

SOUTH COAST AIR QUALITY MANAGEMENT DISTRICT

METHOD 7.1

**DETERMINATION OF NITROGEN OXIDE EMISSIONS
FROM STATIONARY SOURCES**

**OFFICE OF OPERATIONS
TECHNICAL SERVICES DIVISION
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METHOD 7.1

DETERMINATION OF NITROGEN OXIDE EMISSIONS FROM STATIONARY SOURCES

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1. Overview

1.1 Principle

A grab sample is collected in an evacuated flask containing a dilute sulfuric acid-hydrogen peroxide absorbing solution, and the nitrogen oxides except nitrous oxide are measured colorimetrically using the phenoldisulfonic acid (PDS) procedure or ion chromatograph procedures (see Section 5).

1.2 Applicability

This method measures nitrogen oxides (NO_x) emitted from stationary sources. Its range is 2 to 400 mg NO_x (as NO_2) per dry standard cubic meter, without diluting the sample.

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2. Field Procedures

2.1 Sampling Apparatus

Sample collection requires the equipment listed below and shown in Figure 7.1-1.

a. Probe

Borosilicate glass tubing, sufficiently heated to prevent water condensation and equipped with an in-stack or out-stack filter to remove particulate matter. (A plug of glass wool is satisfactory for this purpose.) Stainless steel or Teflon tubing also may be used for the probe. Heating is not necessary if the probe remains dry during the purging period, or less than 2 percent of the NO_x present is NO_2 .

b. Collection Flask

Two-liter borosilicate, round bottom flask, with short neck and 24/40 standard taper opening, protected against implosion or breakage with a T-bore stopcock connected to a 24/40 standard taper joint. Alternatively, this flask may have the short neck replaced with 48 mm (1 1/2 in.) long 12 mm (1/2 in.) glass tubing sealed with rubber tubing and screw clamp. Flasks must be calibrated to the nearest 10 ml.

No difference in NO_x results has been observed between the use of rubber tubing and the use of ground joints. Ground glass joints tend to have more leakage problems than do rubber tubing and screw clamps. When tubing is used, the surface area exposed to the sample should be minimized. See Section 3.9 for calibration procedure.

c. Vacuum Line

Tubing capable of withstanding a vacuum of 75 mm (3 in.) Hg absolute pressure, with "T"

connection and T-bore stopcock or rubber tubing and screw clamp.

d. Vacuum Gauge

The collection flask must be equipped with a vacuum gauge capable of measuring to 760 mm (30 in.) Hg with 2.5 mm (0.1 in.) Hg division.

e. One-way Squeeze Bulb

f. Stopcock and Ground Joint Grease

A high vacuum, high temperature chlorofluorocarbon grease is required when ground glass joints are used. Halocarbon 25-SS is effective.

g. Pump

2.2 Sampling Reagents

a. Sulfuric Acid-Hydrogen Peroxide Solution

See Section 3.2.1 for preparation procedure.

The solution should be prepared daily and not exposed to extreme heat or direct sunlight.

2.3 Preparation of Sampling Equipment

This may be done in the laboratory prior to the test. Use two-liter round bottom flasks. Add 25 ml of absorbing solution to each flask. Evacuate the flask to the vapor pressure of the solution, tightly close the screw clamp and insert a solid glass plug (optional) into the open end of the tubing until ready for sampling.

2.4 Sampling Procedure

Assemble the sampling train as shown in Figure 7.1-1 and place the probe at the sampling point. (Select the sampling point as in Method 3.1, Section 2.2.) Make sure all fittings are tight and leak-free, and if necessary all glass joints have been properly greased with a high-

temperature, chlorfluorocarbon-based stopcock grease.

Turn the flask valve and the pump to the "evacuate" positions. Evacuate the flask to a pressure approaching the vapor pressure of water at the existing temperature. Turn the pump valve to its "vent" position and turn off the pump. Check for leakage by observing the manometer for any pressure fluctuation. A variation more than 10 mm (0.4 in.) Hg over a period of one minute is unacceptable. Do not use the flask until the leakage problem is corrected. If flasks are evacuated prior to setup, the evacuation steps are unnecessary.

Turn the flask valve counterclockwise to its "purge" position. Purge the probe and the vacuum tube using the squeeze bulb. If condensation occurs in the probe and the flask valve area, heat the probe and purge until the condensation disappears. Turn the pump valve to its "vent" position. Turn the flask valve clockwise to its "evacuate" position and record the difference in the mercury levels in the manometer. The absolute internal pressure in the flask (P_i) is equal to

the barometric pressure, minus the manometer reading.

Immediately turn the flask valve to the "sample" position and permit the gas to enter the flask until pressure in the flask and sample line (i.e. duct stack) are equal. (Vacuum gauge should read near zero.) This will usually require about 15 seconds; a longer period indicates a "plug" in the probe, which must be corrected before sampling is continued.

After collecting the sample, turn valve to its "purge" position and disconnect the flask sampling train. Shake the flask for at least 5 minutes. Alternatively, open or close the screw clamps in the appropriate manner to achieve the same results, i.e. (1) purge, (2) vacuum check, (3) sample, (4) seal flask, (5) shake.

When an alternate setup is used, perform all the above operations by opening and closing the appropriate screw clamps.

Record data on a form similar to Figure 7.1-2.

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3. Laboratory Procedures

3.1 Apparatus

3.1.1 Sampling Apparatus

- a. Probe, Collection Flask, Vacuum Line,
Vacuum Gauge, Squeeze Bulb

See Section 2.1.

- b. Pipet

Class A, 25 ml

3.1.2 Sample Recovery

- a. Graduated Cylinder, 50 ml with 1 ml
Divisions

- b. Polyethylene Wash Bottle
- c. Glass Stirring Rod
- d. Test Paper for Indicating pH,
Range 7 to 14
- e. Mercury Manometer, or Calibrated
Electronic Manometer, with Fitting for
Sample Bulb Attachment
- f. Thermometer

Ambient range, °C, traceable to NBS
thermometer.

3.1.3 Analysis

For the analysis, including calibration,
the following equipment is needed:

- a. Volumetric Pipets

Class A, or a microburet to measure 2,
4, 6, 8, 10, 12, 16 and 20 ml of
working calibration solution; one 100
ml, class A pipet.

b. Porcelain Evaporating Dishes

250 ml capacity with lip for pouring,
one for each sample and each standard.
The Coors NO-45006 (shallow-form, 196
ml) is satisfactory.

c. Steam Bath

Low-temperature oven or
thermostatically controlled hot plates
kept below 70°C (158°F) are acceptable
alternatives.

d. Dropping Pipet or Dropper

Three required.

e. Glass Rod

One for each sample, blank, and
standard.

f. Graduated Cylinder

100 ml with 1 ml divisions.

g. Volumetric Flasks

Class A, 1000 ml (four).

h. Spectrophotometer

To measure absorbance at 405 nm, using
a 10 mm cell.

i. Graduated Pipet, 10 ml, 0.1 ml
divisions

j. Test Paper for Indicating pH, Range 7
to 14 pH

k. Analytical Balance

To measure to within 0.1 mg.

l. Centrifuge

To remove solid contained in sample.

m. Graduated Centrifuge Tube, 50 ml, 1 ml
Divisions

3.2 Reagents

Unless otherwise indicated, it is intended that all reagent conform to the specification established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available; otherwise, use the best available grade.

3.2.1 Sampling

To prepare the absorbing solution, cautiously add 2.8 ml concentrated H_2SO_4 to 1 liter of water. Mix well and add 2 ml of 30 percent H_2O_2 . The absorbing solution should be prepared daily. Do not expose to extreme heat or direct sunlight.

3.2.2 Sample Recovery

a. Sodium Hydroxide (NaOH), 1N

Dissolve 40 g NaOH in water and dilute to 1 liter.

b. Water

Deionized, distilled to conform to ASTM specification D1193-77, Type 3. At the option of the chemist, the KMnO_4 test for oxidizable organic matter may be omitted when high concentrations of organic matters are not expected to be present. Reference to water throughout this method implies deionized, distilled water.

3.2.3 Analysis

a. Fuming Sulfuric Acid (H_2SO_4)

15 to 18 percent, by weight, free SO_3 .
HANDLE WITH CAUTION. Used to make phenoldisulfonic acid (PDSA) reagent:
See Section 3.2.3.h.

b. Phenol

White solid. Used to make phenoldisulfonic acid (PDSA) reagent:
See Section 3.2.3.h.

c. Sulfuric Acid (H_2SO_4)

Concentrated, 95 percent minimum assay. Handle with care.

d. Potassium Nitrate (KNO_3)

Dried at 105 to 110°C (220 to 230°F) for a minimum of 2 hours just prior to preparation of standard solution.

e. Standard KNO_3 Solution

Dissolve exactly 0.5495 g of dried KNO_3 in water and dilute to 1 liter with water in a 1000 ml volumetric flask. One milliliter of this standard solution contains the equivalent of 0.250 mg of NO_2 .

f. Working Standard KNO_3 Solution

Dilute 100 ml of the standard solution to 1000 ml with water. One milliliter of the working standard solution is equivalent to 0.025 mg of NO_2 .

g. Water

See Section 2.2.2.

h. Phenoldisulfonic Acid Solution

Dissolve 25 g of pure white phenol in 150 ml concentrated H_2SO_4 , and heat at 100°C (212°F) for 2 hours. Store in a dark stoppered bottle. Protect from ambient moisture at all times.

Phenoldisulfonic acid purchased from a commercial source should be rejected if blank absorbance is greater than 0.030, and if linearity is not obtained during calibration (see Section 3.8).

3.3 Pretest Preparation

All equipment; including the balance, steam bath, centrifuge, spectrophotometer, cleaned glassware, reagents, and safety equipment should be checked for readiness before conducting the following procedure.

3.4 Preparation of Sample Collection Flask

Use two-liter round bottom flasks for sampling. Add 25 ml of absorbing solution to each flask. Reserve a portion of this reagent for a blank and for control preparation. Evacuate the flask to the vapor pressure of the solution, tightly close the screw clamp, and insert a solid glass plug (optional) into the open end of the tubing. Pack the flasks in a sturdy box for transport to the field. Prepare fresh flasks each day.

NOTE: No difference in NO_x results have been observed with use of rubber tubing as compared to glass joints. In addition, rubber tubing has been virtually leak-free as compared to glass joints.

3.5 Sample Collection Flask Leak Check

Check for sample flask leakage during the flask evacuation step (see Section 3.4). The contents of the flask will boil when evacuated if no leak is present. More leak checks may be performed in the field with a manometer or vacuum gauge, though these checks may be avoided by sampling in triplicate or quadruplicate. The analytical

results will indicate which flasks may have leaked and should be rejected.

Check the flask screw clamps (if used) as soon as flasks are returned to the laboratory. Record the presence of slightly loose clamps for consideration in comparing flask analytical results. Very loose clamps are clear cause for rejection.

3.6 Sample Recovery

Shake the sealed collection flasks for 15 minutes on a mechanical shaker, and rotate frequently to provide a thorough scrubbing action. Allow the flasks to stand overnight (or at least 16 hours) to ensure complete oxidation and absorption of the oxides of nitrogen by the solution. When absorption is complete, the oxides of nitrogen (except nitrous oxide) will be converted to HNO_3 . Record the temperature and absolute gas pressure in each flask. Rinse the contents into a 200 ml evaporating dish, using three 15 ml portions of water. Prepare a blank using the same amount of absorbing solution and wash water as used for each sampling flask.

3.7 Analysis

Add 1 N sodium hydroxide to the solution in each evaporating dish, including the blank, until it is barely alkaline ($\text{pH} > 9$) to litmus paper. Evaporate the solution in the evaporating dish to dryness on a steam bath and allow to cool. Add 2 ml phenoldisulfonic acid solution to the dried residue and titrate thoroughly with a glass rod. Make sure the solution contacts all the residue. Add 1 ml water and four drops of concentrated H_2SO_4 . Heat the solution on a steam bath for 3 minutes with occasional stirring. Allow the solution to cool, add 20 ml water, mix well by stirring, and add 10 ml of concentrated NH_4OH , dropwise with constant stirring. Transfer the solution to a 50 ml graduated centrifuge tube, washing the evaporating dish three times with 5 ml portions of water. Dilute to the mark with water, stir thoroughly, and centrifuge. Transfer the clear solution to a spectrophotometer cell.

Measure absorbance of each solution against the reagent blank at a wavelength of 405 nm. If a greater dilution of the sample is required, dilute the blank to the same volume. Thinner cells or dilution blocks may be used. Process

and dilute each sample determination in a manner similar to that used in preparing the corresponding concentration range of the standard curves. In each case, subtract the blank reading from the sample reading. The dilution used for obtaining the calibration curves in the ranges given may have to be varied, depending on the make of spectrophotometer used.

Determine the weight of NO₂, in milligrams, from the light absorption reading on the calibration curve corresponding to dilution used. See Section 3.9 for calibrations.

3.8 Calculations and Reporting

$$\text{NO}_2 = \frac{\text{Net OD} \times \text{Calibration Factor} \times 515 \times 760 \times T}{\text{Net Pressure} \times \text{Net Volume} \times 288.6}$$

where:

$$\text{NO}_2 = \text{NO}_x \text{ as NO}_2, \text{ ppm}$$

$$\text{Net OD} = \text{Sample light absorption} - \text{blank light absorption}$$

Calibration = $\mu\text{g NO}_2/\text{OD}$, from calibration
Factor curve

T = Temperature in the flask, $^{\circ}\text{K}$

Net Pressure = Measured pressure in the flask,
minus the water vapor pressure
at temperature T, mm Hg

Net Volume = Volume of flask - 25 ml (volume
of absorbing solution in the
flask), liters

Report NO_x as NO_2 (ppm), using three significant
figures. Discard decimal digits. Round the
third digit to the nearest 5.

3.9 Calibration

3.9.1 PDSA

For a 0-10 ppm calibration curve, use
pipets or a microburet to transfer 0.0
(blank), 2.0, 4.0, 6.0, 8.0, 10.0, 12.0,
16.0, and 20.0 ml of potassium nitrate
working standard solution into separate
200 ml evaporating dishes, and add 25 ml

of absorbing solution to each evaporating dish. Follow as directed in Section 3.7. Read the light absorption of each solution and subtract the blank reading. If absorption is too high, dilute appropriately with distilled water.

Construct the curve for the concentration range by plotting the net light absorption of the solution as ordinate against milligrams of NO_2 as abscissa, or use a calculator programmed for linear regression analysis:

$$Y = m x + b,$$

where:

m = slope

b = intercept

3.9.2 Flask Calibration

The temperature of the water is measured.
Volume is calculated according to the
formula.

$$v = \frac{w_1 - w_2}{D_t}$$

where:

v = Volume of the bulb, ml

w_1 = Weight of flask and water, g

w_2 = Weight of empty flask, g

D_t = Density of water, g/ml
at temperature, t

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4. Engineering Calculations and Reporting

When mass emission rate of NO_x is required, follow this calculation.

lb of NO_x per hour = A.B.C.D

$$= (\text{ppm NO}_x) (46) (1.58 \times 10^{-7}) (\text{dscfm})$$

A = NO_x concentration in ppm

B = Molecular weight of NO₂, 46 lb/lb-mole

C = Conversion factor, 1.58×10^{-7}

$$= (10^{-6} \text{ ppm}) (60 \text{ min./hr}) (379 \text{ cu ft/lb-mole})$$

D = Dry standard stack gas flow rate per
minute measured, dscfm (follow Method 2.1)

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5. Alternative Laboratory Procedures

5.1 Apparatus

5.1.1 Preparation of Sample Collection Flask

See Section 3.4.

Same as Section 2.1 b.

5.1.2 Sample Recovery

a. Class A 50 ml Volumetric Flask

One for each sample and blank.

b. Polyethylene Wash Bottle

c. Manometer

Capable of reading to 1mm within the 0 to 900mm Hg range.

d. NBS Traceable Thermometer

e. Sample Shaker

5.1.3 Analysis

a. Volumetric Pipets

Class A, one 10 ml for each sample and blank, 100 ml for working standard preparation.

10 ml, 15 ml, 20 ml, 25 ml, 50 ml, and graduated 5 ml Class A pipets, or microburet for calibration standard dilutions.

b. Volumetric Flasks

Class A, one 50 ml flask for each sample and blank, two 50 ml for each

calibration standard, and two 100 ml
for stock and working standard
preparation.

c. Ion Chromatograph

Capable of detecting and resolving 0.1
ppm nitrate in the presence of dilute
($<0.01N$) sulfuric acid.

d. Recorder or Integrator

e. Analytical Balance

Capable of weighing to 0.1 mg.

5.2 Reagents

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

5.2.1 Sampling

Absorbing solution. Same as Section
3.2.1.

5.2.2 Sample Recovery

See Section 3.2.2.

5.2.3 Analysis

a. Potassium Nitrate (KNO_3)

Dried at 105 to 110°C for a minimum of
2 hours, and desiccated to room
temperature just before use.

b. Standard KNO_3 Solution

0.5495 g dried KNO_3 dissolved in 1
liter of water.

c. Working Standard KNO_3 Solution

Dilute 100 ml of KNO_3 standard
solution to 1000 ml with water.

d. Water

See Section 3.2.2.

5.3 Preparation of Sample Collection Flask

See Section 3.4.

5.4 Sample Collection Flask Leak Check

See Section 3.5.

5.5 Sample Recovery

Shake samples and allow to stand overnight as in Section 3.6. Measure and record the temperature and absolute gas pressure in each flask. Recover the contents of each flask into a 50 ml volumetric flask with at least three rinsings, then dilute to volume and mix well.

5.6 Sample Analysis

Dilute a 10 ml aliquot of each sample to 50 ml. Set the instrument response as close as possible to maximum on the highest standard, then run the

calibration curve, the reagent blank, and each sample once. Dilute samples that are too high into range. Samples that are too low require an additional standard dilution and more sensitive instrument settings. Run a control for each set of samples or each ten samples, whichever is fewer. Rerun the calibration curve at the end of the analysis.

5.7 Calibration

A five-point calibration curve in 0.01N H₂SO₄ is made from the working standard as follows:

2 ml KNO₃ working standard solution diluted to 50 ml. Take 2 ml of the working solution and 5 ml of 0.1N H₂SO₄, and dilute to 50 ml with water.

5 ml KNO₃ working standard solution diluted to 50 ml. Take 5 ml of the working solution and 5 ml of 0.1N H₂SO₄, and dilute to 50 ml with water.

10 ml KNO₃ working standard solution diluted to 50 ml. Take 10 ml of the working solution and 5 ml of 0.1N H₂SO₄, and dilute to 50 ml with water.

15 ml KNO_3 working standard solution diluted to 50 ml. Take 15 ml of the working solution and 5 ml of 0.1N H_2SO_4 , and dilute to 50 ml with water.

25 ml KNO_3 working standard solution diluted to 50 ml. Take 25 ml of the working solution and 5 ml of 0.1N H_2SO_4 , and dilute to 50 ml with water.

This corresponds to a sample range of 50 μg NO_2 to 625 μg NO_2 per sample or approximately 12 to 150 ppm.

The calibration curve must bracket all sample concentrations. Dilute a sample that is too high to fall within the range of the calibration curve. For samples that are too low, make another standard solution using 1 ml of the working standard solution (25 μg), delete the highest standard (625 μg), and maximize the instrument response on the next highest standard (375 μg). Rerun the analysis.

Calculate linear regression of total μg NO_2 and peak height using all standard points. Remake and rerun any standard point that deviates by 7 percent or more from expected. A change of instrument response over the course of the run by

10 percent or more invalidates the analysis. A difference of the measured control concentration from the theoretical concentration by 10 percent or more invalidates the analysis.

5.8 Calculations

Calculate the NO₂ in µg for each sample using the linear regression, expressed as:

$$\text{NO}_2 = m \cdot h + b$$

where:

m = Slope

b = Intercept of the regression

h = Sample peak height

Then calculate NO₂ as ppm for each sample, using the following equation:

$$\text{NO}_2 = \frac{\mu\text{g NO}_2 \times 0.515 \times 760 \times T}{\text{Net Pressure} \times \text{Net Volume} \times 288.6}$$

where:

NO_2 = NO_x as NO_2 (ppm v/v)

$\mu\text{g NO}_2$ = Micrograms of NO_2 of the sample
being calculated

T = Temperature of the flask, $^{\circ}\text{K}$

Net Pressure = Measured pressure of the flask,
minus the water pressure, at
temperature T, mm Hg

Net Volume = Volume of the flask, liters

Report NO_x as NO_2 (ppm) using three significant
figures.

Round the third digit to the nearest 5.

5.9 Quality Control

Run suitable blank and control samples with each set of samples or each ten samples, whichever is fewer. Blank consists of reagent reserved from sample preparation.

Suitable control consists of an EPA.QA vial, prepared as directed, and analyzed with the samples. Measured value must be within 10 percent of the theoretical value. A control that falls outside of the range requires instrument recalibration and reanalysis of the sample(s). Change in instrument response of more than 10 percent from the beginning to the end of the run also requires instrument recalibration and reanalysis of the sample(s).

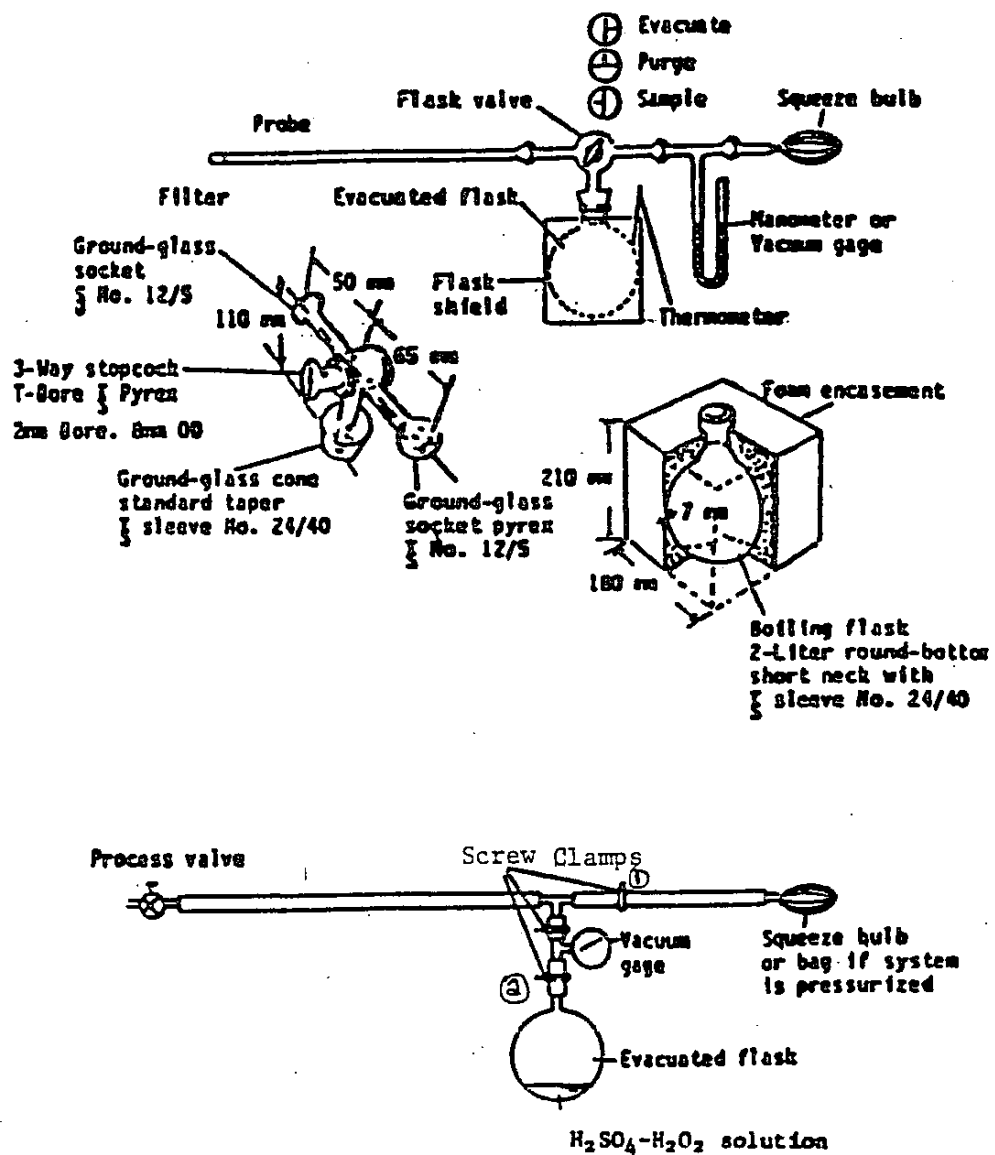


Figure 7.1-1
NO_x Sampling Train

Page No. _____

TEST No. _____

GAS SAMPLING DATA SHEET

Сопразу

Basic/Control Equipment

[illegible]

Sample Collected By _____

Figure 7.1-2

Gas Sampling Data Sheet