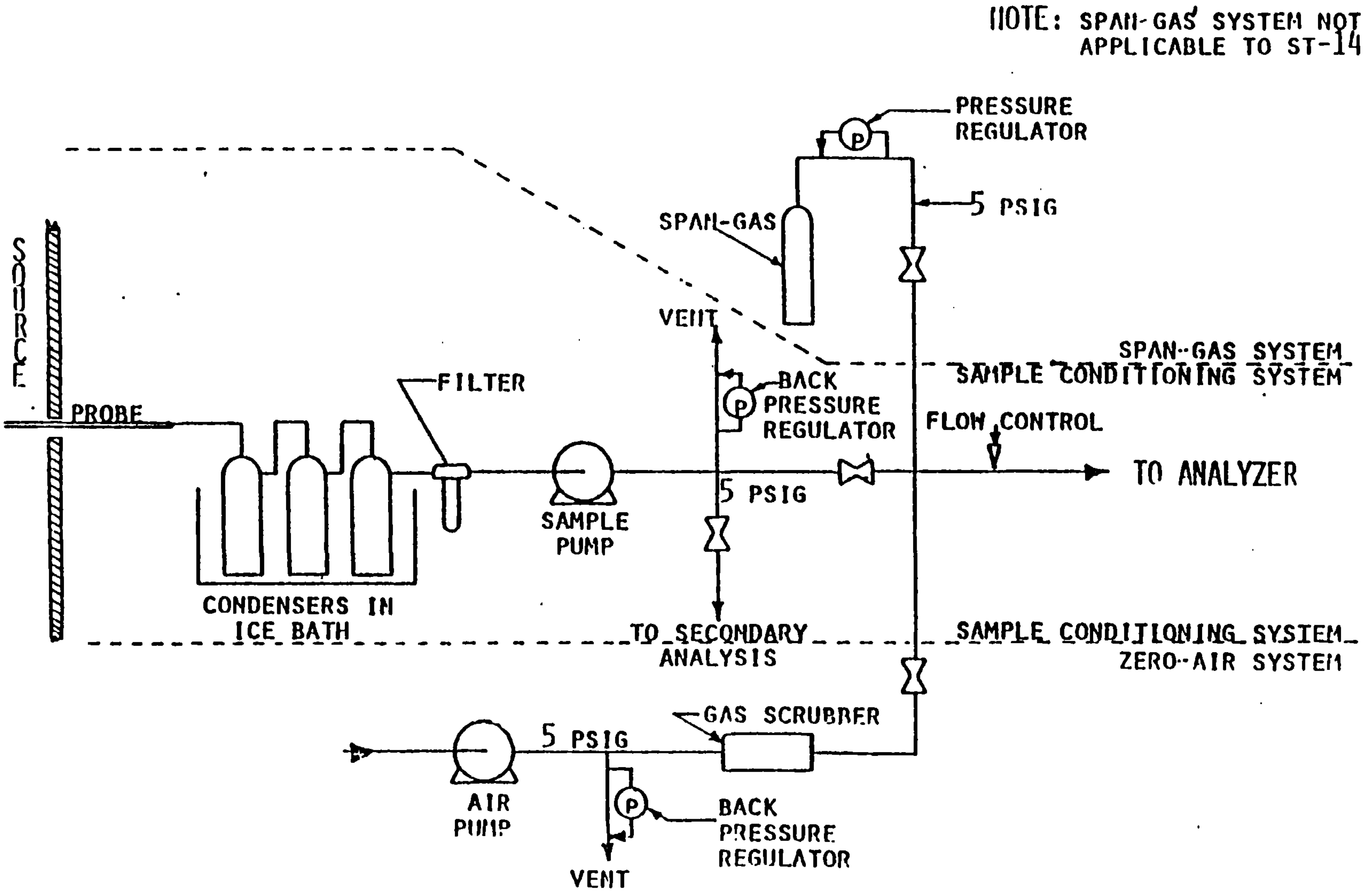

Fig. IV - 68

SAMPLE CONDITIONING, ZERO-AIR AND SPAN-GAS SYSTEMS

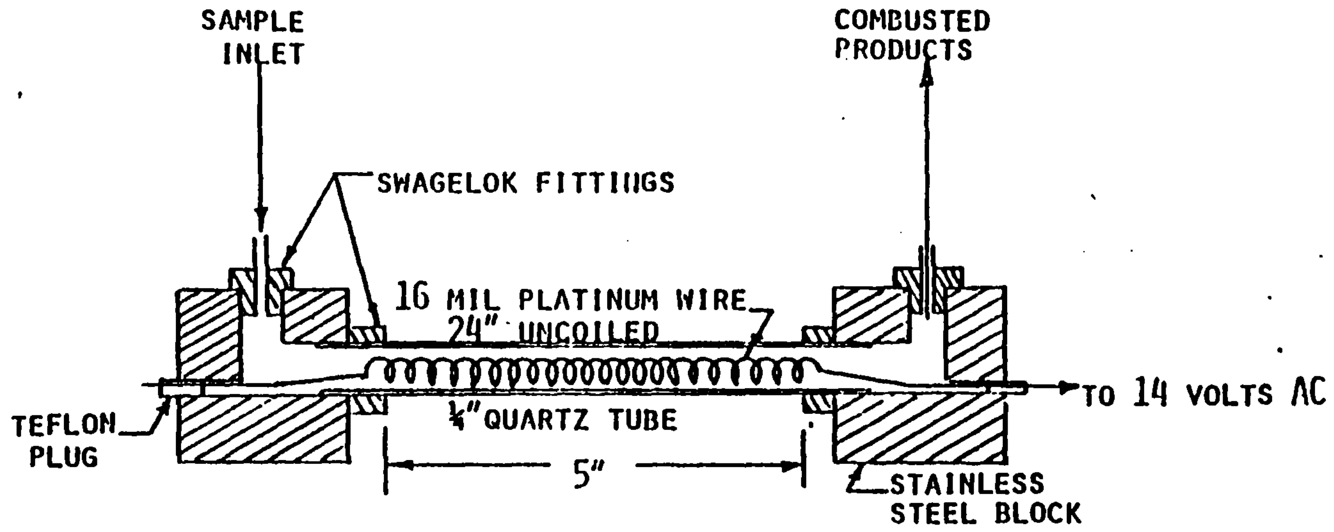

Fig. IV - 69

INTERNALLY HEATED COMBUSTION TUBE

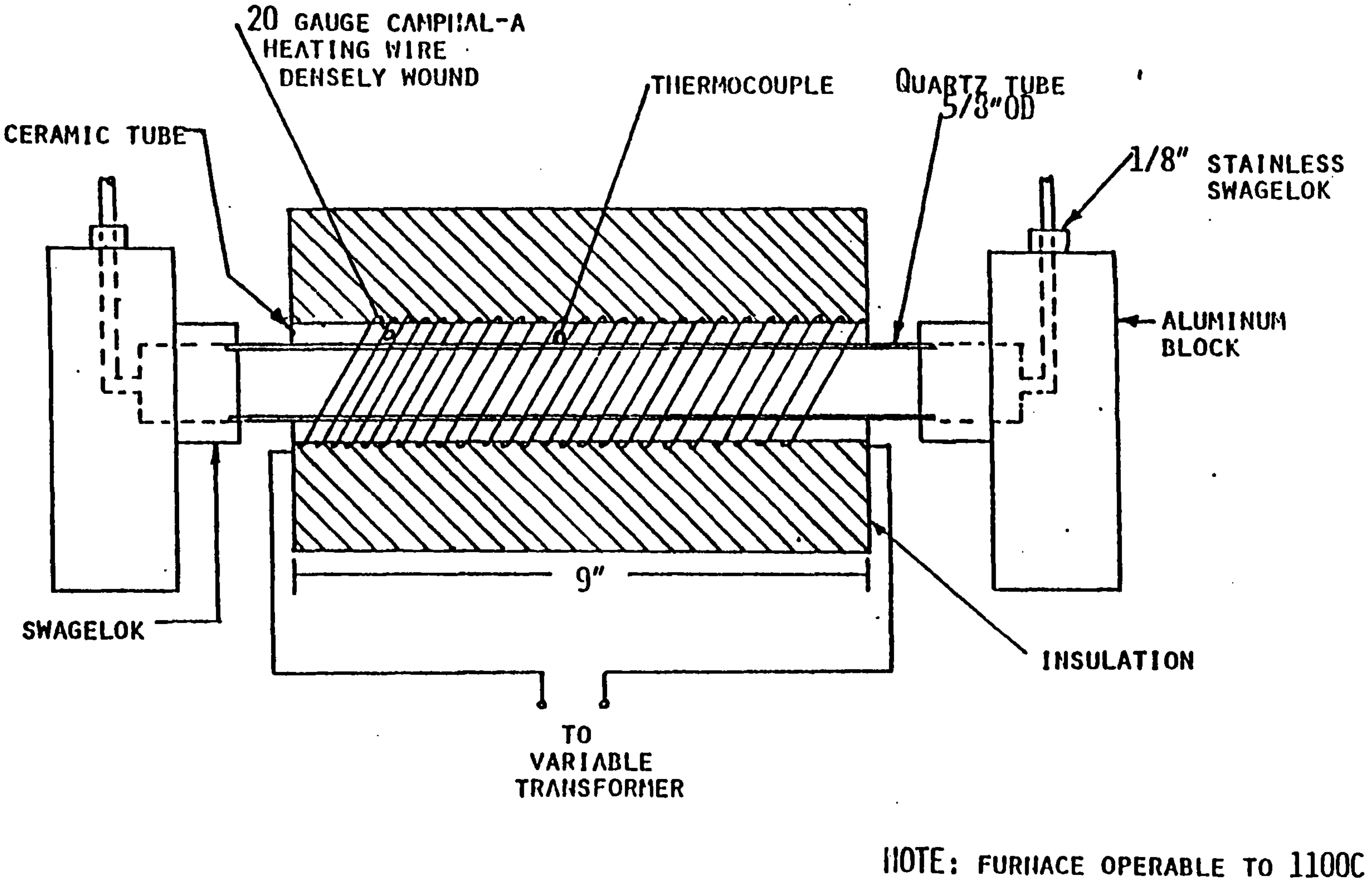

Fig. IV - 70

EXTERNALLY HEATED COMBUSTION TUBE

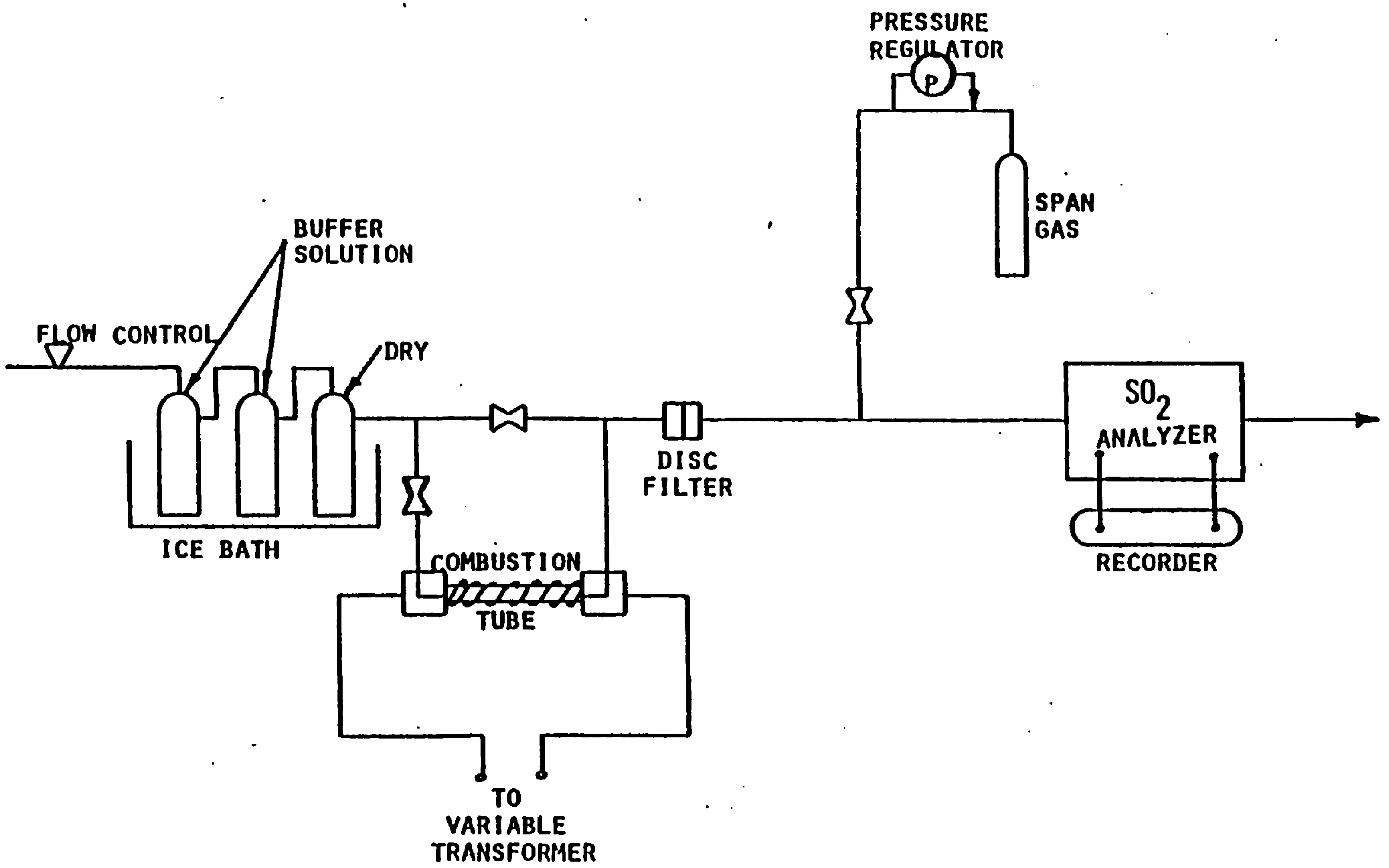

Fig. IV - 71

INSTRUMENTAL ANALYSIS OF TOTAL REDUCED SULFUR

# SUMMARY OF SOURCE TEST RESULTS

## SOURCE INFORMATION

**Firm Name and Address**

**Firm Representative and Title**

**Phone No.**

**Source:**

**Conditions During Tests**

**Operates** hr/day & days/yr

**Operating Parameters**

**Report No.**

**Test Date:**

**Test Times:**

**Run A:**

**Run B:**

**Run C:**

**Test Results and Comments**

| METHOD | TEST | RUN A | RUN B | RUN C | AVG. |
|---|---|---|---|---|---|
| | Run time, minutes | | | | |
| | Stack gas temp., °F. | | | | |
| ST-17 | Stack flowrate, SDCFM | | | | |
| ST-14 | $O_2$ conc., dry basis, % | | | | |
| ST-5 | $CO_2$ conc., dry basis, % | | | | |
| ST-6 | CO conc., dry basis, % | | | | |
| ST-12 | $H_2O$ conc., actual basis, % | | | | |
| ST-21 | Reduced sulfur, as $H_2S$, ppm | | | | |
| | Reduced sulfur, lb/hr. | | | | |

FIG. IV-72

# Source Test Procedure ST-22

## TRIMETHYLAMINE

Ref: Reg. 7-3-3

### 1. Applicability

1.1 This method is used to quantify emissions of Trimethylaming (TMA). It determines compliance with Reg. 7-3-3.

### 2. Principle

2.1 Sample gas is drawn through a solution of 0.1 normal (0.1N) hydrochloric acid which absorbs the TMA. The TMA is subsequently separated and analyzed as specified in Analytical Procedure Lab 14.

### 3. Range and Sensitivity

3.1 The minimum measurable concentration of TMA is 20 ppb at the sample volume specified in this procedure.

3.2 Elevated concentrations of TMA may be determined by increasing the concentration of the absorbing reagent, hydrochloric acid solution. The concentration of reagent to be used may be determined by stoichiometry, allowing a 50% excess.

### 4. Interference

4.1 None known.

### 5. Apparatus

5.1 probe.The probe is constructed of borosilicate glass tubing.

5.2 Absorbers. Use three Greenberg-Smith impingers. The third impinger has a thermometer attached to the inlet stem.

5.3 Cooling system. An ice bath is used to contain the impingers.

5.4 Sample pump. Use a leak-free vacuum pump capable of maintaining a 0.5 CFM flow rate at 15 inches of mercury-vacuum. The pump has a flow control valve and vacuum gauge attached to the inlet.

5.5 Silica gel tube. Use approximately 500cc of silica gel with a Drierite indicator to insure that the gas entering the dry test meter is dry.

5.6 Dry test meter. Use a dry test meter accurate within ±2% of the true volume and equipped with a thermometer to measure the outlet temperature.

5.7 Connections. Use Teflon tubing in making all connections that come in contact with the sample. Vinyl tubing is acceptable for all other connections.

5.8 Barometer. Use a mercury, aneroid, or other barometer that is accurate to within ±0.2 inches of mercury.

5.9 Rotameter. Use a calibrated rotameter to measure the sampling rate.

6. Reagents

6.1 Hydrochloric acid, 0.1 N.

7. Pre-Test Procedures

7.1 Add 100 ml of the HCl solution to each of two impingers.

7.2 Stopper the impingers.

7.3 Retain 100 ml of the hydrochloric acid to analyze as a blank

7.4 Assemble the sampling train as shown in Figure IV-73.

7.5 Leak-test the sampling train by starting the pump, plugging the probe, and adjusting the pump inlet vacuum to 10 inches Hg. The leak rate must not exceed 0.02 CFM through the dry test meter. Before stopping the pump, carefully release the plug in the sample probe to avoid backflow of the impinger solution.

7.6 Record the initial dry test meter reading and barometric pressure as shown in Figure IV-74.

8. Sampling

8.1 Each test run shall be of sixty minute duration when testing emissions from continuous operations. Each test run at batch process operations shall be for 90% of the batch time or sixty minutes, whichever is less.

8.2 Position the probe at the sampling point and start the pump.

8.3 Sample at a constant rate of 14.3 liter/min (0.5 CFM) during the test as determined by the rotameter. Use the rotameter only to establish the initial sampling rate. Then remove it from the system.

8.4 Record the following information at five minute intervals.

Dry test meter temperature
Impinger outlet temperature
Dry test meter reading

8.5 Add ice as necessary to maintain impinger temperatures at 7°C (45°F) or less.

8.6 At the conclusion of each run, stop the pump, remove the probe from the stack, and record the final meter volume.

8.7 Take three consecutive samples.

9. Post-Test Procedures

9.1 Immediately after each test run, stopper the impingers to minimize sample losses.

9.2 Individually analyze the hydrochloric acid solutions and blank for TMA content according to analytical procedure Lab14.

10. Calculations

10.1 Standard sample volume:

$$V_o = \frac{17.71\ V_m P_b}{T_m}$$

where:

$V_o$ = corrected sample volume, SDCF at 70°F and 29.92 inches Hg.
$V_m$ = uncorrected meter volume, ft$^3$
$T_m$ = average run meter temperature, °R
$P_b$ = barometric pressure, inches Hg.
17.71 = a constant correcting to 70F and 29.92 inches H

10.2 TMA concentration:

$$C = \frac{14.4 \times 10^3\ W}{V_o}$$

where:

$C_{TMA}$ = TMA concentration, ppm by volume on a dry basis.
W = total weight of TMA in the impinger catch, for each run, grams.
14.4 = Constant derived from molar volume, molecular weight, and 454 grams/lb.

11. Reporting

11.1 Report the data indicated on Figure IV-75.

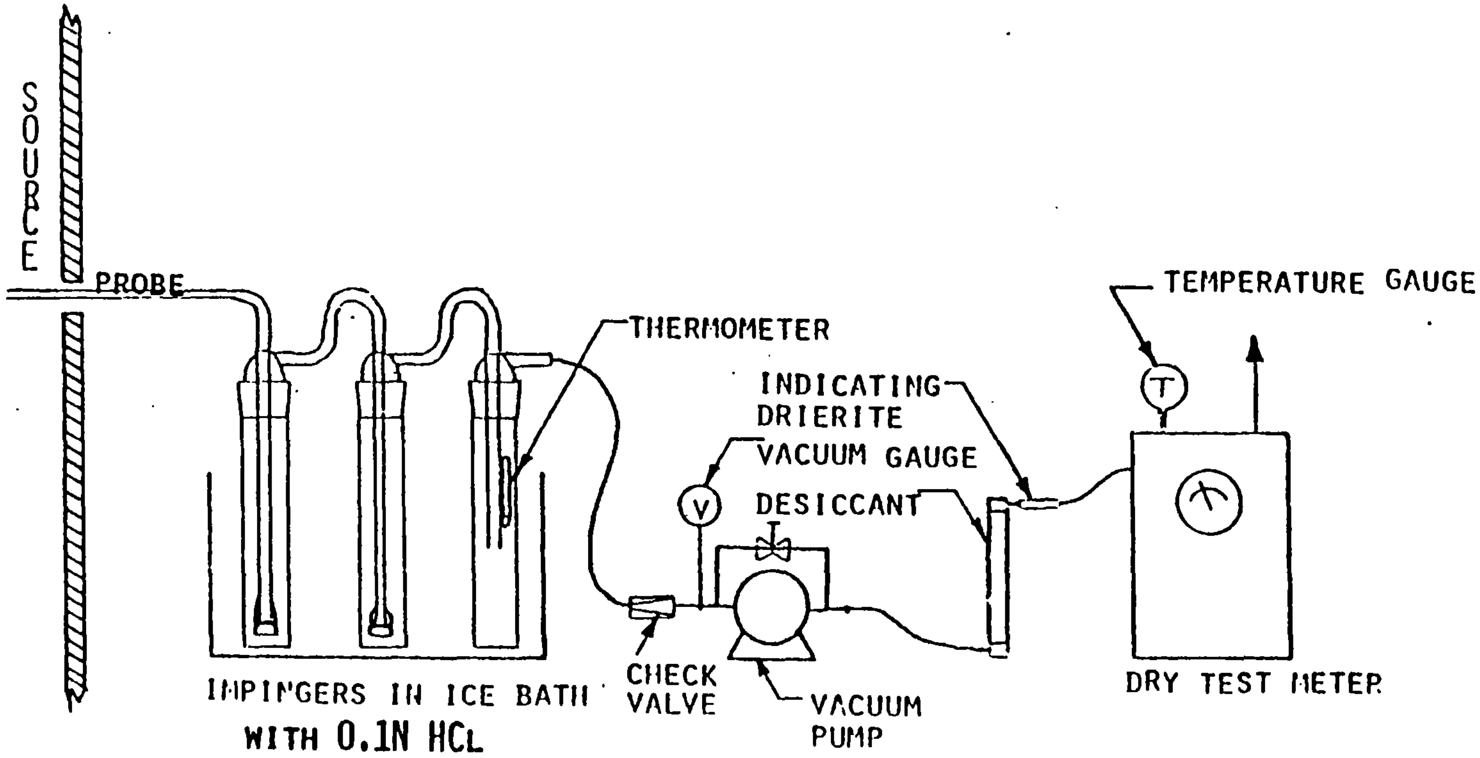

Fig. IV - 73

TRIMETHYLAMINE SAMPLING TRAIN

## BAY AREA AIR Q. TY MANAGEMENT DISTRICT

### Source Test Data Sheet

Source Operation ____________
Plant ____________
Sample Type ____________
Process Cycle ____________
Duct Size ____________
Duct Pressure ____________

Source Test No. ____________
Run No. ____________
Date: ____________

____________ Nozzle Diameter
____________ Pitot Tube
____________ Gas Collector No.
____________ Barometric Pressu
____________ Leak Rate @ 15"Hg

Sampling Train:

| Traverse Point | Dist. From inches | INITIAL TRAVERSE | | | SAMPLING | | | | | | | | | | REMARKS |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | METER | | | | | | |
| | | Duct Temp°F | h $H_2O$ | $\sqrt{h}$ | Traverse Point | h $H_2O$ | $V_s$ FPS | Time | Rate CFH | Temp °F | Volume Ft³ | Vac "Hg | Sat'd Gas Temp°F | $T_s$ Duct Temp°F | |
| | | | | | | | | | | | | | | | |
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$$D_n = 13.7\left[\frac{T_s + 460}{K_p V_s (100-\%H_2O)}\right]^{1/2}$$

$$Q_m = \left[(2.638 \times 10^{-3}) K_p (100-\%H_2O) D_{mn}^2\right]\frac{V_s}{T_s}$$

Condensate ________ gm.
$V_o$ ________
$\%H_2O$ ________
$\%CO_2$ ________
$\%CO$ ________
$\%O_2$ ________

Source Test Team
____________
____________
____________
____________

FIG. I' '4

# SUMMARY OF SOURCE TEST RESULTS

## SOURCE INFORMATION

Firm Name and Address

Firm Representative and Title

Phone No.

Source:

Conditions During Tests

Operates hr/day & days/yr

Operating Parameters

Report No.

Test Date:

Test Times:

Run A:

Run B:

Run C:

Test Results and Comments

| METHOD | TEST | RUN A | RUN B | RUN C | AVG. |
|---|---|---|---|---|---|
| | Run time, minutes | | | | |
| | Stack gas temp., °F. | | | | |
| -22 | TMA concentration, ppm | | | | |

FIG. IV-75

# Source Test Procedure ST-23

## WATER VAPOR

### 1. Applicability

1.1 This method is used to quantify the water vapor content of stack gases. It is applicable in all cases in which such data are needed by any other procedure in this manual.

### 2. Principle

2.1 A gas sample is extracted from the stack at a constant rate. Moisture is removed from the gas through the use of cold condensers. The total condensate is weight determined gravimetrically. The residual water vapor is determined by calculation.

### 3. Range and Repeatability

3.1 The minimum measurable concentration of water vapor is 2% moisture by volume. The maximum measurable concentration is 100% water vapor.

3.2 The sensitivity of the procedure is ±1.0% water vapor.

### 4. Interference

4.1 Compounds which will condense at 45°F. The saturated gas temperature will cause a positive bias.

### 5. Apparatus

5.1 Probe. The probe is constructed of either borosilicate glass or quartz and must be heated as necessary to avoid condensation in the probe. Other probe materials are acceptable when stack conditions allow.

5.2 Condensers. Use three Greenberg-Smith impingers as condensers. The third has a thermometer attached to the inlet stem.

5.3 Cooling system. An ice bath is used to contain all the impingers.

5.4 Sample pump. Use a leak-free vacuum pump capable of a flow rate at 10 inches of Hg vacuum.

5.5 Dry test meter. Use a dry gas meter test meter accurate within ±2% of the true volume and equipped with a thermometer to measure the outlet temperature.

5.6 Connections. All flexible tubing must be leak-free.

6. Pre-Test Procedures

6.1 Tare weights on each of the impingers are recorded to the nearest .1 gram.

6.2 The sampling train is assembled as shown in Figure IV-76. Equipment identification is recorded on the test data sheet.

6.3 It is recommended, but not required that the sampling train be leak-tested before sampling by turning on the pump, plugging the probe and adjusting the pump inlet vacuum to 15" Hg. The leak rate through the dry test meter shall not exceed 0.02 CFM

6.4 Record the initial meter reading before sampling commences.

7. Sampling

7.1 The pump is started and the flow rate adjusted to approximately 0.5 CFM. Maintain a steady sampling rate throughout the test period.

7.2 Sample for thirty minutes or until at least 20cc of condensate have collected in the first impinger.

7.3 At five-minute intervals, record the following:

Test meter temperature
Flow rate
Saturation temperature (from third impinger)
Pump inlet vacuum

7.4 Record the barometric pressure.

8. Post-Test Procedures

8.1 Clean, dry and weigh the impingers.

9. Calculations

9.1 Standard dry sample volume at 90°F, 29.92 inches Hg.

$$V_o = \frac{17.71\, P_b V_m}{T_m}$$

where: 17.71 = a constant correcting to 70F and 29.92 inches Hg.

$V_o$ = standard sample volume, SDCF

$P_b$ = barometric pressure, inches Hg

$T_m$ = average meter temperature

$V_m$ = uncorrected meter volume, $ft^3$

9.2 Stack gas water vapor content

$$H = \frac{(.0474W) + \frac{V_o\ P_{sat}}{P_b - P_i - P_{sat}}}{V_o + (.0474W) + \frac{V_o\ P_{sat}}{P_b - P_i - P_{sat}}} \times 100$$

where: W = total condensate, grams

H = % water vapor

$P_{sat}$ = water saturation pressure, inches Hg determined from average saturation temperature.

$P_i$ = pump inlet vacuum, inches Hg

.0474 = a constant for correcting to standard conditions.

## 10. Reporting

10.1 These values are determined as auxiliary data for other procedures and shall be reported with those test results.

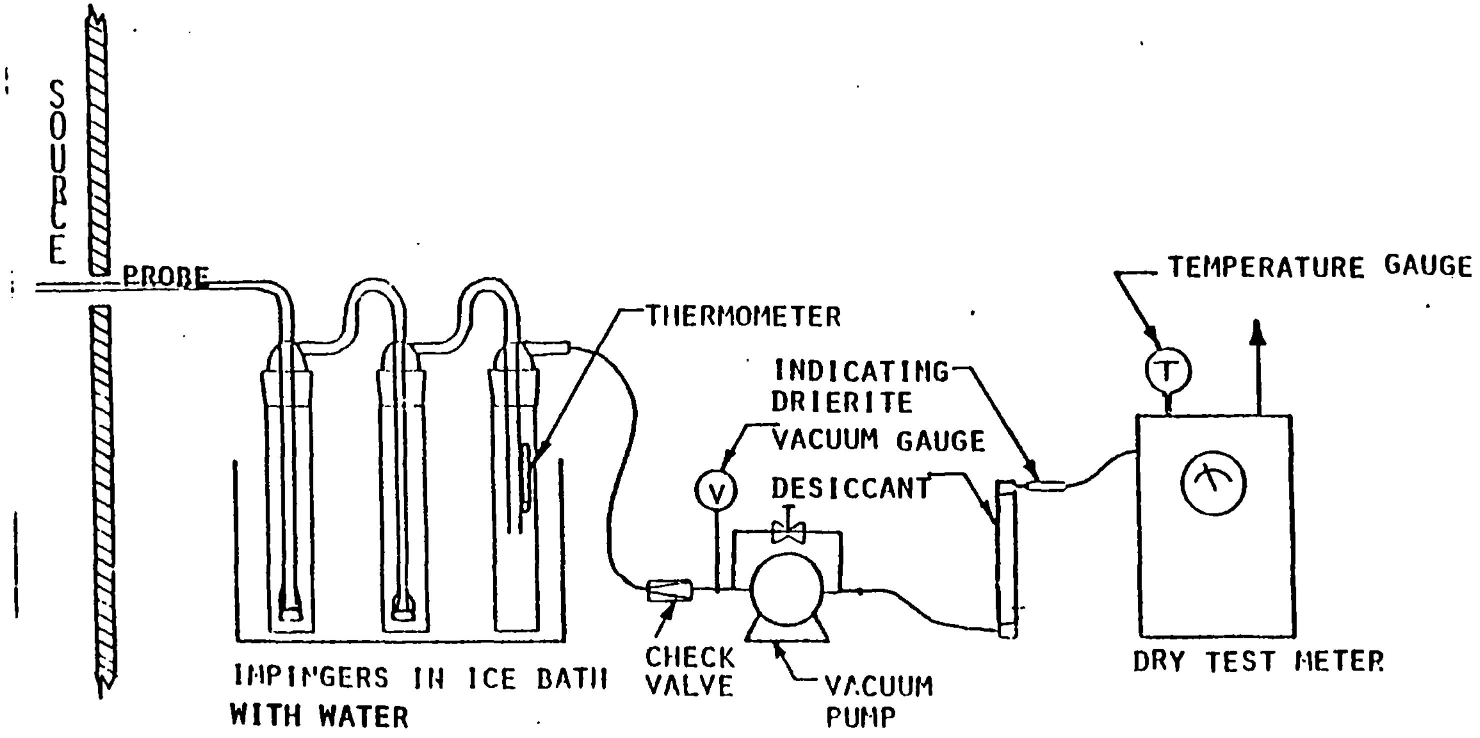

Fig. IV - 76

WATER SAMPLING TRAIN

# Source Test Procedure ST-24

## TANK SAMPLING FOR ORSAT ANALYSIS
## ($CO$, $CO_2$, $O_2$)

REF: Regs. 6-310.1, 8-1-110.3 10-3-301
9-3-301 thru 9-3-304

### 1. Applicability

1.1 This method is used to determine the carbon monoxide, carbon dioxide and oxygen contents of stack gases. It is an acceptable alternate to ST-5, ST-6, and ST-14.

### 2. Principle

2.1 Stack gases are drawn at a constant rate into an evacuated stainless steel tank. A desiccant is used to dry the gases before entering the tank. After testing, the tank is positively pressurized with a known amount of dry nitrogen. The tank contents are then analyzed with an Orsat analyzer, and the results are corrected back to pre-dilution conditions.

### 3. Range

3.1 The minimum measurable concentration of $CO$, $CO_2$ or $O_2$ is 0.2%.

3.2 The procedure is usable for gases up to 100% $CO$, $CO_2$ or $O_2$.

### 4. Interference

4.1 $SO_2$ interfers with $CO_2$ determination.

### 5. Apparatus

5.1 Tank. Use a stainless steel tank, 8-liter capacity or larger, fitted with a stainless steel flow-controlling valve and a vacuum gauge is used.

5.2 Flowmeter. Use a rotameter capable of measuring low sampling rates.

5.3 Desiccant bed. Use Drierite, or equivalent, of sufficient capacity to dry a volume of sample equal to the tank volume.

5.4 Probe. The probe is constructed of either stainless steel or glass.

5.5 Connections. All flexible tubing connections must be leak free.

5.6 Purging Apparatus. Use a squeeze bulb with check valves (see Figure 1) to purge the sample lines with stack gases prior to sampling, as shown in Figure 1.

5.7 Manometer. Use differential manometer with a range of -30 to +20 inches Hg.

5.8 Barometer. Use a temperature compensated aneroid type with a range of 28.0 to 31.0 inches of mercury.

## 6. Pre-Test Procedures

6.1 Prior to the field test, evacuate and seal the tank. If, after a period of not less than two hours, the vacuum gauge indicates a leak, do not use the tank.

6.2 If no leak is found, record the evacuated pressure (gauge), the ambient temperature, and barometric pressure at the time of evacuation.

6.3 In the field, assemble the sampling apparatus as shown in Fig. IV-77. Purge the sampling train until stack gas has completely replaced ambient air. Then remove purging apparatus from the sampling system.

## 7. Sampling

Sample at a constant rate slow enough to fill the evacuated cylinder in approximately 30 minutes.

7.2 For batch processes sample at a constant rate slow enough to fill the evacuated cylinder in approximately 30 minutes or 90% of the batch process time, whichever is less.

7.3 When the tanks is full, seal it for later evaluation.

7.4 Take three consecutive samples if feasible.

## 8. Post-Test Procedures

8.1 Allow the tank to equilibrate at or near the ambient temperature at which is was evacuated. Then record the pressure of its contents and the barometric pressure.

8.2 Pressurize the tank to at least 10 inches of mercury with dry oxygen-free nitrogen. Wait at least ten minutes before reading and recording the pressure.

## 9. Analytical Procedures

9.1 The tank contents are analyzed for oxygen, carbon monoxide and/or carbon dioxide by the Orsat method. Operation of the analysis apparatus shall follow manufacturer's instructions.

9.2 The tank contents are analyzed until successive analyses are constant within .2% (absolute). The constant values shall be reported as the results of the analysis.

## 10. Calculations

10.1 Tank dilution correction factor:

$$F = \frac{P_3 + P_{BF}}{(P_2 + P_{BF}) - (P_1 + P_{BI})}$$

where:

$F$ = correction factor
$P_1$ = residual pressure after evacuation (gauge)
$P_2$ = pressure after sampling, (gauge)
$P_3$ = pressure after addition of nitrogen (gauge)
$P_{BI}$ = barometric pressure at time of evacuation
$P_{BF}$ = barometric pressure at time of pressurization

10.2 Multiply by the factor determined in 10.1, the Orsat analytic results from Section 9.

## 11. Reporting

11.1 These values are determined as auxiliary data for other procedures and shall be reported with those test results.

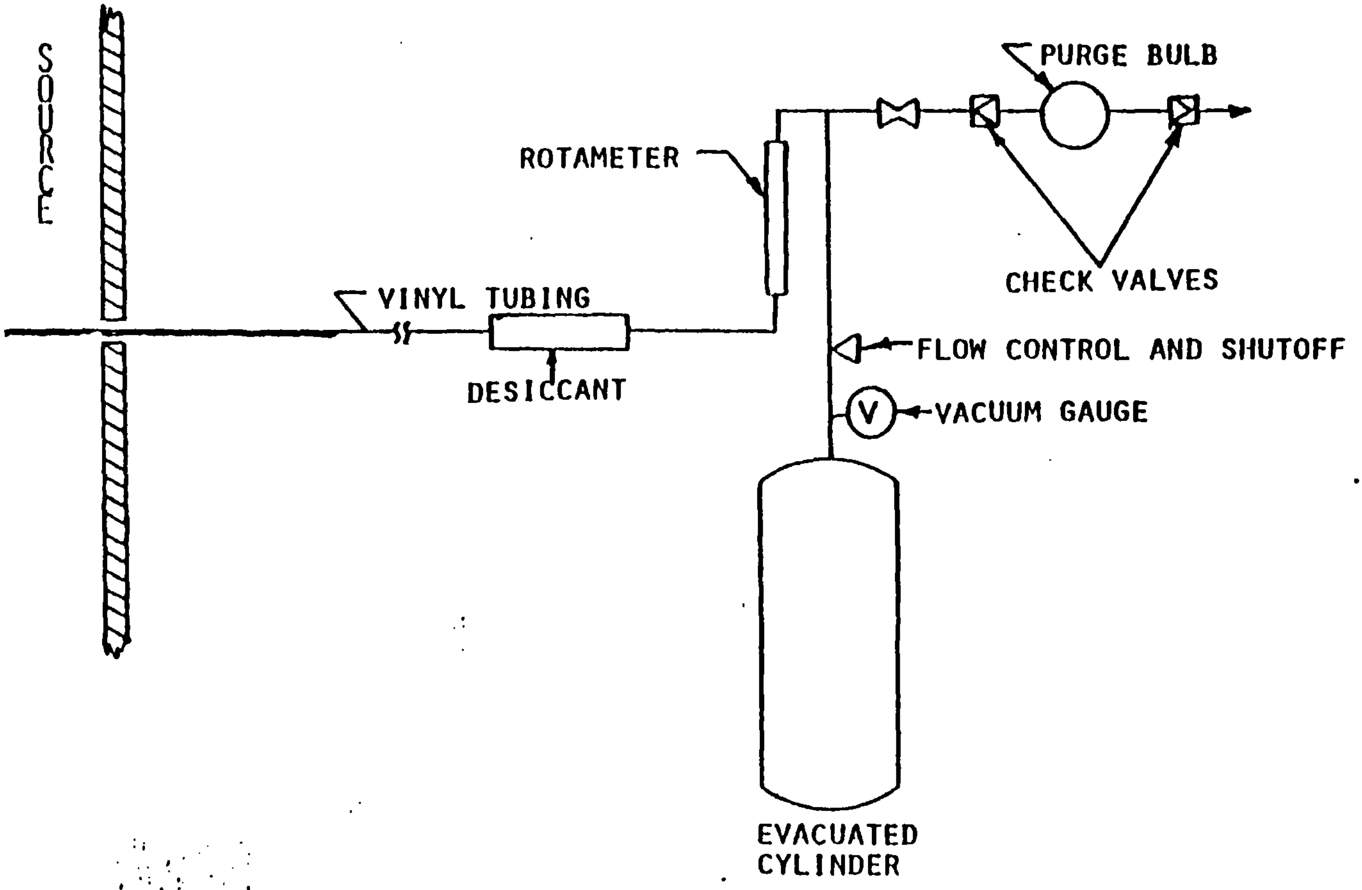

Fig. IV - 77

SAMPLING FOR ORSAT ANALYSIS

# Source Test Procedure ST-25

# FLUORIDE, INTEGRATED SAMPLING

REF: Reg. 10-1-301

## 1. Applicability

1.1 This method is used to quantify emissions of fluoride. It determines compliance with Section 10-1-301 of Regulation 10.

## 2. Principle

2.1 Sample gas is drawn through a solution of 0.1 normal (0.1N) sodium hydroxide which absorbs the fluoride. The fluoride is then analyzed according to Analytical Procedure Lab-24.

## 3. Range

3.1 The minimum measurable concentration of fluoride is 0.05 ppm at the sample volume specified in this procedure.

## 4. Interference

Interferences are accounted for in Lab Procedure 24.

## 5. Apparatus

5.1 Probe. The probe is constructed of borosilicate glass tubing.

5.2 Condensers. Use three Greenberg-Smith impingers as absorber/condensers. The final impinger has a thermometer attached to the inlet stem.

5.3 Cooling system. Use an ice bath to contain the impingers.

5.4 Sample pump. Use a leak-free vacuum pump capable of maintaining a 14.3 liter/min (0.5 CFM) flow rate at 15 inches of mercury. The pump must have a flow control valve and vacuum gauge attached to the inlet.

5.5 Silica gel tube. Use approximately 500cc of silica gel (with a Drierite indicator) to insure that the gas entering the dry test meter is dry.

5.6 Dry test meter. Use a dry gas test meter accurate within ±2% of the true volume and equipped with a thermometer to measure the outlet temperature.

5.7 Connections. Use teflon tubing in making all connections that come in contact with the sample. Vinyl tubing is acceptable for all other connections.

5.8 Barometer. Use a barometer that is accurate to within ±0.2 inches of mercury.

5.9 Rotameter. Use a calibrated rotameter to measure the sampling rate.

## 6. Reagents

6.1 Sodium hydroxide, 0.1N. Dissolve 4.0 grams of sodium hydroxide ml concentrated HCl pellets in sufficiently distilled water to make a 1.0 liter solution.

## 7. Pre-Test Procedures

7.1 Add 100 ml of the NaOH solution to each of two impingers.

7.2 Stopper the impingers.

7.3 Retain 100 ml of the NaOH solution to analyze as a blank.

7.4 Assemble the sampling train as shown in Figure IV-78.

7.5 Leak-test the sampling train by starting the pump, plugging the probe, and adjusting the pump inlet vacuum to 10 inches Hg. The leak rate must not exceed 0.6 liter/min (0.02 CFM) through the dry test meter. Before stopping the pump, carefully release the plug in the sample probe to avoid backflow of the impinger solution.

7.6 Record the initial dry test meter reading and barometric pressure on the sampling data sheet, Figure IV-79.

7.7 If there is evidence of concentration stratification, select the sampling traverse points according to ST-18. Otherwise, sample at single point.

## 8. Sampling

8.1 Each test run shall be of thirty minute duration when testing emissions from continuous operations. Each test run at batch process operation shall be for 90% of the batch time or thirty minutes, whichever is less.

8.2 Position the probe at the sampling point and start the pump.

8.3 Sample at a constant rate of 14.3 liter/min (0.5 CFM) during the test as determined by the rotameter. Use the rotameter only to establish the initial sampling rate. Then remove it from the system.

8.4 Record the following information at five-minute intervals:

Dry test meter temperature
Impinger outlet temperature
Dry test meter volume

8.5 Add ice as necessary to maintain impinger temperatures at 7°C (45°F) or less.

8.6 At the conclusion of each run, stop the pump, remove the probe from the stack, record the final meter reading. Point the probe upward and purge the sample train with ambient air. Rinse the probe and connecting tubing with 50 ml of the NaOH solution and drain into the first impinger. Immediately transfer the impinger solutions into polyethylene bottles for subsequent analyses.

8.7 Take three consecutive samples.

## 9. Post-Test Procedures

9.1 Individually analyze the sodium hydroxide solutions and blank for total fluoride content according to analytical procedure Lab 24.

## 10. Auxiliary Tests

10.1 Stack gas velocity and volumetric flowrate, ST-17.

## 11. Calculations

11.1 Standard sample volume:

$$V_o = \frac{17.71\ V_m P_b}{T_m}$$

Where: $V_o$ = corrected sample volume, SDCF at 70°F and 29.92 inches Hg.
$V_m$ = uncorrected meter volume, $ft^3$
$T_m$ = average run meter temperature, °R
$P_b$ = barometric pressure, inches Hg.
17.71 = a constant correcting to 70°F and 29.92 inches Hg

11.2 Fluoride concentration:

$$C = \frac{2.73 \times 10^3\ (V)}{V_o}$$

Where: C = ammonia concentration, ppm by volume on a dry basis
V = total volume of fluoride in the impinger ca tch for each run, microliters.
$2.73 \times 10^3$ = a constant derived from the molecular weight and correcting to 70F and 29.92 inches Hg

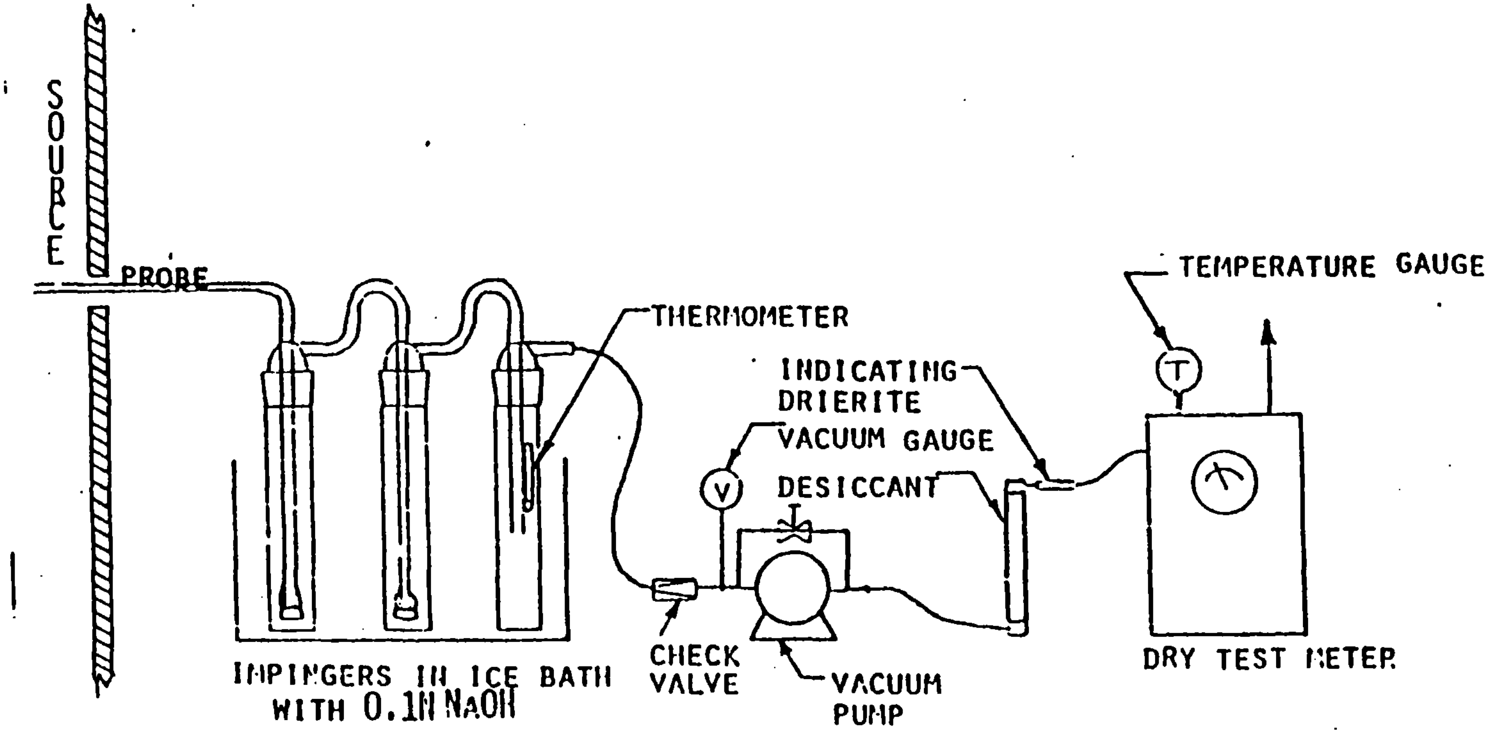

Fig. IV - 78

FLUORIDE SAMPLING TRAIN

# SUMMARY OF SOURCE TEST RESULTS

## SOURCE INFORMATION

Firm Name and Address

Firm Representative and Title

Phone No.

Source:

Conditions During Tests

Operates hr/day & days/yr

Operating Parameters

Report No.

Test Date:

Test Times:

Run A:

Run B:

Run C:

Test Results and Comments

| METHOD | TEST | RUN A | RUN B | RUN C | AVG. |
|---|---|---|---|---|---|
| | Run time, minutes | | | | |
| | Stack gas temp., °F. | | | | |
| ST-25 | Fluoride, ppm | | | | |
| | Flaoride, pounds per ton of product | | | | |

FIG IV-80

11.3 Pounds of fluoride per ton of product:

$$M = \frac{2.94 \times 10^{-6} \text{ (PPM) } (Q_o)}{P}$$

Where: $M$ = pounds of fluoride per ton of product
$Q_o$ = stack gas volumetric flow rate, ST-17
$P$ = production rate, tons per hour (daily average)
$2.94 \times 10^{6}$ = a constant derived from corrections to standard conditions, time and molecular weight.

## 12. Reporting

12.1 Report the data indicated on Figure IV-80.

## Source Test Procedure ST-26

## COKE BURN-OFF RATE

REF: Reg. 10-8-301

### 1. Applicability

1.1 In order to determine compliance with Regulation 10-8-301 for particulate emissions from Fluid Catalytic Cracking Unit Catalyst Regenerators it is necessary to calculate the coke burn-off rate.

### 2. Calculation of Coke Burn-Off Rate

2.1 $$R_c = 0.0186\, Q_{RE}(\%CO_2 + \%CO) + 0.1303\, Q_{RA} - 0.0062\, Q_{RE}\left(\frac{\%CO}{2} + \%CO_2 + \%O_2\right)$$

Where:

$R_c$ = Coke burn-off rate (lb/hr)

0.0186 = material balance factor divided by 100 (lb-min/hr-ft$^3$)

$\%CO_2$ = percent carbon dioxide by volume, dry basis

$\%CO$ = percent carbon monoxide by volume, dry basis

0.1303 = material balance factor divided by 100 (lb-min/hr-ft$^3$)

$Q_{RA}$ = air rate to flued catalyst cracking unit catalyst regenerator, as determined from fluid catalytic cracking unit control room instrumentation (dscf/min)

0.0062 = material balance factor divided by 100 (lb-min/hr-ft$^3$)

### 3. Reference

3.1 40 CFR 60.106. Test Methods and Procedures Part (A) (4).

# Source Test Procedure ST-27

## PRESSURE DROP, PHASE II GASOLINE VAPOR RECOVERY

REF: Reg. 8-7-600

### 1. Applicability

1.1 This method is used to determine the pressure drop in the vapor lines leading from the dispensing nozzle to the underground tank, inclusively. It is applicable in all cases where a Phase II vapor balance system is used.

### 2. Principle

2.1 The pressure drop during refueling is simulated by passing nitrogen through the Phase II recovery system at a constant rate. The resultant pressure drop is measured using a pressure gauge.

### 3. Range

3.1 The minimum and maximum pressure drops that can be measured are dependent upon available pressure gauges. Recommended gauge ranges are 0-2 in. H2O and 0-10 in. $H_2O$.

### 4. Interferences

4.1 Any leaks in the nozzle vapor path, vapor hose, or underground vapor return piping will result in a low pressure drop measurement.

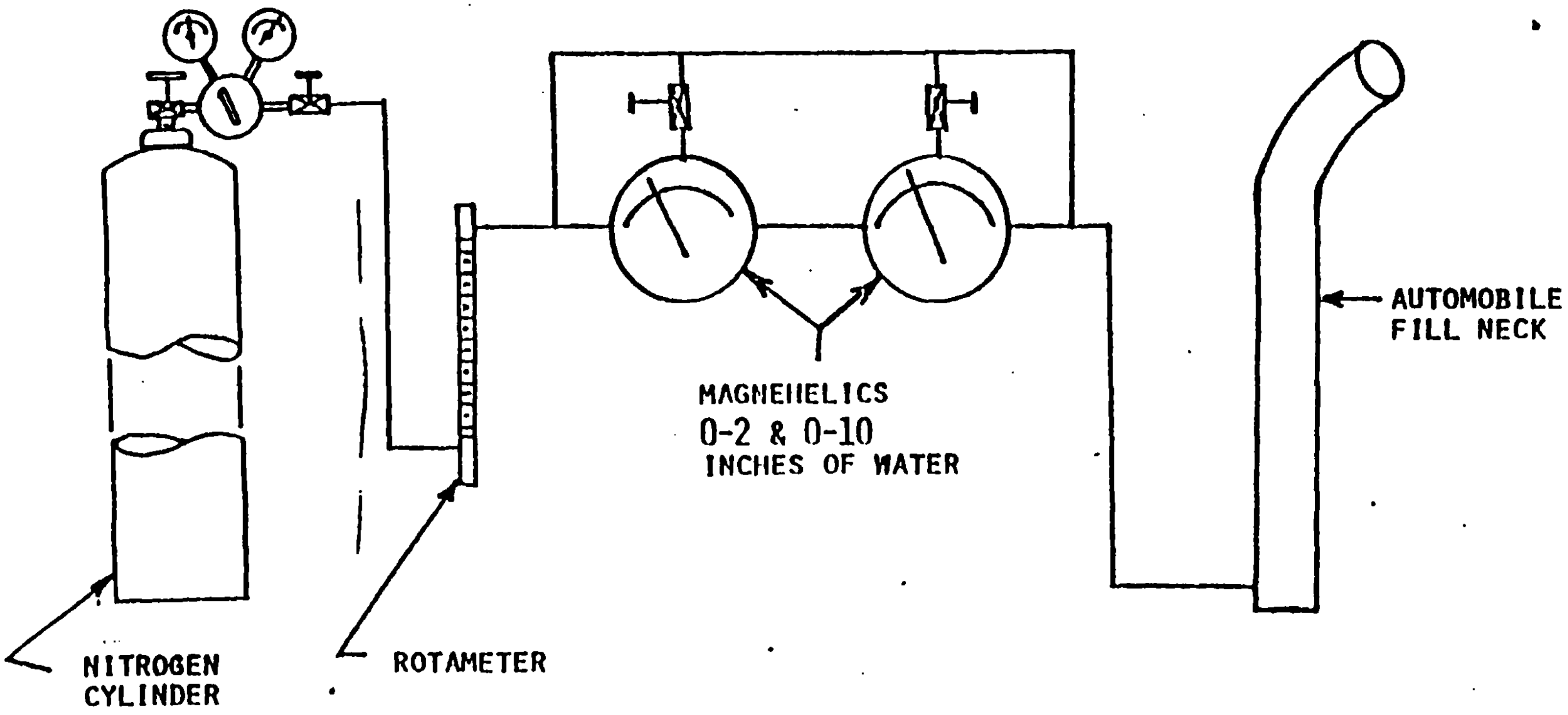

FIGURE IV-81

PRESSURE DROP TEST APPARATUS

BAAPCD

PHASE II - TEST WORKSHEET

TEST NUMBER ____________ DATE ____________________

STATION ______________________________________

ADDRESS ______________________ CITY ____________

MANAGER ______________________ TEL. ____________

| PUMP NUMBER | GASOLINE GRADE | NOZZLE MFG. & MODEL NUMBER | FLOWRATE, CFH | DYNAMIC BACK PRESSURE "$H_2O$ | | STATIC BACK PRESSURE "$H_2O$ | COMMENTS |
|---|---|---|---|---|---|---|---|
| | | | | BEFORE | AFTER | | |
| | | | | | | | |
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FIGURE IV-82

# SUMMARY OF SOURCE TEST RESULTS

## SOURCE INFORMATION

**Firm Name and Address**

**Firm Representative and Title**

**Phone No.**

**Source:**

**Conditions During Tests**

**Operates** hr/day & days/yr

**Operating Parameters**

**Report No.**

**Test Date:**

**Test Times:**

**Run A:**

**Run B:**

**Run C:**

**Test Results and Comments**

| METHOD | PUMP NUMBER | NOZZLE TYPE | DYNAMIC BACK PRESSURE, IN. $H_2O$ BEFORE DRAINING | DYNAMIC BACK PRESSURE, IN. $H_2O$ AFTER DRAINING |
|---|---|---|---|---|

FIG IV-83

# Source Test Procedure ST-28

## HYDROGEN SULFIDE, INTEGRATED SAMPLING

REF: Reg. 10-8-303

### 1. Applicability

1.1 This method is applicable for the determination of hydrogen sulfide ($H_2S$) emissions from stationary sources for compliance with Regulation 10-8-303.

### 2. Principle

2.1 Hydrogen sulfide is collected in a series of impingers and reacted with alkaline cadmium hydroxide ($Cd(OH)_2$) to form cadmium sulfide (CdS). The precipitated CdS is dissolved in hydrochloric acid and absorbed in an iodine solution. The iodine consumed is related to the $H_2S$ content of the gas. The sample train is preceded by an impinger containing hydrogen peroxide to remove $SO_2$ which interfere with the determination.

### 3. Range and Sensitivity

3.1 The minimum measurable concentration of hydrogen sulfide is 0.0002 grains/SDCF

### 4. Interferences

4.1 High concentrations of $SO_2$ or other acid gases could saturate the peroxide impinger and interfere.

### 5. Apparatus

5.1 Probe. The probe is constructed of borosilicate glass tubing.

5.2 Absorbers. Use five Greenberg-Smith impingers. The final impinger has a thermometer attached to the inlet stem.

5.3 Cooling system. An ice bath is used to contain the impingers.

5.4 Sample pump. Use a leak free vacuum pump capable of maintaining a 0.5 CFM flow rate at 15 inches of mercury. The pump has a flow control and vacuum gauge attached to the inlet.

5.5 Silica gel tube. Use approximately 500 cc of silica gel with a drierite indicator to insure dry gas entering the dry gas meter.

5.6 Dry test meter. Use a dry test meter accurate within ±2% of the true volume and equipped with a thermometer to measure the outlet temperature.

5.7 Connections. Use Teflon tubing in making all connections that come in contact with the sample. Vinyl tubing is acceptable for all other connections.

5.8 Barometer. Use a barometer that is accurate within ±0.2 inches of mercury.

5.9 Rotameter. Use a calibrated rotameter to measure the sampling rate.

6. Reagents

6.1 Hydrogen peroxide ($H_2O_2$) solution, 3%. Prepare a solution of 3% by volume hydrogen peroxide in distilled water.

6.2 Cadmium hydroxide ($Cd(OH)_2$). Mix 4.3 g cadmium sulfate hydrate ($3CdSO_4 \cdot 8H_2O$) and 0.3g of sodium hydroxide (NaOH) in 1 liter of distilled water.

7. Pre-test Procedures

7.1 Add 100 ml of 3% $H_2O_2$ to one impinger.

7.2 Add 100 ml of $Cd(OH)_2$ to each of three impingers.

7.3 Assemble the sampling train as shown in Figure IV-84.

7.4 Leak-test the sampling train by starting the sample pump, plugging the probe, and adjusting the pump inlet vacuum to 10 inches Hg. The leak rate must not exceed 0.02 CFM through the meter. Before stopping the pump, carefully release the plug in the sample probe to avoid backflow of the impinger solution.

7.5 Record the initial dry test meter reading and barometric pressure as shown in Figure IV-85.

8. Sampling

8.1 Each test run shall be of thirty minute duration when testing emissions from continuous operations. Each test run at batch process operations shall be for 90% of the batch time or thirty minutes, whichever is less. If the yellow color of cadmium sulfide is visible in the third cadmium hydroxide impinger discontinue sampling.

8.2 Position the probe at the sampling point and start the pump.

8.3 Sample at a constant rate of 14.3 liter/min (0.5 CFM) during the test as determined by the rotameter. Use the rotameter only to establish the initial sampling rate. Then remove it from the system.

8.4 Record the following information at five-minute intervals:

dry test meter temperature
impinger outlet temperature
dry test meter reading

8.5 Add ice as necessary to maintain impinger temperatures at 7°C or less.

8.6 At the conclusion of each run, stop the pump, remove the probe from the stack, and record the final meter reading.

8.7 Take three consecutive samples.

## 9. Post-Test Procedures

9.1 Disconnect the impinger train from the probe and purge the train with clean ambient air for 15 minutes to ensure all $H_2S$ is removed from the hydrogen peroxide.

9.2 Stopper the impingers to minimize sample losses.

9.3 Individually analyze the cadmium hydroxide solutions for hydrogen sulfide according to analytical procedure Lab 18.

## 10 Calculations

10.1 Standard Sample Volume:

$$V_o = \frac{17.71\ V_m P_b}{T_m}$$

where:

$V_o$ = corrected sample volume, SDCF at 70°F and 29.92 in Hg.
$T_m$ = average meter temperature, °R, (°F+460)
$V_m$ = uncorrected meter volume, $ft^3$
$P_b$ = barometric pressure, inches Hg.
17.71 = constant correcting to standard conditions $\frac{(530^{\circ}R)}{(29.92 \text{ inches Hg})}$

10.2 Hydrogen Sulfide concentration:

$$C_{H_2S} = \frac{W \times 15.43}{V_o}$$

where: $C_{H_2S}$ = Hydrogen sulfide concentration, grains/SDCF

$W$ = total weight of hydrogen sulfide in the impinger catch, for each run, grams

15.43= factor converting grams to grains

## 11. Reporting

11.1 Report the data indicated on Figure IV-86.

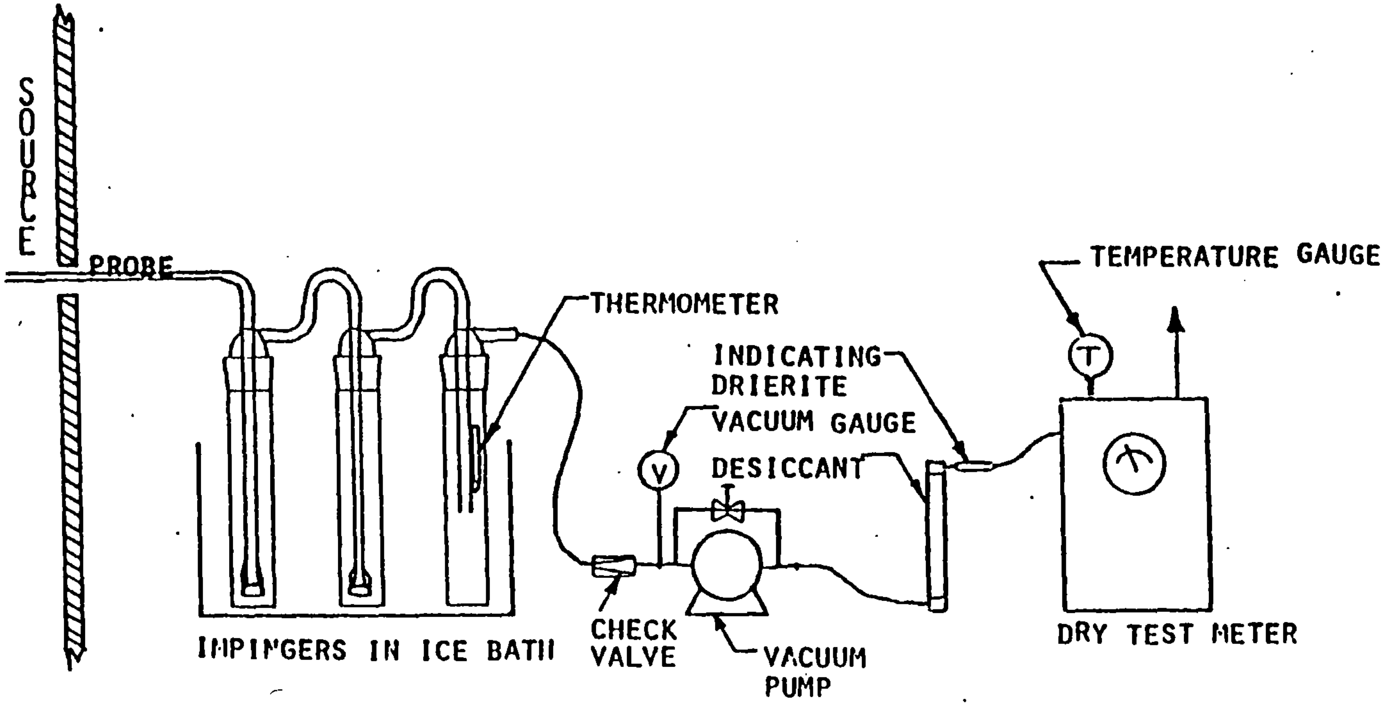

FIG. IV-84

HYDROGEN SULFIDE SAMPLING TRAIN

## BAY AREA AIR POLLUTION CONTROL DISTRICT

### Source Test Data Sheet

Source Operation ____________
Plant ____________
Sample Type ____________
Process Cycle ____________
Duct Size ____________
Duct Pressure ____________

Source Test No. ____________
Run No. ____________
Date: ____________

____________ Nozzle Diameter
____________ Pitot Tube
____________ Gas Collector No
____________ Barometric Press
____________ Leak Rate @ 15"H

Sampling Train:

| Traverse Point | Dist. From Inches | INITIAL TRAVERSE | | | SAMPLING | | | | | | | | | | REMARKS |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Duct Temp°F | h $H_2O$ | $\sqrt{h}$ | Traverse Point | h $H_2O$ | $V_s$ FPS | Time | METER | | | Vac "Hg | Sat'd Gas Temp°F | $T_s$ Duct Temp°F | |
| | | | | | | | | | Rate CFH | Temp °F | Volume Ft$^3$ | | | | |
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$$D_n = 13.7\left[\frac{T_s + 460}{K_p V_s (100-\%H_2O)}\right]^{1/2}$$

$$Q_m = \left[(2.638 \times 10^{-3}) K_p (100-\%H_2O) D_{mm}^2\right]\frac{V_s}{T_s}$$

Condensate ________ gm.
$V_o$ ________
$\%H_2O$ ________
$\%CO_2$ ________
$\%CO$ ________
$\%O_2$ ________

Source Test Team
____________
____________
____________
____________

FIG IV-85

# SUMMARY OF SOURCE TEST RESULTS

## SOURCE INFORMATION

Firm Name and Address

Firm Representative and Title

Phone No.

Source:

Conditions During Tests

Operates hr/day & days/yr

Operating Parameters

Report No.

Test Date:

Test Times:

Run A:

Run B:

Run C:

Test Results and Comments

| METHOD | TEST | RUN A | RUN B | RUN C | AVG. |
|---|---|---|---|---|---|
| ST-28 | Hydrogen Sulfide, gr/SDCF | | | | |

FIG IV-86

# MANUAL OF PROCEDURES

## VOLUME V

## CONTINUOUS EMISSION MONITORING
## POLICY AND PROCEDURES

# Manual of Procedures

## VOLUME V

## Continuous Emission Monitoring

## Policy and Procedures

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D. 47-53 Field Accuracy Test Procedure

E. 54-55 Monthly Report Form

# Continuous Emission Monitoring

## Policy and Procedures

## 1. Introduction

The purpose of this Volume of Manual of Procedures is to advise persons subject to the Regulations of the Bay Area Air Quality Management District of the requirements which must be met by continuous emission monitoring installations.

This volume is an elaboration of the requirements in the Regulations and has been adopted by the Board of Directors of this District. Persons failing to comply with its provisions will be subject to penalty action as provided for in the Health and Safety Code of the State of California.

## 2. Applicability.

The procedures set forth in this Volume are applicable to the requirements for those monitors specified by District regulations. Generally, these regulations are designed to fulfill the requirements of State and Federal Law, i.e., Sections 42700 of the California Health and Safety Code along with California Air Resources Board Resolution 75-59 and Title 40, U.S. Code of Federal Regulations, Part 51, Appendix P. and Part 60.

These documents are available to the public. Persons subject to these monitoring requirements are encouraged to obtain them and review their contents.

## 3. Instrumentation.

### 3.1 General

The Air Pollution Control Officer (APCO) shall approve plans and specifications for monitor selection and placement.

In all cases where gaseous monitors are installed it will be necessary to determine mass emission rates. Flow rate may be determined either by installing a stack gas velocity monitor or by calculations. Any such calculations must be clear, easy to verify, and of demonstrated reliability.

All monitors on sources subject to an emission standard shall be equipped with an analog chart recorder. Chart speeds shall be such that violations of the standard are readily discernible.

The instrument span shall be two to four times the anticipated stack concentration. If necessary to provide a clear record of any violations, the instruments shall be dual range with automatic attenuation and an event marker to indicate span on the chart recorder.

In certain situations it may be possible to use a single monitor on a combination of sources or, in the case of an extractive system, to use one monitoring system on multiple sources. The APCO will approve any such applications on a case-by-case basis.

### 3.2 Specifications

Factors taken into consideration when the APCO evaluates a proposed monitor installation will be the performance specifications shown in Appendicies A, B, and C, if applicable, and the state of the art.

### 3.3 Placement

The monitoring location shall be such that a representative sample is obtainable. The APCO may provide alternates to these requirements in cases of hardship or physical impossibility.

## 4. Installation Schedules

Occasionally additional monitors may be required by written notification from the APCO. For the purpose of installation scheduling, the effective date shall be the date of the letter from the APCO.

The following timetable shall apply to such installations.

### 4.1 Submittal of Plans and Specifications

A person shall respond to the Air Pollution Control Officer in writing within 45 days from the date of notification that a monitor is required. Such response shall include the plans and specifications of monitor selection and placement and shall include a descriptive brochure from the manufacturer containing performance specifications and an engineering drawing depicting the placement.

### 4.2 Proof of Intent to Purchase

Within 45 days of the date of notification by APCO of approval of plans and specifications, a person shall furnish the Air Pollution Control Officer documentary proof of intent to purchase, in the form of a copy of a purchase order.

### 4.3 Completion of Installation

Within 180 days of submission of intent to Purchase the installation the preliminary field calibration shall have been completed; and the Air Pollution Control Officer so notified.

### 4.4 Completion of Testing Requirements

Within 45 days of completion of installation, all required tests shall have been completed and reported to the APCO. It may be preferable that part of the required testing be done by the manufacturer at the factory.

### 4.5 Time Extensions

Time extensions may be granted at the discretion of the APCO.

## 5. Operation

### 5.1 General

Instrument malfunctions are to be reported on the monthly report indicating times, type and a brief description of the repairs. Periods of inoperation greater than 24 hours must be reported by phone to the District dispatcher by the following working day, followed by notification of completion of repairs. Repairs must be made as soon as possible. Downtimes in excess of fifteen days shall be deemed a failure to monitor.

A record shall be maintained for each monitor describing maintenance, calibration and inspection.

The Source Test Section of this District will conduct periodic, Field Accuracy tests to assure proper maintenance and accuracy.

### 5.2 Calibration

Daily calibration and span checks shall be made as recommended by the manufacturer, except for velocity sensing instrumentation which shall be calibrated on a monthly basis. Daily records shall be kept and adjustments shall be made if the drift is greater than ten percent of the applicable emission standard or, if none applies, ten percent of span.

Calibration gases shall be traceable to NBS standards where such reference gases are available. Every three months from the date of manufacture, gases must be re-analyzed by the reference methods indicated in the Appendicies, unless the manufacturer guarantees a longer shelf life. Gases should not be used after their stated shelf life has expired. For extractive systems, the calibration gases must be introduced as close to the tip of the probe as possible.

### 5.3.Maintenance

All monitoring systems shall be maintained in a good state of repair. At the discretion of the APCO, either complete performance specification tests or field accuracy tests may be required after repairs have been made on the system.

## 6. Testing Requirements

Testing requirements depend on the type of monitor and source. Performance tests shall be conducted at the completion of installation and preliminary field calibrations. A copy of the test results shall be furnished to the APCO and one copy shall be retained in owners file.

### 6.1 Performance Specification Tests

Performance Specification Tests are detailed tests designed to insure that an instrument meets performance specifications for accuracy, zero and span drift, response time and stability. These tests are required on the following monitors on indicated sources.

| Monitor | SOURCES |
|---|---|
| $SO_2$ | Fossil Fuel Fired Steam Generators, $H_2SO_4$ plants |
| $NO_x$ | Fossil Fuel Fired Steam Generators, $HNO_3$ plants |
| $O_2$ or $CO_2$ | Fossil Fuel Fired Steam Generators. |
| Opacity | All |

Applicable Performance Specification Test Procedures are appended as A, B, and C. These procedures are identical to EPA Performance Specification Tests 1,2 and 3.

### 6.2 Field Accuracy Tests

Field Accuracy Tests are a portion of the Performance Specification Test which are designed to insure the accuracy of the monitoring system. They are applicable to all systems except transmissometers. The accuracy requirement is that the monitoring system must be within ±20% or 10% of the applicable emission standard, whichever is greater, when compared to the Field Accuracy Test Procedure. This means that not only the component monitors, but also, the resultant mass emission rate must meet this specification.

Field Accuracy Test Procedure is shown as Appendix D.

## 7. Records Retention

All persons subject to monitoring requirements must maintain a file of all pertinent information, emission measurements, system performance specification and field accuracy tests, calibration checks; adjustments and maintenance.

These records must be retained for not less than two years and made available to the APCO upon request. Source Test personnel may inspect them during periodic Field Accuracy Tests.

## 8. Reports

### 8.1 Performance Specification Test Report

This test is to be conducted by the person responsible for the installation. One copy of the test results is to be furnished to the APCO upon completion. The APCO will notify the person of the acceptability of the report.

### 8.2 Field Accuracy Test Report

This test may be conducted either by the person responsible for the monitor or the APCO. Copies of the test results are to be furnished by either party to the other upon completion of the test.

### 8.3 Report of Excesses

Any indicated excess of any emission standard to which the stationary source is required to conform, as indicated by the monitoring device, shall be reported by the operator of the source by telephone to the District dispatcher within 96 hours after such occurrence. The report should include the nature, extent, cause and corrective action taken.

For the purpose of determining an indicated excess in the case of a gaseous pollutant an excess will be considered to have occurred if the average of any clock hour exceeds the standard, except for start-up of sulfuric acid plants. Prior to July 31, 1981, sulfur dioxide emissions during start-up of sulfuric acid plants shall be averaged over the first six hours of operation for purposes of determining compliance. After July 31, 1981, the start-up averaging time shall be four hours.

In the case of opacity, an indicated excess will be considered to have occurred if any cumulative period over three minutes within any clock hour was in excess of the opacity standard.

Where computerized data processing systems are used the APCO may approve alternate requirements.

### 8.4 Monthly Monitoring Report

The data from monitors required by this District will be used as proof of violations of applicable emission standards, to relate sources to ground level monitoring excesses and provide emission inventory information. Therefore, the emissions to be reported will vary with the type of monitor. The following is a list of the type of emissions that must be reported for each pollutant:

| Pollutant | Emission Type |
|---|---|
| Opacity | Excesses only |
| $NO_x$ | Mass Emission Rate (Ton/day) plus $NO_x$ concentration at 3% $O_2$ for Regulated boilers. |
| $SO_2$ | Average 24 hour concentration, maximum one hour concentration, Mass Emission rate, Tons/day, and emissions based on production rate. |

All concentration data is to be reported on a dry basis. A water monitor is not necessary for the dry basis calculation. Data from previous tests, process parameters or calculations may be used.

In addition to the emission data, the monthly monitoring report shall include:

a: the date and time identifying each period the system was inoperative, except for daily calibrations, and the nature of the repairs.

b: A Summary of the excesses including a negative declaration if applicalbe.

The monthly calibration data on the flow sensor need not be reported and is to be kept available in files.

An example of the reporting format is shown as Appendix E.

This report is due within 30 days after the end of the month.

# PERFORMANCE SPECIFICATION . TEST 1

Performance Specification 1 - Performance specifications and specification test procedures for transmissometer systems for continuous measurement of the opacity of stack emissions.

## 1. Principle and Applicability

1.1 Principle. The opacity of particulate matter in stack emissions is measured by a continuously operating emission measurement system. These systems are based upon the principle of transmissometry which is a direct measurement of the attenuation of visible radiation (opacity) by particulate matter in a stack effluent. Light having specific spectral characteristics is projected from a lamp across the stack of a pollutant source to a light sensor. The light is attenuated due to absorption and scatter by the particulate matter in the effluent. The percentage of visible light attenuated is defined as the opacity of the emission. Transparent stack emissions that do not attenuate light will have a transmittance of 100 or an opacity of 0. Opaque stack emissions that attenuate all of the visible light will have a transmittance of 0 or an opacity of 100 percent. The transmissometer is evaluated by use of neutral density filters to determine the precision of the continuous monitoring system. Tests of the system are performed to determine zero drift, and response time characteristecs of the system.

1.2 Applicability. This performance specification is applicable to the continuous monitoring systems specified in the subparts for measuring opacity of emissions. Specification for continuous measurement of visible emissions are given in terms of design, performance, and installation parameters, installation requirements, and data computation procedures for evaluating the acceptability of the continuous monitoring systems subject to approval by the APCO.

## 2. Apparatus

2.1 Calibrated Filters. Optical filters with neutral spectral characteristics and known optical densities to visible light of screens known to produce specified optical densities. Calibrated filters with accuracies certified by the manufacturer to within ± 3 percent opacity shall be used. Filters required are low, mid, and high-range filters with nominal optical densities as follows when the transsometer is spanned at opacity levels specified by applicable subparts:

| Span Value (percent opacity) | Calibrated filter optical densities with equivalent opacity in parenthesis | | |
|---|---|---|---|
| | Low Range | Mid-Range | High-Range |
| 50 | 0.1 (20) | 0.2 (37) | 0.3 (50) |
| 60 | .1 (20) | .2 (37) | .3 (50) |
| 70 | .1 (20) | .3 (50) | .4 (60) |
| 80 | .1 (20) | .3 (50) | .6 (75) |
| 90 | .1 (20) | .4 (60) | .7 (80) |
| 100 | .1 (20) | .4 (60) | .9 (87 1/2) |

It is recommended that filter calibrations be checked with a well-collimated photopic transmissometer of known linearity prior to use. The filters shall be of sufficient size to attenuate the entire light beam of the transmissometer.

2.2 Data Recorder. Analog chart recorder or other suitable device with input voltage range compatible with the analyzer system output. The resolution of the recorder's data output shall be sufficient to allow completion of the test procedures within this specification.

2.3 Opacity measurment System. An in-stack transmissometer (folded or single path) with the optical design specifications designated below, associated control units and apparatus to keep optical surfaces clean.

3. Definitions.

3.1 Continuous Monitoring System. The total equipment required for the determination of pollutant opacity in a source effluent. Continuous monitoring systems consist of major subsystems as follows:

3.1.1 Sampling Interface. The portion of a continuous monitoring system for opacity that protects the analyzer from the effluent.

3.1.2 Analyzer. That portion of the continuous monitoring system which senses the pollutant and generates a signal output that is a function of the pollutant opacity.

3.1.3 Data Recorder. That portion of the continuous monitoring system that processes the analyzer output and provides a permanent record of the output signal in terms of pollutant opacity.

3.2 Transmissometer. The portions of a continuous monitoring system for opacity that include the sampling interface and the analyzer.

3.3 Span. The value of opacity at which the continuous monitoring system is set to produce the maximum data display output. The span shall be set at an opacity specified in each applicable subpart.

3.4 Calibration Error. The difference between the opacity reading indicated by the continuous monitoring system and the known values of a series of test standards. For this method the test standards are a series of calibrated optical filters or screens.

3.5 Zero Drift. The change in continuous monitoring system output over a stated period of time of normal continuous operation when the pollutant concentration at the time of the measurements is zero.

3.6 Calibration Drift. The change in the continuous monitoring system output over a stated period of time of normal continuous operation when the pollutant concentration at the time of the measurements is the same known upscale value.

3.7 System Response. The time interval from a step change in opacity in the stack at the input to the continuous monitoring system to the time at which 95 percent of the corresponding final value is reached as displayed on the continuous monitoring system data recorder.

3.8 Operational Test Period. A minimum period of time over which a continuous monitoring system is expected to operate within certain performance specifications without unscheduled maintanence, repair, or adjustment.

3.9 Transmittance. The fraction of incident light that is transmitted through an optical medium of interest.

3.10 Opacity. The fraction of incident light that is attenuated by an optical medium of interest. Opacity (O) and transmittance (T) are related as follows:

$$O = 1 - T$$

3.11 Optical Density. A logarithmic measure of the amount of light that it attenuated by an optical medium of interest. Optical density (D) is related to the transmittance and opacity as follows:

$$D = -\log_{10} T$$

$$D = -\log_{10} (1-O)$$

3.12 Peak Optical Response. The wave-length of maximum sensitivity of the instrument.

3.13 Mean Spectral Response. The wave-length which bisects the total area under the curve obtained pursuant to paragraph 9.2.1

3.14 Angle of View. The maximum (total) angle of radiation detection by the photodetector assembly of the analyzer.

3.15 Angle of Projection. The maximum (total) angle that contains 95 percent of the radiation projected from the lamp assembly of the analyzer.

3.16 Pathlength. The depth of effluent in the light beam between the receiver and the transmitter of the single-pass transmissometer, or the depth of effluent between the transciever and reflector of a double-pass transmissometer. Two pathlengths are referenced by this specification:

3.16.1 Monitor Pathlength. The depth of effluent as the installed location of the continuous monitoring system.

3.16.2 Emission Outlet Pathlength. The depth of effluent at the location emissions are released to the atmosphere.

4. Installation Specification.

4.1 Location. Thr transmissometer must be located across a section of duct or stack that will provide a particulate matter flow through the optical volume of the transmissometer that is representative of the particulate matter flow through the duct or stack. It is recommended that the monitor pathlength or depth of effluent for the transmissometer include the entire diameter of the duct or stack. In installations using a shorter pathlength, extra caution must be used in determining the measurement location representative of the particulate matter flow through the duct or stack.

4.1.1 The transmissometer location shall be downstream from all particulate control equipment.

4.1.2 The transmissometer shall be located as far from bends and obstructions as practical.

4.1.3 A transmissometer that is located in the duct or stack following a bend shall be installed in the plane defined by the bend where possible.

r.1.4 The transmissometer should be installed in an accessible location.

4.1.5 When required by the APCO , the owner or operator of a source must demonstrate that the transmissometer is located in a section of duct or stack where a representative particulate matter distributation exists. The determination shall be accomplished by examining the opacity profile of the effluent as a series of positions across the duct or stack while the plant is in operation at maximum or reduced operating rates or by other tests acceptable to the APCO.

4.2 Slotted Tube. Installations that require the use of a slotted tube shall use a slotted tube of sufficient size and blackness so as not to interfere with the free flow of effluent through the entire optical volume of the transmissometer or reflect light into the transmissometer photodetector. Light reflections may be prevented by using blackened baffles within the slotted tube to prevent the lamp radiation from impinging upon the tube walls, by restricting the angle of projection of the light and the angle of view of the photodetector assembly to less than the cross-sectional area of the slotted tube, or by other methods. The owner or operator must show that the manufacturer of the monitoring system has used appropriate methods to minimuze light reflections for systems using slotted tubes.

4.3 Data Recorder Output. The continuous monitoring system output shall permit expanded display of the span opacity on a standard 0 to 100 percent scale. Since all opacity standards are based on the opacity of the effluent exhausted to the atmospher the system output shall be based upon the emission outlet pathlength and permanently recorded. For affected facilities whose monitor pathlength is different from the facility's emission outlet pathlength, a graph shall be provided with the installation to show the relationships between the continuous monitoring system recorded opacity based upon the emission outlet pathlength and the opacity of the effluent at the analyzer location (monitor pathlength ). Tests for measurement of opacity that are required by this performance specification are based upon the monitor pathlength. The graph necessary to convert the data recorder output to the monitor pathlength basis shall be established as follows:

$$\log (1-O_1) = (l_1/l_2) \log (1-O_2)$$

where:

$O_1$ = the opacity of the effluent based upon $l_1$.

$O_2$ = the opacity of the effluent based upon $l_2$.

$l_1$ = the emission outlet pathlength.

$l_2$ = the monitor pathlength.

## 5. Optical Design Specifications.

The optical design specifications set forth in Section 6.1 shall be met in order for a measurement system to comply with the requirements of this method.

## 6. Determination of Conformance with Design Specifications.

6.1.1 Peak Spectral Response. The peak spectral response of the continuous monitoring systems shall occur between 500 nm and 600 nm. Response at any wavelength below 400 nm or above 700 nm shall be less than 10 percent of the peak response of the continuous monitoring system.

6.1 The continuous monitoring system for measurement of opacity shall be demonstrated to conform to the design specifications set forth as follows:

6.1.2 Mean Spectral Response. The mean spectral response of the continuous monitoring system shall occur between 500 nm and 600 nm.

6.1.3 Angle of View. The total angle of view shall be no greater than 5 degrees.

6.1.4 Angle of Projection. The total angle of projection shall be no greater than 5 degrees.

6.2 Conformance with requirements under Section 6.1 of this specification may be demonstrated by the owner or operator of the affected facility or by the manufacturer of the opacity measurement system. Where conformance is demonstrated by the manufacturer, certification that the tests were performed, a description of the test procedures, and the test results shall be provided by the manufacturer. If the source owner or operator demonstrates conformance, the procedures used and results obtained shall be reported.

6.3 The general test procedures to be followed to demonstrate conformance with Section 6 requirements are given as follows: (These procedures will not be applicable to all designs and will require modification in some cases. Where analyzer and optical design is certified by the manufacturer to conform with the angle of view or angle of projection specifications the respective procedures may be omitted.)

6.3.1 Spectral Response. Obtain spectral data for detector, lamp, and filter components used in the measurement system from their respective manufacturers.

6.3.2 Angle of View. Set the receiver up as specified by the manufacturer. Draw an arc with radius of 3 meters. Measure the receiver response to a small (less than 3 centimeters) non-directional light source at 5-centimeter intervals on the arc for 26 centimeters on either side of the detector centerline. Repeat the test in the vertical direction.

6.3.3 Angle of Projection. Set the projector up as specified by the manufacturer. Draw an arc with radius of 3 meters. Using a small photoelectric light detector (less than 3 centimeters), measure the light intensity at 5-centimeter intervals on the arc for 26 centimeters on wither side of the light source centerline of projection. Repeat the test in the vertical direction.

7. Continuous Monitoring System Performance Specifications.

The continuous monitoring system shall meet the performance specifications in Table 1-1 to be considered acceptable under this method.

TABLE 1-1. Performance Specifications

| Parameter | Specifications |
|---|---|
| a. Calibration error | $\leq$ 3 pct opacity.[1] |
| b. Zero drift (24h) | $\leq$ 2 pct opacity.[1] |
| c. Calibration drift (24 h) | $\leq$ 2 pct opacity.[1] |
| d. Response time | 10 s (maximum) |
| e. Operational test period | 168 h. |

[1] Expressed as sum of absolute mean value and the 95 pct confidence interval of a series of tests.

8. Performance Specification Test Procedures. The following test procedures shall be used to determine conformance with the requirements of paragraph 7:

8.1 Calibration Error and Response Time Test. These tests are to be performed prior to installation of the system on the stack and may be performed at the affected facility or at other locations provided that proper notification is given. Set up and calibrate the measurement system as specified by the manufacturer's written instructions for the monitor pathlength to be used in the installation. Span the analyzer as specified in applicable subparts.

8.1.1 Calibration Error Test. Insert a series of calibration filters in the transmissometer path at the midpoint. A minimum of three calibration filters (low, mid, and high-range) selected in accordance with the table under paragraph 2.1 and calibrated within 3 percent must be used. Make a total of five nonconsecutive readings for each filter. Record the measurement system output readings in percent opacity. (See Figure 1-1).

8.1.2 System Response Test. Insert the high-range filter in the transmissometer path five times and record the time required for the system to respond to 95 percent of final zero and high-range filter values. (See Figure 1-2).

8.2 Field Test for Zero Drift and Calibration Drift. Install the continuous monitoring system on the affected facility and perform the following alignments:

8.2.1 Preliminary Alignments. As soom as possible after installation and once a year thereafter when the facility is not in operation perform the following optical and zero alignments:

8.2.1.1 Optical Alignment. Align the light beam from the transmissometer upon the optical surfaces located across the effluent (i.e., the retroflector or photodetector as applicable) in accordance with the manufacturer's instructions.

8.2.1.2 Zero Alignment. After the transmissometer has been optically aligned and the transmissometer mounting is mechanically stable (i.e., no movement of the mounting due to thermal contraction of the stack, duct, etc.) and a clean stack condition has been determined by a steady zero opacity condition, perform the zero alignment. This alignment is performed by balancing the continuous monitor system response so that any simulated zero check coincides with an actual zero check performed across the monitor pathlength of the clean stack.

8.2.1.3 Span. Span the continuous monitoring system at the opacity specified in subparts and offset the zero setting at least 10 percent of span so that negative drift can be quantified.

8.2.2 Final Alignments. After the preliminary alignments have been completed and the affected facility has been started up and reaches normal operating temperature, re-check the optical alignment in accordance with 8.2.1.1 of this specification. If the alignment has shifted, realign the optics, record any detectable shift in the opacity measured by the system that can be attributed to the optical realignment, and notify the APCO. This condition may not be objectionable if the affected facility operates within a fairly constant and adequately narrow range of operating temperatures that does not produce significant shifts in optical alignment during normal operation of the facility. Under circumstances where the facility operations produce fluctuations in the effluent gas temperature that result in significant misalignments, the APCO may require improved mounting structures or another location for installation of the transmissometer.

8.2.3 Conditioning Period. After completing the post-startup alignments, operate the system for an initial 168-hour conditioning period in a normal operational manner.

8.2.4 Operational Test Period. After completing the conditioning period, operate the system for an additional 168-hour period retaining the zero offset. The system shall monitor the source effluent at all times except when being zeroed or calibrated. At 24-hour intervals the zero and span shall be checked according to the manufacturer's instructions. Minimum procedures used shall provide a system check of the analyzer internal mirrors and all electronic circuitry including the lamp and photodetector assembly and shall include a procedure for producing a simulated zero opacity condition and a simulated upscale (span) opacity condition as viewed by the receiver. The manufacturer's written instructions may be used providing that they equal or exceed these minimum procedures. Zero and span the transmissometer, clean all optical surfaces exposed to the effluent, realign optics, and make any necessary adjustments to the calibration of the system daily. These zero and calibration adjustments and optical realignments are allowed only at 24-hour intervals or at such shorter intervals as the manufacturer's written instructions specify. Automatic corrections made by the measurement system without operator interventions are allowed at any time. The magnitude of any zero or span drift adjustments shall be recorded. During this 168-hour operational test period, record the following at 24-hour intervals: (a) the zero reading and span readings after the system is calibrated (these readings should be set at the same value at the beginning of each 24-hour period); (b) the zero reading after each 24 hours of operation, but before cleaning and adjustment; and (c) the span reading after cleaning and zero adjustment, but before span adjustment. (See Figure 1-3).

## 9. Calculation, Data Analysis, and Reporting.

### 9.1 Procedure for Determination of Mean Values and Confidence Intervals.

9.1.1 The mean value of the data set is calculated according to equation 1-1.

$$X = \frac{1}{n} \sum_{i=i}^{n} x_i$$

Equation 1-1

where $x_1$ = absolute value of the individual measurements.

= sum of the individual values.

X = mean value, and

n = number of data points.

9.1.2 The 95 percent confidence interval (two-sided) is calculated according to equation 1-2:

$$C.I._{95} = \frac{t_{.975}}{n\sqrt{n-1}} \sqrt{n(\Sigma x_1^2) - (\Sigma x_1)^2}$$

Equation 1-2

where

$x_i$ = sum of all data points,

$t_{.975}$ = $t_1$ - a/2 and

$C.I._{95}$ = 95 percent confidence interval estimate of the average mean value.

Values for $t_{.975}$

| n | $t_{.975}$ | n | $t_{.975}$ |
|---|---|---|---|
| 2 | 12.706 | 10 | 2.262 |
| 3 | 4.303 | 11 | 2.228 |
| 4 | 3.182 | 12 | 2.201 |
| 5 | 2.776 | 13 | 2.179 |
| 6 | 2.571 | 14 | 2.160 |
| 7 | 2.477 | 15 | 2.145 |
| 8 | 2.365 | 16 | 2.131 |
| 9 | 2.306 | | |

The values in this table are already corrected for n-1 degrees of freedom. Use n equal to the number of samples as data points.

9.2 Data Analysis and Reporting.

9.2.1 Spectral Response. Combine the spectral data obtained in accordance with paragraph 6.3.1 to develop the effective spectral response curve of the transmissometer. Report the wavelength at which the peak response occurs, the wavelength at which the mean response occurs, and the maximum response at any wavelength below 400 nm and above 700 nm expressed as a percentage of the peak response as required under paragraph 6.2

9.2.2 Angle of View. Using the data obtained in accordance with paragraph 6.3.2, calculate the response of the receiver as a function of viewing angle in the horizontal and vertical directions (26 centimeters of arc with a radius of 3 meters equal 5 degrees). Report relative angle of view curves as required under paragraph 6.2.

9.2.3 Angle of Projection. Using the data obtained in accordance with paragraph 6.3.3, calculate the response of the photoelectric detector as a function of projection angle in the horizontal and vertical directions. Report relative angle of projection curves as required under paragraph 6.2.

9.2.4 Calibration Error. Using the data from paragraph 8.1 (figure 1-1), subtract the known filter opacity value from the value shown by the measurement system for each of the 15 readings. Calculate the mean and 95 percent confidence interval of the five different values at each test filter value according to equations 1-1 and 1-2. Report the sum of the absolute mean difference and the 95 percent confidence interval for each of the three test filters.

Figure 1-1, Calibration Error Test

Calibrated Neutral Density Filter Data
(See paragraph 8.1.1)

Low Range ________% opacity Mid Range ________% opacity High Range ______%Opacity
Span Value________% opacity

Date of Test ________________ Location of Test ________________

| Calibrated Filter[1] | Analyzer Reading % Opacity | Differences[2] % Opacity |
|---|---|---|

1. ____________________
2. ____________________
3. ____________________
4. ____________________
5. ____________________
6. ____________________
7. ____________________
8. ____________________
9. ____________________
10. ____________________
11. ____________________
12. ____________________
13. ____________________
14. ____________________
15. ____________________

| | Low | Mid | High |
|---|---|---|---|
| Mean Difference | ____ | ____ | ____ |
| Confidence Interval | ____ | ____ | ____ |
| Calibration error = Mean Difference[3]+C.I. | ____ | ____ | ____ |

---

[1] Low, mid or high range
[2] Calibration filter opacity - analyzer reading
[3] Absolute value

9.2.5 Zero Drift. Using the zero opacity values measured every 24 hours during the field test (paragraph 8.2), calculate the differences between the zero point after cleaning, aligning, and adjustment, and the zero value 24 hours later just prior to cleaning, aligning, and adjustment. Calculate the mean value of these points and the confidence interval using equations 1-1 and 1-2. Report the sum of the absolute mean value and the 95 percent confidence interval.

9.2.6 Calibration Drift. Using the span value measured every 24 hours during the field test, calculate the differences between the span value after cleaning, aligning, and adjustment of zero and span, and the span value 24 hours later just after cleaning, aligning, and adjustment of zero and before adjustment of span. Calculate the mean value of these points and the confidence interval using equations 1-1 and 1-2. Report the sum of the absolute mean value and the confidence interval.

9.2.7 Response Time. Using the data from paragraph 8.1, calculate the time interval from filter insertion to 95 percent of the final stable value for all upscale and downscale traverses. Report the mean of the 10 upscale and downscale test times.

9.2.8 Operational Test Period. During the 168-hour operational test period, the continuous monitoring system shall not require any corrective maintenance, repair, replacement, or adjustment other than that clearly specified as required in the manufacturer's operation and maintenance manuals as routine and expected during a one-week period. If the continuous monitoring system is operated within the specified performance parameters and does not require corrective maintenance, repair, replacement, or adjustment other than as specified above during the 168-hour test period, the operational test period shall have veen successfully concluded. Failure of the continuous monitoring system to meet these requirements shall call for a repetition of the 168-hour test period. Portions of the tests which were satisfactorily completed need not be repeated. Failure to meet any performance specification(s) shall call for a repetition of the one-week operational test period and that specific portion of the tests required by paragraph 8 related to demonstrating compliance with the failed specification. All maintenance and adjustments required shall be recorded. Output readings shall be recorded before and after all adjustments.

## 10 References.

10.1 "Experimental Statistics," Department of Commerce, National Bureau of Standards Handbook 91, 1963 pp. 3-31, paragraphs 3-3.1.4.

10.2 "Performance Specifications for Stationary-Source Monitoring Systems for Gases and Visible Emissions," Environmental Protection Agency, Research Triangle Park, N.C., EPA-650/7-74-013, January 1974.

Zero Setting____________________(See paragraph 8.2.1) Date of Test________

Span Setting____________________

| Date and Time | Zero Reading (Before cleaning and adjustment) | Zero Drift ( Zero) | (after cleaning & zero adjustment but before span adjustment) | Calibrate Drift ( Span) |
|---|---|---|---|---|
| | | | | |
| | | | | |
| | | | | |
| | | | | |
| | | | | |
| | | | | |
| | | | | |
| | | | | |
| | | | | |
| | | | | |

Zero Drift = Mean Zero Drift* ____________ + CI (Zero)________ =_________.

Calibration Drift = Mean Span Drift*_________+ CI (Span)________ =__________.

---

*Absolute value

Figure 1-3. Zero and Calibration Drift Test

Date of Test ____________ Location of Test ____________

Span Filter ________________________ % Opacity

Analyzer Span Setting ____________________ % Opacity

Upscale 1. ____________________ Seconds

2. ____________________ Seconds

3. ____________________ Seconds

4. ____________________ Seconds

5. ____________________ Seconds

Downscale 1. ____________________ Seconds

2. ____________________ Seconds

3. ____________________ Seconds

4. ____________________ Seconds

5. ____________________ Seconds

Average response ________________ Seconds

Figure 1-2. Response Time Test

## PERFORMANCE SPECIFICATION TEST 2

Performance Specification 2 - Performance specifications and specification test procedures for Monitors of $SO_2$ and $NO_x$ from stationary sources.

### 1. Principle and Applicability.

1.1 Principle. The concentration of sulfur dioxide or oxides of nitrogen pollutants in stack emissions is measured by a continuously operating emission measurement system. Concurrent with operation of the continuous monitoring system, the pollutant concentrations are also measured with reference methods (Appendix A). An average of the continuous monitoring system data is computed for each reference method testing period and compared to determine the relative accuracy of the continuous monitoring system. Other tests of the continuous monitoring system are also performed to determine calibration error, drift, and response characteristics of the system.

1.2 Applicability. This performance specification is applicable to evaluation of continuous monitoring systems for measurement of nitrogen oxides or sulfur dioxide pollutants. Tests specifications contain test procedures, installation requirements, and data computation procedures for evaluating the acceptability of the continuous monitoring systems.

### 2. Apparatus.

2.1 Calibration Gas Mixtures. Mixtures of known concentratio of pollutant gas in a diluent gas shall be prepared. The pollutant gas shall be sulfur dioxide or the appropriate oxide(s) of nitrogen specified by paragraph 6 and within subparts. For sulfur dioxide gas mixtures, the diluent gas may be air or nitrogen. For nitric oxide (NO) gas mixtures, the diluent gas shall be oxygen-free (<10ppm) nitrogen, and for nitrogen dioxide ($NO_2$) gas mixtures the diluent gas shall be air. Concentrations of approximately 50 percent and 90 percent of span are required. The 90 percent gas mixture is used to set and to check the span and is referred to as the span gas.

2.2 Zero Gas. A gas certified by the manufacturer to contain less than 1 ppm of the pollutant gas or ambient air may be used.

2.3 Equipment for measurement of the pollutant gas concentration using the reference method specified in the applicable standard.

2.4 Data Recorder. Analog chart recorder or other suitable device with input voltage range compatible with analyzer system output. The resolution of the recorder's data output shall be sufficient to allow completion of the test procedures within the specification.

2.5 Continuous monitoring system for $SO_2$ or $NO_x$ pollutants as applicable.

3. Definitions.

3.1 Continuous Monitoring System. The total equipment required for the determination of a pollutant gas concentration in a source effluent. Continuous monitoring systems consist of major subsystems as follows:

3.1.1 Sampling Interface. That portion of an extractive continuous monitoring system that performs one or more of the foloowing operations: acquisition, transportation, and conditioning of a sample of the source effluent or that portion of an in-situ continuous monitoring system that protects the analyzer from the effluent.

3.1.2 Analyzer. That portion of the continuous monitoring system which senses the pollutant gas and generates a signal output that is a function of the pollutant concentration.

3.1.3 Data Recorder. That portion of the continuous monitoring system that provides a permanent record of the output signal in terms of concentration units.

3.2 Span. The value of pollutant concentration at which the continuous monitoring system is set to produce the maximum data display output. The span shall be set at the concentration specified in each applicable subpart.

3.3 Accuracy (Relative). The degree of correctness with which the continuous monitoring system yields the value of gas concentration of a sample relative to the value given by a defined reference method. This accuracy is expressed in terms of error, which is the difference between the paired concentration measurements expressed as a percentage of the mean reference value.

3.4 Calibration Error. The difference between the pollutant concentration indicated by the continuous monitoring system and the known concentration of the test gas mixture.

3.5 Zero Drift. The change in the continuous monitoring system output over a stated period of time of normal continuous operation when the pollutant concentration at the time for the measurements is zero.

3.6 Calibration Drift. The change in the continuous monitoring system output over a stated time period of normal continuous operations when the pollutant concentration at the time of the measurements is the same known upscale value.

3.7 Response Time. The time interval from a step change in pollutant concentration at the imput to the continuous monitoring system to the time at which 95 percent of the corresponding final value is reached as displayed on the continuous monitoring system data recorder.

3.8 Operational Period. A minimum period of time over which a measurement system is expected to operate within certain performance specifications without unscheduled maintenance, repair, or adjustment.

3.9 Stratification. A condition identified by a difference in excess of 10 percent between the average concentration in the duct or stack and the concentration at any point more than 1.0 meter from the duct or stack wall.

4. Installation Specifications. Pollutant continuous monitoring systems ($SO_2$ and $NO_x$) shall be installed at a sampling location where measurements can be made which are directly representative (4.1), or which can be corrected so as to be representative (4.2) of the total emissions from the affected facility. Conformance with this requirement shall be accomplished as follows:

4.1 Effluent gases may be assumed to be nonstratified if a sampling location eight or more stack diameters (equivalent diameters) downstream of any air in-leakage is selected. This assumption and data correction procedures under paragraph 4.2.1 may not be applied to sampling locations upstream of an air preheater in a stream generating facility under Subpart D of this part. For sampling locations where effluent gases are either demonstrated (4.3) or may be assumed to be nonstratified (eight diameters), a point (extractive systems) or path (in-situ systems) of average concentration may be monitored.

4.2 For sampling locations where effluent gases cannot be assumed to be nonstratified (less than eight diameters) or have been shown under paragraph 4.3 to be stratified, results obtained must be consistently representative (e.g. a point of average concentration may shift with load changes) or the data generated by sampling at a point (extractive systems) or across a path (in-situ systems) must be corrected (4.2.1 and 4.2.2) so as to be representative of the total emissions from the affected facility. Conformance with this requirement may be accomplished in either of the following ways:

4.2.1 Installation of a diluent continuous monitoring system ($O_2$ or $CO_2$ as applicable) in accordance with the procedures under paragraph 4.2 of Performance Specification 3 of this appendix. If the pollutant and the diluent monitoring systems are not of the same type (both extractive or both in-situ), the extractive system must use a multipoint probe.

4.2.2 Installation of extractive pollutant monitoring systems using multipoint sampling probes or in-situ pollutant monitoring systems that sample or view emissions which are consistently representative of the total emissions for the entire cross section. The Administrator may require data to be submitted to demonstrate that the emissions sampled or viewed are consistently representative for several typical facility process operating conditions.

4.3 The owner or operator may perform a traverse to characterize any stratification of effluent gases that might exist in a stack or duct. If no stratification is present, sampling procedures under paragraph 4.1 may be applied even though the eight diameter criteria is not met.

4.4. When single point sampling probes for extractive systems are installed within the stack or duct under paragraphs 4.1 and 4.2.1, the sample may not be extracted at any point less than 1.0 meter from the stack or duct wall. Multipoint sampling probes installed under paragraph 4.2.2 may be located at any points necessary to obtain consistently representative samples.

5. Continuous Monitoring System Performance Specifications.

The continuous monitoring system shall meet the performance specifications in Table 2-1 to be considered acceptable under this method.

TABLE 2-1. PERFORMANCE SPECIFICATIONS

| Parameter | Specification |
|---|---|
| 1. Accuracy[1] | ≤ 20 pct of the mean value of the reference method test data. |
| 2. Calibration error[1] | ≤ 5 pct of each (50 pct, 90 pct) calibration gas mixture value. |
| 3. Zero drift (2h)[1] | 2 pct of span |
| 4. Zero drift (24h)[1] | Do. |
| 5. Calibration drift (2h)[1] | Do. |
| 6. Calibration drift (24h)[1] | 2.5 pct. of span |
| 7. Response time | 15 min maximum. |
| 8. Operational period | 168 h minimum |

[1] Expressed as sum of absolute mean value plus 95 pct confidence interval of a series of tests.

6. Performance Specification Test Procedures. The following test procedures shall be requirenemts of paragraph 5. For $NO_x$ analyzers that oxidize nitric oxide (NO) to nitrogen dioxide ($NO_2$), the response time test under paragraph 6.3 of this method shall be performed using nitric oxide (NO) span gas. Other tests for $NO_x$ continuous monitoring systems under paragraph 6.1 and 6.2 and all tests for sulfur dioxide systems shall be performed using the pollutant span gas specified by each subpart.

6.1 Calibration Error Test Procedure. Set up and calibrate the complete continuous monitoring system according to the manufacturer's written instructions. This may be accomplished either in the laboratory or in the field.

6.1.1 Calibration Gas Analyses. Triplicate analyses of the gas mixtures shall be performed within two weeks prior to use using Reference Methods 6 for $SO_2$ and 7 for $NO_x$. Analyze each calibration gas mixture (50%, 90%) and record the results on the example sheet shown in Figure 2-1. Each sample test result must be within 20 percent of the averaged result or the tests shall be repeated. This step may be omitted for non-extractive monitors where dynamic calibration gas mixtures are not used. (6.1.2).

6.1.2 Calibration Error Test Procedure. Make a total of 15 nonconsecutive measurements by alternately using zero gas and each calibration gas mixture concentration (e.g., 0%, 50%, 0%, 90%, 50%, 90%, 50%, 0%, etc.). For nonextractive continuous monitoring systems, this test procedure may be performed by using two or more calibration gas cells whose concentrations are certified by the manufacturer to be functionally equivalent to these gas concentrations. Convert the continuous monitoring system output readings to ppm and record the results on the example sheet shown in Figure 2-2.

6.2 Field Test for Accuracy (Relative), Zero Drift, and Calibration Drift. Install and operate the continuous monitoring system in accordance with the manufacturer's written instructions and drawings as follows:

6.2.1 Conditioning Period. Offset the zero setting at least 10 percent of the span so that negative zero drift can be quantified. Operate the system for an initial 168-hour conditioning period in normal operating manner.

6.2.2 Operational Test Period. Operate the continuous monitoring system for an additional 168-hour period retaining the zero offset. The system shall monitor the source effluent at all times except when being zeroed, calibrated, or backflushed.

6.2.2.1 Field Test for Accuracy (See Appendix D).

6.2.2.2 Field Test for Zero Drift and Calibration Drift. For extractive systems, determine the values given by zero and span gas pollutant concentrations at two-hour intervals until 15 sets of data are obtained. For nonextractive measurement systems, the zero value may be determined by mechanically producing a zero condition that provides a system check of the analyzer internal mirrors and all electronic circuitry including the radiation source and detector assembly or by inserting three or more calibration gas cells and computing the zero point from the upscale measurements. If this latter technique is used, a graph(s) must be retained by the owner or operator for each measurement system that shows the relationship between the upscale measurements and the zero point. The span of the system shall be checked by using a calibration gas cell certified by the manufacturer to be functionally equivalent to 50 percent of span concentration. Record the zero and span measurements (or the computed zero drift) on the example data sheet shown in Figure 2-4. The two-hour periods over which measurements are conducted need not be consecutive but may not overlap. All measurements required under this paragraph may be conducted concurrent with tests under paragraph 6.2.2.1.

6.2.2.3 Adjustments. Zero and calibration corrections and adjustments are allowed only at 24 hour intervals or at such shorter intervals as the manufacturer's written instructions specify. Automatic corrections made by the measurement system without operator intervention or initiation are allowable at any time. During the entire 168-hour operational test period, record on the example sheet shown in Figure 2-5 the values given by zero and span gas pollutant concentrations before and after adjustment at 24-hour intervals.

6.3 Field Test for Response Time.

6.3.1 Scope of Test. Use the entire continuous monitoring system as installed, including sample transport lines if used. Flowrates, line diameters, pumping rates, pressures (do not allow the pressurized calibration gas to change the normal operating pressure in the sample line), etc., shall be at the nominal values for normal operation as specified in the manufacturer's written instructions. If the analyzer is used to sample more than one pollutant source (stack), repeat this test for each sampling point.

6.3.2 Response Time Test Procedure. Introduce zero gas into the continuous monitoring system sampling interface or as close to the sampling interface as possible. When the system output reading has stabilized, switch quickly to a known concentration of pollutant gas. Record the time from concentration switching to 95 percent of final stable response. For non-extractive monitors, the highest available calibration gas concentration shall be switched into and out of the sample path and response times recorded. Perform this test sequence three (3) times. Record the results of each test on the example sheet shown in Figure 2-6.

## 7. Calculations, Data Analysis and Reporting.

### 7.1 Procedure for determination of mean values and confidence intervals.

7.1.1 The mean value of a data set is calculated according to equation 2-1.

$$\overline{X} = \frac{1}{n} \sum_{i=1}^{n} X_i$$

Equation 2-1.

where:

$X_i$ = absolute value of the measurements

$\sum$ = sum of the individual values

$\overline{X}$ = mean value, and

$n$ = number of data points

7.1.2 The 95 percent confidence interval (two-sided) is calculated according to equation 2-2:

$$C.I._{95} = \frac{t_{.975}}{\sqrt{n \quad n-1}} \sqrt{n(\sum I_i^2) - (\sum X_i)^2}$$

Equation 2-2.

where:

$X_i$ = sum of all data points

$t_{.975}$ = $t_1 - a/2$, and

$C.I._{95}$ = 95 percent confidence interval estimate of the average mean value.

VALUES FOR $t_{.975}$

| n | $t_{.975}$ |
|---|---|
| 2 | 12.706 |
| 3 | 4.303 |
| 4 | 3.182 |
| 5 | 2.776 |
| 6 | 2.571 |
| 7 | 2.447 |
| 8 | 2.365 |
| 9 | 2.306 |
| 10 | 2.262 |
| 11 | 2.228 |
| 12 | 2.201 |
| 13 | 2.176 |
| 14 | 2.160 |
| 15 | 2.145 |
| 16 | 2.131 |

The values in this table are already corrected for n-1 degrees of freedom. Use in equal to the number of samples as data points.

### 7.2 Data Analysis and Reporting

7.2.1 Accuracy (See Appendix D).

7.2.2 Calibration Error. Using the data from paragraph 6.1, subtract the measured pollutant concentration determined under paragraph 6.1.1 (Figure 2-1) from the value shown by the continuous monitoring system for each of the five readings at each concentration measured under 6.1.2 (Figure 2-2). Calculate the mean of these difference values and the 95 percent confidence intervals according to equations 2-1 and 202. Report the calibration error (the sum of the absolute value of the mean difference and the 95 percent confidence interval) as a percentage of each respective calibration gas concentration. Use example sheet shown in Figure 2-2.

7.2.3 Zero Drift (2-hour). Using the zero concentration values measured each two hours during the field test, calculate the differences between consecutive two-hour readings expressed in ppm. Calculate the mean difference and the confidence interval using as the sum of the absolute mean value and the confidence interval as a percentage of span. Use example sheet shown in Figure 2-4.

7.2.4 Zero Drift (24 Hour). Using the zero concentration values measured every 24 hours during the field test, calculate the differences between the zero point after zero adjustment and the zero value 24 hours later just prior to zero adjustment. Calculate the mean value of these points and the confidence interval using equations 2-1 and 2-2. Report the zero drift (the sum of the absolute mean and confidence interval) as a percentage of span. Use example sheet shown in Figure 2-5.

7.2.5 Calibration Drift (2-hour). Using the calibration values obtained at two-hour intervals during the field test, calculate the differences between consecutive two-hour readings expressed as ppm. These values should be corrected for the corresponding zero drift during that two-hour period. Calculate the mean and confidence interval of these corrected difference values using equations 2-1 and 2-2. Do not use the differences between non-consecutive readings. Report the calibration drift as the sum of the absolute mean and confidence interval as a percentage of span. Use the example sheet shown in Figure 2-4.

7.2.6 Calibration Drift (24 hour). Using the calibration values measured every 24 hours during the field test, calculate the differences between the calibration concentration reading after zero and calibration adjustment, and the calibration concentration reading 24 hours later after zero adjustment but before calibration adjustment. Calculate the mean value of these differences and the confidence interval using equations 2-1 and 2-2. Report the calibration drift (the sum of the absolute mean and confidence interval) as a percentage of span. Use the example sheet shown in Figure 2-5.

7.2.7 Response Time. Using the charts from paragraph 6.3, calculate the time interval from concentration switching to 90 percent to the final stable value for all upscale and downscale tests. Report the mean of the three upscale test times and the mean of the three downscale test times. The two average times should not differ by more than 15 percent of the slower time. Report the slower time as the system response time. Use the example sheet shown in Figure 2-6.

7.2.8 Operational Test Period. During the 168-hour performance and operational test period, the continuous monitoring system shall not require any corrective maintenance repair, replacement, or adjustment other than that clearly specified as required in the operation and maintenance manuals as routine and expected during a one-week period. If the continuous monitoring system operates within the specified performance parameters and does not require corrective maintenance, repair, replacement or adjustment other than as specified above during the 168 hour test period, the operational period will be successfully concluded. Failure of the continuous monitoring system to meet this requirement shall call for a repetition of the 168-hour test period. Portions of the test which were satisfactorily completed need not be repeated. Failure to meet any performance specifications shall call for a repetition of the one-week performance test period and that portion of the testing which is related to the failed specification. All maintenance and adjustments required shall be recorded. Output readings shall be recorded before and after all adjustments.

## 8. References.

8.1 "Monitoring Instrumentation for the Measurement of Sulfur Dioxide in Stationary Source Emissions," Environmental Protection Agency, Research Triangle Park, N.C., February 1973.

8.2 "Instrumentation for the Determination of Nitrogen Oxides Content of Stationary Source Emissions," Environmental Protection Agency, Research Triangle Park, N.C., Volume 2, APTD-0942, January 1972.

8.3 "Experimental Statistics," Department of Commerce, Handbook 91, 1963, pp. 3-31, paragraphs 3-3.1.4.

8.4 "Performance Specificaitons for Stationary-Source Monitoring Systems for Gases and Visible Emissions,: Environmental Protection Agency, Research Triangle Park, N.C., EPA-650/2-74-013, January 1974.

Date________________________ Reference Method Used_______

Mid-Range Calibration Gas Mixture

Sample 1____________________ppm

Sample 2____________________ppm

Sample 3____________________ppm

Average_____________________ppm

High-Range (span) Calibration Gas Mixture

Sample 1____________________ppm

Sample 2____________________ppm

Sample 3____________________ppm

Average_____________________ppm

Figure 2-1. Analysis of Calibration Gas Mixtures

## Figure 2-2. Calibration Error Determination

Calibration Gas Mixture Data (From Figure 2-1

Mid (50%) ________ppm  High (90%) __________ppm

| Run # | Calibration Gas Concentration, ppm | Measurement System Reading, ppm | Differences,[1] ppm |
|---|---|---|---|
| 1. | | | |
| 2. | | | |
| 3. | | | |
| 4. | | | |
| 5. | | | |
| 6. | | | |
| 7. | | | |
| 8. | | | |
| 9. | | | |
| 10. | | | |
| 11. | | | |
| 12. | | | |
| 13. | | | |
| 14. | | | |
| 15. | | | |

| | Mid | High |
|---|---|---|
| Mean difference | ______ | ___________ |
| Confidence interval | +_________ | +___________ |

Calibration error = Mean difference[2] +C.I. x100 / Average Calibration Gas Concentration_______% ___________

---

[1] Calibration gas concentration - measurement system reading

[2] Absolute value

Figure 2-3. Accuracy Determination ($SO_2$ and $NO_x$)

| Test No. | Date and Time | Reference Method Samples | | | | | Analyzer 1-hour Average (ppm)* | | Differenc (ppm) | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | $SO_2$ Sample 1 (ppm) | $NO_x$ Sample 1 (ppm) | $NO_x$ Sample 2 (ppm) | $NO_x$ Sample 3 (ppm) | $NO_x$ Average (ppm) | $SO_2$ | $NO_x$ | $SO_2$ | $NO_x$ |
| 1 | | | | | | | | | | |
| 2 | | | | | | | | | | |
| 3 | | | | | | | | | | |
| 4 | | | | | | | | | | |
| 5 | | | | | | | | | | |
| 6 | | | | | | | | | | |
| 7 | | | | | | | | | | |
| 8 | | | | | | | | | | |
| 9 | | | | | | | | | | |

Mean reference method test value ($SO_2$) ______

Mean reference method test value ($NO_x$) ______

Average of the differences ______ ______

Mean differences** = ______ ppm ($SO_2$), = ______ ppm ($NO_x$).

95% Confidence intervals = = ± ______ ppm ($SO_2$), = ± ______ ppm ($NO_x$)

Accuracies = $\frac{\text{Mean difference (absolute value) + 95\% confidence interval}}{\text{Mean reference method value}}$ x 100= ______ % ($SO_2$), = ______ % ($NO_x$)

* Explain and report method used to determine integrated averages.

** Mean differences = the average of the differences minus the mean reference method test value.

Figure 2-4. Zero and Calibration Drift (2 Hour)

| Data Set No. | Time | | Date | Zero Reading | Zero Drift ( zero) | Span Reading | Span Drift ( Span) | Calibration Drift ( Span-Zero) |
|---|---|---|---|---|---|---|---|---|
| | Begin | End | | | | | | |
| 1 | | | | | | | | |
| 2 | | | | | | | | |
| 3 | | | | | | | | |
| 4 | | | | | | | | |
| 5 | | | | | | | | |
| 6 | | | | | | | | |
| 7 | | | | | | | | |
| 8 | | | | | | | | |
| 9 | | | | | | | | |
| 10 | | | | | | | | |
| 11 | | | | | | | | |
| 12 | | | | | | | | |
| 13 | | | | | | | | |
| 14 | | | | | | | | |
| 15 | | | | | | | | |

Zero Drift = Mean Zero Drift* ____________ + CI (Zero) ______________ ÷ Span x 100 = ___________.

Calibration Drift = Mean Span Drift* ______________ + CI (Span) ____________ ÷ Span x 100= ___________

*Absolute Value.

| Date and Time | Zero Reading | Zero Drift ( Zero) | Span Reading (After zero adjustment) | Calibration Drift ( Span) |
|---|---|---|---|---|
| | | | | |
| | | | | |
| | | | | |
| | | | | |
| | | | | |
| | | | | |
| | | | | |
| | | | | |
| | | | | |
| | | | | |

Zero Drift = Mean Zero Drift* ______________ ± C.I. (Zero) ______________________

÷ Instrument Span x 100 = ________________.

Calibration Drift = Mean Span Drift* ________________ + C.I. (Span) ______________________

÷ Instrument Span x 100 = ______________________.

* Absolute Value

Figure 2-5. Zero and Calibration Drift (24 Hour)

Date of Test ____________

Span Gas Concentration ____________ppm

Analyzer Span Setting ____________ppm

1 ____________seconds

Upscale 2 ____________seconds

3 ____________seconds

Average upscale response ____________seconds

1____________ seconds

2____________ seconds

3 ____________ seconds

Average downscale response ____________seconds

System average response time (slower time) = ____________seconds

$$\text{\% deviation from slower system average response} = \frac{\text{average upscale minus average downscale}}{\text{slower time}} \text{X}100\% = \_\_\_ .$$

Figure 2-6. Response Time

## PERFORMANCE SPECIFICATION TEST 3

Performance Specification 3 - Performance specifications and specification test procedures for monitors of $CO_2$ and $O_2$ from stationary sources.

1. Principle and Applicability.

1.1 Principle. Effluent gases are continuously sampled and are analyzed for carbon dioxide or oxygen by a continuous monitoring system. Tests of the system are preformed during a minimum operating period to determine zero drift, calibration drift, and response time characteristics.

1.2 Applicability. This performance specification is applicable to evaluation of continuous monitoring systems for measurement of carbon dioxide or oxygen. These specifications contain test procedures, installation requirements, and data computation procedures for evaluating the acceptability of the continuous monitoring systems subject to approval by the APCO. Sampling may include either extractive or non-extractive (in-situ) procedures.

2. Apparatus.

2.1 Continuous Monitoring System for Carbon Dioxide or Oxygen.

2.2 Calibration Gas Mixtures. Mixture of known concentrations of carbon dioxide or oxygen in nitrogen or air. Midrange and 90 percent of span carbon dioxide or oxygen concentrations are required. The 90 percent of span gas mixture is to be used to set and check the analyzer span and is referred to as span gas. For oxygen analyzers, if the span is higher than 21 percent $O_2$, ambient air may be used in place of the 90 percent of span calibration gas mixture. Triplicate analyses of the gas mixture (expect ambient air) shall be performed within two weeks prior to use using Reference Method 3 or this part.

2.3 Zero Gas. A gas containing less than 100 ppm of carbon dioxide or oxygen.

2.4 Data Recorder. Analog chart recorder or other suitable device with imput voltage range compatible with analyzer system output. The resolution of the recorder's data output shall be sufficient to allow completion of the test procedures within this specification.

3. Definitions.

3.1 Continuous Monitoring System. The total equipment required for the determination of carbon dioxide or oxygen in a given source effluent. The system consists of three major subsystems:

3.1.1 Sampling Interface. That portion of the continuous monitoring system that performs one or more of the following operations: delineation, acquisition, transportation, and conditioning of a sample of the source effluent or protection of the analyzer from the hostile aspects of the sample or source environment.

3.1.2 Analyzer. That portion of the continuous monitoring system which senses the pollutant gas and generates a signal output that is a function of the pollutant concentration.

3.1.3 Data Recorder. That portion of the continuous monitoring system that provides a permanent record of the output signal in terms of concentration units.

3.2 Span. The value of oxygen or carbon dioxide concentration at which the continuous monitoring system is set that produces the maximum data display output. For the purposes of this method, the span shall be set no less than 1.5 to 2.5 times the normal carbon dioxide or normal oxygen concentration in the stack gas of the affected facility.

3.3 Midrange. The value of oxygen or carbon dioxide concentration that is representative of the normal conditions in the stack gas of the affected facility at typical operating rates.

3.4 Zero Drift. The change in the continuous monitoring system output over a stated period of time of normal continuous operation when the carbon dioxide or oxygen concentration at the time for the measurements is zero.

3.5 Calibration Drift. The change in the continuous monitoring system output over a stated time period of normal continuous operation when the carbon dioxide or oxygen continuous monitoring system is measuring the concentration of span gas.

3.6 Operational Test Period. A minimum period of time over which the continuous monitoring system is expected to operate within certain performance specifications without unscheduled maintenance, repair, or adjustment.

3.7 Response Time. The time interval from a step change in concentration at the input to the continuous monitoring system to the time at which 95 percent of the corresponding final value is displayed on the continuous monitoring system data recorder.

4. Installation Specification.

Oxygen or carbon dioxide continuous monitoring systems shall be installed at a location where measurments are directly representative of the total effluent from the affected facility or representative of the same effluent sampled by a $SO_2$ or $NO_x$ continuous monitoring system. This requirement shall be complied with by use of applicable requirements in Performance Specification 2 of this appendix as follows:

4.1 Installation of Oxygen or Carbon Dioxide Continuous Monitoring Systems Not Used to Convert Pollutant Data. A sampling location shall be selected in accordance with the procedures under paragraphs 4.2.1 or 4.2.2, or Performance Specification 2 of this appendix.

4.2 Installation of Oxygen or Carbon Dioxide Continuous Monitoring Systems Used to Convert Pollutant Continuous Monitoring System Data to Units of Applicable Standards. The diluent continuous monitoring system (oxygen or carbon dioxide) shall be installed at a sampling location where measurements that can be made are representative of the effluent gases sampled by the pollutant continuous monitoring system(s). Conformance with this requirement may be accomplished in any of the following ways:

4.2.1 The sampling location for the diluent system shall be near the sampling location for the pollutant continuous monitoring system such that the same approximate point (s) (extractive systems) or path (in-situ systems) in the cross section is sampled or viewed.

4.2.2 The diluent and pollutant continuous monitoring systems may be installed at different locations if the effluent gases at both sampling locations are nonstratified as determined under paragraphs 4.1 or 4.3, Performance Specification 2 of this appendix and there is no in-leakage occurring between the two sampling locations. If the effluent gases are stratified at either location, the procedures under paragraph 4.2.2, Performance Specification 2 of this appendix shall be used for installating continuous monitoring systems at that location.

5. Continuous Monitoring System Performance Specification.

The continuous monitoring system shall meet the performance specifications in Table 3-1 to be considered acceptable under this method.

6. Performance Specification Test Procedures.

The following test procedures shall be used to determine conformance with the requirements of paragraph 4. Due to the wide variation existing in analizer designs and principles of operation, these procedures are not applicable to all analyzers. Where this occurs, alternative procedures, subject to the approval of the . APCO ., may be employed. Any such alternative procedures must fulfill the same purposes (verify response, drift, and accuracy) as the following procedures, and must clearly demonstrate conformance with specifications in table 2-1.

6.1 Calibration Check. Establish a calibration curve for the continuous monitoring system using zero, midrange, and span concentration gas mixtures. Verify that the resultant curve of analyzer reading compared with the calibration gas value is consistent with the expected response curve as described by the analyzer manufacturer. If the expected response curve is not produced, additional calibration gas measurements shall be made, or additional steps undertaken to verify the accuracy of the response curve of the analyzer.

6.2 Field Test for Zero Drift and Calibration Drift. Install and operate the continuous monitoring system in accordance with the manufacturer's written instructions and drawings as follows:

Table 3-1. Performance Specifications

| Parameter | Specification |
|---|---|
| 1. Zero drift (2h)[1] | 0.4 pct $O_2$ or $CO_2$ |
| 2. Zero drift (24h)[1] | 0.5 pct $O_2$ or $CO_2$ |
| 3. Calibration drift (2h)[1] | 0.4 pct $O_2$ or $CO_2$ |
| 4. Calibration drift (24h)[1] | 0.5 pct $O_2$ or $CO_2$ |
| 5. Operational period | 168 h minimum |
| 6. Response time | 10 min. |

[1] Expressed as sum of absolute mean value plus 95 pct confidence interval of a series of tests.

6.2.1 Conditioning Period. Offset the zero setting at least 10 percent of span so that negative zero drift may be quantified. Operate the continuous monitoring system for an initial 168-hour conditioning period in a normal operational manner.

6.2.2 Operational Test Period. Operate the continuous monitoring system for an additional 168 hour period maintaining the zero offset. The system shall monitor the source effluent at all times except when being zeroed, calibrated, or backpurged.

6.2.3 Field Test for Zero Drift and Calibration Drift. Determine the values given by zero and midrange gas concentrations at two-hour intervals until 15 sets of data are obtained. For non-extractive continuous monitoring systems, determine the zero value given by a mechanically produced zero condition or by computing the zero value from upscale measurements using calibrated gas cells certified by the manufacturer. The midrange checks shall be performed by using certified calibration gas cells functionally equivalent to less than 50 percent of span. Record these readings on the example sheet shown in Figure 2-1. These two-hour periods need not be consecutive but may not overlap. In-situ $CO_2$ of $O_2$ analyzers which cannot be fitted with a calibration gas cell may be calibrated by alternative procedures acceptable to the APCO . Zero and calibration corrections and adjustments are allowed only at 24-hour intervals or at such shorter intervals as the manufacturer's written instructions specify. Automatic corrections made by the continuous monitoring system without operator intervention or initiation are allowable at any time. During the entire 168-hour test period, record the values given by zero and span gas concentrations before and after adjustment at 24 hour intervals in the example sheet shown in Figure 3-2.

6.3 Field Test for Response Time.

6.3.1 Scope of Test.

This test shall be accomplished using the continuous monitoring system as installed including sample transport lines if used. Flow rates, line diameters, pumping rates, pressures (do not allow the pressurized calibration gas to change the normal operating pressure in the sample line), etd., shall be at the nominal values for normal operation as specified in the manufacturer's written instructions. If the analyzer is used to sample more than one source (stack), this test shall be repeated for each sampling point.

6.3.2 Response Time Test Procedure

Introduce zero gas into the continuous monitoring system sampling interface or as close to the sampling interface as possible. When the system output reading has stabilized, switch quickly to a known concentration of gas at 90 percent of span. Record the time from concentration switching to 95 percent of final stable response. After the system response has stabilized at the upper level, switch quickly to a zero gas. Record the time from concentration switching to 95 percent of final stable response. Alternatively, for nonextractive continuous monitoring systems, the highest available calibration gas concentration shall be switched into and out of the sample path and response times recorded. Perform this test sequence three (3) times. For each test, record the results on the data sheet shown in Figure 3-3.

## 7. Calculations, Data Analysis, and Reporting.

7.1 Procedure for determination of mean values and confidence intervals.

7.1.1 The mean value of a data set is calculated according to equation 3-1.

$$\bar{X} = \frac{1}{n} \sum_{i=i}^{n} X$$

Equation 3-1

where:

$X_i$ = absolute value of the measurements,

$\sum$ = sum of the individual values,

$\bar{x}$ = mean value, and

n = number of data points.

7.2.1 The 95 percent confidence interval (two-sided) is calculated according to equation 3-2:

$$C.I._{95} = \frac{t_{.975}}{n\sqrt{n-1}} \sqrt{n(\sum X_1^2) - (\sum X_1)^2}$$

Equation 3-2.

where:

$\sum X$ = sum of all data points,

$t_{.975} = t_1 - a/2$, and

$C.I._{95}$ = 95 percent confidence interval estimates of the average mean value.

Values for $t_{.975}$

| n | $t_{.975}$ |
|---|---|
| 2 | 12.706 |
| 3 | 4.303 |
| 4 | 3.182 |
| 5 | 2.766 |
| 6 | 2.571 |
| 7 | 2.447 |
| 8 | 2.365 |
| 9 | 2.306 |
| 10 | 2.262 |
| 11 | 2.228 |
| 12 | 2.201 |
| 13 | 2.179 |
| 14 | 2.160 |
| 15 | 2.145 |
| 16 | 2.131 |

The values in this table are already corrected for n-1 degrees of freedom. Use n equal to the number of samples as data points.

## 7.2 Data Analysis and Reporting.

7.2.1 Zero Drift (2 hour). Using the zero concentration values measured each two hours during the field test, calculate the differences between the consecutive two-hour readings expressed in ppm. Calculate the mean difference and the confidence interval using equations 3-1 and 3-2. Record the sum of the absolute mean value and the confidence interval on the data sheet shown in Figure 3-1.

7.2.2 Zero Drift (24 hour). Using the zero concentration values measured every 24 hours during the field test, calculate the difference between the zero point after zero adjustment and the zero value 24 hours later just prior to zero adjustment. Calculate the mean value of these points and the confidence interval using equations 3-1 and 3-2. Record the zero drift (the sum of the absolute mean and confidence interval) on the data sheet shown in Figure 3-2.

7.2.3 Calibration Drift (2 hour). Using the calibration values obtained at two-hour intervals during the field test, calculate the differences between consecutive two-hour readings expressed as ppm. These values should be corrected for the corresponding zero drift during that two-hour period. Calculate these corrected difference values using equations 3-1 and 3-2. Do not use the differences between non-consecutive readings. Record the sum of the absolute mean and confidence interval upon the data sheet shown in Figure 3-1.

7.2.4 Calibration Drift (24 hours). Using the calibration values measured every 24 hours during the field test, calculate the differences between the calibration concentration reading after zero and calibration adjustment and the calibration concentration reading 24 hours later after zero adjustment but before calibration adjustment. Calculate the mean value of these differences and the confidence interval using equations 3-1 and 3-2. Record the sum of the absolute mean and confidence interval on the data sheet shown in Figure 3-2.

7.2.5 Operational Test Period. During the 168-hour performance and operational test period, the continuous monitoring system shall not receive any corrective maintenance, repair, replacement, or adjustment other than that clearly specified as required in the manufacturer's written operation and maintenance manuals as routine and expected during a one-week period. If the continuous monitoring system operates within the specified performance parameters and does not require corrective maintenance, repair, replacement or adjustment other than as specified above during the 168-hour test period, the operational period will be successfully concluded. Failure of the continuous monitoring system to meet this requirement shall call for a repetition of the 168 hour test period. Portions of the test which were satisfactorily completed need not be repeated. Failure to meet any performance specifications shall call for a repetition of the one-week performance test period and that portion of the testing which is related to the failed specification. All maintenance and adjustments required shall be recorded. Output readings shall be recorded before and after all adjustments.

7.2.6 Response Time. Using the data developed under paragraph 5.3, calculate the time interval from concentration switching to 95 percent to the final stable value for all upscale and downscale tests. Report the mean of the three upscale test times and the mean of the three downscale test times. The two average times should not differ by more than 15 percent of the slower time. Report the slower time as the system response time. Record the results on Figure 3-3.

## 8. References.

8.1 "Performance Specifications for Stationary Source Monitoring Systems for Gases and Visible Emissions", Environmental Protection Agency, Research Triangle Park, N.C., EPA-650/2-74-013, January 1974.

8.2 "Experimental Statistics," Department of Commerce, National Bureau of Standards Handbook 91, 1963, pp. 3-31, paragraphs 3-3.1.4.

## Figure 5-1. Zero and Calibration Drift (2 hour)

| Data Set No | Time Begin | End | Date | Zero Reading | Zero Drift ( Zero) | Span Reading | Span Drift ( Span) * | Calibration Drift ( Span- Zero) |
|---|---|---|---|---|---|---|---|---|
| 1 | | | | | | | | |
| 2 | | | | | | | | |
| 3 | | | | | | | | |
| 4 | | | | | | | | |
| 5 | | | | | | | | |
| 6 | | | | | | | | |
| 7 | | | | | | | | |
| 8 | | | | | | | | |
| 9 | | | | | | | | |
| 10 | | | | | | | | |
| 11 | | | | | | | | |
| 12 | | | | | | | | |
| 13 | | | | | | | | |
| 14 | | | | | | | | |
| 15 | | | | | | | | |

Zero Drift = Mean Zero Drift* ______________ + CI (Zero) ______________ = ______________.

Calibration Drift = Mean Span Drift* ______________ + DI (Span) ______________ = ______________.

* Absolute Value.

| Date and Time | Zero Reading | Zero Drift ( Zero) | Zero Reading (After Zero adjustment) | Calibration Drift ( Span) |
|---|---|---|---|---|
| | | | | |
| | | | | |
| | | | | |
| | | | | |
| | | | | |
| | | | | |
| | | | | |
| | | | | |
| | | | | |
| | | | | |

Zero Drift = Mean Zero Drift* ____________ + C.I.(Zero) ____________

= ____________.

Calibration Drift = Mean Span Drift* ____________ +C.I.(Span) ____________.

= ____________.

*Absolute Value

Figure 3-2. Zero and Calibration Drift (24 hour)

Date of Test ____________

Span Gas Concentration ____________ ppm

Analyzer Span Setting ____________ ppm

Upscale
1. ____________ seconds
2. ____________ seconds
3. ____________ seconds

Average upscale response ____________ seconds

Downscale
1. ____________ seconds
2. ____________ seconds
3. ____________ seconds

Average downscale response ____________ seconds

System average response time (slower time) = ____________ seconds

$$\text{\% deviation from slower system average response} = \frac{\text{Average upscale minus average downscale}}{\text{slower time}} \times 100\%$$

= ____________.

Figure 3-3. Response

# FIELD ACCURACY TEST
# PROCEDURE FOR CONTINUOUS EMISSION MONITORS

## 1. Applicability

1.1 This procedure is used to evaluate the accuracy of continuous mass emission monitoring systems for sulfur dioxide, nitrogen oxides, carbon monoxide, carbon dioxide, oxygen or any other gaseous compounds whose monitoring may be required by the Bay Area Air Quality Management District. Both the accuracy of the gas species concentration analyzer and the accuracy of the stack gas flow rate monitor are tested.

## 2. Principle

2.1 A continuous gas sample, representative of atmospheric emissions, is extracted from the source and conditioned to remove moisture and particulate material. A small portion of the conditioned sample is passed through a continuous analyzer sensitive to the species of interest. The average concentration of the specie determined over 90 minutes is compared with a similar reading determined by the continuous emission monitoring system.

2.2 Carbon dioxide and carbon monoxide are analyzed by non-dispersive infra-red spectoscopy (NDIR). Sulfur dioxide is analyzed by ultraviolet (UV) absorption spectroscopy. Oxides of nitrogen are analyzed as NO by chemiluminescent detection. Oxygen is analyzed by galvanic measurement at a sample/fuel cell interface.

2.3 A pitot tube is used to measure the velocity pressure in the stack, from which the stack gas volumetric flow rate is calculated.

## 3. Interferences

3.1 The various analytical methods have potential interferences as described below.

3.1.1 Carbon dioxide - methanol, ethanol and water. (No interferences exist with the analyzer mentioned in 1.1.1)

3.1.2 Carbon monoxide - cyanogen, methyl azide

3.1.3 Nitrogen oxides - other nitrogen compounds (except ammonia)

3.1.4 Sulfur dioxide - elemental sulfur, sulfur trioxide, carbon disulfide.

3.1.5 Oxygen - halogens and halogenated compounds.

3.2 If interferences are anticipated with the use of any method herein, the Source Test Section of the BAAPCD should be consulted or else an alternate method(s) as described in MOP., Vol IV, Source Test Policy and Procedures shall be used.

4. Sampling Ports and Facilities

1.1 Sampling ports and facilities shall be provided for purposes of field accuracy tests of continuous monitoring systems according to the requirements of Sections 2.3 and 2.4 of "Source Test Policy" in Manual of Procedures, Vol IV, Source Test Policy and Procedures.

5. Apparatus

5.1 Instrumentation

5.1.1 The analyzers, by test species, are indicated below.

5.1.1.1 Carbon dioxide - Use Infrared Industries Inc. Infrared Gas Analyzer Model 703, or equivalent.

5.1.1.2 Carbon Monoxide - Use MSA Co. LIRA Model 202 carbon monoxide analyzer, or equivalent.

5.1.1.3 Oxides of nitrogen - Use Thermo Electron Corporation chemiluminiscent Analyzer Model 10A, or equivalent.

5.1.1.4 Sulfur dioxide - Use E.I. DuPont de Nemours and Co. Photometric Analyzer Model 400, or equivalent.

5.1.1.5 Oxygen - Use Teledyne Analytical Instruments Model 326 Analyzer, or equivalent.

5.1.2 Potentiometric recorder - The recorder monitors and records the continuous output from the analyzers.

5.2 Sample conditioning, zero air, and span gas system.(Figure 1)

5.2.1 Materials and construction - Except as specified, all valves, fittings, lines and other sample-contacting surfaces shall be Teflon or stainless steel.

5.2.2 Sample probe - Use a borosilicate glass tube fitted at the downstream end with a tubing connector. The length of the probe shall be at least equal to the radius of the stack being tested. If stack temperature exceeds 800°F., substitute quartz for the borosilicate tube. Other sample probes are acceptable subject to prior approval by the Source Test Section.

5.2.3 Moisture condensers - Use modified Greenberg-Smith impingers with the impaction plate removed and the inlet tube shortened to 3 or 4 inches. At least two condensers shall be connected in series. Other condensers are acceptable if they are as efficient as impingers.

5.2.4 Ice bath - Immerse the condensers in an ice bath during sampling.

5.2.5 Particulate filter - Use a Balston type 95 holder with grade B filter, or equivalent, in the sample system.

5.2.6 Pumps - Use leak-free, Teflon-lined diaphragm pumps, Thomas Industries Model No. 908CA18TFE, or equivalent, in the sample and zero air systems. The pumps msut have a free-flow capacity of at least 28 liters/min (1.0 CFM).

5.2.7 Back pressure regulator - Use a back-pressure regulator to maintain sample and zero gas pressures to the analyzers at 5 psig.

5.3 Zero Air System (Figure 1)

5.3.1 This system provides clean dry atmospheric air for analyzer calibration.

5.3.2 Gas scrubber - Use a bed of silica gel, Ascarite (or soda-lime), and charcoal to remove moisture, carbon dioxide, and hydrocarbons from the zero air system.

5.4 Span gas-cylinder of appropriate species with inert balance at a concentration between 20% and 80% of full scale on the analyzer. The concentration shall be traceable to primary standards.

5.5 Velocity Measurement - Refer to Source Test Procedure ST-17, (M.O.P., Vol IV).

6. Pre-Test Procedures

6.1 Instrument warm-up - time shall be per manufacturer's recommendation or until stability is achieved.

6.2 Leak Test - The sampling system shall be leak-tested by turning on the sample pump, plugging the probe and ascertaining that the sample pressure to the analyzer falls to zero. Other leak tests are acceptable subject to prior approval by the Source Test Section.

6.3 Calibration, Zero - Zero air shall be introduced at the manufacturer's recommended flow rate, and the analyzer shall be zero-adjusted, except the oxygen analyzer shall be adjusted to read 20.9%.

6.4 Calibration, Span - Span gas shall be introduced at the rate in 6.3, and the analyzer span shall be accordingly adjusted (except the oxygen analyzer.)

6.5 Concentration Traverse - The stack shall be traversed with the probe to determine whether the concentration of any of the species of interest is radially variant. The probe shall be positioned at approximately 1/5, 2/5, 3/5, 4/5 and 5/5 of the stack diameter, long enough at each point to record a representative measure of the concentration of each test species. If the concentration of any test species varies at any single point by over 10% of the average over all points, the stack shall be traversed during sampling according to paragraph 7.2.

## 7. Sampling

7.1 Sampling shall be done continuously for a 90 minute period. The analyzer(s) shall be zero and span-checked at the beginning and end of the test period according to paragraphs 6.3 and 6.4.

7.2 If stack traversing is necessary (see paragraph 6.5), the traverse points shall be as specified in Source Test Procedure ST-18 (M.O.P., Vol. IV). Each traverse point shall be sampled for an equal length of time.

7.3 The continuous emission monitor shall not be adjusted during the test period.

## 8. Auxiliary Tests

8.1 Water Vapor - The moisture content of the stack gas shall be measured once during the field accuracy test period according to Source Test Procedure ST-23 (M.O.P., Vol. IV) unless it is reliably known by other means.

8.2 Stack Gas Flowrate - The flow rate shall be determined according to Source Test Procedure ST-17 once during the test period. The exact time intervals during which the stack velocity pressure is measured shall be recorded on the stack flow rate monitor chart.

## 9. Calculations (each test period)

9.1 The calculations herein assume that the stack monitors report data at actual stack (wet) conditions.

9.2 The time-averaged (dry basis) test concentration of each species, $C_T$, shall be computed.

9.3 The stack gas water vapor content, H(%), shall be computed as in Source Test Procedure ST-23.

9.4 The test standard dry stack gas flowrate, $Q_o$, shall be computed as in Source Test Procedure ST-17.

9.5 The time-averaged concentration (actual basis) of each species as measured by the continuous monitor(s), $C_M$, shall be computed.

9.6 The average monitor concentration(s) shall be changed to a dry basis as:

$$C'_M = \frac{C_M \times 100}{100 - H}$$

9.7 The actual stack gas flow rate as reported by the monitor at the time of the velocity pressure test shall be corrected to standard dry conditions as

$$Q'_M = \frac{Q_M \times 530^\circ R \times P \times 100}{29.92 \text{ in. Hg} \times T \times (100 - H)}$$

where: $Q_M$ = actual stack gas flow rate as reported by monitor, CFM.

$P$ = stack static pressure, inches of Hg. (abs)

$T$ = stack temperature, °R.

## 10. Reporting

10.1 The data indicated in Table I shall be reported for each test period and as the average of the test periods.

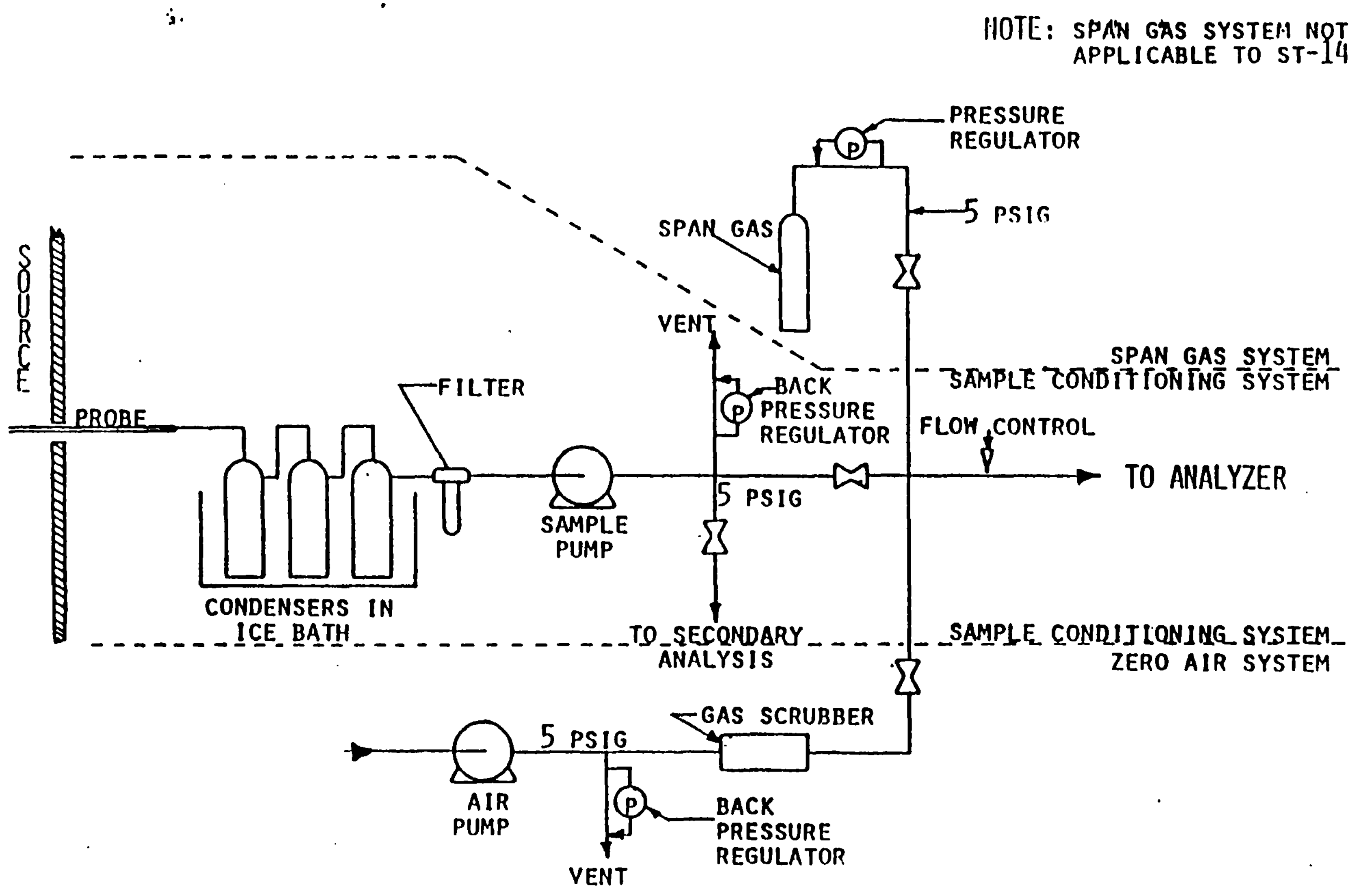

FIGURE 1.

SAMPLE CONDITIONING, ZERO AIR AND SPAN GAS SYSTEMS

## TABLE 1 - Field Accuracy Reporting Data

Firm Name and Address:

Firm Representative and Title:

Source:

Testing Firm and Personnel:

Test Date:

Test Times: Run A Run B Run C

Test Method used on each component Tested:

$SO_2$
$NO_x$
$CO_2$
$O_2$

Summary of Field Accuracy Results:

| | Test Method Results | | | | Source Monitor Results | | | |
|---|---|---|---|---|---|---|---|---|
| | Run A | Run B | Run C | Avg. | Run A | Run B | Run C | A |
| Flowrate, SDCFM | | | | | | | | |
| Water Content % | | | | | | | | |
| $SO_2$, ppm (dry) | | | | | | | | |
| $SO_2$, lb/hr. | | | | | | | | |
| $NO_x$, ppm (dry) | | | | | | | | |
| $NO_x$ (as $NO_2$) lb/hr. | | | | | | | | |
| $CO_2$, % (dry) | | | | | | | | |
| $O_2$, % (dry) | | | | | | | | |

BAY AREA
AIR QUALITY MANAGEMENT DISTRICT

## MONTHLY CONTINUOUS EMISSION MONITORING REPORT

COMPANY:

SOURCE:

MONTH:

POLLUTANT:

1. EMISSION DATA

| DAY | AVERAGE 24Hr. CONCENTRATION, ppm | MINIMUM 1 Hr. CONCENTRATION, ppm | DAILY MASS EMISSION, TONS | EMISSION BASED ON PRODUCTION* |
|---|---|---|---|---|
| 1 | | | | |
| 2 | | | | |
| 3 | | | | |
| 4 | | | | |
| 5 | | | | |
| 6 | | | | |
| 7 | | | | |
| 8 | | | | |
| 9 | | | | |
| 10 | | | | |
| 11 | | | | |
| 12 | | | | |
| 13 | | | | |
| 14 | | | | |
| 15 | | | | |
| 16 | | | | |
| 17 | | | | |
| 18 | | | | |
| 19 | | | | |
| 20 | | | | |
| 21 | | | | |
| 22 | | | | |
| 23 | | | | |
| 24 | | | | |
| 25 | | | | |
| 26 | | | | |
| 27 | | | | |
| 28 | | | | |
| 29 | | | | |
| 30 | | | | |
| 31 | | | | |

*For Sulfuric Acid plants and Sulfur Recovery Units use pounds per short ton of production based on a daily average. This data requirement is not applicable to other sources or those emission points serving multiple sources.

## II. STATEMENT OF EXCESS EMISSIONS
(Negative declaration Required, Including Opacity)

| DATE | TIME | DURATION | MAGNITUDE | REMARKS |
|---|---|---|---|---|
| | | | | |

## III. MONITOR MALFUNCTION

| DATE | TIME | DURATION | PROBLEM/CORRECTIVE ACTION |
|---|---|---|---|
| | | | |

Signature and Date

# MANUAL OF PROCEDURES

## VOLUME VI

## AIR MONITORING PROCEDURES

MANUAL OF PROCEDURES

VOL. VI

# AIR MONITORING PROCEDURES

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## 1. GROUND LEVEL MONITORING FOR SULFUR DIOXIDE AND HYDROGEN SULFIDE

REF: Regs. 1-510
9-1-501, 9-1-604
9-2-501, 9-2-601

1.1 General. This section outlines the procedures to be used for atmospheric sampling of hydrogen sulfide and sulfur dioxide.concentrations in order to fulfill requirements of Regulation 9-1-110.2 and Regulation 9-2-301.

1.2 Instrumentation. When required under Regulation 9-1-501 or Regulation 9-2-501, the person responsible for emissions shall provide recording instrumentation at not less than three sites chosen to monitor the ambient air in the area surrounding the emission source and one meteorological station to record wind speed and direction. Additional instruments may be required in specific cases where necessary to meet the intent of the appropriate section. The instruments must be sufficient in number to give reasonable assurance that any ground level limits exceeding those permitted will be detected. All analytical instrumentation must be capable of detecting ground level concentrations which exceed the allowable limits. All instrumentation shall be continuous and equipped with a strip chart recorder.

1.2.1 Sulfur Dioxide Instrument Specifications. The instruments shall be of a type which will continuously detect and record minute-by-minute fluctuations of concentrations of sulfur dioxide in the range from 0.01 ppm (vol) to 1.00 ppm (vol).

1.2.2 Hydrogen Sulfide Instrument Specifications. The recording instruments shall be of a type which will continuously detect and record minute-by-minute fluctuations of concentrations of $H_2S$ in the range from 0.01 ppm (vol) to 0.10 ppm (vol), or to 0.20 ppm (vol).

1.2.3 Meteorological Instrument Specifications. Meteorological instruments shall be capable of continuously measuring and recording wind direction to within ten degrees of arc, and wind speed to within one mile per hour (mph) at wind speeds less than 25 mph and with a threshold no greater than 3 mph. The width of the wind recording charts shall be adequate to determine the wind components as specified.

1.3 Siting. The instruments shall be installed and operated in locations which adequately represent maximum ground level concentrations of the measured air pollutants. Sites will be chosen to intercept most frequent ground level maximum concentrations, but in conformance with Regulation 1-510. Proper siting will be taken to require that a preponderant downwind exposure over the calendar year be accumulated by the instruments of a given network, during their hours of operation. Downwind exposure exists when the mean wind direction lies in the arc within 22.5 degrees of a direct line from source to monitor. The effective source height and the prevalent stability class associated with the most frequent wind directions are used to calculate the most probable distances for maximum ground level concentrations. A station may be placed at or within the property line if the location is otherwise acceptable and provided that the person responsible for the stations agrees in writing that such location shall, for the purposes of District requirements, be deemed to be off the property from which the emissions occur.

The wind measuring site (or sites) shall be located at the source or with the ground level monitors. In either case, they must be high enough and openly exposed so as to be free of interference from buildings, trees, or local terrain. Final approval of the siting of ground level monitors and meteorological instrumentation shall be with the APCO.

1.4 Maintenance. Regulation 1-510 requires that the person responsible for monitoring provide care and maintenance in order to assure that the instruments function properly and accurately measure ground level concentrations. A record of consistent instrument downtime may be considered failure to meet this requirement. The APCO may require submission of maintenance records.

1.5 Calibration. Regulation 1-510 requires that the person responsible for monitoring perform periodic calibrations to assure that the instruments provide acceptable monitoring of ground level concentrations. Additionally, a field calibration shall be performed after any relocation of an analyzer or major repair work. For sulfur dioxide the reference method for calibration is specified in Section 1.5.6 of this volume; for hydrogen sulfide, in Section 1.5.7.

As a quality assurance measure, District personnel will periodically inspect sites, and may perform calibration audits on the ground level monitors to determine accuracy. Accuracy of a calibration is expressed as the deviation between the analyzer response obtained under test conditions and the results of the reference procedure when samples of the same test gas are taken at approximately the same time. Deviation is calculated as a percent of the reference results.

$$\% \text{ Deviation} = \frac{\text{Analyzer value} - \text{Reference value}}{\text{Reference value}} \times 100$$

The acceptable limit for sulfur dioxide analyzer calibrations is ± 10% deviation. The acceptable limit for hydrogen sulfide analyzer calibrations is ± 15% deviation.

A record of unacceptable calibrations will be considered failure to meet the requirement. The APCO may require submission of calibration records.

1.5.1 Dynamic Calibration Procedure. A dynamic calibration is a performance test of the entire analyzer system under simulated operating conditions. The analyzer system includes the analyzer, recorder and/or data transmission system, and the sampling system with its sample lines and sample filters.

The procedure is to allow the analyzer system to sample a zero air to establish an analyzer zero response (baseline) and to sample test-gas mixtures of known concentration from a calibration gas system (see Fig. 1) to establish an upscale response. A test-gas mixture with concentration approximately equal to midscale of the analyzer range should be used. The reference methods Sulfur Dioxide Analytical Precedure 1.5.6, Hydrogen Sulfide Analytical Procedure 1.5.7 contained in this volume are used to verify test-gas concentrations.

The test-gas concentration and the analyzer response are used in the formula in Calibration 1.5 to determine the percent deviation. The analyzer response is the net reading derived by subtracting the zero response (baseline) from response to the test gas. The analyzer should be corrected to make its response conform to the known test-gas concentration. After adjustments are made, it is necessary to repeat the sampling process to reestablish both the zero and upscale analyzer responses. Linearity and low level response are determined by varying the diluent air calibration gas ratios to provide test gas concentrations throughout the entire range of the analyzer.

1.5.2 Zero (Diluent) Air. Zero air is used to establish a baseline point of reference and as a diluent in preparation of test gas mixtures. This air must be free of any substances which can alter the test gas mixtures or can

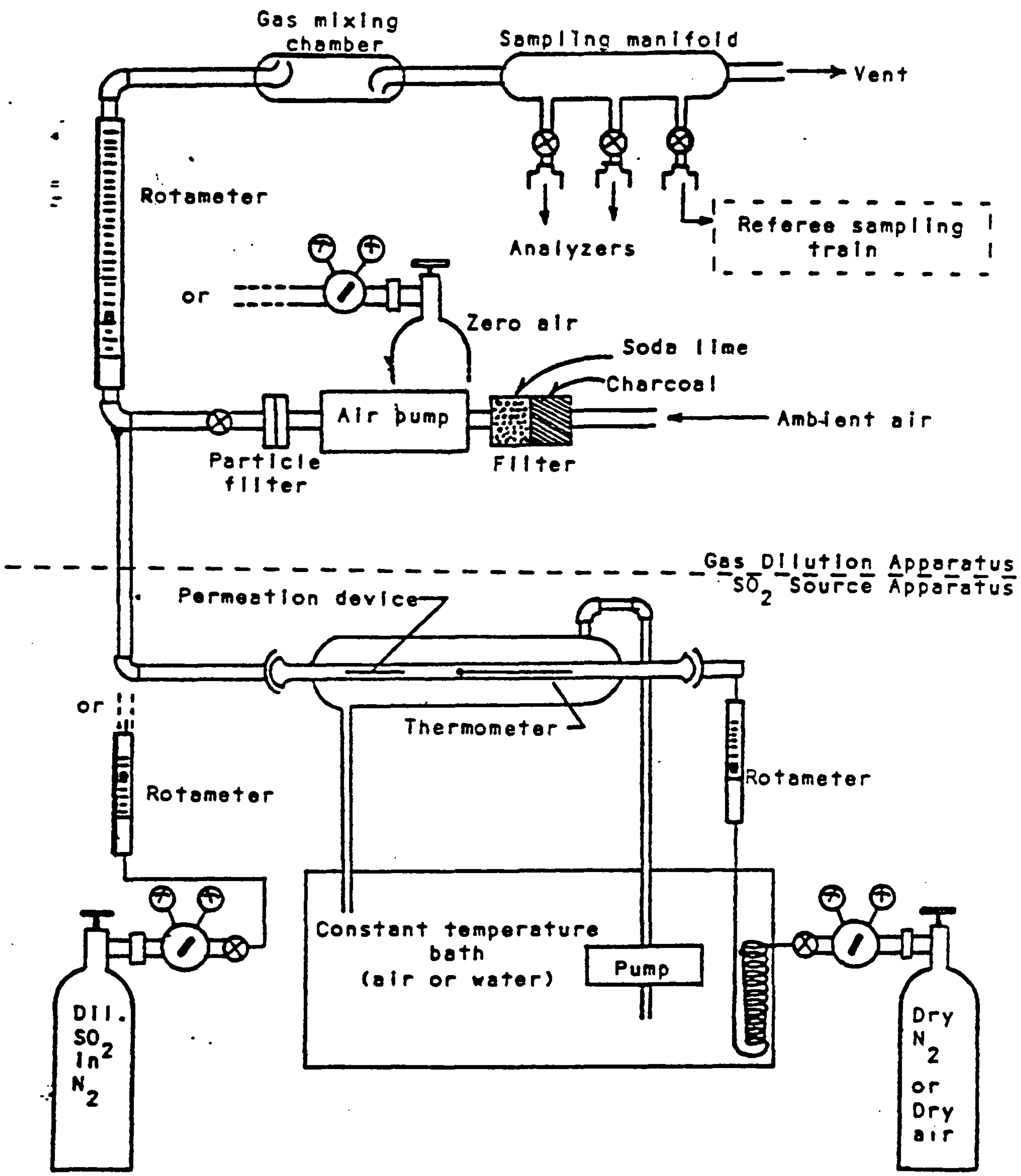

Figure I.

CALIBRATION GAS SYSTEM

affect the analyzer response or the reference method. Zero air can be obtained in pressurized gas cylinders or by properly filtering and drying air obtained with an air pump.

1.5.3 Calibration Gas System. A calibration gas system consists of a source of diluent air, a source of calibration gas, a mixing chamber and a delivery manifold from which analyzers and reference sampling trains can sample the test gas. The test gas is prepared by thoroughly mixing the calibration gas and diluent air in various known proportions. The calibration gas can be obtained from a permeation device or from a pressurized cylinder containing a suitable concentration of the calibration gas.

The calibration gas system should be positioned as close as is practical to the analyzer and reference sampling apparatus to minimize losses. Sample lines, flow metering devices, mixing chambers, all other parts of the calibration system, as well as the analyzer system should be of materials which will not affect the test gas concentration. All components used in the calibration procedure should be allowed sufficient time to stabilize before reference samples are taken and before analyzer response is determined.

### Pressurized Gas Standards

Gas standards in pressurized cylinders can be used as a gas source to be diluted in a calibration gas system or used directly when the concentration is within the operating range of the analyzer. Cylinders can be prepared in the laboratory or obtained commercially in various concentrations with or without analysis based on reference methods. Such gas standards should be restandardized against the reference method at a minimum of once every six months. Reference samples must be taken each time if a nonstandardized gas source is used in the performance of an instrument calibration.

Permeation Device

A permeation device, based on the diffusion of a gas through a plastic membrane, can be used as a gas source in a calibration gas system. The diffusion rate is a function of temperature and therefore constant temperature must be maintained throughout the calibration. Permeation devices are available commercially with or without analysis based on the reference method. Certified permeation devices should be standardized gravimetrically or against the accepted reference method at a minimum of once every six months. Reference samples must be taken each time if a nonstandardized permeation device is used.

Precautions to be taken with permeation devices include:

a. Storage of the device in a dry nitrogen atmosphere, preferably between 20 to 25°C.

b. Use of a dry, analyte-free carrier gas.

c. Handling of a permeation device only in a well vented atmosphere.

d. Allowance of a minimum of 24 hours for a permeation to establish temperature equilibrium before use.

1.5.4 Calculations.

a. Conversion Factors

$$\frac{\mu g\ SO_2}{2.6\ \mu g/\mu l} = \mu l\ SO_2$$

$$\frac{\mu g\ H_2S}{1.4\ \mu g/\mu l} = \mu l\ H_2S$$

b. To calculate parts per million concentration from the known emission rate of a permeation device, use the following equation:

$$PPM = \frac{P}{Qd}$$

Where: P = permeation rate in µl/minute

Qd = rate of diluent in liters/minute

c. To calculate parts per million concentration when using a pressurized gas standard, use the following equation:

$$PPM = \frac{F_1 \times C}{F_1 + Fo}$$

Where: Fo = diluent air flow in ml/minute

$F_1$ = calibration gas flow in ml/minute

C = concentration of calibration gas in ppm

1.5.5 Calibration Records. Calibration records shall be maintained containing the information necessary to determine test gas concentrations and to determine the percent deviation of an analyzer's response to known test-gas concentrations.

### 1.5.6 Sulfur Dioxide Reference Procedure

Principle

The method is based on the absorption of sulfur dioxide contained in a dilute calibration stream by a solution of sodium tetrachloromercurate (TCM). A stable complex is formed, which is then reacted with formaldehyde pararosaniline resulting is a colored pararosaniline derivative. The optical density, spectrophotometrically, is proportional to the amount of sulfur dioxide initially absorbed.

Reagents

1. Absorbing Solution (TCM)

Dissolve 27.2 g of mercuric chloride and 11.7 g of sodium chloride in distilled water and dilute to 1 liter. The absorbing reagent is stable for 6 months.

2. Pararosaniline Hydrochloride Solution

Dissolve 0.15 g of pararosaniline in 1 liter of distilled water containing 81 ml of concentrated hydrochloric acid. Mix well and allow to stand for two days before using. A new standard curve should be prepared for each new batch. This reagent is stable for 6 months.

3. Formaldehyde Solution 0.2%

Dilute 0.5 ml of 37% formaldehyde solution to 100 ml with distilled water. This solution should be prepared prior to use.

## Apparatus

1. Midget impingers, such as Ace Glass Inc. Cat. No 7531.
2. Air pump with flow control and with a minimum capacity of 2 liters per minute through a midget impinger.
3. Spectrophotometer, suitable for measurement at 560 ± 25 nm.
4. Flowmeter, 0 to 2 liter per minute range.
5. Stopwatch.

## Sample Collection

1. Preset the air pump to a flowrate of approximately 1 liter per minute. Prepare the sampling train by connecting the flowmeter to the sample manifold (Fig. 1, 1.5.3).
2. Pipet 10.0 ml of absorbing solution into a midget impinger. Connect the impinger to the flowmeter, and attach the air pump to the exit tube of the impinger.
3. When the calibration stream is stable and at the desired concentration level, start the air pump and the stopwatch. Immediately make the minor adjustment for a desired flow rate of 1.0 liter/min. and maintain flow for a time interval sufficient to collect from 5 to 13 μg of $SO_2$. For stream concentrations approaching or greater than 1.0 ppm, a flow rate of 0.5 liter per minute may be used.

4. Take at least two samples for each calibration point.

Analysis

1. To the contents of each impinger add 1.0 ml of 0.2% formaldehyde solution and 1.0 ml of pararosaniline hydrochloride solution. Thoroughly mix and allow 30 minutes for color development.

2. Prepare a 10.0 ml reagent blank in the same manner as the collected samples.

3. With the spectrophotometer at 560 nm, set the reagent blank at 100% transmission.

4. Read the % transmission of each sample and from a standard curve, obtain the total micrograms of $SO_2$ collected.

Preparation of Standard Curve

1. Dissolve 0.4000 g of sodium meta bisulfite (Assay 65.5% as $SO_2$) in distilled water and bring to 1 liter in a 1 liter volumetric flask. This yields a solution of approximately 260 μg of $SO_2$/ml.

2. Standardize using standard solutions of iodine and thiosulfate (Ref. 2).

3. Make proper dilutions with TCM absorbing solution to obtain a working standard containing 2.6 μg $SO_2$ per ml.

4. Add respectively 0, 1.0, 2.0, 3.0, 4.0, and 5.0 ml of the working standard to a series of graduated test tubes. Add sufficient volumes of absorbing solution to make 10.0 ml of total volume.

5. Develop color as described above in the Analysis Section.

6. Plot % transmission vs. micrograms $SO_2$ on semi-logarithmic graph paper to obtain the standard curve.

Calculations

$$\text{PPM } SO_2 = \frac{\mu g \ SO_2 \text{ From Standard Curve}}{\text{Sample Vol. (in liters)} \times 2.6}$$

References

1. West, P., Gaeke, Anal. Chem. 28, 1816-19, 1956.

2. Kolthoff and Sandell, Textbook of Quantitative Inorganic Analysis, Third Edition, 1952, MacMillan Co.

### 1.5.7 Hydrogen Sulfide Reference Procedure

Principle

The method is based on the absorption of hydrogen sulfide, contained in a dilute calibration stream, by a suspension of cadmium hydroxide and arabino galactan. The formed cadmium sulfide is then reacted with N-N Dimethyl-P-phenylenediamine dihydrochloride and ferric chloride to make methylene blue. The methylene blue formed, proportional to the hydrogen sulfide absorbed, is measured spectrophotometrically.

Reagents

1. Absorbing Solution

Dissolve 2.7 g of anhydrcus cadmium sulfate and 10 g of arabino galactan in approximately 500 ml of distilled water. Dissolve 0.3 g of sodium hydroxide in approximately 100 ml distilled water. Mix the two solutions slowly while stirring. Add distilled water to make 1 liter of absorbing solution. The absorbing solution is stable for 3 months.

2. Test Amine Solution

Dissolve 0.375 g of N-N dimethyl-P-phenylenediamine dihydrochloride in 100 ml of 1:1 (v/v) sulfuric acid. The solution is stable for 6 months.

3. Ferric Chloride Solution

Dissolve 100g of $FeCl_3.6\ H_2O$ in sufficient water to make 100 ml of solution. The solution is stable for 6 months.

Apparatus

1. Midget impingers, such as Ace Glass Inc. Cat. No. 7531.
2. Air pump with flow control and with a minimum capacity of 2 liters per minute through a midget impinger.
3. Spectrophotometer, suitable for measurement at 670 ± 25 nm.
4. Flowmeter, 0 to 2 liter per minute range.
5. Stopwatch.

Sample Collection

1. Preset the air pump to a flowrate of approximately 1 liter per minute. Prepare the sampling train by connecting the flowmeter to the sample manifold (Fig. 1, 1.5.3).

2. Pipet 10.0 ml of thoroughly shaken absorbing solution into a midget impinger. Connect the impinger to the flowmeter and attach the air pump to the exit tube of the impinger.

3. When the calibration stream is stable and at the desired concentration level, start the air pump and the stopwatch. Immediately make the minor adjustment for a desired flow rate of 0.7 liter/min. and maintain flow for a time interval sufficient to collect from 3 to 8 µg of $H_2S$.

4. Take at least two samples for each calibration point.

Analysis

1. Add consecutively 0.3 ml of test amine solution, and one drop of ferric chloride solution to the contents of each impinger. Thoroughly mix to insure that the precipitate has been dissolved, and allow 30 minutes for color development.

2. Prepare a 10.0 ml reagent blank in the same manner as the samples.

3. With the spectrophotometer set at 670 nm, set the reagent blank at 100% T.

4. Read the % transmission of each sample and from a standard curve, obtain the total micrograms of $H_2S$ collected.

Preparation of Standard Curve

1. Dry a crystal of $Na_2S.9\ H_2O$ with clean absorbent paper and break into small pieces.

2. Dissolve 0.71 g of sodium sulfide in distilled water and bring to 1 liter in a 1 liter volumetric flask. This yields a solution containing approximately 100 μg $H_2S$ per ml.

3. Standardize immediately prior to use, using standard solutions of iodine and thiosulfate (Ref. 3).

4. Make proper dilutions with distilled water so as to obtain a working standard solution containing about 10 μg $H_2S$ per ml.

5. Add respectively 0, 0.2, 0.4, 0.6, 0.8, and 1.0 ml of the $H_2S$ working standard to a series of graduated test tubes. Add sufficient volumes of absorbing solution to make 10.0 ml of total volume.

6. Develop color as described above in the Analysis Section.

7. Plot % transmission vs. micrograms $H_2S$ on semi-logarithmic paper to obtain the standard curve.

Calculations

$$\text{PPB } H_2S = \frac{\mu g \ H_2S \text{ From Standard Curve} \times 10^3}{\text{Sample Vol. (liters)} \times 1.4}$$

References

1. Jacobs, et al, Anal. Chem. 29, 1349, 1957

2. Bamesberger, Adams Environ. Sci. and Tech. 3, 258-61 (1969)

3. Kolthoff and Sandell, Textbook of Quantitative Inorganic Analysis, Third Edition, 1952, MacMillan Co.

1.6 Reporting. Data recorded by the required instrumentation shall be examined at least once every seven days to determine whether the allowable limits have been exceeded, and to determine whether the instrumentation has operated properly. Instrument downtime exceeding a continuous 24 hour period and recorded data exceeding allowable limits shall be reported to the APCO within the next mormal working day following examination.

A summary of data obtained during each calendar month shall be submitted to the APCO within 30 days following the end of the month. The summary shall include excesses over allowable limits, mass emission rate from sources, and notations for instrument downtime or other loss of data.

## 2. ATMOSPHERIC SAMPLING OF GROUND LEVEL LEAD CONCENTRATIONS

REF: Regs. 1-510, 11-1-501,
11-1-602 to 11-1-603

2.1 General. This section outlines the procedures to be used for calculation of mass emission limits and for atmospheric sampling of ground level lead concentrations in order to fulfill requirements of Regulations 11-1-302 and 11-1-303.

2.2 Mass Emission Limitations. Emission limitations required to meet Regulation 11-1-302 shall be determined by use of formulas 4.1 and 5.13, and figures 3-3 and 3-9, in "Workbook of Atmospheric Dispersion Estimates," by D. Bruce Turner, Public Health Service Publication No. 999-AP-26, Revised 1969, published by the U.S. Department of Health, Education and Welfare. In using said equations and figures, a neutral or "D" stability category shall be assumed, a wind shall be assumed that remains throughout the averaging period directed within a 22.5° sector of the compass rose at an average speed of two meters per second, and an ambient air temperature of 293°K shall be assumed.

2.3 Instrumentation. The person responsible for emissions of lead, who has elected to be regulated by Regulation 11-1-303 shall provide, install and maintain not less than four directionally controlled high-volume samplers located in the area surrounding the source and shall provide at least one recording meteorological station equipped to record wind speed and wind direction.

2.3.1 Instrument Specification. High-volume samplers, as described in Appendix B, "Reference Method for the Determination of Suspended Particulates in the Atmosphere (High-Volume Method)", Federal Register, Vol. 36, No. 84, Friday, April 30, 1971, shall be fitted with a control device which will cause the sampler to operate only during those periods when the ambient airflow to the sampler is from a specified sector. Means shall be added to record the elapsed time of sampler operation.

2.3.2 Meteorological Instrument Specifications. Meteorological instruments shall be capable of continuously measuring and recording wind direction to within ten degrees of arc, and wind speed to within one mile per hour (mph) at wind speeds less than 25 mph, and with a threshold no greater than 3 mph. The width of the wind recording charts shall be adequate to determine the wind components as specified.

2.4 Instrument Siting. High-volume samplers shall be positioned in pairs along vectors of wind direction passing over the source. The number of wind vectors required for monitoring of a site shall be determined from a wind rose applicable to the site. The wind rose shall be as described in "Some Applications of Statistics to Meteorology", by Hans Panofsky and Glenn Briar, Mineral Industries Extension Service, Pennsylvania State University, pages 15-16, 1958. Two such wind roses shall be used, one for the period November through April, and one for the period May through October. The requirements of this section apply to each one independently.

On each wind rose, a primary vector is drawn in the direction of the most frequent winds, and passing through the emission point. This vector is the centerline of a sector of 45° of arc (vector direction plus and minus 22.5°). Similar treatment of at least one additional vector shall be provided to ensure that the sectors as a group encompass at least one-half of the exposure indicated by the wind rose.

A pair of samplers shall be installed along each vector. One shall be upwind, and its data will be used in determining background concentrations; the other shall be downwind, and its data will be used in determining source-impacted concentrations. These samplers shall be located as close as possible to the points at which maximum ground level concentrations are predicted by dispersion analysis to occur most frequently. In no case shall the location of the sampler be on the property on which the emissions occur unless the person responsible for monitoring agrees in writing that such location shall, for the purpose of District requirements, be deemed off the property.

Meteorological instruments shall be placed as close to the emission source as is practicable while providing a reasonably unobstructed exposure to the flow of ambient air.

Positioning of all instruments shall be determined in consultation with the APCO.

2.5 Instrument Operation. The monitoring system shall be operated for 24 consecutive hours, at least once every three days. During this period, meteorological instruments shall be operated continuously; and all samplers in the system shall be ready to operate, and shall operate whenever the wind direction is within the sector for which controls are set. Samplers shall be operated, and samples obtained, in accordance with the specifications as described in Appendix B, "Reference Method for the Determination of Suspended Particulates in the Atmosphere (High-Volume Method)", Federal Register, Vol. 36, No. 84, Friday, April 30, 1971.

2.5.1 Filter Media. Glass-fiber filters having an initial collection efficiency of at least 99 percent for particles of 0.3 μm. diameter are suitable for sample collection.

2.6 Maintenance. Care and maintenance shall be such that the instruments will function properly and record the lead concentrations in the area.

2.7 Calibration. Calibrations shall be performed to assure that the volume of air sampled is accurately known. High-volume sampler calibrations shall be performed by use of the Calibration Procedure in Appendix B - Reference Method for the Determination of Suspended Particulates in the Atmosphere (High-Volume Method), Federal Register, Vol. 36, No. 84, Friday, April 30, 1971 or any equivalent method.

2.8 Analysis. Lead collected on the filters shall be analyzed by Laboratory Procedure No. 4A "Determination of Lead Content in Atmospheric Particulate Matter". The APCO may require submission of filter samples for comparative analysis.

2.8.1 Data Analysis. Arithmetic means of lead concentrations shall be computed from all samples obtained during a thirty day period. Two separate arithmetic means shall be computed, one for all the background samples and one for all samples influenced by the source. All means shall be running means, updated at each subsequent 24-hour sample to include data for a thirty day period.

2.9 Reporting. A summary of data obtained from sampling and analysis and from the meteorological instrumentation, shall be submitted to the APCO within 30 days following the end of the month.