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Industrial hygiene sampling and analytical methods were developed and validated under a follow-up research effort to develop measurement methods which failed to validate under the joint NIOSH/OSHA Standards Completion Program. This is the fifth set of 10 methods in an effort to develop methods for 130 substances. Monitoring methods for the following substances are included:

S199	Mercury	S354	Copper (fume)
S321	Nitric Oxide	S320	Nitrogen Dioxide
S319	Nitric Acid	S334	Phosphorus (yellow)
S327	Formaldehyde	S371	Methoxyclor
S288	Hydrogen Cyanide	S374	Methylcyclohexanol

17. Key Words and Document Analysis. 17a. Descriptors

Chemical analysis
Sampling

*Mercury
*Nitric Oxide
*Nitric Acid
*Formaldehyde
*Hydrogen Cyanide
*Copper (fume)
*Nitrogen Dioxide
*Phosphorus (yellow)
*Methoxyclor
*Methylcyclohexanol

17b. Identifiers/Open-Ended Terms

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Ten NIOSH Analytical Methods Set-5

A joint National Institute for Occupational Safety and Health (NIOSH)/Occupational Safety and Health Administration (OSHA) Standards Completion Program will complete standards for approximately 400 air contaminants presently listed in Tables Z-1, Z-2, and Z-3 of 29 CFR Part 1910.1000 by adding other requirements of a standard required under Section 6(b)(7) and 8(c)(3) of the Occupational Safety and Health Act of 1970 (PL 91-596). These completed standards will then contain, in addition to the permissible exposure limit given in 1910.1000, appropriate provisions requiring monitoring of worker exposure, engineering control, personal protection, employee training, medical surveillance, and recordkeeping.

As a part of the Standards Completion Program, NIOSH engaged in a two-year study under contract CDC-99-74-45 to validate sampling and analytical procedures for use in monitoring worker exposure to substances listed in Tables Z-1, Z-2, and Z-3. One hundred seventy of the methods failed to validate under the guidelines of the SCP. One hundred thirty of the 170 methods which failed are being developed and validated in a follow-up project. These 10 methods have been validated and thus may be used for determining compliance with the standard or the need for control, for research, or whenever there is a need to measure airborne concentrations in the workplace. These analytical methods should not be considered the only methods which may be used to evaluate worker exposure. Other methods meeting the accuracy requirements in the standard may also be used.

These analytical methods will be periodically modified as new developments in Science and technology require.

Mercury
Nitric Oxide
Nitric Acid
Formaldehyde
Hydrogen Cyanide

Copper (fume)
Nitrogen Dioxide
Phosphorus (yellow)
Methoxyclor
Methylcyclohexanol

U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
Public Health Service
Center for Disease Control
National Institute for Occupational Safety and Health
Division of Physical Sciences and Engineering
Cincinnati, Ohio

July 1978

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Mercury

Analyte:	Mercury	Method No.:	S199
Matrix:	Air	Range:	0.046-0.18 mg/cu m
OSHA Standard:	0.1 mg/cu m - Ceiling	Precision ($\overline{CV}_T$):	0.061
Procedure:	Adsorption on silvered Chromosorb P, thermal desorption, flameless AA	Validation Date:	7/8/77

1. Principle of the Method

1.1 A known volume of air is drawn through a glass tube containing silvered Chromosorb P (AgCP) to trap mercury vapors. A cellulose ester membrane filter is connected to the front of the sorbent tube to collect particulate mercury interference.

1.2 The sample is analyzed by thermally desorbing the mercury and passing it through the absorption cell of a flameless atomic absorption spectrophotometer.

2. Range and Sensitivity

2.1 This method was validated over the range of 0.0456-0.1800 mg/cu m at an atmospheric temperature of 23°C and atmospheric pressure of 760 mm Hg, using a 3-L sample. The method is capable of measuring smaller amounts. A longer AA absorption cell path length may be needed for levels below 0.01 mg/cu m. The range of the absorption cell must be determined by calibration.

2.2 The upper limit of the range of the method depends in most part upon the capacity of the AA detector with the particular absorption cell used. The detector may be saturated at amounts of mercury greater than those in the acceptable range for the absorption cell. To extend the range, a shorter absorption cell path length may be needed. Scale expansion can extend the measurable range to a limited degree. It is unlikely that the absorptive capacity of the AgCP will affect the upper limit of the range of the method in view of the analytical limitations.

Breakthrough is defined as the time that the effluent concentration from the collection tube (containing 30 mg of AgCP) reaches 5% of the concentration in the test gas mixture. Breakthrough did not occur after sampling for 3.5 hours at an average sampling rate of

0.184 liter/minute and relative humidity of 85% and temperature of 25°C. The breakthrough test was conducted at a concentration of 0.244 mg/cu m.

3. Interferences

3.1 Loading the prefilter with excess particulate will increase air flow resistance through the sampler. This may overload the battery-operated sampling pumps.

3.2 It has been reported that AgCP absorbs methyl mercury chloride. Most other organomercury compounds are not retained.

3.3 Strong oxidizing vapors and gases, particularly chlorine, which attack silver, reduce the efficiency of the sampling tube, but do not interfere in the analysis of the sample. These interferences should not be a problem under normal sampling conditions.

3.4 When other compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 0.0456-0.1800 mg/cu m was 0.061. This value corresponds to a 0.0006 mg/cu m standard deviation at the OSHA standard level. Statistical information can be found in Reference 11.1. Details of the test procedures are found in Reference 11.2.

4.2 On the average the concentrations obtained in the laboratory validation study at 0.5X, 1X, and 2X the OSHA standard level were 0.7% higher than the "true" concentrations for 17 samples. Any difference between the "found" and "true" concentrations may not represent a bias in the sampling and analytical method, but rather a random variation from the experimentally determined "true" concentration. Therefore, the method has no bias. The Coefficient of Variation is a good measure of the accuracy of the method since the recoveries and storage stability were good. Storage stability studies on samples collected from a test atmosphere at a concentration of 0.0927 mg/cu m indicate that collected samples are stable for at least 7 days.

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal and the tubes are analyzed by means of a quick, instrumental method.

5.2 A disadvantage of the method is that the range is limited by the path length of the AA absorption cell(s) used in the analytical system.

5.3 The precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

5.4 A disadvantage of the method is the care needed to avoid contamination of the outer surfaces of the sampling tubes.

5.5 Another disadvantage is that the complete sample is used in the anasis. However, the sample may be recollected on a AgCP tube after passage through the AA absorption cell and reanalyzed.

6. Apparatus

6.1 Personal Sampling Pump: A calibrated personal sampling pump whose flow rate can be determined within 5% at the recommended flow rate.

6.2 Silvered Chromosorb P (AgCP) Tubes: These tubes are available on special order from SKC, Inc.* If sampling tubes are to be prepared, the preparation of AgCP is described in Section 8.2. The sorbent tube consists of a glass tube with both ends unsealed, (2 cm long with a 6-mm O.D. and a 4-mm I.D.) containing 30 mg of AgCP. A plug of glass wool, preferably quartz glass wool, is placed at the ends of the tube. The sampling tube is thermally desorbed in the thermal desorption apparatus as described in the analytical procedure to rid the sorbent of any background interferences. The tube is removed from the thermal desorption unit and allowed to cool. Caution: The tubes are hot when they are removed from the thermal desorption unit and should be dropped directly into a vial for cooling and storage. The sampling tube is sealed in the vial until it is used.

6.3 Prefilter unit: The sample tube is preceded by a 0.8-micrometer/37-mm cellulose ester membrane filter to collect particulate mercury. The filter is placed in a cassette filter holder, and the filter is supported by a cellulose backup pad.

6.4 Thermal Desorption Unit and Analysis System: A detailed description of the apparatus and instructions for installation and operation are given in Appendix A.

6.5 Flameless atomic absorption mercury analyzer with recorder set at 253.7 nm; Coleman Mercury Analysis System (MAS-50) or equivalent atomic absorption spectrophotometer.

6.6 Absorption Cell: 4.0 cm length (3.7 cm inside diameter), made of Pyrex glass with quartz windows. Satisfactory results may be obtained with different path length cells. The system used must be calibrated over the expected concentration range.

6.7 Microliter Syringes: 10-microliter for preparing standards.

6.8 Pipets: Delivery type, 1.0-mL and other convenient sizes.

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* SKC, Inc., Rd. 1 #395 Valley View Rd., Eighty Four, PA 15330

6.9 Volumetric Flasks: 10-mL and other convenient sizes for preparing standard solutions.

6.10 Thermometer.

6.11 Manometer.

6.12 Stopwatch.

7. Reagents

All reagents must be ACS reagent grade or better.

7.1 Mercuric chloride. Other stable mercury salts or conventional atomic absorption standards may be used.

7.2 Nitric acid.

7.3 Distilled or deionized water.

7.4 The following reagents are used in the preparation of AgCP:

7.4.1 Chromosorb P, non-acid washed, 30/60 mesh. Chromosorb P is a diatomaceous earth material primarily used as a gas chromatographic support. It is manufactured by Johns-Manville and is available from most gas chromatography equipment suppliers.

7.4.2 Silver nitrate.

7.4.3 Ammonium hydroxide.

7.4.4 Potassium hydroxide.

7.4.5 Dextrose.

8. Procedure

8.1 Cleaning of Equipment. Glassware used for preparing standards should be detergent washed, thoroughly rinsed with dilute nitric acid, distilled water, and dried.

8.2 Preparation of Silvered Chromosorb P (AgCP):

Caution: Use face shield and rubber gloves.

8.2.1 Dissolve 20 g silver nitrate in 300 mL of distilled water (Solution A) in a 1000-mL beaker.

8.2.2 Place a magnetic stirring bar in the solution and stir on a magnetic stirrer.

8.2.3 Slowly add concentrated ammonium hydroxide until a dark brown precipitate of silver oxide forms.

8.2.4 While stirring, add concentrated ammonium hydroxide dropwise until the solution just clears. Disregard any small specks which may form.

8.2.5 Take another 2 g of silver nitrate and dissolve in 30 mL distilled water in a separatory funnel (Solution B). Add this solution dropwise to the mixture in the 1000 mL beaker (Section 8.2.4) until the solution turns straw yellow.

8.2.6 Slowly add 100 mL of potassium hydroxide solution (14 g KOH in 100 mL of water) while constantly stirring.

8.2.7 Add concentrated ammonium hydroxide dropwise until the solution in the 1000-mL beaker just clears.

8.2.8 Add more Solution B until a thin straw yellow or light brown precipitate forms. Again disregard any small specks.

8.2.9 Remove the 1000-mL beaker from the stirrer and filter the solution (Solution C) through glass wool.

8.2.10 Dissolve 7.8 g dextrose in 120 mL of distilled water in a 1000-mL Erlenmeyer flask and add 40 g of Chromosorb P to the dextrose solution.

8.2.11 Swirl the Chromosorb P in the dextrose solution until the surfaces are wet and then carefully decant any excess dextrose solution.

8.2.12 Slowly add the silver solution (Solution C - Section 8.2.9) to the Chromosorb P, stopper the flask, and shake vigorously until all the surfaces come in contact with the silver solution.

8.2.13 Decant and discard the excess silver solution.

8.2.14 Rinse and decant the silvered Chromosorb P (AgCP) three times with distilled water.

8.2.15 Dry the AgCP in a drying oven at 60°C. Note: Dry in an atmosphere free of sulfides.

8.3 Calibration of Sampling Pumps. Each personal sampling pump must be calibrated with a representative AgCP tube and prefilter in the line to minimize errors associated with uncertainties in the volume sampled.

8.4 Collection and Shipping of Samples

8.4.1 Clean lint free gloves or laboratory wipers should be used when handling the sampling tubes. After the sampling tubes have been prepared and stored, they should be stable indefinitely. Immediately before sampling, remove the sample tube from the vial.

8.4.2 The sample tube is preceded by a 0.8-micrometer/37-mm cellulose ester membrane filter to collect particulate mercury. The filter is placed in a cassette filter holder, and the filter is supported by a cellulose backup pad. The prefilter is

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connected to the sample tube with a short piece of flexible tubing.

8.4.3 The sample tube should be placed nearer the sampling pump and in a vertical position during sampling to avoid channeling through the the AgCP.

8.4.4 Air being sampled should not be passed through any hose or tubing before entering the filter holder. A minimum amount of flexible tubing should be used to connect the filter holder to the sample tube.

8.4.5 A sample size of 3 L is recommended. Sample at a flow rate between 0.01 and 0.2 liter/minute. Do not sample at a flow rate less than 0.01 liter/minute. For ceiling measurements, sample for 15 minutes. Record sampling time, flow rate, and type of sampling pump used.

8.4.6 The temperature, pressure, and relative humidity of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.

8.4.7 After sampling, disconnect the filter cassette from the sampling tube. Return the AgCP tube to the glass vial. Insert cotton into the vial to prevent breakage of the tube during shipping. Gloves or wipers should be used when handling the sample tube. The prefilter should be discarded after sampling, and the filter cassette holder should be cleaned for future use.

8.4.8 With each batch of ten samples, submit one tube from the same lot of tubes used for sample collection. This tube must be subjected to exactly the same handling as the samples except that no air is drawn through it. This tube should be labeled as the blank.

8.4.9 Vials containing the sample tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.4.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap or equivalent. This sample should not be transported in the same container as the AgCP sample tubes.

8.5 Analysis of Samples

8.5.1 Preparation of Analysis System. Turn on the atomic absorption spectrophotometer and allow the instrument to stabilize. Turn on the heating tape and the vacuum pump. Observe the rotameter to insure that the flow through the critical orifice has not been interrupted. It should be at approximately 1.0 liter/minute. Turn on the cooling air and adjust the flow to 20 liters/minute. Turn on the recorder, and allow it to stabilize. Adjust the spectrophotometer to the desired 0 and 100% T settings. Purge the thermal desorption system before analyzing samples by heating the first desorption section for 60 seconds and allowing it to cool for 60 seconds. Heat the second section for 30 seconds, and allow the desorption unit to cool for 1 minute before analyzing samples.

Note: The thermal desorption system must be optimized so that 100% of the mercury is desorbed from the AgCP tube in one heating (Appendix A).

8.5.2 Preparation of Samples. Remove the clamp between the loading mechanism and desorption unit and insert the AgCP sample tube. Push the sample tube into the first desorption section using the plunger of the loading mechanism and replace the clamp.

8.5.3 Desorption of Samples. Turn the switch to heat the first section of the thermal desorption unit and heat the sampling tube for 60 seconds; allow it to cool for 60 seconds. Turn the switch to heat the second section for 30 seconds. Any mercury desorbed from the sample tube should produce an absorption signal at this time. Allow the thermal desorption unit to cool for about 30 seconds before opening the clamp on the loading mechanism to unload the used sample tube.

Caution: The sample tube is very hot when it comes out of the desorption unit. Do not touch the tube with bare hands. Drop the hot tube into a dry beaker to cool.

Note: If the used sample tube does not drop when the plunger is removed, a narrow spatula may be used to loosen the tube. The AgCP sample tubes are reusable.

8.5.4 The absorption signal is recorded as a very sharp peak on the recorder. The height of the sample peak is measured, and the mercury level is read from a standard curve prepared as discussed below.

9. Calibration and Standards

A series of standards, varying in concentration over the range corresponding to approximately 0.1 to 3 times the OSHA standard for the sample under study, is prepared and analyzed under the same conditions and during the same time period as the unknown samples. Curves are established by plotting micrograms versus peak height. Standards must be analyzed at the same time that the sample analysis is done. This will minimize the effect of known day-to-day variations and variations during the same day of the AA response.

9.1 Stock Solution: Prepare a stock standard solution containing 1.35 mg/mL mercuric chloride in 1% nitric acid. This is equivalent to 1.0 mg/mL mercury. Conventional atomic absorption standards, any stable mercury salt, or metallic mercury (dissolved in concentrated nitric acid) may be used.

9.2 Standard Working Solution A: 0.1 mg/mL, prepared by diluting 1.00 mL of stock solution to 10 mL with 1% nitric acid.

9.3 Standard Working Solution B: 0.03 mg/mL, prepared by diluting 3.00 mL of stock solution to 100 mL with 1% nitric acid.

9.4 Aliquots of 1 to 10 microliters are withdrawn from the working standards by microliter syringe and injected directly onto the AgCP in the sample tube. Prepare at least 5 working standards to cover the range of 0.03-0.09 microgram mercury. This range is based on a 3-L sample. No more than 10 microliters of the standard should be injected on the AgCP because of the small volume of sorbent. The standards are immediately desorbed and analyzed.

9.5 Prepare a standard calibration curve by plotting micrograms of mercury versus peak height. A minimum of five standards, replicated three times at each level, should be used in preparing the calibration curve.

10. Calculations

10.1 Read the weight, in micrograms, corresponding to each peak height from the standard curve.

10.2 Corrections for the blank must be made for each sample.

micrograms = micrograms sample - micrograms blank

where:

micrograms sample = micrograms found in sample tube
micrograms blank = micrograms found in blank tube

10.3 For personal sampling pumps with rotameters only, the following correction should be made.

$$\text{Corrected Volume} = f \times t \left(\sqrt{\frac{P_1}{P_2} \times \frac{T_2}{T_1}} \right)$$

where:

f = flow rate sampled
t = sampling time
P_1 = pressure during calibration of sampling pump (mm Hg)

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P_2 = pressure of air sampled (mm Hg)
T_1 = temperature during calibration of sampling pump (°K)
T_2 = temperature of air sampled (°K)

10.4 The concentration of mercury in the air sampled can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{micrograms (Section 10.2)}}{\text{Corrected air volume sampled (liters)}}$$

11. References

11.1 Documentation of NIOSH Validation Tests, National Institute for Occupational Safety and Health, Cincinnati, Ohio (DHEW-NIOSH-Publication No. 77-185), 1977. Available from Superintendent of Documents, U.S. Government Printing Office, Washington, D.C., Order No. 017-033-00231-2.

11.2 Backup Data Report for Mercury, prepared under NIOSH Contract No. 210-76-0123.

Appendix A

Description, Installation, and Operation of the Two-Stage Thermal Desorption Unit for the Determination of Mercury

Introduction

The thermal desorption unit described here was designed for the determination of mercury collected on 4-mm I.D. sampling tubes containing silvered Chromosorb P (AgCP). Sampling tubes are inserted into the first section of the desorption unit where the mercury is thermally desorbed and transferred to a second section. The second section contains gold granules which amalgamate all the mercury released by the first section and allow impurities to pass. Mercury is then thermally desorbed from the second section and passed into a flameless atomic absorption spectrophotometer where the amount of desorbed mercury is determined.

Description

With the exception of the electrical components and the loading spring, the entire thermal desorption unit is made of either quartz or Pyrex glass. A diagram of the unit giving the critical dimensions is shown in Figure S199-A1. Each important part of the thermal desorption unit is numbered in the diagram and the numbers represent the following:

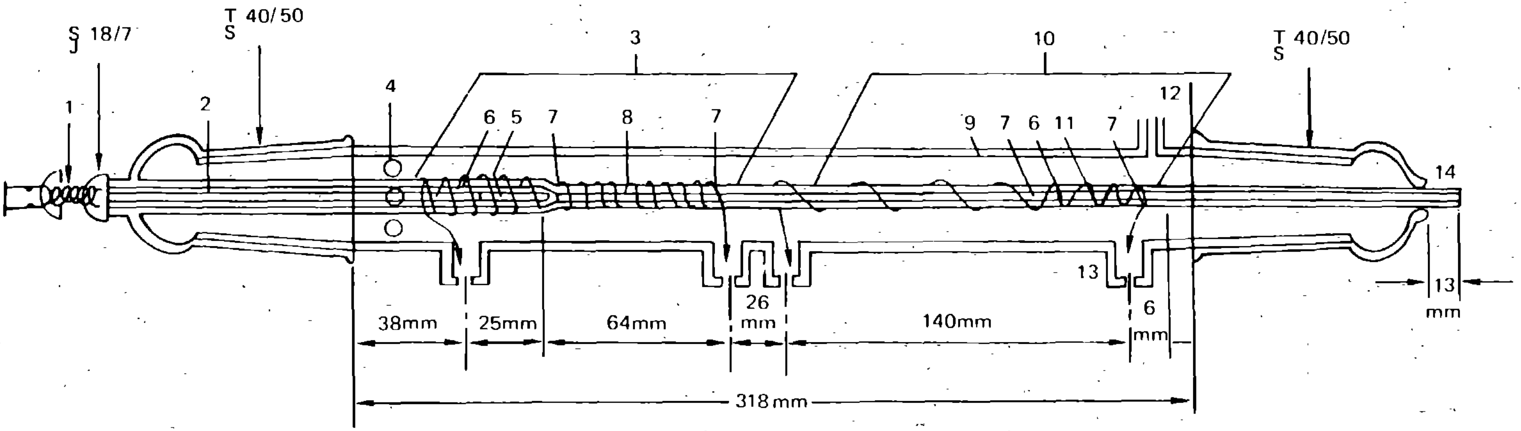
1-2. Loading mechanism (Figure S199-A2) - Made from a glass 18/7 female standard socket joint with steel spring (#1), and a plunger tube (3-mm or 4-mm O.D. quartz glass - #2). The length of the plunger is cut to reach the sample desorption section.

3. Sample desorption section - Made from 8-mm I.D. and 5-mm I.D. quartz tubing. The junction between the two sizes of tubing is tapered on the inside so that sampling tube tips fit snugly against the junction.

4. Cooling vent holes - About seven 4-mm holes are placed around the outer jacket of the unit to allow cooling air to flow from the second heating coil to the first coil.

5. Sampling tube - Sampling tubes are positioned inside the first desorption section during mercury desorption. The spring on the loading mechanism is adjusted to press the sampling tubes lightly in place.

6. Nichrome wire coils - Twenty-eight coils of 18 gauge nichrome wire are wrapped around the first desorption section to heat the sampling tubes during the thermal desorption step.



1. LOADING MECHANISM
2. QUARTZ GLASS PLUNGER TUBE
3. SAMPLE DESORPTION SECTION
4. COOLING AIR VENT HOLES
5. SAMPLING TUBE
6. NICHROME WIRE COILS
7. QUARTZ GLASS WOOL PLUGS
8. CUPRIC OXIDE (CuO)
9. COOLING JACKET
10. SECOND DESORPTION SECTION
11. GOLD SECTION
12. COOLING AIR INTAKE
13. WIRE HOLES AND SOLDERLESS CONNECTORS
14. OUTLET

Figure S199-A1 THERMAL DESORPTION UNIT

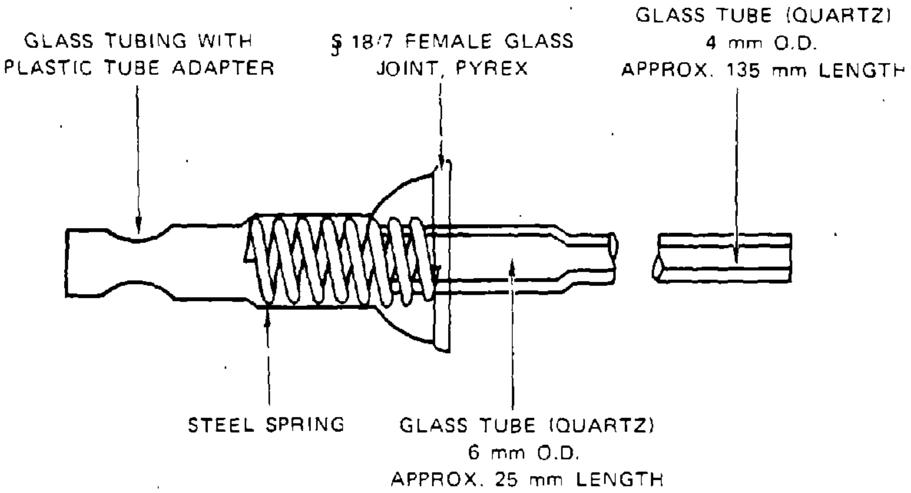


Figure S199-A2 LOADING MECHANISM

7. Quartz glass wool plugs - Quartz glass wool plugs are used to separate each section. Although the plugs should be large enough to hold the materials, they should not be packed too tightly.

8. Cupric oxide (CuO) - A 40-mm section of rod shaped CuO is placed just downstream from the sampling tubes. When heated, the CuO oxidizes organic vapors desorbed from the sampling tube. The CuO is held by a quartz glass wool plug which fits against a crimp in the glass tubing.

9. Cooling jacket - The pyrex glass outer covering not only directs the flow of cooling air, but also acts as electrical insulation for the heating coils.

10. Second desorption section - This section is made from the 5-mm I.D. quartz glass tubing extending from the first desorption section. The contents are held in place by a crimp in the glass tube.

11. Nichrome wire coils - Thirty coils of size 20 nichrome wire are wrapped around the second desorption section. The coils are wrapped to allow most of the generated heat to concentrate over the gold granules of the second desorption section.

12. Gold section - This section consists of a 25-mm length of powdered gold mixed one-to-one with 20/40 mesh sea sand. The sand is added to the gold to prevent fusing of the gold granules and to allow better air flow through the section.

13. Cooling air intake - A 6-mm I.D. piece of glass tubing is used for connecting plastic tubing from the cooling air supply.

14. Wire lead throughs and solderless connectors - Wires to the heating coils enter the cooling jacket through 5-mm holes at the ends of glass nipples on the side of the jacket. The solderless connectors between the wires and the coils are placed inside the jacket to prevent exposing uninsulated wire outside the cooling jacket. The insulated wires to the connectors are sealed in place with a heat resistant sealer.

15. Outlet - The outlet from the desorption unit is butt connected with a Tygon overseal to a glass tube which leads to a flameless atomic absorption spectrophotometer (MAS-50). The end of the quartz tube slides through an opening at the end of the cooling jacket. The opening is kept to a minimum to limit the escape of cooling air.

Installation

A diagram of the installed thermal desorption unit system is shown in Figure S199-A3.

1. Power connections - The wires to the heating coils should be heavy enough to carry the current necessary to heat the coils (about #12). Power to the heating coils is controlled by a three position switch with an off position, an on position for the sample desorption section and on position for the gold section. Power to the switch comes from a 120 Vac Input, 20 A variable transformer set at between 20 and 30 Vac. The exact setting is determined by testing the thermal desorption unit for complete desorption of mercury from the sample tube in one heating. Complete desorption usually occurs when the sample tube reaches a maximum of 650°C. The time required for heating may vary slightly from what is stated in the method (60 sec). These variations are due to the spacing between heating coils and the concentration of heat near the sample tube and/or desorption sections.

2. Air supply - The air which passes through the heated sections of the thermal desorption unit is drawn from the room by a vacuum pump. The pump is attached to a ballast tank to prevent fluctuations in air flow.

   Before entering the desorption unit, room air passes through a drying tube containing anhydrous $Mg(ClO_4)_2$ or any other suitable drying agent. The dimensions of the drying tube and all subsequent filters may vary but should not interfere with the air flow through the system. The drying agent should be changed periodically depending on the humidity of the work area. The dried air passes through a filter containing activated charcoal and 30/60 mesh silvered Chromosorb P or Mersorb charcoal to remove organic vapors and metallic mercury.

   The dry, filtered air then passes through the thermal desorption unit, through the flameless atomic absorption optical cell and into a filter containing Mersorb charcoal which collects any mercury desorbed by the desorption unit. Air from this charcoal filter then passes through a flowmeter and into the ballast tank of the vacuum pump. The flowmeter covers a 0 to 5 liter/min range and a critical orifice controls the flow of air through the system.

3. Cooling air - Cooling air for the heating coils is supplied by an air compressor. A flowmeter controls the flow rate at 20 liters/min. The air enters the desorption unit from a plastic tube into the air intake near the second desorption section.

4. Detection system - Mercury desorbed from the gold section of the thermal desorption system enters the optical cell of a flameless atomic absorption spectrophotometer through a glass tube. The glass tube connecting the desorption unit with the optical cell is maintained at 70°C using a heating tape. Power for the heating tape is supplied by a 120 Vac, 8 A variable transformer.

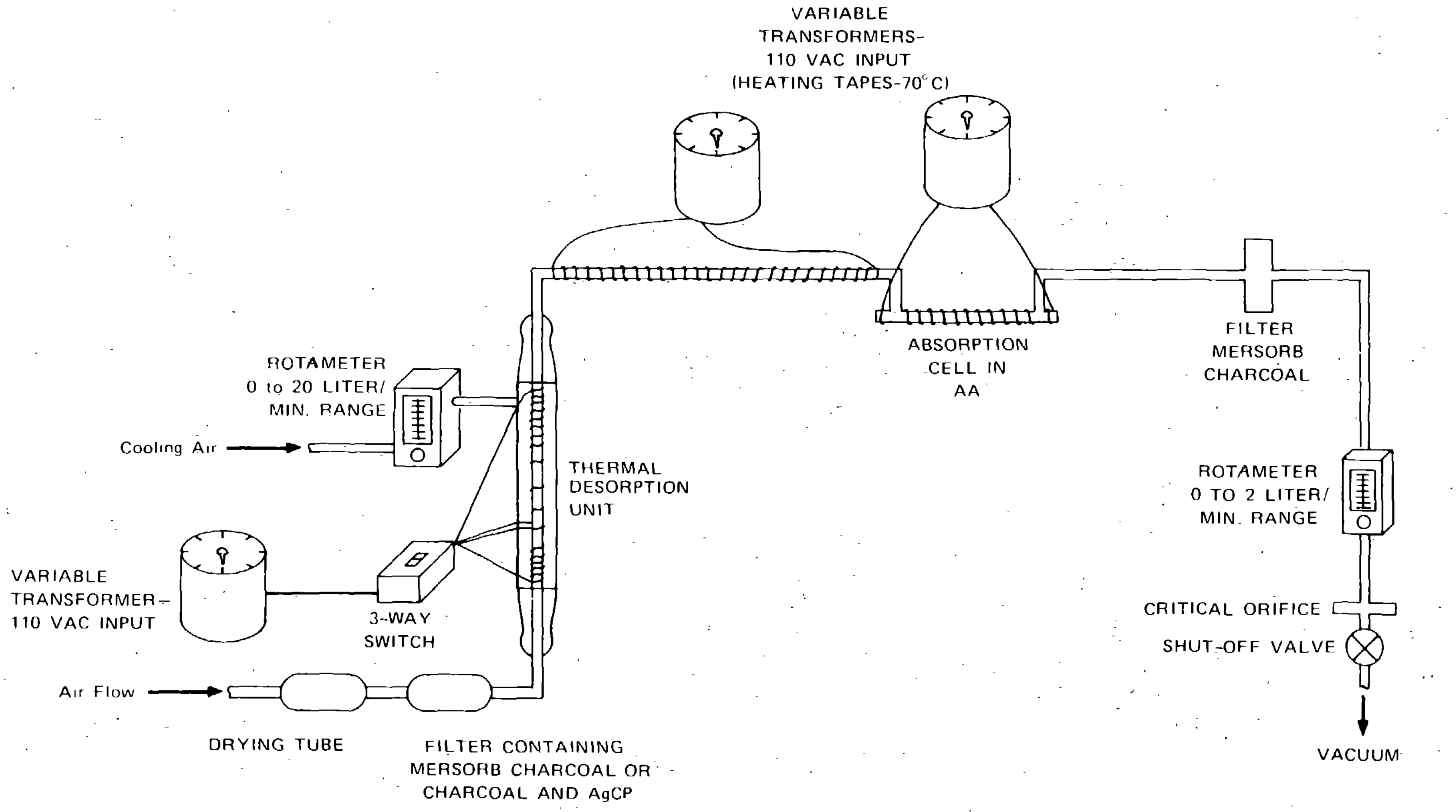


Figure S199-A3 MERCURY ANALYSIS SYSTEM

Any reliable flameless atomic absorption spectrophotometer or mercury analysis system set to absorb the 253.7 nm wavelength of mercury may be used to detect the mercury vapor released from the desorption unit.

Operation

1. Turn on the atomic absorption spectrophotometer and allow to stabilize.

   Note: The time required for stabilization varies with the individual instruments.

2. Turn on the heating tape.

3. Turn on the vacuum pump.

4. Observe the rotameter to insure flow through the critical orifice has not been interrupted. It should be approximately 1.0 liter/min.

5. Turn on the cooling air and adjust cooling air flowmeter to 20 liters/min.

6. Turn on the recorder and allow to stabilize.

7. Adjust the spectrophotometer to the desired 0 and 100% T settings.

8. Purge the system before analyzing samples by heating the first desorption section of the desorption unit for 60 seconds, allow to cool 60 seconds, and then heating the second section for 30 seconds.

9. Allow the desorption unit to cool for one minute before analyzing samples.

10. Remove the clamp between the loading mechanism and desorption unit and insert the sampling tube.

11. Push the sampling tube into the first desorption section of the desorption unit using the plunger of the loading mechanism and replace the clamp.

12. Switch the 3-way power switch to heat the first section of the thermal desorption unit and heat the sampling tube for the required time (usually 60 seconds).

13. After the first section is heated, allow unit to cool for 60 seconds and then switch the 3-way power switch to heat the second desorption section of the thermal desorption unit. This section is usually heated for about 30 seconds.

    Note: At this time the recorder will record the absorption signal of any mercury desorbed from the sampling tube.

14. Turn the 3-way switch to the off position.

15. Allow the thermal desorption unit to cool for about 30 seconds and open the clamp on the loading mechanism to unload the used sampling tube.

    Caution: The sampling tube is very hot when it comes out of the desorption unit. Do not touch the tube with bare hands. Drop the hot tube into a dry beaker to cool.

    Note: If the used sampling tube does not drop when the plunger is removed, turn off the air flow through the desorption unit using the shutoff valve and remove the tube with a metal rod.

16. Reload the desorption unit with another sampling tube.

17. Repeat steps 11 through 16 for each analysis.

Sampling Data Sheet No. S199

July 8, 1977

Substance

Mercury

Standard

Ceiling: 0.1 mg/cu m

Analytical Method

A known volume of air is drawn through a glass tube containing silvered Chromosorb P (AgCP) to trap the mercury vapors present. The mercury is thermally desorbed from the AgCP and passed through the absorption cell of a flameless atomic absorption spectrophotometer for analysis. The method was validated over the range of 0.0456-0.1800 mg/cu m for a 3-L sample at 23°C and 760 mm Hg atmospheric temperature and pressure.

Sampling Equipment

Sampling equipment includes a calibrated personal sampling pump whose flow can be determined accurately (±5%) in the range of 0.01 to 0.2 liter/minute. A tube (2.0-cm long with a 6-mm O.D. and a 4-mm I.D.) containing 30 mg of specially prepared 30/60 mesh AgCP, is used to collect the samples. The sample tubes must be specially prepared as described in NIOSH Method No. S199, and thermally desorbed before use. Before and after sampling, these tubes are stored in clean capped glass vials. A 0.8-micrometer/37-mm mixed cellulose ester membrane prefilter is used to collect particulate mercury.

Sample Size

A sample size of 3 liters is recommended. Sample at a flow rate between 0.01 and 0.2 liter/minute. Do not sample at a flow rate less than 0.01 liter/minute. Sample for 15 minutes.

Sampling Procedure

1. White gloves or laboratory wipers should be used when handling the sampling tubes. After the sampling tubes have been prepared and stored, they should be stable indefinitely. Immediately before sampling, remove the sample tube from the vial.

2. The sample tube is preceded by a 0.8 micrometer/37-mm cellulose ester membrane filter to collect particulate mercury. The filter is placed in a styrene filter holder, and the filter is supported by a cellulose backup pad. The prefilter is connected to the sample tube with a short piece of flexible tubing.

3. The sample tube should be placed nearer the sampling pump and in a vertical position during sampling to avoid channeling through the AgCP.

4. Air being sampled should not be passed through any hose or tubing before entering the filter holder. A minimum amount of flexible tubing should be used to connect the filter holder to the sample tube.

5. Set the flow rate as accurately as possible using the manufacturer's directions. Record the temperature, relative humidity, and pressure of the atmosphere being sampled. If the pressure reading is not available, record the elevation. Also report the type of sampling pump that is used.

6. After sampling, disconnect the filter cassette from the sampling tube. Return the AgCP tube to the glass vial. Insert cotton into the vial to prevent breakage of the tube during shipping. Gloves or wipers should be used when handling the sample tube. The prefilter should be discarded after sampling, and the filter cassette holder should be cleaned for future use.

7. With each batch of ten samples, submit one tube from the same lot of tubes used for sample collection. This tube must be subjected to exactly the same handling as the samples except that no air is drawn through it. This tube should be labeled as the blank.

Special Considerations

1. To avoid contamination of the outer surfaces of the sampling tube, white gloves or laboratory wipers should be used when handling the tubes.

2. Loading the prefilter with excess particulate will increase air flow resistance through the sampler. This may overload the battery-operated sampling pumps.

3. It has been reported that AgCP absorbs methyl mercury chloride and that most other organomercury compounds are not retained.

4. Strong oxidizing vapors and gases, particularly chlorine, which attack silver, reduce the efficiency of the sampling tube, but do not interfere in the analysis of the sample. These interferences should not be a problem under normal sampling conditions.

5. When other compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

Bulk Samples

A bulk sample of the suspected compound should be submitted to the laboratory in a glass container with a Teflon-lined cap. Label of the bulk sample should match air samples for identification purposes.

Shipping Instructions

Vials containing the sample tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping. Never transport, mail, or ship the bulk sample in the same container as the sample or blank tubes.

Reference

Mercury, NIOSH Method No. S199.

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Backup Data Report No. S199
July 8, 1977

Substance:	Mercury
OSHA Standard:	0.1 mg/cu m - Ceiling
Chemical Used for Validation:	Mercury Masero Laboratories; Palo Alto, CA

General

The procedure for collection and analysis of air samples of mercury is described in NIOSH Method No. S199. This method consists of collection of the sample on silvered Chromosorb P (AgCP), thermal desorption of the mercury, and analysis by passing the mercury through an absorption cell of a flameless atomic absorption spectrophotometer. This method has been tested for validity for a 3-L air sample using the criteria for validation outlined in Reference 1. Using these criteria, the absolute total error (sampling and analysis) is less than 25% at the OSHA standard level 95% of the time.

The protocol used for testing this method was to:

Analyze 18 samples (6 each at 0.5X, 1X, and 2X the OSHA standard) spiked with the appropriate amounts of mercury to represent 3-L air samples.

Analyze 18 samples collected from dynamically generated test atmospheres (6 samples collected at each of 0.5X, 1X, and 2X the OSHA standard).

Determine the breakthrough capacity of AgCP at high relative humidity.

Test the storage stability of six collected samples.

Assess the precision and accuracy of the method.

Details of these procedures are discussed below.

Analysis

A description of the method of analysis is given in NIOSH Method No. S199. The results of the analytical tests are in Table S199-4. Sample tubes used in the validation study were manufactured by SKC, Inc.

Sampling and Analysis

Test atmospheres of mercury in air were generated with an apparatus fabricated specifically for generating known concentrations of mercury. The apparatus, shown in Figure S199-1, was constructed entirely of glass and consisted of a mercury vapor generator, a temperature-controlled condenser, dilution and mixing chambers, and a sampling chamber. A constant uniform output of mercury was generated with the use of Monel screen specially coated with mercury. The concentration of mercury generated was based upon the known vapor pressure of mercury at the condenser temperature.

A special technique was required to coat the Monel screen with mercury. The Monel screen was first submerged in concentrated HCl to prepare the surface. The HCl was then displaced with mercury. The prepared Monel was readily oxidized if exposed to the air. The mercury-coated Monel was rinsed with water until the rinse water was neutral, and dried in a nitrogen stream.

The generator, containing the coated Monel screen, was heated to 30°C and a flow of nitrogen gas at 200 mL/min was passed through the chamber. The generator was connected to a condenser, also containing coated Monel screen, which was maintained at a temperature of 18.0 ± 0.1°C. The nitrogen passing through the condenser became saturated with mercury vapor at the condenser temperature. The saturated nitrogen was then diluted with a known flow of air to the appropriate OSHA level. The generated mercury atmosphere entered the mixing column and finally the sampling chamber.

The concentration of mercury vapor in the test chamber was calculated using the known vapor pressure of mercury at the condenser temperature, the nitrogen flow, and the dilution air flow. The samples were collected as described in Method No. S199 using AgCP sampling tubes. Separate generations were made to obtain each OSHA level.

Six samples were collected for 15 minutes at each level to obtain 3-L air samples. An additional six samples were collected at 1X the OSHA standard level and were used for the storage stability test. The results of the analysis of these samples are presented in Table S199-5.

Storage Stability Study

A study was done to assess whether mercury would be successfully stored for one week after collection. A second set of six samples at 1X the OSHA standard level was collected at the same time as the samples that were used for validation. These sample tubes were capped and stored on the laboratory bench for one week before analysis. The results of the analyses are given in Table S199-1.

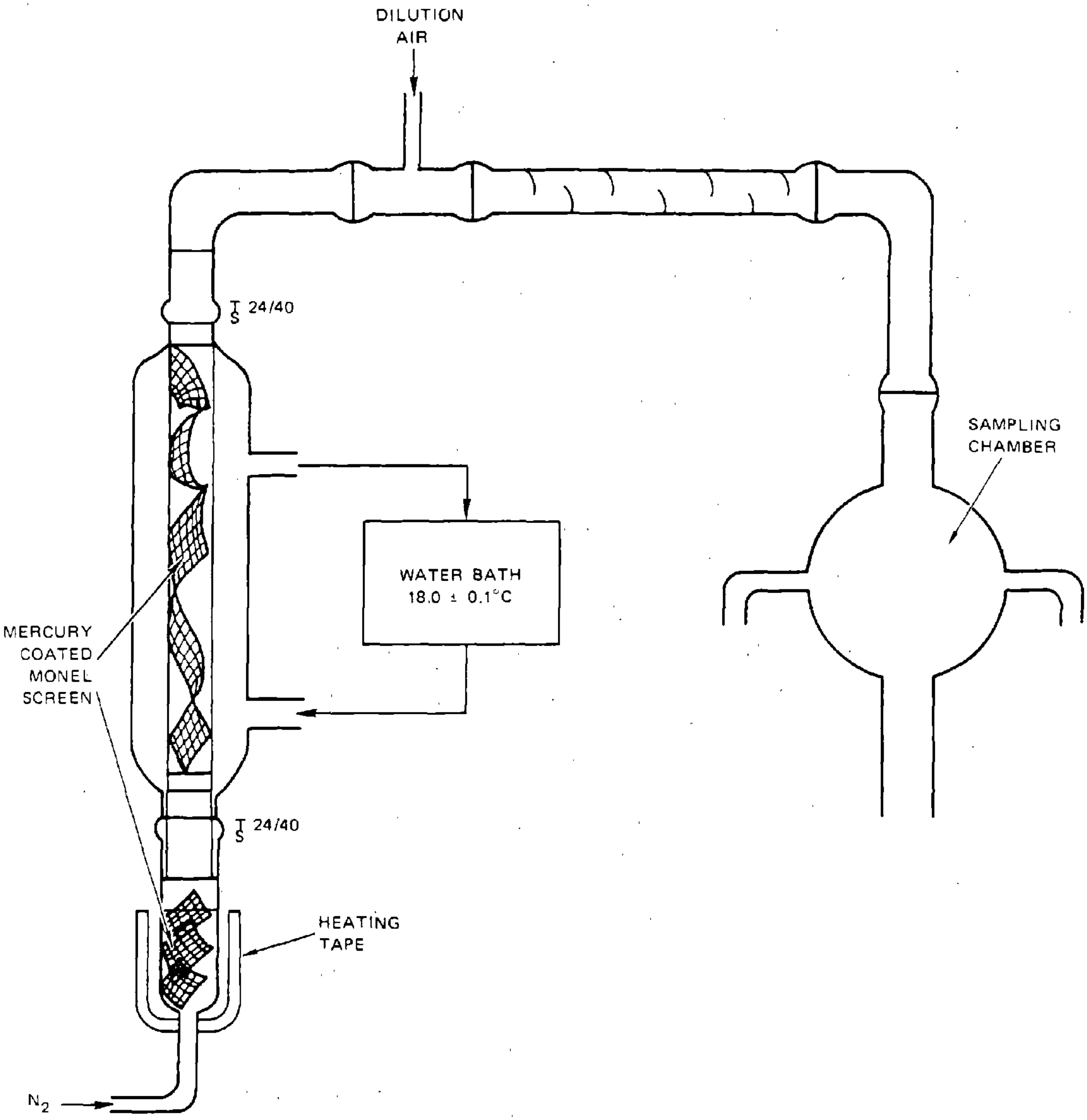


FIGURE S199-1 MERCURY VAPOR GENERATION APPARATUS

Table S199-1

Storage Stability Test

	Samples Analyzed Immediately mg/cu m	Samples Analyzed After Seven Days mg/cu m
	0.0987	0.1020
	0.1008	0.1033
	0.1033	0.1122
	0.0994	0.1063
	0.1003	0.1056
	0.1003	0.0997
mean	0.1005	0.1048
std dev	0.0016	0.0044
CV	0.016	0.042

The criterion for acceptance was that the mean of the six samples stored at room temperature for seven days should be within ±10% of the mean of the set analyzed at the beginning of the storage period. The two means compare within 4%; thus, storage stability was adequate.

Breakthrough Tests

A breakthrough test was performed at a relative humidity of 85%. Details of the method of generating atmospheres containing high relative humidities are given in Attachment A.

Breakthrough is defined as the time that the effluent concentration from the collection tube (containing 30 mg of AgCP) reaches 5% of the concentration in the test gas mixture. The criterion for acceptance is that the volume of air that has passed through the tube at the time of breakthrough must be greater than 1.5 times the volume of air that would be passed through the tube during collection of a field sample, when the substance of interest in the test atmosphere is at 2X the OSHA standard level.

The breakthrough time was measured by testing 14 sampling tubes in parallel, each containing 30 mg of AgCP followed by a backup tube containing 30 mg of AgCP. The tubes were placed in the sample generation apparatus. The test atmosphere was sampled through each set of tubes at the flow rate to be used during sample collection. After start of the test, a sample tube and corresponding backup tube was analyzed every 15 minutes. Saturation of the AA detector begins to occur after 1.0 microgram of mercury is collected in the tube, making it impossible to measure the amount sampled on the front tube after 25 minutes at 2X the OSHA standard level. To overcome this difficulty, sequential control samples were taken for each 15-minute interval, and the total accumulated amount of mercury collected on the breakthrough test sample was found by adding the amounts measured on the control samples.

The amount of mercury collected on the control samples and backup tubes was determined by thermal desorption with flameless AA analysis. The data collected during the breakthrough test is presented in Table S199-2.

Table S199-2

Breakthrough Test

Time (hours)	Micrograms Hg Collected in 15-min Sequential Samples	Amount Collected on Front AgCP Sample Tube (Cumulative Total of Sequential Samples	Backup AgCP Tube
0.25	0.655	0.655	N.D.*
0.50	0.655	1.310	N.D.
0.75	0.640	1.950	N.D.
1.00	0.596	2.546	N.D.
1.25	0.596	3.142	N.D.
1.50	0.648	3.790	N.D.
1.75	0.602	4.392	N.D.
2.00	0.673	5.065	N.D.
2.25	0.640	5.705	N.D.
2.50	0.702	6.407	N.D.
2.75	0.706	7.113	N.D.
3.00	0.673	7.786	N.D.
3.25	0.690	8.476	N.D.
3.50	0.702	9.178	N.D.

* N.D. = Not detected at a detection limit of 0.01 microgram.

Breakthrough did not occur when the average sampling rate was 0.184 liter/minute and the relative humidity was 85%. The concentration tested was 0.244 mg/cu m. The breakthrough test was discontinued after 210 minutes, because of a limited number of sampling ports.

Discussion

The recommended mercury analysis system (Reference 2), including the thermal desorption unit, flow system, and absorption cell, was tested and modified before valid results were obtainable. The first section in the desorption unit where the sample tube is thermally desorbed, was initially wired improperly so that insufficient heat was concentrated over the sample tube. Incomplete desorptions were obtained after lengthy heatings. This section was rewired and conditions were optimized to obtain complete desorption in one short heating. The narrow range of sensitivity, partially a result of the thermal desorption system, was also a factor to be considered. When mercury was desorbed from the gold (second) section in the thermal desorption unit, a very sharp immediate response was obtained. The flow through the system or the length of the lines did not appear to affect the maximum response. The absorption cell path length affected the AA detector response more than any other factor. A 17.5-cm path length cell was initially used. The usable range was from 0.01 to 0.4 microgram mercury, which was unacceptable.

To sample at 0.2 liter/minute for 15 minutes near the OSHA level, a wider sensitivity range was necessary. A 4.0-cm path length cell was used to obtain a range of 0.01 to 1.0 microgram mercury. The response curve tended to level out at mercury amounts greater than the upper limit of the acceptable range, indicating saturation of the AA detector.

The recovery of mercury from AgCP has been demonstrated in this study and previously (Reference 3) to be 100% within experimental error when the AgCP is heated to 650-700°C. Samples collected on AgCP of accurately known mercury vapor concentrations have been analyzed and compared to mercury standards spiked from a standard solution directly onto AgCP. Results obtained were essentially the same. Since complete recovery of mercury from AgCP has been thoroughly demonstrated under the proper conditions, it is not recommended that the individual user of the method perform analytical method recovery tests.

The originally proposed method included the use of Carbosieve B (CB) as a pre-sorbent for organomercury compounds. Much work was performed on CB before its use was found to be unacceptable because of mercury retention. The AA response of a known amount of mercury desorbed from CB was the same as that from AgCP. The temperature required to desorb mercury (or mercury compounds) from the CB was 300°C, much less than the 650°C required to desorb mercury from AgCP. If the temperature was raised over 300°C, the CB was oxidized. CB tubes required thermal desorption before use since mercury or compounds absorbing at the same wavelength as mercury were found on blank tubes.

A high humidity breakthrough test was performed with 14 samples each taken by a CB pre-sorbent tube followed by two AgCP tubes in series. The average level generated was 0.244 mg/cu m at 85% relative humidity. Breakthrough of mercury to the second AgCP tube did not occur in the 3.5-hour test. The pre-sorbent CB tube retained less than 1% of the total mercury collected on each sampling devise.

Mercury was then generated dry at 0.190 mg/cu m and seven samples were collected with a CB tube/AgCP tube combination. Mercury was retained on the CB tubes in the range of 0 to 53%, averaging 16%. A second generation was performed at 0.185 mg/cu m and seven samples collected as above. Immediately after collection, the sample tubes were purged with nitrogen at 1 liter/minute for 5 minutes to pass any mercury on the CB tube to the AgCP tube. The amount of mercury found on the CB tubes after purging ranged from 2 to 50%, averaging 23%. Based upon the inconsistent retention of mercury on CB, it was decided to use only the AgCP tube to collect mercury.

Independent Method

The concentration of mercury in the generator was determined by theoretical calculations based upon mercury vapor pressure data published in the Handbook of Chemistry and Physics, 48th ed. The following parameters were used to determine the "taken" concentration in the generator.

Table S199-3

Generation Parameters

Condenser Temperature: 18.0°C

Vapor Pressure of Mercury at 18.0°C: 0.001009 mm Hg

Atmospheric Pressure: 760 mm Hg

	0.5X	1X	2X
Nitrogen carrier flow (L/min):	0.188	0.193	0.188
Dilution air flow (L/min):	46.0	23.0	11.5
Mercury concentration (mg/cu m):	0.0456	0.0927	0.180

Precision and Accuracy

The statistical procedures and a definition of the terms used are described in Reference 4.

The precision of the analytical method was assessed using the data in Table S199-4. The pooled Coefficient of Variation ($\overline{CV}_1$) for three sets of analytical samples was found to be 0.051.

Precision and accuracy of the total sampling and analytical method was evaluated using the data in Table S199-5 and the results obtained from breakthrough tests and storage stability tests. The pooled Coefficient of Variation ($\overline{CV}_2$) for the three sets of samples collected from test atmospheres is 0.027. To obtain a measure of the accuracy of the method, the mean value of the concentration found by analysis at each level was compared with the value for the concentration taken

The average recovery (concentration found divided by concentration taken) for all three levels was 100.7%. The value for the taken concentration was obtained as described under the Independent Method Section. The difference between the taken and found concentrations is considered to result from experimental uncertainties in the value for the taken concentration and does not represent a bias in the method. Further confidence in the accuracy of the tested method is established by the results of the breakthrough test and the storage stability test, described above.

The total Coefficient of Variation ($\overline{CV}_T$) is 0.061.

Table S199-4

Data Sheet: Mercury

Analysis

Level	0.5X			1X			2X		
	µg taken	µg found	A.M.R.	µg taken	µg found	A.M.R.	µg taken	µg found	A.M.R.
	0.1500	0.1400	0.933	0.300	0.298	0.993	0.600	0.617	1.028
	0.1500	0.1480	0.987	0.300	0.311	1.037	0.600	0.611	1.018
	0.1500	0.1400	0.933	0.300	0.316	1.053	0.600	0.625	1.042
	0.1500	0.1450	0.967	0.300	0.335	1.117	0.600	0.605	1.008
	0.1500	0.1520	1.013	0.300	0.284	0.947	0.600	0.617	1.028
	0.1500	0.1670	1.113	0.300	0.308	1.027	0.600	0.607	1.012
n =			6			6			6
mean			0.991			1.029			1.023
std dev			0.067			0.057			0.012
CV_1			0.068			0.055			0.012

$\overline{CV}_1$ 0.051

$\overline{CV}_{A+\overline{AMR}}$ 0.055

Table S199-5

Data Sheet: Mercury

Sampling and Analysis

Test Level	Found			Taken	
	µg	Liters	mg/cu m*	mg/cu m	Percent Recovery
0.5X	0.1320	3.08	0.0429	0.0456	
	0.1300	3.06	0.0425	0.0456	
	0.1350	3.23	0.0418	0.0456	
	0.1290	2.94	0.0439	0.0456	
	0.1180	2.61	0.0452	0.0456	
	0.1330	3.10	0.0429	0.0456	
		n = 6			
		mean	0.0432		94.7
		std dev	0.0012		
		CV_2	0.028		
1X	0.312	3.16	0.0987	0.0927	
	0.258	2.56	0.1008	0.0927	
	0.310	3.00	0.1033	0.0927	
	0.310	3.12	0.0994	0.0927	
	0.303	3.02	0.1003	0.0927	
	0.301	3.00	0.1003	0.0927	
		n = 6			
		mean	0.1005		108.4
		std dev	0.0016		
		CV_2	0.016		
2X	0.581	3.02	0.1924	0.1800	
	0.551	2.94	0.1874	0.1800	
	0.494	2.61	0.1893	0.1800	
	0.572	3.10	0.1845	0.1800	
	0.539	3.08	0.1750	0.1800	
	Sample was lost.				
		n = 5			
		mean	0.1857		103.2
		std dev	0.0066		
$\overline{CV}_2$ 0.027		CV_2	0.036		

* All values have passed the Grubbs' outlier test at the 1% confidence level as described in Reference No. 4.

References

1. Contract 210-76-0123, National Institute for Occupational Safety and Health, Division of the Department of Health, Education and Welfare, U. S. Government.

2. NIOSH Manual of Analytical Methods, Method P&CAM 175, (Revised 3/9/77).

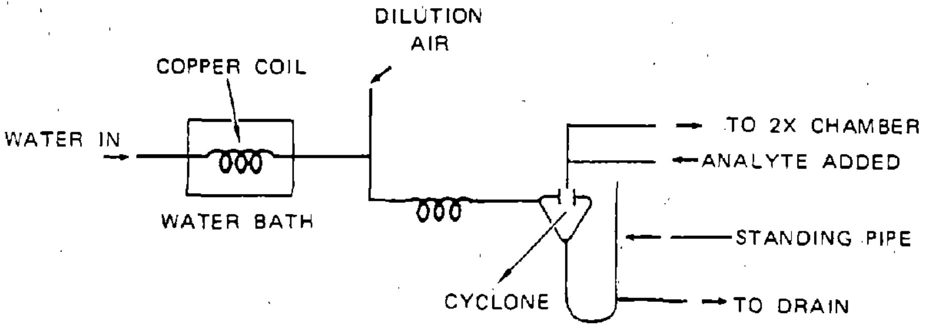
3. Trujillo, Patricia E. and Evan E. Campbell, "Development of a Multistage Air Sampler for Mercury," *Anal. Chem.*, *47*, 1629, (1975).

4. Documentation of NIOSH Validation Tests, National Institute for Occupational Safety and Health, Cincinnati, Ohio (DHEW-NIOSH-Publication No. 77-185), 1977. Available from Superintendent of Documents, U.S. Government Printing Office, Washington, D.C., Order No. 017-033-00231-2.

Attachment A

Generation of Known Humidity Test Atmospheres

A diagram of the apparatus used for generating high humidity atmospheres is shown below.



A regulated flow of tap water at approximately 15°C flows through a copper coil contained in a thermostated water bath. After emerging from the water bath it enters a 5-foot length of 5/16-inch Tygon tubing. The dilution air is introduced into this same tubing and becomes water saturated at the temperature of the bath. This water-air mixture passes into a cyclone, where excess water is removed from the air stream and drains from the bottom of the cyclone. The U-shaped tube and standing pipe provide a water seal at the bottom of the cyclone to prevent loss of air by this route. The humid air passes through the top of the cyclone. A controlled flow of the analyte enters the air stream at the outlet of the cyclone at a rate such that the 2X concentration is obtained.

The temperature of the water bath is kept 1°C lower than the temperature of the room. Thus, the air is saturated with water vapor at the lower temperature and reaches a relative humidity of less than 100% as it warms to room temperature after leaving the cyclone.

The relative humidity of the air in the sampling chamber is measured by the dry and wet bulb thermometer method. A flow of 32 liters/minute of the test atmosphere is drawn from the sampling chamber over the thermometers.

To ensure that a sufficiently high flow rate of air passes over the thermometers to give an accurate measurement, both thermometers are enclosed in glass tubing with an internal diameter of 11 mm.

From the readings of the relative temperatures of these two thermometers, the relative humidity at the temperature of the dry thermometer is found by consulting relative humidity tables.

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Nitric Oxide

Analyte:	Nitrite ion, NO_2^-	Method No.:	S321
Matrix:	Air	Range:	11.1 - 48 ppm
OSHA Standard:	25 ppm (30 mg/cu m)	Precision ($\overline{CV}_T$):	0.062
Procedure:	Oxidation to nitrogen dioxide, collection on triethanolamine-coated molecular sieve, desorption with triethanolamine, spectrophotometric analysis	Validation Date:	8/5/77

1. Principle of the Method

1.1 A known volume of air is drawn through a sampling tube containing in series: 400 mg triethanolamine-impregnated molecular sieve; 1.2 g Draeger oxidizer; 400 mg triethanolamine-impregnated molecular sieve. The first section removes ambient nitrogen dioxide. The Draeger oxidizer transforms nitric oxide to nitrogen dioxide and the last section adsorbs the nitrogen dioxide.

1.2 The last triethanolamine-impregnated molecular sieve section in each tube is transferred to a flask, and the nitrogen dioxide is desorbed and hydrolyzed in an aqueous triethanolamine solution to yield nitrite ion. An aliquot is treated with hydrogen peroxide, sulfanilamide and N-(1-naphthyl)-ethylenediamine dihydrochloride and the reacted nitrite ion is measured spectrophotometrically.

2. Range and Sensitivity

2.1 This method was validated over the range of 11.14-47.7 ppm at an atmospheric temperature of 19°C and atmospheric pressure of 764 mm Hg using a 1.5-liter sample volume. This sample volume is based on the adsorptive capacity of the triethanolamine-impregnated molecular sieve to collect nitric oxide vapors at high relative humidity. This method is capable of measuring much smaller amounts, since the collection and desorption efficiency has been shown to be adequate at levels of approximately 0.5 ppm NO_2 and 9 ppm NO (Reference 11.1).

2.2 The upper limit of the sampling and analytical method is dependent on the oxidation efficiency of the Draeger oxidizer and adsorptive capacity of the triethanolamine-impregnated molecular sieve section. Breakthrough is defined as the time that the effluent concentration from the collection tube reaches 5% of the concentration in the test gas mixture. After sampling 108 minutes at 20.94 mL/minute from an atmosphere containing 46.1 ppm NO at 84% relative humidity, 3.8% breakthrough occurred. The recommended sampling volume is thus less than two-thirds the 5% breakthrough capacity. It is expected that the sampling tube will not be suitable at concentrations much in excess of 2X the OSHA standard. Of course, other oxidizable compounds in the air may also reduce the collection efficiency of the sampling tubes.

2.3 The detection limit under the prescribed sampling conditions is approximately 0.19 ppm NO.

3. Interferences

3.1 Nitrogen dioxide is an interference in this method at some undetermined concentration in excess of 50 ppm. This is due to the unknown capacity of nitrogen dioxide on the first triethanolamine-impregnated molecular sieve section of the sampling tube. Since this is far in excess of the recommended OSHA standard of 1 ppm, such an occurrence is probably not common in the workplace.

3.2 Interference due to collection of nitric oxide on the first section of triethanolamine-impregnated molecular sieve is observed to correspond to less than 1% of the NO at 2X the OSHA standard.

3.3 Any compound which is collected on the second triethanolamine-impregnated molecular sieve section and which reacts with the colorimetric reagents may act as a positive or negative interference. If such an interference exists, its impact must be determined by independent analysis.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV_T}$) for the total sampling and analytical method in the range of 11.14-47.7 ppm was 0.0621. This value corresponds to a 1.552 ppm standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in References 11.2 and 11.3.

4.2 On the average, the concentrations obtained at the OSHA standard level using the overall sampling and analytical method were 5.4% higher than the "true" concentrations for a limited number of laboratory experiments. Any difference between the "found" and "true" concentrations may not represent a bias in the sampling and analytical method, but rather a random variation from the experimentally determined "true" concentration. Another possibility is that the stoichiometric factor for conversion of nitrogen dioxide (gas) to nitrite ion (0.63) is not correct. Several authors have reported values from 0.5-0.9. The value determined by Blacker (Reference 11.4) under similar experimental conditions is 0.63. The analytical data described in Reference 11.3 corroborates this value and, therefore, it has been used for method validation. Storage stability studies conducted on samples collected from an atmosphere containing 19.9 ppm NO indicate that collected samples are stable at least 7 days. For these reasons, no recovery correction should be applied to the final result.

5. Advantages and Disadvantages

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal due to the analytical specificity.

5.2 The method utilizes a readily available visible spectrophotometer.

5.3 If the concentration of nitrogen dioxide present in the environment sampled exceeds the proposed OSHA standard (1 ppm), its concentration may be determined with the same sampling tube as used for nitric oxide analysis.

5.4 If the nitric oxide concentration exceeds 2X the OSHA standard, the collection device will not quantitatively collect all of the analyte present.

5.5 The precision of the method is affected by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated with one tube only.

6. Apparatus

6.1 A calibrated personal sampling pump whose flow can be determined within ±5% at the recommended flow rate of 25 milliliters per minute. The pump must be calibrated with a sampling tube in line.

6.2 Sampling Tubes. Glass tube with both ends flame-sealed, 17 cm long with 7 mm O.D. and 5 mm I.D., containing the sections listed below and shown schematically in Figure S321-1. The pressure drop across the tube is about 3 cm of H_2O at a flow rate of 25 milliliters per minute.

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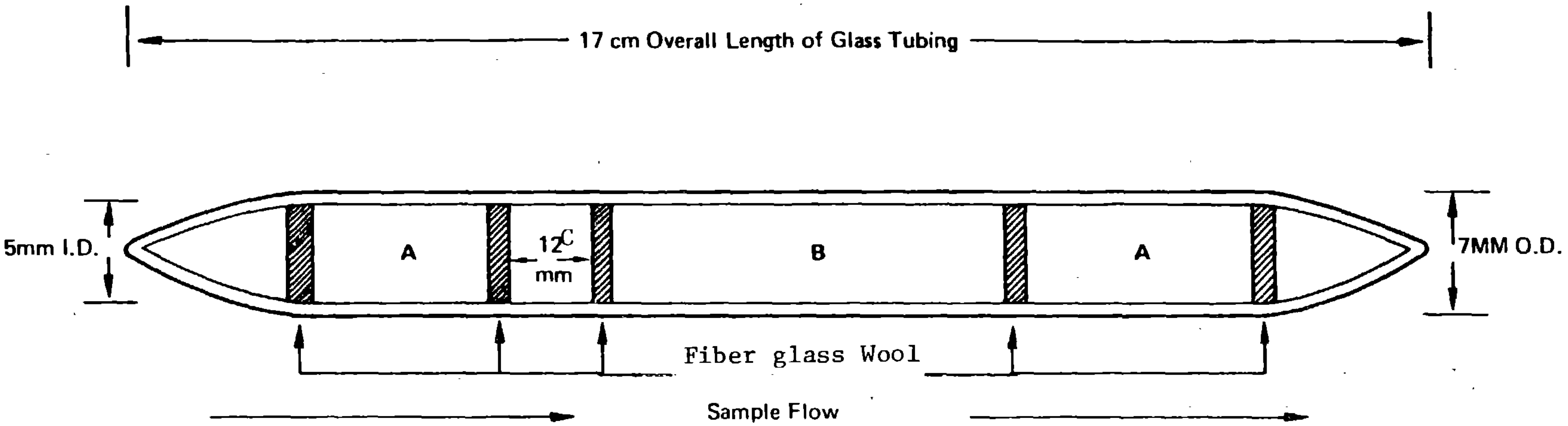

A. 400 mg Triethanolamine — Impregnated Type 13 X, 30-40 Mesh Molecular Sieve

B. 1.2 g of Oxidation Material No. 1900277 from Draeger Company of Germany, supplied by National Mine Service Co.

C. 12 mm glass spacer tube, 4.0 mm O.D., 2.6 mm I.D.

NITRIC OXIDE SAMPLING TUBE

FIGURE S321-1

6.2.1 Small plugs of glass wool as shown in Figure S321-1.

6.2.2 400-mg triethanolamine-impregnated Type 13X, 30-40 mesh molecular sieve.

6.2.3 12-mm glass spacer tube with 4.0 mm O.D., and 2.6 mm I.D.

6.2.4 1.2 g, oxidizer, No. 1900277, oxidation material produced by Draeger Company. Available from National Mine Service Company, 3001 Koppers Bldg., Pittsburgh, PA 15219.

The triethanolamine-impregnated molecular sieve can be prepared as follows: Add 25 g triethanolamine to a 250-mL beaker; add 4 g glycerol, 50 mL acetone and sufficient distilled water to bring up to 100 mL. To the mixture add about 50 mL Type 13X, 30-40 mesh molecular sieve. Stir and let stand in a covered beaker for about 30 minutes. Decant the excess liquid and transfer the molecular sieve to a porcelain pan which is then placed under a heating lamp until most of the moisture has evaporated. Complete the drying in an oven at 110°C for one hour. The sorbent should be free flowing. Store in a closed glass container.

6.3 A spectrophotometer capable of measuring absorbance or transmittance at 540 nm.

6.4 Two matched 1-cm silica cells.

6.5 Volumetric flasks, 50-mL and other convenient sizes.

6.6 Beakers, 100-mL.

6.7 Pipets, 1, 5 and 10-mL and other convenient sizes to make standard dilutions.

6.8 Balance.

6.9 Barometer.

6.10 Thermometer.

6.11 Stopwatch.

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7. Reagents

All reagents should be ACS reagent grade or better. They are the same as described in Reference 11.1.

7.1 Liquid Absorber. Prepare by dissolving 15.0 g triethanolamine in approximately 500 mL distilled water, adding 0.5 mL n-butanol, and diluting to 1 liter.

7.2 Hydrogen Peroxide Solution 0.02% (V/V). Prepare by diluting 0.2 mL, 30% hydrogen peroxide to 250 mL with distilled water.

7.3 Sulfanilamide Solution. Prepare by dissolving 10 g sulfanilamide in 400 mL distilled water, adding 25 mL concentrated phosphoric acid and diluting to 500 mL.

7.4 NEDA Solution. Prepare by dissolving 0.5 g N-(1-napthyl) ethylenediamine dihydrochloride in distilled water and diluting to 500 mL.

7.5 Stock Nitrite Solution, 100 ppm NO_2^-. Prepare by dissolving 0.1500 g sodium nitrite in 1 liter of water.

7.6 Working Nitrite Solution, 2 ppm NO_2^-. Prepare by diluting 2 mL of the stock nitrite solution to 100 mL with absorbing solution.

8. Procedure

8.1 Cleaning of Equipment

8.1.1 Before use, all glassware should be initially soaked in a mild detergent to remove any residual grease or chemicals.

8.1.2 After initial cleaning, the glassware should be thoroughly rinsed with warm tap water, 6 M nitric acid, tap water, distilled water, in that order, and then dried.

8.2 Calibration of Personal Sampling Pumps. Each personal pump must be calibrated with a representative sampling tube in the line. The tube is described in Section 6.2. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Immediately before sampling, break the two ends of the sampling tube to provide an opening of at least one half of the internal diameter of the tube (5 mm).

8.3.2 The tube should be oriented so that the inner glass tube (12 mm) is farthest from the pump.

8.3.3 The tube should be placed in a vertical direction during sampling to minimize channeling through the sorbent.

8.3.4 Air being sampled should not be passed through any hose or tubing before entering the tube.

8.3.5 A sample size of 1.5 liters is recommended. Sample at a flow rate of exactly 0.025 liter per minute for 60 minutes. The flow rate should be known with accuracy of at least ±5%. No other flow rate is suitable.

8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If the pressure reading is not available, record the elevation.

8.3.7 The exposed tube should be labeled appropriately and capped with supplied plastic caps.

8.3.8 With each batch of five or fewer samples, submit one sampling tube which has been handled in the same manner as the sample tubes (break, seal, transport), except that no air is sampled through this tube. This tube should be labeled as blank.

8.3.9 Capped sampling tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, the broken ends of each tube are widened to facilitate removal of the sorbent. The glass wool is removed carefully and discarded, making sure that no sorbent is lost in the process. The triethanolamine-impregnated molecular sieve in back (farthest from the 12-mm inner glass tube) is transferred to a 50-mL volumetric flask. If it is desired to quantify the NO_2 concentration (see restriction noted in Section 5.3) as well as the NO concentration, the triethanolamine-impregnated molecular sieve in front may be transferred to a separate 50-mL volumetric flask. These two sections may be analyzed separately.

8.4.2 Extraction of the Sample. Prior to analysis, liquid absorber is added to the flask to bring the volume to 50 mL. The flask is shaken vigorously for about 30 seconds and the solids allowed to settle.

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A blank is prepared similarly with a TEA/molecular sieve section from an unexposed sampling tube.

8.4.3 Spectrophotometer Operation. Turn on the spectrophotometer and allow sufficient time for warmup. Follow the instrument manufacturer's recommendations for specific operating parameters. Adjust the wavelength to 540 nm and set the zero and 100% transmittance scale using a 1-cm cell filled with distilled water. Check these settings prior to making any measurement to check on instrument drift.

8.4.4 Analytical Procedure

1. Pipet 10 mL of the extracted sample into a 50 mL volumetric flask.
2. Add 1.0 mL hydrogen peroxide solution, 10.0 mL sulfanilamide solution, and 1.4 mL NEDA solution with thorough mixing after each addition.
3. Allow ten minutes for complete color development.
4. Transfer some of the sample to a 1-cm absorption cell.
5. Measure the absorbance or transmittance at 540 nm using a reagent blank to set zero absorbance.

9. Calibration and Standards

9.1 Using freshly prepared working nitrite solution, prepare at least five calibration standards in absorbing solution to cover a nitrite concentration range of 1 to 18 μg nitrite per 10 mL.

9.2 Prepare these standards fresh daily by appropriate dilution of the working nitrite solution using absorbing solution for all dilutions. A reagent blank containing no nitrite should also be prepared.

9.3 Proceed as in Section 8.4.4.

9.4 Prepare a calibration curve by plotting the absorbance of the standards after subtraction of the reagent blank versus the concentration of each standard in μg NO_2^- per 10 mL on linear graph paper.

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10. Calculations

10.1 Correction for the sample blank (obtained by extraction and analysis of the sampling tube marked "blank") must be made for each sample.

$$\text{Abs}_{\text{corr}} = \text{Abs}_{\text{sample}} - \text{Abs}_{\text{sample blank}}$$

10.2 Read the amount of nitrite ion, in µg NO_2^- per 10 mL, corresponding to the Abs_{corr} from the standard curve (Section 9.4).

10.3 Multiply the amount of nitrite ion per 10 mL by the factor shown below to obtain the µL NO_2 (gas) per 50 mL (total sample) at 25°C and 760 mm Hg.

$$\mu\text{L } NO_2\text{(gas) in sample} = \mu\text{g } NO_2^-/10 \text{ mL} \times \frac{5}{1.88 \times 0.63}$$

where:

1 µL NO_2(gas) = 1.88 µg NO_2(gas) at 25°C and 760 mm Hg, and

1 µg NO_2(gas) = 0.63 µg $NO_2^- \equiv$ "stoichiometric factor"

10.4 Determine the volume of air sampled at ambient conditions in liters based on the appropriate information, such as flow rate in liters per minute multiplied by sampling time. If a pump using a rotameter for flow rate control was used for sample collection, a pressure and temperature correction must be made for the indicated flow rate. The expression for this correction is:

$$\text{Corrected Volume} = f \times t \left(\sqrt{\frac{P_1}{P_2} \times \frac{T_2}{T_1}}\right)$$

where:

f = sampling flow rate

t = sampling time

P_1 = pressure during calibration of sampling pump (mm Hg)

P_2 = pressure of air sampled (mm Hg)

T_1 = temperature during calibration of sampling pump (°K)

T_2 = temperature of air sampled (°K)

10.5 The concentration of analyte in the air sampled can be expressed in ppm (at standard conditions of 25°C and 760 mm Hg).

$$\text{ppm NO} = \frac{\mu\text{L NO (gas)} \quad \text{(see Section 10.3)}}{\text{Air volume sampled (liters)} \times \frac{P}{760} \times \frac{298}{T}}$$

Another method of expressing concentration is mg/cu m

$$\text{mg/cu m} = \text{ppm} \times \frac{30.01}{24.45}$$

where:

P = Pressure (mm Hg) of air sampled

T = Temperature (°C) of air sampled

760 = Standard Pressure (mm Hg)

298 = Standard Temperature (°C)

24.45 = Molar volume (liter/mole) of air at 25°C and 760 mm Hg

30.01 = Molecular weight of nitric oxide

11. References

11.1 M.A. Willey, C. McCammon, Jr., and L. Doemeny, *Am. Ind. Hyg. Assoc. J.* (38), 358 (1977).

11.2 Documentation of NIOSH Validation Tests, National Institute for Occupational Safety and Health, Cincinnati, Ohio (DHEW-NIOSH-Publication No. 77-185), 1977. Available from Superintendent of Documents, Washington, D. C., Order No. 017-033-00231-2.

11.3 S321 Backup Data Report for Nitric Oxide, prepared under NIOSH Contract No. 210-76-0123.

11.4 J.H. Blacker, *Am. Ind. Hyg. Assoc. J.* (34), 390 (1973).

Sampling Data Sheet No. S321
August 5, 1977

Substance

Nitric oxide

Standard

Time-weighted average: 25 ppm (30 mg/cu m)

Analytical Method

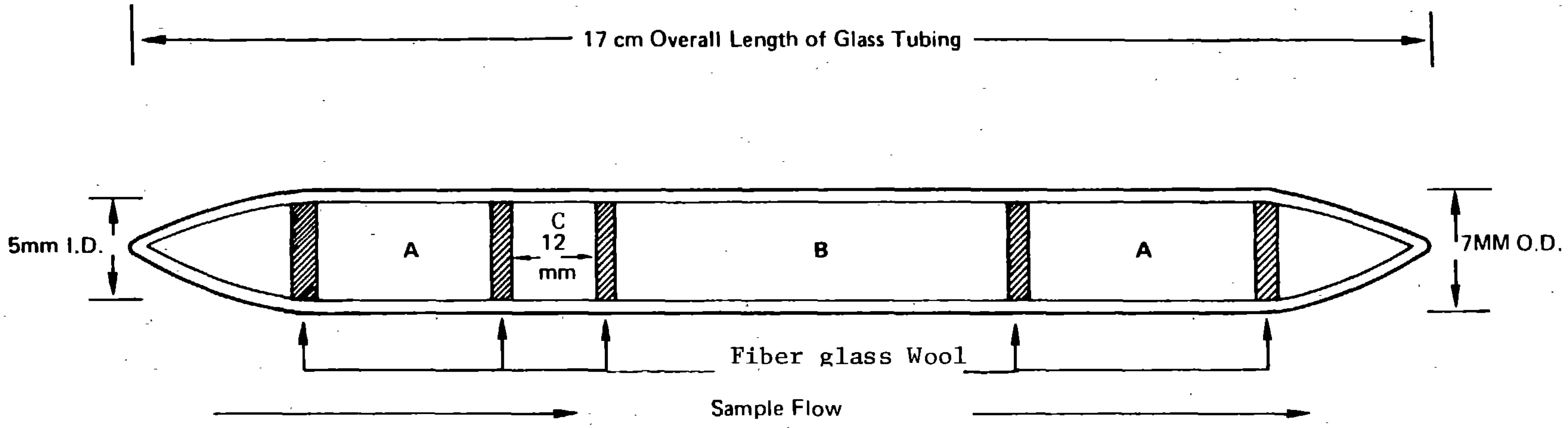
A known volume of air is drawn through a three-section sampling tube containing triethanolamine-impregnated molecular sieve and Draeger oxidizer to collect the nitric oxide after oxidation to nitrogen dioxide. The spectrophotometric method has been validated over the range of 11.14-47.7 ppm for a 1.5-liter sample at 19°C and 764 mm Hg atmospheric temperature and pressure.

Sampling Equipment

The sampling equipment needed consists of a three-section sampling tube containing triethanolamine-impregnated molecular sieve and Draeger oxidizer and a personal sampling pump calibrated with a representative sampling tube in the line. The pump flow rate should be set accurately, ±5%, at 0.025 liter per minute. A suitable tube holder should be used to protect the worker from the sharp edges of the glass sampling tube.

The sampling tube used to collect the sample consists of a glass tube flame-sealed at both ends, 17 cm long with a 7-mm OD and a 5-mm ID, packed with two 400-mg sections of triethanolamine-impregnated molecular sieve and one 1.2-g section of Draeger oxidizer. Sections are separated by glass wool and a 12-mm inner glass tube as shown in Figure S321-1. The pressure drop across the tube is approximately 3 cm of water at a flow rate of 0.025 liter per minute.

The triethanolamine-impregnated molecular sieve can be prepared as follows: Add 25 g triethanolamine to a 250-mL beaker; add 4 g glycerol, 50 mL of acetone and sufficient distilled water to bring up to 100 mL. To the mixture add about 50 mL Type 13X, 30-40 mesh molecular sieve. Stir and let stand in a covered beaker for about 30 minutes. Decant the excess liquid and transfer the molecular sieve to a porcelain pan which is then placed under a heating lamp until most of the moisture has evaporated. Complete the drying in an oven at 110°C for one hour. The sorbent should be free flowing. Store in a closed glass container.



A. 400 mg Triethanolamine – Impregnated Type 13 X, 30–40 Mesh Molecular Sieve

B. 1.2 g of Oxidation Material No. 1900277 from Draeger Company of Germany, supplied by National Mine Service Co.

C. 12 mm glass spacer tube, 4.0 mm O.D., 2.6 mm I.D.

NITRIC OXIDE SAMPLING TUBE

Figure S321-1

Sample Size

A sample size of 1.5 liters is recommended. (See Special Considerations.) Sample at a flow rate of 0.025 liter per minute for 60 minutes.

Sampling Procedure

1. Immediately before sampling, the ends of the tubes should be broken so as to provide openings approximately one-half the internal diameter of the tubes.

2. The 12-mm inner glass tube should be positioned farthest from the sampling pump. The sampling tube should be placed in a vertical position during sampling to avoid channeling and subsequent premature breakthrough of the analyte.

3. Air being sampled should not be passed through any hose or tubing before entering the front section of the sampling tube.

4. A low flow rate pump is used. Set the flow rate as accurately as possible using the manufacturer's directions. Record all the necessary information to determine flow rate or volume and also record the initial and final sampling time. Record the temperature and pressure of the atmosphere being sampled. If pressure reading is not available, record the elevation.

5. The sampling tubes should be labeled properly and capped with the supplied plastic caps immediately after sampling.

6. One sampling tube should be handled in the same manner as the sample tubes (break, seal, and transport), except for the taking of an air sample. This tube should be labeled as a blank. Submit one blank for every batch of five samples.

Sampling Considerations

1. Where two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

2. Collection efficiency is not acceptable at a flow rate much in excess of 0.025 liter per minute if the concentration of nitric oxide approaches or exceeds twice the OSHA standard level. Therefore, the sampling rate must be set carefully.

Shipping Instructions

Capped sampling tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

Reference

Nitric oxide, NIOSH Method No. S321.

Backup Data Report No. S321
August 5, 1977

Substance:	Nitric oxide
OSHA Standard:	25 ppm (30 mg/cu m)
Chemical Used for Validation:	Nitric oxide, 1.03%, Scott Specialty Gas, Inc.

General Considerations

The method for nitric oxide (NO) has been tested in accordance with the various criteria for validation described in Reference 1 and in conformity with the statistical analysis described in Reference 2. The statistical criteria established for this program are related to the present suggested standard for air monitoring accuracy, i.e., the absolute total error (sampling and analysis) should be less than 25% in at least 95% of the samples analyzed at the level of the OSHA standard. In order to satisfy the statistical criteria, a measure of accuracy and precision was established, i.e., overall recovery must be 100 ±10% and CV_T must be less than or equal to 0.105. The fine points of the statistical basis for this program are discussed in Reference 2.

The protocol for validation of a method for nitric oxide consisted of the following experimental studies:

- Comparison of the collection efficiency of nitric oxide gas on various sampling tubes containing two 400-mg sections of triethanolamine-impregnated molecular sieve and a section of MSA oxidizer or Draeger oxidizer,
- Analysis of a set of eighteen analytical samples (six samples at each of the three test levels), prepared by drawing known amounts of nitric oxide in air through three-section sampling tubes to collect the equivalent of 1.5-liter collections at 0.5, 1 and 2X the OSHA standard,
- Analysis of a set of eighteen samples (six samples at each of the three test levels) collected from a dynamically generated test atmosphere to represent 60 minute samples (1.5 liters) at 0.5, 1 and 2X the time-weighted average concentration,
- Independent verification of the concentration of a set of six samples collected from a dynamically generated test atmosphere at the OSHA standard level,
- Determination of the breakthrough capacity of three-section sampling tubes at high relative humidity,
- Testing of the storage stability of collected samples,

- Assessment of the precision and accuracy of the method.

The details with respect to each of these items are discussed in the following sections. The method tested experimentally and documented in this report has passed all the requirements of the program.

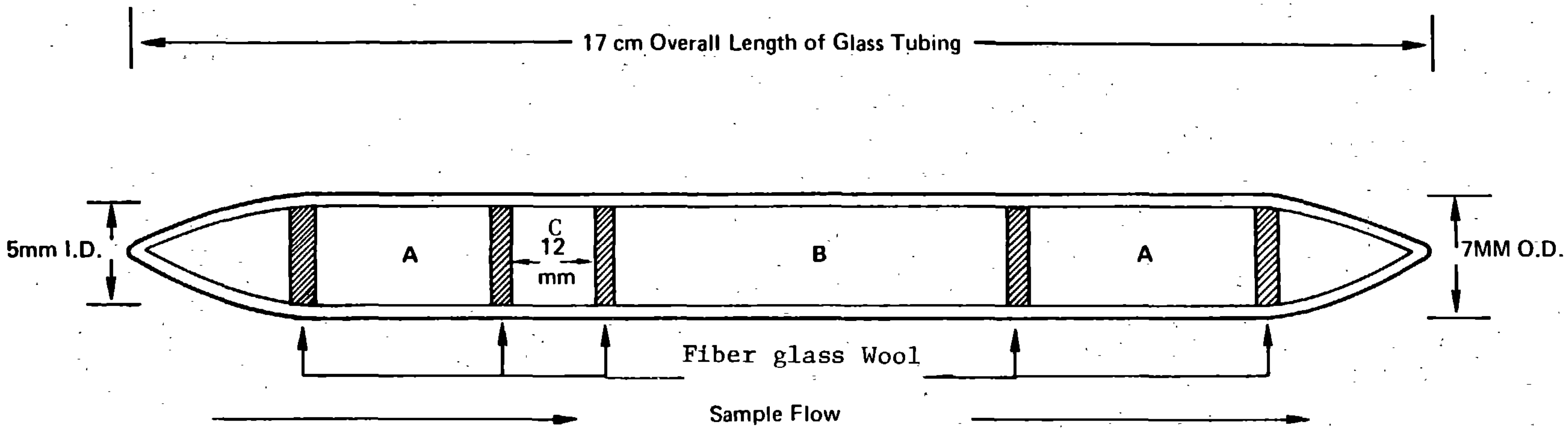
Principle of the Method

The method validated for the analysis of nitric oxide in air is based on collection on a three-section sampling tube containing two 400-mg sections of triethanolamine (TEA)-impregnated molecular sieve and a 1.2-g section of Draeger oxidizer (Figure S321-1). The sample is collected at a flow rate of 25 mL/minute. Ambient nitrogen dioxide (NO_2) is removed quantitatively by the first TEA section, NO is oxidized quantitatively to NO_2 by the solid oxidizer, and the NO_2 is quantitatively collected on the second TEA section. The NO_2 trapped on the second section is removed with an absorbing solution and the concentration determined by spectrophotometric analysis of nitrite ion.

Comparison of Collection Media

Recent work by Levaggi, et al. (Reference 3), and Blacker (Reference 4) resulted in a method for measuring NO_2 by absorbing it in a triethanolamine solution or on TEA-impregnated molecular sieve. Current techniques for the measurement of NO generally involve oxidizing it to NO_2 and determining the concentration of NO_2 spectrophotometrically. Willey, et al. (Reference 5), have described a solid sorbent sampling tube for NO_2 and NO which combines this previous work and allows simultaneous collection of NO and NO_2 in the concentration range of the proposed NIOSH standards. Although NO_2 is collected efficiently (96%) in the range of 0.5 to 5 ppm by this method, the collection efficiency for NO decreases with increasing concentration in the range from 9 to 50 ppm. In order to meet the statistical criteria of the NIOSH Standard Completion Program, sampling conditions had to be determined to improve the poor collection efficiency (67%) observed at 50 ppm NO (2X the OSHA standard).

Initial experiments to determine collection efficiency at 50 ppm NO involved sampling at a flow rate of 25 mL/min (Willey, et al., had used a flow rate of 50 mL/min) in hopes of achieving quantitative collection. Three-section sampling tubes prepared by MSA according to the design described by Willey et al. were supplied to us by NIOSH. Five replicate samples were collected at 25 mL/min for two hours in 82% relative humidity. The collection efficiency was only about 2%, as shown below. The data are shown as micrograms of nitrite ion (NO_2^-) since that is the species measured.



A. 400 mg Triethanolamine – Impregnated Type 13 X, 30-40 Mesh Molecular Sieve

B. 1.2 g of Oxidation Material No. 1900277 from Draeger Company of Germany, supplied by National Mine Service Co.

C. 12mm glass spacer tube, 4.0 mm O.D., 2.6 mm I.D.

NITRIC OXIDE SAMPLING TUBE

Figure S321-1

μg NO_2^- taken	μg NO_2^- found	Recovery (%)
177	3.25	1.8
177	4.00	2.3
177	5.00	2.8
177	2.50	1.4
177	4.25	2.4

The collection efficiency was also measured by collecting 50 ppm NO in a dry atmosphere and similar results were obtained.

Glass tubes (7-mm OD) were packed with 800 mg of Draeger oxidizer to determine the oxidation efficiency of this material. Five replicate samples were collected with an oxidizer tube and an MSA tube in series. The front TEA sections of the MSA tube were analyzed to determine the percent of NO oxidized by the Draeger oxidizer. One-hour samples were collected at 21 mL/min from a test atmosphere of 48 ppm NO. The collection efficiency under these conditions is shown below.

μg NO_2 added	μg NO_2^- found	Conversion Recovery (%)
143	56.4	39.4
143	59.8	41.8
143	55.6	38.9
143	57.3	40.1
143	57.3	40.1

The recovery was improved but was still not sufficient to meet the statistical requirements. It should, of course, be noted that the preceding recoveries were based on calculated (not measured) generator concentrations.

Another collection from about 50 ppm NO was made at 22 mL/min for 60 minutes. However, during this experiment the generator concentration was measured by an Energetic Sciences "Enolyzer" which was calibrated with a commercially available 49.8 ppm NO gas standard. Also, the oxidizer section was increased to 1.0 g. The results of this collection are shown below.

μg NO_2^- taken	μg NO_2^- found	Conversion Recovery (%)
78.9	78.0	98.9
78.9	77.0	97.6
78.9	71.9	91.1
78.9	75.3	95.4
78.9	72.9	92.4
78.9	74.2	94.0

The data indicate that a 1.0-g oxidizer section is sufficient to yield acceptable recovery during a 60-minute collection at 2X the OSHA standard (50 ppm). However, in order to provide sufficient collection efficiency and breakthrough capacity in humid air, the oxidizer section was increased to 1.2 g of Draeger oxidizer. The capacity of this tube is shown in the following section on breakthrough tests. Tubes packed with two 400-mg sections of TEA/molecular sieve and 1.2 g Draeger oxidizer have a pressure drop of 3 cm H_2O at 25 mL/min.

Analysis

A detailed description of the procedure for analysis, preparation of sample collection devices and the preparation of calibration standards is given in NIOSH Method No. S321 (Reference 6).

The reliability of the analytical method was tested, based on the analysis of eighteen samples. The analytical samples were prepared by drawing a 49.8 ppm NO gas mixture through sampling tubes at 25 mL/min for 15, 30 and 60 minutes to represent the equivalent of a 1.5-liter sample at 0.5, 1, and 2X the OSHA standard, respectively.

The front and back TEA/molecular sieve sections were treated with triethanolamine solution so as to desorb the NO_2. An aliquot of the resulting solution was treated with hydrogen peroxide, sulfanilamide and (N-1-(naphthyl)-ethylene-diamine)dihydrochloride. Spectrophotometric analysis was done with a Perkin-Elmer Coleman 55 Spectrophotometer at 540 nm using a treated blank to zero the instrument. The absorbance was observed to be directly proportional to the nitrite ion concentration in the sample. Appropriate standard solutions, prepared from a 100-ppm nitrite stock standard, were analyzed on the same day as the samples. The data for the full set of eighteen analytical samples are shown in Table S321-1.

Table S321-1

Data Sheet: Nitric Oxide

Analysis

Level	0.5S			1S			2S	
µL added	µL found	Recovery	µL added	µL found	Recovery	µL added	µL found	Recovery
18.40	17.71	0.962	36.8	37.9	1.030	73.6	73.0	0.992
19.26	20.42	1.060	38.5	43.2	1.122	77.1	75.3	0.977
17.45	16.65	0.954	34.9	33.4	0.957	69.7	74.8	1.073
18.46	16.17	0.876	37.0	35.4	0.957	73.9	74.5	1.008
17.76	17.39	0.979	35.5	36.1	1.017	71.0	68.9	0.970
17.50	18.19	1.039	35.0	32.9	0.940	70.1	66.1	0.943

	0.5S	1S	2S
n =	6	6	6
mean	0.978	1.004	0.994
std dev	0.0658	0.0682	0.0445
CV_1	0.0673	0.0679	0.0448

$\overline{CV}_1$ 0.0610

$\overline{CV}_{A+\overline{DE}}$ 0.0659

Breakthrough Tests

Breakthrough is defined as the time at which the effluent concentration from the collection tube is 5% of the concentration in the test gas mixture. The criterion for acceptance of sampling tube capacity is that the volume of air that has passed through the tube at the time of breakthrough must be at least 1.5 times the volume of air that would be passed through the tube during collection of a field sample, when the substance of interest in the test atmosphere is at 2X the OSHA standard level.

Breakthrough experiments were done in a test atmosphere of 84% relative humidity. The procedure for determining breakthrough of NO consisted of (1) generating a test atmosphere of NO at a concentration of 46.1 ppm (measured with an Enolyzer), (2) placing two 3-section sampling tubes in series to act as a primary collector and a breakthrough monitor, (3) collecting six replicate samples at a flow rate of 20.94 milliliters per minute for 108 minutes (2.262 liters), and (4) analyzing the TEA/molecular sieve sections of each set of sampling tubes.

The tests were conducted at an atmospheric temperature of 19.7 °C and an atmospheric pressure of 764.4 mm Hg. The analytical data for each set of tubes is shown in Table S321-2. The amount of NO collected on the first tube (collection tube) corresponds to a mean concentration of 43.8 ppm NO while that collected in the second tube (breakthrough monitor) corresponds to a mean concentration of 1.725 ppm NO. The fact that no NO_2 (<0.19 ppm) was collected on the front TEA section of each tube indicates that the observed breakthrough is due to inefficient oxidation of NO to NO_2 rather than inefficient collection of NO_2. The data indicate that the breakthrough in a volume of 2.262 liters (1.5 times the recommended collection volume equals 2.250 liters) is 3.79%.

It is thus recommended that a sample volume of 1.5 liters be used for field collection of NO.

Sampling and Analysis

Test atmospheres were generated using the vapor dilution system described in Attachment A. A steady stream of 1.03% nitric oxide in nitrogen was delivered from a gas cylinder via a calibrated rotameter at a flow rate of approximately 0.48 liters per minute into a dry air stream flowing at a rate of 0.105 cu m per minute. The three sample lines were maintained at dilution ratios of 0.228, 0.489 and 1.000 to produce 0.5, 1 and 2X OSHA standard test levels. The delivery rate of the nitric oxide was determined by calibrating the rotameter using a soap-bubble flow meter.

Table S321-2

Breakthrough Analysis of NO Sampling Tube[*]

Tube	TEA Section	µL NO[**]
Collection Tube	Front - 1	<0.427
	2	<0.427
	3	<0.427
	4	<0.427
	5	<0.427
	6	<0.427
	Back - 1	95.2
	2	101.9
	3	102.9
	4	89.6
	5	98.6
	6	105.6
	mean	99.0
	std dev	5.83
	CV	0.0589
Breakthrough Tube	Front - 1	<0.427
	2	<0.427
	3	<0.427
	4	<0.427
	5	<0.427
	6	<0.427
	Back - 1	4.27
	2	3.77
	3	3.63
	4	3.84
	5	4.05
	6	3.84
	mean	3.90
	std dev	0.2264
	CV	0.0580

$$\% \text{ Breakthrough} = \frac{3.90\ \mu\text{L}}{99.0 + 3.90\ \mu\text{L}} = 3.79$$

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[*] NO sampling tube contains 400 mg TEA/molecular sieve followed by 1.2-g Draeger oxidizer and another 400 mg TEA/molecular sieve.

[**] Samples were collected for 108 minutes at a flow rate of 21 mL/min. A total volume of 2.262 L was collected a a challenge concentration of 46.1 ppm NO.

Six samples were collected simultaneously at each test level at a flow rate of 25 mL/min for 60 minutes (1.5 liters). The samples were analyzed as described in Section 8.4 of NIOSH Method No. S321. The data obtained for these eighteen samples are shown in Table S321-3.

Storage Stability

Studies were done to assess the stability of nitric oxide samples upon storage for seven days at atmospheric conditions. Twelve samples, representative of the OSHA standard level, were collected simultaneously from the vapor generator. The generator concentration (19.8 ppm NO) was independently measured with an Energetic Sciences "Enolyzer." Six samples were analyzed one day after collection, and the other six samples were stored and analyzed seven days after collection. The comparative data given in Table S321-4 indicate that the samples are stable over the seven-day period. The average value found for nitric oxide was 19.98 ppm for the one-day-old samples versus 19.89 ppm for the seven-day-old samples; a recovery of 99.5%.

Independent Verification of Generator Concentration

In addition to establishing the generator concentration of nitric oxide by determining the gas delivery rate and the dilution air flow at the main line and dilution lines, a calibrated Energetic Sciences Enolyzer Model 7100 was used to independently measure the NO concentration at each level during generation experiments. The Enolyzer was calibrated with a certified gas standard (49.8 ppm NO) supplied by Scott Specialty Gas, Inc.

At least six measurements of generator concentration in the 1S dilution arm (and several measurements in the 0.5 and 2S arm) were made during sample collections. The data shown in Table S321-5 were obtained during collection of the sampling and analysis set described above. The data verify the accuracy of this method within the criteria of 100 ±10% agreement.

Precision and Accuracy

The precision of the method was determined by using the statistical procedures described in Reference 2 and the data in Tables S321-1 and S321-3.

Bartlett's test for homogeneity of variances of 0.5, 1 and 2X the OSHA standard for sampling and analysis was applied to the data for nitric oxide. The data (Table S321-3) gave a chi-squared value of 0.918. This chi-squared value indicates that it is feasible to pool the coefficents of variation. Thus, $\overline{CV}_T$ is calculated based on the pooled data.

TABLE S321-3

Data Sheet: Nitric Oxide Sampling and Analysis

Test Level	-------- Found	-----------		Taken	
	µL	Liters	ppm	ppm	Recovery
0.5S	16.39	1.501	10.92	11.05	
	17.78	1.571	11.32	11.05	
	16.51	1.422	11.61	11.05	
	16.09	1.507	10.68	11.05	
	16.12	1.448	11.13	11.05	
	15.98	1.429	11.18	11.05	
		n = 6			
		mean	11.14		1.008
		std dev	0.321		
		CV_2	0.02882		
1S	39.4	1.562	25.22	23.56	
	36.6	1.493	24.52	23.56	
	38.3	1.521	25.20	23.56	
	37.0	1.499	24.71	23.56	
	38.8	1.508	25.75	23.56	
	37.7	1.462	24.44	23.56	
		n = 6			
		mean	24.97		1.060
		std dev	0.505		
		CV_2	0.02022		
2S	71.5	1.439	49.7	45.3	
	74.7	1.522	49.1	45.3	
	67.9	1.483	45.8	45.3	
	74.0	1.541	48.0	45.3	
	71.0	1.527	46.5	45.3	
	69.7	1.473	47.3	45.3	
		n = 6			
		mean	47.7		1.054
		std dev	1.500		
		CV_2	0.0314		
		$\overline{CV}_2$	0.02723		

Table S321-4

Stability of Generated/Collected NO Samples

Samples Stored 1 Day			Samples Stored 7 Days		
μL NO Found	Liters	ppm	μL NO Found	Liters	ppm
28.03	1.478	18.96	28.88	1.479	19.53
29.89	1.484	20.14	28.03	1.423	19.70
29.73	1.400	21.24	30.21	1.468	20.58
28.08	1.426	19.69	28.88	1.402	20.60
31.06	1.548	20.06	29.57	1.435	20.61
27.87	1.408	19.79	27.61	1.507	18.32
	n = 6			n = 6	
	mean	19.98		mean	19.89
	std dev	0.746		std dev	0.909
	CV	0.0373		CV	0.0457

TABLE S321-5

Independent Verification of Generator Concentration

ppm NO			
	ppm Taken: Enolyzer		ppm Found: Spectrophotometric Method
	22.9		25.22
	23.6		24.52
	23.5		25.20
	24.1		24.71
	24.2		25.75
	23.7		24.44
n =	6	n =	6
mean	23.7	mean	24.97
std dev	0.468	std dev	0.505
CV	0.01975	CV	0.02022

The precision of the method is expressed in terms of the coefficients of variation for the analytical method, the sampling and analysis method, and the overall method which includes a pump error of 0.05. These values are shown below:

$$\overline{CV}_1 = 0.0610 \qquad \overline{CV}_2 = 0.02723 \qquad \overline{CV}_T = 0.0621$$

The experimentally determined $\overline{CV}_T$ value is a good estimate not only of the precision but also of the accuracy of the method. This assumption is suggested by the data for the set of six samples described in the section on Independent Verification and other data collected during generation of NO. For those samples where the Taken concentration is based on the "Enolyzer" data, the agreement between the Found and Taken values can be summarized as shown below.

	----- ppm NO	------	
Level	Taken	Found	Agreement (Found ÷ Taken)
0.5S	10.6	11.14	1.051
1S	23.7	24.97	1.054
2S	47.5	47.7	1.004
		Average =	1.036

The differences between the Taken and Found concentrations is considered to result from experimental uncertainties in the value for the Taken concentration and does not represent a bias in the method. Further confidence in the accuracy of the tested method is established by the results of the collection efficiency test and the storage stability test, described in the appropriate sections.

References

1. Statement of Work, Article 1, Contract No. 210-76-0123, NIOSH, Department of Health, Education and Welfare, U. S. Government.

2. Documentation of NIOSH Validation Tests, National Institute of Occupational Safety and Health, Cincinnati, Ohio (DHEW-NIOSH-Publication No. 77-185), 1977. Available from Superintendent of Documents, U. S. Government Printing Office, Washington, D. C., Order No. 017-033-00231-2.

3. D. A. Levaggi, W. Sui and M. Feldstein, _J. Air Poll. Cont. Assoc._, 23, 30 (1973).

4. J. H. Blacker, *Am. Ind. Hyg. Assoc. J.*, 34, 390 (1973).

5. M. A. Willey, C. McCammon, Jr. and L. Doemeny, *Am. Ind. Hyg. Assoc. J.*, 38, 358 (1977).

6. Nitric Oxide, NIOSH Method No. S321, prepared under NIOSH Contract 210-76-0123.

ATTACHMENT A

VAPOR DILUTION/SAMPLING SYSTEM

The vapor generation/dilution system used for the validation studies of several vapors and gases, such as this analyte, is shown schematically in Figure S321-A-1. The system basically consists of a main line air stream to which are added predetermined amounts of various liquids, gases or aerosols to generate the desired vapor concentrations. From the main line, three dilution arms branch off in which the desired multiples 0.5, 1.0 and 2.0 times the OSHA Standard concentration level are established. Six sampling devices are connected in parallel to the 0.5S dilution line and six to the 2S dilution line; twelve sampling devices are connected to the 1S dilution line. All these devices are connected via critical flow orifices (CFO's) to the corresponding vacuum lines.

Air flow rates through the system are established by means of critical flow orifices (CFO's) and flow restrictors. The primary air system derived from the house air compressor is maintained at 20.0 psig. The appropriate orifice diameters are chosen to maintain an air flow of approximately 0.1 cu m/min in the Main Line and an addition of 0.05 cu m/min to each of the dilution lines. The main line is maintained at 8 cm H_2O pressure by means of a needle valve. Appropriate flow restrictor diameters are chosen for the 0.5S, 1S and 2S dilution lines so as to give the desired final concentrations of vapor in air.

The system was designed to generate either 4X or 2X the OSHA Standard concentration in the Main Line. When a 4X level is generated, 0.05 cu m/min of dilution air is added to each dilution line. Orifices are selected so that the 0.5S, 1S and 2S lines have flows equal to approximately 0.007, 0.017 and 0.050 cu m/min respectively of the Main Line concentration added to the dilution air, thus giving the desired final concentrations. Where a Main Line concentration of 2X the OSHA Standard is generated, no dilution air is added to the 2S dilution line--0.017 cu m/min is simply allowed to flow through this line--and 0.050 cu m/min of dilution air is added to the 0.050 cu m/min and 0.017 cu m/min of Main Line mixture admitted to the 1S and 0.5S dilution lines, respectively.

All materials which the vapor may contact before collection are 316 or 304 stainless steel. A glass heater is included where the liquids are added to the main line. Shutoff ball valves are placed in the dilution lines to allow their independent operation and the calibration of air flows. The Main Line has a 2.54-cm (1 in) O.D., and the dilution lines are 1.90-cm (0.75 in) O.D. Diameters were chosen to give turbulent flow with an approximate minimum Reynolds number of 3000.

Air Supply

Air from the house compressor is treated by passing it sequentially through a cotton filter, a silica gel bed, a charcoal bed and a high efficiency glass fiber filter for removal of water, hydrocarbons and particulate. This air is then connected to a manifold containing six takeoff

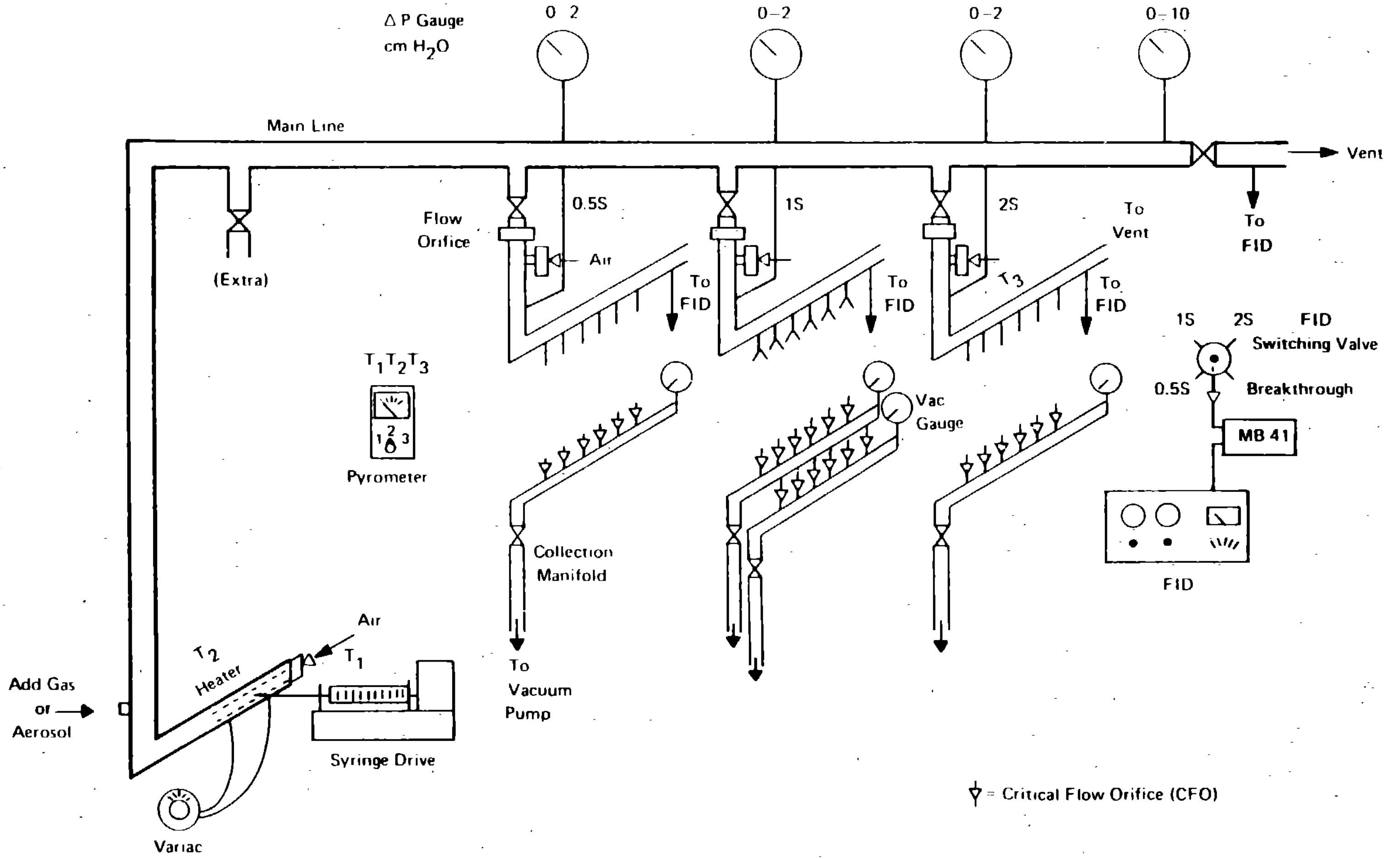

Figure S321-A-1. Vapor Generation/Dilution/Sampling System

ball valves. The pressure (20 psig) at the manifold is maintained with a Nullmatic Moore 40H50 regulator and monitored with an Ashcroft 0-60 psig test gauge. The air supply is used for each of the dilution system connections as well as for the flame ionization detector monitor flame and "zero" air.

Sample Collection Manifold

Sample flow through the sampling devices connected to the dilution lines is established by connecting each device by means of a short piece of flexible tubing to a CFO which is connected to a 1.27 cm (1/2 in) O.D. vacuum manifold. Each dilution line has a separate manifold which derives its vacuum from a Model 0322 Gast vacuum pump. The orifices are jewel orifices pressed into a threaded Teflon rod. One end of the rod is screwed into a tee on the manifold, and the other has a hose tabulation fitting connected to it. The orifice is protected from plugging by means of a piece of 100 mesh stainless steel screen.

Vent System

All excess vapor-laden air is collected via a 3.81-cm (1.5 in) PVC manifolding system where it is passed through a 0.3 x 0.3 x 0.6-M charcoal bed. Flow is established by means of a pressure blower on the exit side of the charcoal bed, and it is vented to the laboratory hood exhaust.

Calibration

Air Flows

Main Line -- The air flow delivered by the Main Line CFO was determined by measurement with a Singer Dry Test Meter. The meter had previously been calibrated with a spirometer primary standard. Using the 0.310-cm diameter orifice at 20 psig air pressure, the flow was found to be 0.1086 cu m/min corrected to 25°C and 760 mm Hg.

Dilution Lines -- The air flow through each of the dilution line CFO's and restrictor orifices was similarly measured with the Dry Test Meter to assure that they met design parameters, but these values did not provide the primary basis for determination of vapor concentration.

Collection CFO's -- Since the flow rate through the sample collection CFO's was lower (0.2 and 1.0 liter per minute) than appropriate for use with the Dry Test Meter, the flow rate of each of these orifices was measured using an SKC soap bubble meter which was independently calibrated by gravimetrically measuring water capacity.

All volume measurements have been referenced to normal temperature and pressure of 25°C and 760 mm Hg.

Dilution Ratios

The concentration of vapor in the dilution lines is determined from the concentration calculated in the Main Line and the dilution ratio determined between the dilution lines and the main line. These dilution ratios were measured by adding a controlled amount of propane gas to the Main Line and then measuring the relative concentration in each of the lines using a Beckman Model 402 heated hydrocarbon analyzer. The procedure was repeated several times and is regularly checked during the program.

In the case where 4X or 2X concentration level conditions were generated, the dilution ratios reported below were observed.

		Relative Concentration		
Case Generated	Main Line	2S	1S	0.5S
4X	1.000	0.5097	0.2557	0.1311
2X	1.000	1.000	0.499	0.227

Each of these sets of values represents a different set of air flow and orifice selection conditions as previously discussed. Point to point comparison of the six sample ports on each manifold showed less than a 1% variation in concentration among them.

Monitors

To provide a ready check on operating conditions, several gauges or monitors have been included in the system. Dwyer Magnehelic gauges monitor the pressure on the Main Line and each of the dilution lines. A 0-10 cm H_2O gauge is used on the Main Line (Setpoint 8 cm) and 0-2 cm H_2O gauges are used for the dilution lines. The purpose of these latter gauges is to provide a check against possible back pressure developing in these lines which would affect the dilution ratios.

The flame ionization detector (FID) is used to determine the time at which the Main Line concentration has reached equilibrium and to monitor the concentration level during breakthrough studies and sample collection.

Breakthrough Studies

A. Low Relative Humidity (Dry Air)

For the measurement of sorbent tube capacity for a given vapor (breakthrough) six sorbent tubes containing only the 100 mg "front half" section of sorbent are connected in parallel to the 2S dilution line and to a 0.635-cm (1/4-in) O.D. stainless steel six-port manifold. Flow through the manifold is controlled by a CFO and is established using a Metal Bellows Corp. Model MB41 pump. Flow through the orifice was

measured as 1.14 liters per minute providing a 0.19-liter per minute flow to each of the tubes. (A separate set of orifice allows a similar determination at a flow rate of 1.0 liter per minute through each tube.) Equal flow through each of the tubes is insured by carefully selecting and/or adjusting packing in the tubes to have an equal pressure drop when precalibrated at a 0.2-liter per minute flow rate.

Once a steady state vapor concentration is established, the 2S concentration level is used to set the 100% point on the hydrocarbon analyzer. Then the valve is switched, and the flow from the breakthrough manifold is passed through the hydrocarbon analyzer and monitored either until 5% of the 2S level is observed or for a period of four hours--whichever occurs first.

B. High Relative Humidity

For the generation of a high relative humidity atmosphere, at least 80% R.H., water vapor is delivered into the generator Main Line via one of the side arms as shown in Figure S321-A-2. A peristaltic pump, Cole-Parmer Masterflex, Model No. 7013, is used to deliver water into a heated copper coil (1/8 in x 10 feet) contained in a tube furnace; the furnace temperature is maintained above 110°C and monitored by a thermocouple and optical pyrometer. Water is delivered at the rate of 1.9 g per minute to blend with the analyte-containing dry air stream flowing at a rate of 0.100 cu m per min to produce an atmosphere of at least 80% R.H. at 25°C and 760 mm Hg.

All other aspects of the breakthrough test procedure are as described above.

Procedure

The overall procedure for a given sample is as follows:

1. Line air flow and dilution ratios are verified.
2. Sample delivery rate is determined by appropriate calibration.
3. Sample is fed into Main Line until vapor concentration equilibrium is established.
4. The breakthrough experiment is performed and subsequent sample collection volumes adjusted if necessary.
5. The four sets of six samples from the three concentration levels are collected simultaneously.

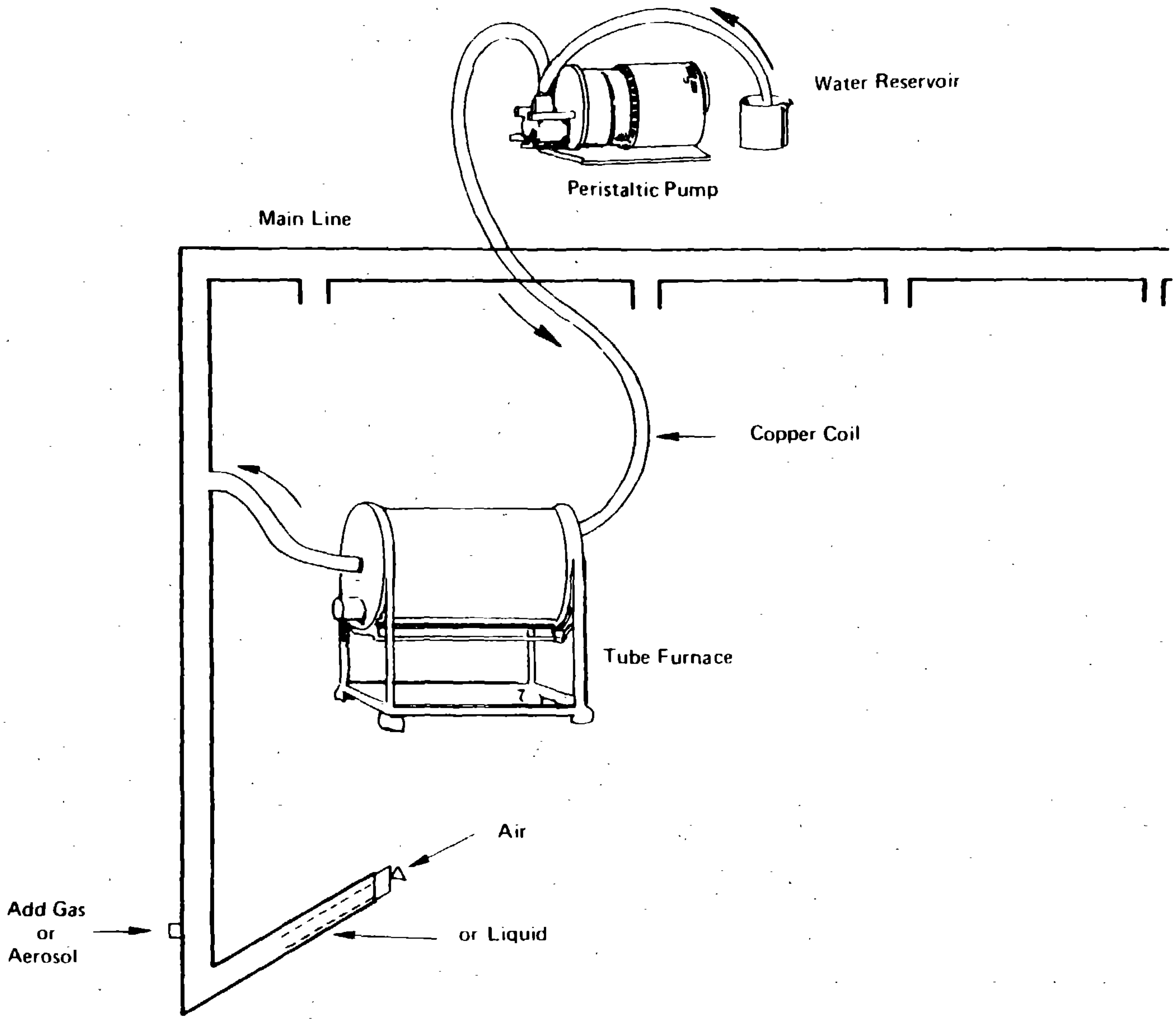

Figure S321-A-2 Generation of High Humidity Atmospheres

Nitric Acid

Analyte:	Nitrate Ion	Method No:	S319
Matrix:	Air	Range:	2.60 - 10.8 mg/cu m
OSHA Standard:	5 mg/cu m	Precision ($\overline{CV}_T$):	0.082
Procedure:	Impinger collection, ion specific electrode	Validation Date:	8/5/77

1. Principle of the Method

1.1 Samples are collected by drawing a known volume of air through a midget impinger containing distilled water.

1.2 The contents of the impinger are analyzed by direct potentiometry using an ion specific electrode.

1.3 The concentration of nitric acid in the sample is determined by comparison of the potential obtained for the sample solution to a calibration curve obtained by measurement of standard solutions.

1.4 A calibration standard is run before and after each sample to assure that reliable results are obtained.

2. Range and Sensitivity

2.1 This method was validated over the range 2.60 - 10.8 mg/cu m using a 180-liter air sample.

2.2 The lower limit of detection for nitrate using the nitrate ion specific electrode is 6×10^{-6} M or 0.4 μg/ml according to the electrode manufacturer.

3. Interference

Constituents of the buffer solution complex, precipitate, decompose or otherwise remove the common interfering anions including Br^-, Cl^-, F^-, I^-, PO_4^{-3}, and NO_2^- (Reference 11.1). However, high concentrations of any of these species should be avoided.

4. Precision and Accuracy

4.1 The coefficient of Variation ($\overline{CV}_T$) for the total sampling and analytical method in the range of 2.60 - 10.8 mg/cu m was 0.0824. This value corresponds to a 0.4 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in References 11.2 and 11.3.

4.2 A collection efficiency of 97% was determined for HNO_3 in water; thus, no bias was introduced in the sample collection step from this source.

4.3 The average concentrations "found" at the OSHA standard levels using the overall sampling and analytical method were 4.3% lower than the "true" concentrations found for a limited number of samples analyzed by an alternate method (Reference 11.3). In addition, samples were found to be stable when stored for seven days. Thus, CV_T is a satisfactory measure of the precision of the sampling method.

5. Advantages and Disadvantages

5.1 Advantages of the method include simplicity, specificity, and speed.

5.2 Disadvantages of the method are associated with the collection device, the midget impinger. Not only is it inconvenient, but there is the possible loss of sample if the impinger is not maintained in an upright position during sampling.

6. Apparatus

6.1 Sampling Apparatus

6.1.1 Personal Sampling Pump. A calibrated personal sampling pump, the flow of which can be determined within ±5% at the recommended flow rate (Reference 11.3). The pump is protected from splashover or water condensation by a piece of glass wool loosely packed within the tubing used to connect the pump and midget impinger.

6.1.2 Midget impinger.

6.1.3 Distilled water.

6.1.4 Pipet, 20-ml or other suitable device for filling the impinger.

6.1.5 Barometer.

6.1.6 Thermometer.

6.1.7 Stopwatch.

6.2 Orion 92-07 Nitrate Liquid Ion Exchange Membrane Electrode or equivalent.

6.3 Orion 90-02 Double Junction Reference Electrode or equivalent.

6.4 Orion Model 801 Digital pH/mV Meter or equivalent.

6.5 Volumetric flasks, 25-ml.

6.6 Pipets, 20-ml, 5-ml.

6.7 Beakers, 50-ml.

6.8 Magnetic stirrer and Teflon-coated stirring bars.

7. Reagents

All reagents must be ACS reagent grade or better.

7.1 Buffer Solution. Dissolve 4.3g aluminum sulfate, 1.6g boric acid, 3.9g silver sulfate, and 2.4g sulfamic acid in distilled water and dilute to 500 ml. The purpose of this buffer is explained in Reference 11.1.

7.2 Nitric Acid Standards

7.2.1 Nitric Acid Stock Solution. Pipet 5 ml of concentrated nitric acid into a 500-ml volumetric flask and dilute to the mark with distilled water. The concentration of the stock solution should be determined accurately by titration of 15-ml aliquots with 0.1N Sodium hydroxide using phenolphthalein as an indicator. Duplicate titrations should agree within 0.1 ml. Calculate the molarity of the stock solution using the equation

$$\text{Molarity} = \frac{(\text{Molarity of NaOH}) \times (\text{ml of NaOH})}{15 \text{ ml}}$$

7.2.2 Nitric Acid Working Solution. Pipet 5 ml of the nitric acid stock solution into a 500-ml volumetric flask and dilute to the mark with distilled water.

7.2.3 Working Standards. Working standards corresponding to the amounts of nitric acid collected at the 0.5, 1, and 2X the OSHA standard can be prepared by pipeting 5, 10, and 20 ml respectively of the nitric acid working solution into three 25-ml volumetric flasks, each of which contains 5 ml of the buffer solution, and diluting to the mark with distilled water. The concentrations of the working standards are calculated by multiplying the concentration of the nitric acid stock solution by the appropriate dilution factors.

7.3 Saturated Sodium Sulfate Solution. Add sufficient sodium sulfate to distilled water to form a saturated solution. The supernatant is used for the outer chamber filling solution in the double junction reference electrode.

8. Procedure

8.1 Cleaning of Equipment. All glassware should be washed with detergent and rinsed thoroughly with distilled water.

8.2 Calibration of Personal Pump. Each personal pump must be calibrated with a representative midget impinger in the line.

8.3 Collection and Shipping of Samples

8.3.1 Connect a midget impinger containing 20 ml of distilled water to a sampling pump using a piece of flexible tubing. The tubing should be loosely plugged with a piece of glass wool to protect the sampling pump from splashover and condensation.

8.3.2 The impinger must be maintained in a vertical position during sampling.

8.3.3 Air being sampled should not be passed through any hose or tubing before entering the impinger.

8.3.4 A sample size of 180 liters is recommended. Sample at a flow rate of 1.0 liter per minute for 180 minutes. The flow rate should be known with an accuracy of at least ±5%.

8.3.5 Record the ambient temperature and barometric pressure.

8.3.6 Remove the impinger stem and tap the stem gently against the inside wall of the impinger bottle to recover as much of the sampling solution as possible. Rinse the impinger stem with 1 ml of distilled water and add the wash to the impinger bottle. Seal the impinger with a hard, non-reactive stopper (preferably Teflon). Do not seal with rubber. The stoppers on the impingers should be tightly sealed to prevent leakage during shipping.

8.3.7 With each batch of 10 samples submit one impinger containing 20 ml of distilled water. This impinger should be handled in the same manner as the samples except that no air is drawn through it. Label this impinger as the blank.

8.4 Analysis of Samples

8.4.1 Pipet 5 ml of the buffer solution into a 25-ml volumetric flask.

8.4.2 Transfer the contents of the impinger to the volumetric flask and dilute to the mark with distilled water.

8.4.3 Empty the contents of the volumetric flask into a 50-ml beaker. Add a magnetic stirring bar.

8.4.4 Potentiometric Measurements

8.4.4.1 Immerse the nitrate ion electrode and reference electrode in the sample solution and record the millivolt reading. Both samples and standards should be stirred while readings are taken. The reading should be taken after the meter has stabilized to ± 0.1 mV/10 sec. Follow the instrument manufacturer's instruction manual for proper operation and measurement procedures.

8.4.4.2 Samples should be interspersed between standards as described in Section 9.2.

8.4.5 Appropriate blanks must be analyzed by the same procedure used for the samples.

9. Calibration and Standards

9.1 Nitric acid standards should be prepared as described in Section 7.2. A series of at least three standards should be analyzed prior to the measurement of samples. Plot the potentials in millivolts developed in the standards (on the linear axis) against the molarity of the standards (on the log axis) on semilogarithmic graph paper. The slope of the best straight line fitted to the standards measurements should be equal to 59.2 mV ±1 mV/10-fold change in concentration. If the slope of the line does not fall within these limits, consult the troubleshooting section of the electrode manufacturer's instruction manual.

9.2 Samples should be interspersed between standards having concentrations which bracket the concentrations of the samples. At the conclusion of the analysis of a series of samples, calculate the average response in millivolts for each standard. Plot the data as described in Section 9.1. The resulting calibration line is used to calculate the concentrations of the samples.

10. Calculations

10.1 Determine the molarity of nitric acid in the sample from the calibration line. Calculate the weight of nitric acid in micrograms corresponding to the molarity of the sample using the equation

$$\text{Molarity} \times (1.575 \times 10^6) = \mu g$$

10.2 Corrections for the blank must be made for each sample impinger.

$$\mu g = \mu g \text{ sample} - \mu g \text{ blank}$$

where:

μg sample = μg found in sample impinger

μg blank = μg found in blank impinger

10.3 Determine the volume of air sampled at ambient conditions in liters based on the appropriate information, such as flow rate in liters per minute multiplied by sampling time. If a pump using a rotameter for flow rate control was used for sample collection, a pressure and temperature correction must be made for the indicated flow rate. The expression for this correction is:

$$\text{Corrected Volume} = f \times t \left(\sqrt{\frac{P_1}{P_2} \times \frac{T_2}{T_1}} \right)$$

where:

f = sample flow rate

t = sampling time

P_1 = atmospheric pressure during calibration of sampling pump (mm Hg)

P_2 = atmospheric pressure of air during sampling (mm Hg)

T_1 = ambient temperature during calibration of sampling pump (°K)

T_2 = ambient temperature of air sampled (°K)

10.4 The concentration of nitric acid in the sampled air can be expressed in mg/cu m (= µg/liter) as follows:

$$\text{mg/cu m} = \frac{\mu\text{g (Section 10.2)}}{\text{Air volume sampled (Section 10.3)}}$$

Another method of expressing concentration is ppm (corrected to standard conditions of 25°C and 760 mm Hg):

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{\text{MW}} \times \frac{760}{\text{P}} \times \frac{(\text{T} + 273)}{298}$$

where:

P = barometric pressure (mm Hg) of air sampled

T = temperature (°C) of air sampled

24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg

MW = molecular weight

760 = standard pressure (mm Hg)

298 = standard temperature (°K)

11. References

11.1 P.J. Milham, A.S. Awad, R.E. Paull, and J.H. Bull, Analyst, 95, 751 (1970).

11.2 Documentation of NIOSH Validation Tests, National Institute for Occupational Safety and Health, Cincinnati, Ohio (DHEW-NIOSH-Publication No. 77-185), 1977. Available from Superintendent of Documents, U.S. Government Printing Office, Washington, D.C., Order No. 017-033-00231-2.

11.3 Backup Data Report for Nitric Acid, No. S319, prepared under NIOSH Contract No. 210-76-0123.

11.4 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

Sampling Data Sheet No. S319
August 5, 1977

Substance

Nitric Acid

Standard

8-hour time weighted average: 2 ppm (5 mg/cu m)

Analytical Method

A known volume of air is drawn through a midget impinger containing 20 ml of distilled water to trap nitric acid vapors and aerosols present. The impinger solutions are analyzed by direct potentiometry using the nitrate ion specific electrode. The method has been validated over the range of 2.60-10.8 mg/cu m for a 180-liter sample.

Sampling Equipment

Required sampling equipment includes a midget impinger containing 20 ml of distilled water and a personal sampling pump. The pump should be calibrated with a representative impinger in the line; the flow rate should be determined accurately to within ±5% at 1.0 liter per minute. The flexible tubing connecting the impinger to the pump should be loosely plugged with a piece of glass wool to protect the sampling pump from splashover and condensation.

Sample Size

A sample size of 180 liters is recommended. Sample at a flow rate of 1.0 liter per minute for 180 minutes.

Sampling Procedure

1. Pipet 20 ml of distilled water into a midget impinger.

2. Attach the impinger to the sampling pump with a short piece of flexible tubing. The tubing should be loosely plugged with a piece of glass wool to protect the sampling pump from splashover and condensation. The impinger must be maintained in a vertical position during sampling.

3. Air being sampled should not be passed through any hose or tubing before entering the impinger.

4. Set the pump flow rate as accurately as possible using the manufacturer's directions. Record all the information necessary to determine flow rate or volume and also record the initial and final sampling time. Record the temperature and barometric pressure of

the atmosphere being sampled. If pressure reading is not available, record the elevation.

5. Remove the impinger stem and tap the stem gently against the inside wall of the impinger bottle to recover as much of the sampling solution as possible. Rinse the impinger stem with 1 ml of distilled water and add the wash to the impinger bottle. Seal the impinger with a hard, non-reactive stopper (preferably Teflon). Do not seal with rubber. The stoppers on the impingers should be tightly sealed to prevent leakage during shipping.

6. With each batch of 10 samples submit one impinger containing 20 ml of distilled water. This impinger should be handled in the same manner as the samples except that no air is drawn through it. Label this impinger as the blank.

Special Considerations

Where two or more air contaminants are known or suspected to be present in the air, such information, including their suspected identifies, should be transmitted with the sample. The following anions are known interferences: Br^-, Cl^-, F^-, I^-, PO_4^{-3} and NO_2^-.

Shipping Instructions

The sealed impinger bottles containing the sample solutions and blanks should be shipped in a suitable container, designed to prevent damage in transit.

Reference

Nitric Acid, NIOSH Method No. S319.

Backup Data Report No. S319
August 5, 1977

Substance: Nitric Acid

OSHA Standard: 5.0 mg/cu m

Chemical Used for Validation: Nitric Acid, 69.0 - 71.0%, Fisher Scientific Co.

General Considerations

The method for nitric acid has been tested in accordance with the various criteria for validation described in Reference 1 and in conformity with the statistical analysis described in Reference 2. The statistical criteria established for this program are related to the present suggested standard for air monitoring accuracy, i.e., the absolute total error (sampling and analysis) should be less than 25% in at least 95% of the samples analyzed at the level of the OSHA standard. In order to satisfy the statistical criteria, a measure of accuracy and precision was established, i.e., overall recovery must be 100 ±10% and unbiased $\overline{CV}_T$ must be less than or equal to 0.105. The fine points of the statistical basis for this program are discussed in Reference 2.

The protocol for validation of a method for nitric acid consisted of the following experimental studies:

- Determination of the collection efficiency of midget impingers containing distilled water,
- Analysis of a total of 18 samples (6 at each of the 3 test levels--0.5, 1 and 2X the OSHA standard) spiked with the appropriate amount of nitric acid to represent a sample volume of 180 liters,
- Analysis of a total of 18 samples collected from dynamically generated test atmospheres (6 at each of the 3 test levels--0.5, 1 and 2X the OSHA standard) for the same sample volume as above,
- Testing of the storage stability of collected samples,
- Assessment of the precision and accuracy of the method.

The details with respect to each of these items are discussed in the following sections. The method tested experimentally and documented in this report has passed all the requirements of this program.

Preliminary Experiments

The stainless steel vapor generation/dilution/sampling system ordinarily used for experiments with vapors was <u>not</u> used for nitric acid in order to prevent deleterious effects on the system due to the chemical action of nitric acid or interference of any residual nitric acid in the system with other compounds in subsequent experiments. A separate generation apparatus, described in Appendix A, employing a glass sampling manifold was assembled and used for all experiments with nitric acid.

Initial experiments were directed toward the evaluation of silica gel as a solid absorbent for nitric acid vapors (Reference 3). The capacity of pre-assembled silica gel tubes (SKC Inc., Cat. No. 226-10) was determined using the glass generation apparatus. The combined effluent from six absorbent tubes was drawn through a modified midget impinger through which distilled water was pumped at a constant, pre-determined rate. The concentration of nitric acid in the impinger overflow was monitored continuously using a pH meter, so that the occurrence of breakthrough could be determined immediately. The ability of this system to respond adequately to a concentration equivalent to 5% of twice the OSHA standard was verified experimentally. Response time for this concentration was approximately five minutes. However, in the actual evaluation of silica gel capacity for nitric acid, no breakthrough was detected after sampling an atmosphere having a concentration equal to 2X the OSHA standard for eight hours at 0.2 liter per minute.

The analytical method was evaluated using samples prepared by spiking the front sections of 18 identical silica gel tubes (6 each at 0.5, 1 and 2X the OSHA standard) with microliter aliquots of a nitric acid stock solution. The amounts of nitric acid added to the tubes corresponded to the amounts of nitric acid collected in a 4-hour sampling period using a collection rate of 0.2 liter per minute. The nitric acid was desorbed by emptying the front section of the silica gel tube into a 50-ml beaker containing 5 ml of distilled water. The mixture was stirred for 2 minutes using a miniature Teflon-coated stirring bar. Five ml of ionic strength adjustment buffer (Reference 4) were pipetted into the mixture and the nitrate and reference electrodes were immersed in the resulting solution. The first mV reading that was constant to ±0.1 mV for 10 seconds was recorded. Calibration curves were constructed using standards prepared from a nitric acid stock solution and analyzed according to the procedure described above. The concentrations of nitric acid in the samples were determined from the calibration curves. The data for the 18 analytical samples are shown in Table S319-1.

Test atmosphere samples were generated in lots of six. Samples were collected at 0.2 liter per minute for 240 minutes. The generator concentration was determined by replacing the flow-through impinger used in the breakthrough experiment with a standard midget impinger containing 20 ml of distilled water. Nitric acid collected in the impinger was titrated with standard alkali. The data for six samples collected from an atmosphere having a concentration equal to 2X the OSHA standard are shown in Table S319-2.

Two sets of six samples each were collected at the OSHA standard level. Three samples from each set were analyzed on the day of collection and the remaining samples were stored for seven days prior to analysis. No special efforts were taken to store the samples in a dark place, but an

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Table S319-1

Nitric Acid - Silica Gel Adsorbent Tube Collection

Analysis

Level	0.5S			1S			2S	
µg added	µg found	Recovery	µg added	µg found	Recovery	µg added	µg found	Recovery
125.9	134.9	1.071	251.7	249.7	0.992	504	519	1.030
125.9	120.4	0.956	251.7	261.0	1.037	504	505	1.002
125.9	139.3	1.106	251.7	303.9	1.207	504	487	0.966
125.9	146.3	1.162	251.7	273.0	1.085	504	496	0.984
125.9	136.2	1.082	251.7	285.6	1.135	504	501	0.994
125.9	134.9	1.071	251.7	280.6	1.115	504	- (sample lost)	
n =		6			6			5
mean		1.075			1.095			0.9995
std dev		0.0675			0.0757			0.02365
CV_1		0.0628			0.0691			0.02377

$\overline{CV}_1$ 0.0571

$\overline{CV}_{A+\overline{DE}}$ 0.0617

Table S319-2

Nitric Acid - Silica Gel Adsorbent Tubes Sampling and Analysis

Test Level	Found			Taken	Recovery
	µg	Liters	mg/cu m	mg/cu m	
2S	455	52.3	8.70	8.48	
	450	52.3	8.60	8.48	
	480	55.2	8.70	8.48	
	476	52.3	9.10	8.48	
	496	52.6	9.43	8.48	
	472	52.1	9.06	8.48	
		n =	6		1.053
		mean	8.93		
		std dev	0.3210		
		CV_2	0.0358		

adhesive label wrapped around each tube for identification effectively prevented light from reaching the silica gel. When examined visually prior to analysis, the stored samples showed evidence of chemical reaction; the wire spring holding the glass wool plug in place ahead of the front silica gel section was corroded and the first 1-2 mm of silica gel were colored light yellow. The data for these sets are shown in Table S319-3.

The average recoveries for Sets A and B were 0.797 and 0.460 respectively. While the reasons for the difference in recoveries between the two sets are not apparent, the recovery for either set is unacceptably low. Because of this problem, work with silica gel was terminated, and a complete set of 18 analytical samples was not collected.

It may be possible to eliminate the storage stability problem simply by removing the wire spring from pre-assembled silica gel tubes prior to sampling. In any case, the acceptable $\overline{CV}_1$ and $\overline{CV}_2$ values and recoveries shown in Tables S319-1 and S319-2 suggest that the silica gel adsorbent tube approach may merit further attention in future studies.

Principle of the Method

The method validated for the analysis of nitric acid vapor in air is based on collection in water and analysis of the resulting solution with a nitrate ion specific electrode. A sample size of 180 liters is recommended.

Analysis

A detailed description of the procedure used for analysis is given in NIOSH Method No. S319.

The reliability of the analytical method tested was based on the analysis of 18 analytical samples. These samples were prepared by adding aliquots of a nitric acid stock solution to distilled water. The aliquots added (10, 20, 40-microliters) contained respectively 0.504, 1.007 and 2.014 mg of nitric acid representing the equivalent of a 180-liter air sample at 0.5, 1 and 2X the OSHA standard.

The data for the 18 analytical samples is shown in Table S319-4.

Sampling and Analysis

Test atmosphere samples were generated in lots of 7 using the system described in Attachment B.

Collection Efficiency

The collection efficiency of midget impingers containing distilled water was determined by collecting samples using 6 sets of 2 impingers connected in series. Samples were collected for 180 minutes at 1.0 liter per minute from a test atmosphere having a concentration equal to 2X the OSHA standard. The amount of nitric acid in the front

Table S319-3

Nitric Acid - Silica Gel Adsorbent Tubes
Storage Stability

	Samples Analyzed on Day of Collection (mg/cu m)	Samples Analyzed 7 Days after Collection (mg/cu m)
Set A	223.2	174.6
	219.4	211.6
	221.3	143.1
	Mean 221.3	Mean 176.4
Set B	299.4	174.7
	348.7	132.5
	Mean 357.5	Mean 155.0
	335.2	154.1

Table S319-4

Nitric Acid

Analysis

Level	0.5S			1S			2S	
µg added	µg found	Recovery	µg added	µg found	Recovery	µg added	µg found	Recovery
504	496	0.984	1007	1003	0.996	2014	2112	1.049
504	493	0.978	1007	1007	1.000	2014	2120	1.053
504	513	1.018	1007	1019	1.012	2014	2120	1.053
504	510	1.012	1007	1019	1.012	2014	2068	1.027
504	507	1.006	1007	1032	1.025	2014	2042	1.014
504	510	1.012	1007	1035	1.028	2014	2094	1.040
n =		6			6			6
mean		1.002			1.012			1.039
std dev		0.01656			0.01284			0.01588
CV_1		0.01653			0.01269			0.01528

$\overline{CV}_1$ 0.01492

$\overline{CV}_{A+\overline{DE}}$ 0.01612

impingers was determined and compared to the amount of nitric acid found in the back impingers; the average collection efficiency calculated in this manner was 96.8%. The data for this experiment is shown in Table S319-5.

Additional test atmosphere samples were collected using midget impingers, each containing 20 ml of distilled water, at 1.0 liter per minute for 180 minutes. Twenty-one samples, seven each at 0.5, 1, and 2X the OSHA standard, were collected. One sample from each lot of seven was used for the independent method of determining the generator concentration. The remaining eighteen samples were analyzed within one day of collection as described in Section 8.4 of NIOSH Method No. S319. The data for the eighteen generated samples is shown in Table S319-6.

Storage Stability Studies

Studies were done to assess the stability of nitric acid sample solutions for seven days under ambient conditions. Due to equipment limitations (only seven samples could be taken at once with the glass generating system used), two sets of six samples were collected at the OSHA standard level. Three samples from each set were analyzed on the day of collection and the remaining six samples were analyzed seven days after the day of collection. No special efforts were taken to store the samples in a dark place. The data for these samples is given in Table S319-7.

The data in Table S319-7 show that the six samples stored for seven days met the criterion for acceptance, i.e., the mean of six samples stored at room temperature for seven days should be within ±10% of the mean of six samples analyzed at the beginning of the storage period. In this case, the two means agree within 9%, indicating adequate stability on storage.

Independent Determination of Generator Concentration

The concentration of nitric acid generated by the vapor generation system was determined by titration with 0.01N sodium hydroxide of the nitric acid collected in 20 ml of distilled water in a midget impinger. One sample for determination of generator concentration was collected at 1.0 liter per minute for 180 minutes and analyzed along with each set of six generated samples. The pH of the sample solution was recorded as a function of volume of titrant added during the titration, and the equivalence point was determined graphically. The "taken" concentrations at 0.5, 1, and 2X the OSHA standard determined by this method were 2.603, 5.98, and 10.83 mg/cu m respectively. The average recoveries calculated by comparison of the "taken" values obtained as described above to the "found" values determined as described in Section 8.4 of NIOSH Method No. S319 indicate satisfactory agreement between the independent and validated methods.

Table S319-5

Nitric Acid - Impinger Collection Efficiency

µg Found			
Front	Backup	Total	Collection Efficiency
2157	61.7	2219	0.972
2268	54.2	2322	0.977
2316	78.1	2394	0.967
2456	98.0	2554	0.962
2036	84.1	2120	0.960
2125	71.0	2196	0.968

Average Collection Efficiency ... 0.968

Table S319-6

Data Sheet: Nitric Acid
Sampling and Analysis

Test Level	---------Found-----------			Taken	
	µg	Liters	mg/cu m	mg/cu m	Recovery
0.5S	411	196.2	2.095	2.603	
	436	196.2	2.222	2.603	
	448	192.6	2.326	2.603	
	488	198.0	2.465	2.603	
	485	192.6	2.518	2.603	
	488	196.2	2.487	2.603	
		n =	6		
		mean	2.352		0.904
		std dev	0.1686		
		CV_2	0.0716		
1S	1003	196.2	5.11	5.98	
	1016	196.2	5.18	5.98	
	1096	192.6	5.69	5.98	
	1183	198.0	5.97	5.98	
	1074	192.6	5.58	5.98	
	1041	196.2	5.31	5.98	
		n =	6		
		mean	5.47		0.915
		std dev	0.332		
		CV_2	0.0607		
2S	2157	196.2	10.99	10.83	
	2268	196.2	11.56	10.83	
	2316	192.6	12.02	10.83	
	2456	198.0	12.40	10.83	
	2036	192.6	10.57	10.83	
	2125	196.2	10.83	10.83	
		n =	6		
		mean	11.40		1.053
		std dev	0.720		
		CV_2	0.0632		
		$\overline{CV}_2$	0.0653		

Table S319-7

Nitric Acid - Impingers
Storage Stability

	Samples Analyzed on Day of Collection (mg/cu m)	Samples Analyzed 7 Days after Collection (mg/cu m)
Set A	4.92	5.00
	5.32	4.53
	5.59	4.81
Set B	5.74	5.14
	5.12	4.76
	5.28	4.85
	Mean 5.33	Mean 4.85

Precision and Accuracy

The precision of the method was determined by applying the statistical procedures described in Reference 2 and the data in Tables S319-4 and 6.

Bartlett's test for homogeneity of variances was applied to the CV data for sampling and analysis for nitric acid. The data (Table S319-4) gave a chi squared value of 0.1252, indicating that it is feasible to pool the coefficients of variation. Thus, $\overline{CV}_T$ is calculated based on the pooled data.

The precision of the method is expressed in terms of the coefficients of variation for the analytical method, the sampling and analytical method, and the overall method which includes a pump error of 0.05. These respective values are shown below.

$\overline{CV}_1 = .01492 \qquad \overline{CV}_2 = .0653 \qquad \overline{CV}_T = .0824$

The accuracy of the method was determined by comparison of the average value found by analysis of each set of six samples at each of the three test levels with the taken generator concentration determined as discussed in the preceding section. The data summarized below show good agreement [Found (Electrode) ÷ Taken (Titration)] with an average of 95.7%.

Table S319-8

Comparison of Validated Method and Independent Method

Found by Titration mg/cu m	Found by Electrode mg/cu m	Found (Electrode) / Taken (Titration)
2.603	2.352(1)	0.904
5.98	5.47(1)	0.915
10.83	11.40(1)	1.053

(1) average of six determinations

References

1. Statement of Work, Article 1, Contract No. 210-76-0123. NIOSH Department of Health, Education and Welfare, 4676 Columbia Parkway, Cincinnati, Ohio 45226.

2. Documentation of NIOSH Validation Tests, National Institute for Occupational Safety and Health, Cincinnati, Ohio (DHEW-NIOSH-Publication No. 77-185), 1977. Available from Superintendent of Documents, U.S. Government Printing Office, Washington, D.C., Order No. 017-033-00231-2.

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3. Failure Report No. S319, Nitric Acid.

4. P. J. Milham, A. S. Awad, R. E. Paull, and J. H. Bull, Analyst, 95, 751 (1970).

ATTACHMENT A

VAPOR GENERATION/DILUTION/SAMPLING SYSTEM FOR ADSORBENT TUBE COLLECTION OF NITRIC ACID VAPOR

The vapor generation/dilution/sampling system used for adsorbent tube collection of nitric acid vapor is shown schematically in Figure S319-A-1. The particular equipment configuration shown in the figure was used for the breakthrough studies; slight modifications were made as noted below for the collection of test atmosphere samples. The basic components of the system are described below.

Air Supply

Air from the house compressor was passed sequentially through a cotton filter, a silica gel tower, and a high efficiency glass fiber particulate filter. The air pressure was controlled with a constant pressure regulator downstream from the filters. Air flow from the regulator was controlled by a 100-liter per minute critical flow orifice (CFO).

Vapor Generation

Air flow from the 100 lpm CFO was split at a tee. The larger portion of the air was directed to the glass dilution/sampling manifold. The remainder of the air stream was directed to a midget bubbler containing concentrated nitric acid. The relative flows through the two legs of the tee were controlled by a needle valve and a flowmeter in the leg connected to the midget bubbler. Air from the flowmeter was directed to the top of the midget bubbler and through the sintered glass tip into concentrated nitric acid. Nitric acid vapor entrained by the air passed into the glass dilution/sampling manifold where it combined with the remainder of the air stream. Desired concentrations of nitric acid vapor in air were obtained by varying the flow through the bubbler using the flowmeter.

Sampling Manifold

Silica gel adsorbent tubes were connected to the glass dilution/sampling manifold with Teflon Swagelok® unions. In the breakthrough experiment, the effluent end of the adsorbent tubes were connected by latex tubing to the sampling ports of an identical glass sampling manifold, which was maintained under a slight vacuum. That portion of the air flow which was not sampled by the adsorbent tubes was vented through the open end of the sampling manifold.

The effluent from all six tubes was combined and directed into a midget impinger containing distilled water. The total flow through the tubes was controlled by a one lpm CFO downstream from the impinger. The CFO was connected to a carbon vane sampling pump.

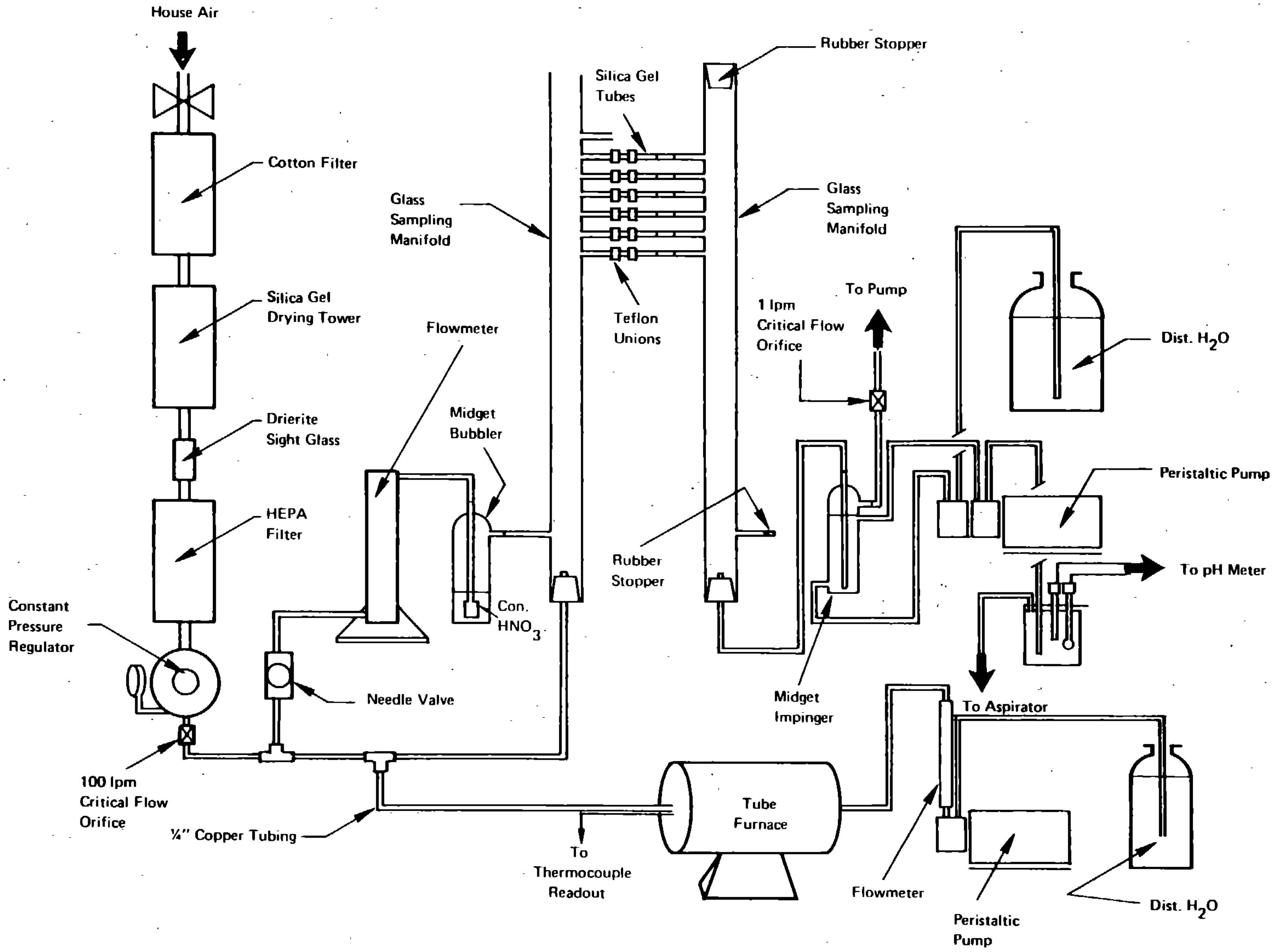

FIGURE S319–A–1 NITRIC ACID VAPOR GENERATION APPARATUS ADSORBENT TUBE COLLECTION

Water Addition

For the determination of breakthrough capacity, a humid atmosphere was generated by addition of water vapor to the air. Distilled water was fed by a peristaltic pump into a tube furnace. Water vapor exiting from the furnace was combined with that portion of the air which was directed to the sampling manifold without passing through the bubbler containing concentrated nitric acid. The relative humidity of the air was determined using a Beckwith Humi-Chek® mounted at the open end of the glass dilution/sampling manifold. With this configuration, the highest relative humidity that could be achieved before droplets appeared on the inner walls of the sampling manifold was 40%. The effects of the 80% relative humidity atmosphere required for challenging the sampling devices was simulated by doubling the proposed sampling time and monitoring for breakthrough over that period.

Detection of Breakthrough

The combined effluent from the six adsorbent tubes was collected at one lpm in distilled water in a modified midget impinger. The impinger was modified by addition of a one-inch long 8mm pyrex tube near the bottom of the sample bottle and an identical tube near the top of the bottle on the opposite side. Distilled water from a reservoir was pumped into the sample bottle through the bottom arm. Water overflowing from the upper arm on the sample bottle was pumped at the same rate into a 50-ml beaker, so that the amount of water in the sample bottle remained constant at about 20 ml. The water level in the beaker was controlled by a piece of glass tubing mounted in a perpendicular position over the water and connected to an aspirator. A glass electrode and a calomel reference electrode were immersed in the 50-ml beaker. The water in the beaker was stirred continuously using a magnetic stirrer. The pumping rate was adjusted to maintain a pH $\simeq$ 5; any increase in the amount of nitric acid in the combined effluent from the six adsorbent tubes would be observed as an increase in the rate of change of pH. In trial experiments, deliberate increases in nitric acid vapor concentration equivalent to the increase in concentration expected on breakthrough were detected within five minutes.

System Modifications for Generation of Test Atmospheres

For the routine generation of test atmospheres, the modified midget impinger was replaced with a standard midget impinger containing 20 ml of distilled water. Air flow through the impinger was controlled by a one lpm CFO connected to a carbon vane sampling pump. Nitric acid collected in the impinger was determined at the end of the sampling period by titration with 0.01N sodium hydroxide.

ATTACHMENT B

VAPOR GENERATION/DILUTION/SAMPLING SYSTEM FOR IMPINGER COLLECTION OR NITRIC ACID VAPOR

The vapor generation/dilution/sampling system used for studies of impinger collection of nitric acid vapor is shown schematically in Figure S319-B-1. The air supply, vapor generation, and sampling manifold components of this system were identical to those of the system described in detail in Attachment A.

Seven midget impingers, each containing 20 ml of distilled water, were connected to the sampling ports on the glass sampling manifold with latex tubing. Each impinger was also connected with latex tubing to a one lpm critical flow orifice (CFO). The CFO's were mounted in a copper manifold which was connected to a carbon vane sampling pump. One of the impingers from each set of samples was used to determine the generator concentration. Nitric acid collected in the impinger was determined at the end of the sampling period by titration with 0.01N sodium hydroxide.

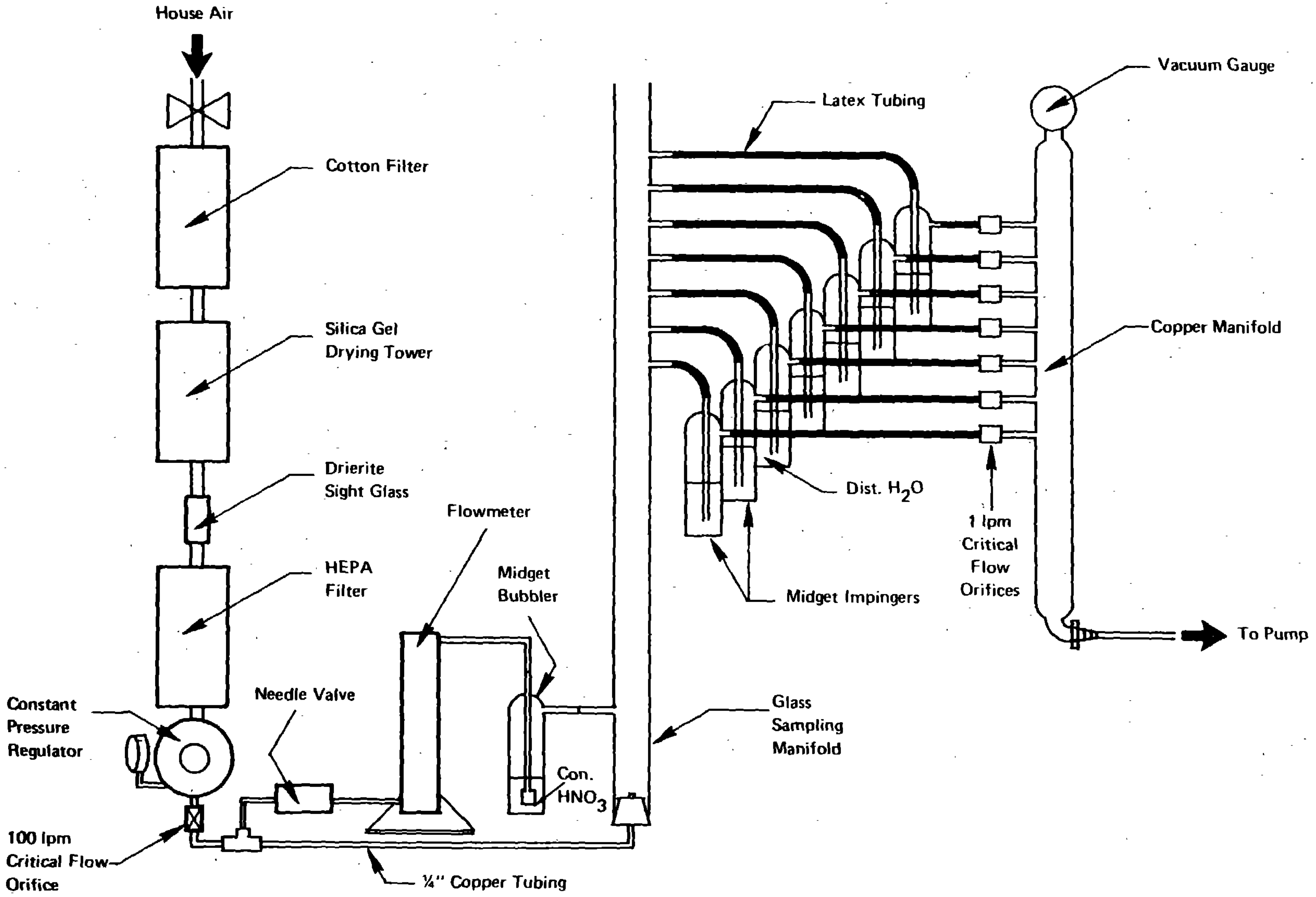

FIGURE S319–B–1 NITRIC ACID VAPOR GENERATION APPARATUS IMPINGER COLLECTION

Formaldehyde

Analyte:	Formaldehyde derivative	Method No.:	S327
Matrix:	Air	Range:	1.4-6.2 ppm (8-hr T.W.A.) 4.6-19.8 ppm (Peak)
OSHA Standard:	3 ppm (8-hr T.W.A.) 10 ppm (Peak) 5 ppm (Ceiling)	Precision $(\overline{CV}_T)$:	0.052 (8-hr T.W.A.) 0.058 (Peak)
Procedure:	Bubbler collection, derivatization with Girard T reagent, polarography	Validation Date:	9/2/77

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1. Principle of the Method

1.1 A known volume of air is drawn through a midget bubbler containing a buffered solution of Girard T reagent. Formaldehyde is derivatized with the Girard T reagent.

1.2 The formaldehyde-Girard T reagent derivative is measured by polarography.

2. Range and Sensitivity

2.1 This method was validated over the range of 1.4-6.2 ppm at an atmospheric temperature and pressure of 21°C and 759 mm Hg, using an 18-L sample, representing an 8-hour time-weighted average (T.W.A.) collection. This method was also validated over the range of 4.62-19.84 ppm for 30-minute peak samples at an atmospheric temperature and pressure of 21°C and 757 mm Hg.

2.2 The upper limit of the method is dependent on the concentration of Girard T reagent. While collection efficiency has not been tested outside of the method range, a 80-fold molar excess of Girard T reagent should be maintained over the total amount of formaldehyde sampled.

3. Interferences

3.1 When other compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

3.2 The use of polyvinyl chloride tubing preceding the midget bubbler should be kept to a minimum. Products from the tubing may interfere in the method.

3.3 Other volatile aldehydes such as acrolein, crotonaldehyde, and benzaldehyde may cause significant interference.

4. Precision and Accuracy

4.1 The Coefficient of Variation $(\overline{CV}_T)$ for the total analytical and sampling method in the range of 1.4-6.2 ppm (8-hr T.W.A.) was 0.052. This corresponds to a 0.16 ppm standard deviation at 1X the 8-hr T.W.A. OSHA standard. The Coefficient of Variation (CV_T) for the total analytical and sampling method in the range of 4.62-19.84 ppm (peak) was 0.058. This corresponds to a 0.58 ppm standard deviation at 1X the ceiling OSHA standard. Statistical information can be found in Reference 11.2.

4.2 On the average the concentrations obtained in the laboratory validation study at 0.5X, 1X, and 2X the 8-hr T.W.A. OSHA standard were 3.5% higher than the "true" concentrations for 18 samples. The concentrations obtained at 0.5X, 1X, and 2X the peak OSHA standard were 1.1% lower than the "true" concentrations for 18 samples. Any difference between the "found" and "true" concentrations may not represent a bias in the sampling and analytical method, but rather a random variation from the experimentally determined "true" concentration. Therefore, the method has no bias. The Coefficient of Variation is a good measure of the accuracy of the method since the recoveries and storage stability were good. Storage stability studies on samples collected from a test atmosphere at a concentration of 3.02 ppm indicate that collected samples are stable for at least 7 days. Collection efficiency of the midget bubbler was determined to be 1.00, so no correction for collection efficiency is needed.

5. Advantages and Disadvantages of the Method

5.1 The formaldehyde-Girard T reagent derivative has adequate storage stability.

5.2 Collected samples are analyzed by a quick instrumental method.

5.3 A disadvantage of the method is the awkwardness in using midget bubblers for collecting personal samples. If the worker's job performance requires much body movement, loss of the collection solution during sampling may occur.

5.4 The bubblers are more difficult to ship than adsorption tubes or filters due to possible breakage and leakage of the bubblers during shipping.

6. Apparatus

6.1 A glass midget bubbler.

6.2 Personal Sampling Pump: A calibrated personal sampling pump whose flow rate can be determined to an accuracy of 5%. The sampling pump is protected from splashover or solvent condensation by a trap. The trap is a midget bubbler or impinger with the stem broken off which is used to collect spillage. The trap is attached to the pump with a metal holder. The outlet of the trap is connected to the pump by flexible tubing.

6.3 Thermometer.

6.4 Manometer.

6.5 Volumetric Flasks: 1-L and other convenient sizes for preparing standard solutions.

6.6 Pipets: Convenient sizes for preparing stock standard solutions and for measuring the collection medium.

6.7 Buret: 0-50 mL capacity with graduations of 0.1 mL.

6.8 Erlenmeyer Flask: 250 mL.

6.9 Ice Bath.

6.10 Magnetic Stirrer.

6.11 Syringes: Convenient sizes for preparing spiked standard samples.

6.12 Polarograph which is capable of DC or sampled DC polarography with reference to a saturated calomel electrode.

6.13 China Marker.

6.14 Teflon tubing (15 cm x 7-mm I.D.) or Teflon plugs for sealing the inlet and outlet of the bubbler stem before shipping.

7. Reagents

7.1 Citric acid, reagent grade.

7.2 Disodium hydrogen phosphate, reagent grade.

7.3 Girard T reagent, reagent grade.

7.4 Triton X-100, 0.075% solution. Dilute 750 microliters of Triton X-100 to 1 liter with distilled water. Triton X-100 is a commonly used polarographic maximum suppressor.

7.5 Buffered Girard T reagent. Dissolve 13.257 g disodium hydrogen phosphate, 10.773 g citric acid, 3.926 g Girard T reagent in a 1-L volumetric flask. Add 6.6 mL of the Triton X-100 solution and dilute to 1 liter with distilled water. The pH of the resulting solution is 4.5.

7.6 Formaldehyde, 37% solution, reagent grade.

7.7 Formaldehyde Solution A, 1 mg/mL. Dilute 2.7 mL 37% formaldehyde solution to 1 liter with distilled water.

7.8 Iodine, 0.1 N (approximate). Dissolve 25 g of potassium iodide in about 25 mL of distilled water, add 12.7 g of iodine and dilute to 1 liter.

7.9 Iodine, 0.01 N. Dilute 100 mL of the 0.1 N iodine solution to 1 liter. Standardize against sodium thiosulfate.

7.10 Starch Solution, 1%. Make a paste of 1 g of soluble starch and 2 mL of water and slowly add the paste to 100 mL of boiling water. Cool, add several milliliters of chloroform as a preservative, and store in a stoppered bottle. Discard if a mold growth is noticed.

7.11 Sodium Carbonate Buffer Solution. Dissolve 80 g of anhydrous sodium carbonate in about 500 mL of distilled water. Slowly add 20 mL of glacial acetic acid and dilute to 1 liter.

7.12 Sodium Bisulfite, 1%. Dissolve 1 g of sodium bisulfite in 100 mL of distilled water.

7.13 Sodium Thiosulfate, 0.05 N. Dissolve 12.410 g sodium thiosulfate in 1 liter of distilled water.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water, and dried.

8.2 Calibration of Personal Sampling Pumps. Each personal sampling pump must be calibrated with a representative filter cassette, bubbler, and splashover trap in the line to minimize errors associated with uncertainties in the volume sampled.

8.3 Collection and Shipping of Samples

8.3.1 Pipet 15 ml of Girard T reagent solution buffered at a pH of 4.5 into each midget bubbler. Mark the liquid level on the bubbler with a china marker.

8.3.2 The outlet of the midget bubbler is attached to the pump's inlet or a trap which may be used to protect the pump during personal sampling. The trap is a midget impinger or bubbler with the stem broken off which is used to collect spillage. The trap is attached to the pump with a metal holder. The outlet of the trap is connected to the pump by flexible tubing.

8.3.3 Air being sampled should not be passed through any hose or tubing before entering the midget bubbler. (Polyvinyl chloride tubing is known to give interferences in the method).

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8.3.4 At levels corresponding to the 8-hour time-weighted average standard, a sample size of 18 liters is recommended. Sample at a flow rate of 0.2 liter/minute. Levels corresponding to the peak standard should be collected for 30 minutes at approximately 0.2 liter/minute.

8.3.5 Turn the pump on and begin sample collection. Terminate sampling at the predetermined time and record sample flow rate, collection time, and ambient temperature and pressure. If pressure reading is not available, record the elevation. Also record the type of sampling pump used.

8.3.6 The inlet and outlet of the bubbler stem should be sealed by connecting a piece of Teflon tubing between them or inserting Teflon plugs in the inlet and outlet. Do not seal with rubber. The standard taper joint of the bubbler should be taped securely to prevent leakage during shipping. Care should be taken to minimize spillage or loss of sample by evaporation at all times.

8.3.7 With each batch of ten samples, submit one bubbler containing 15 mL of the collection medium prepared from the same stock as that used for sample collection. This bubbler must be subjected to exactly the same handling as the samples except that no air is drawn through it. Label this bubbler as the blank.

8.3.8 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap or equivalent. This sample should not be transported in the same container as the bubblers.

8.3.9 Do not return the material in the trap.

8.4 Analysis of Samples

8.4.1 Each sample is analyzed separately. Remove the bubbler stem and tap the stem lightly against the flask to drain the contents into the bubbler flask. If necessary, bring the liquid volume to the 15-mL mark with distilled water. Swirl the bubbler flask to mix the contents well.

8.4.2 Transfer the mixed solution to a clean, dry polarographic receptacle which contains a small amount of mercury (approximately 0.3 mL) on the bottom. Place the receptacle on the polarograph and purge the sample for 5 minutes with oxygen-free nitrogen at a flow rate of 200 mL/minute.

8.4.3 Analyze the sample by sampled DC polarography using the following conditions:

Drop Time: 1 second
Scan Rate: 5 mV/second
Scan from -0.7 V to -1.3 V versus a saturated calomel electrode.

8.4.4 Rinse the electrodes with distilled water between samples.

8.4.5 Measure the diffusion current from the reduction of the formaldehyde-Girard T reagent derivative. The half-wave potential, $E_{\frac{1}{2}}$, of the formaldehyde-Girard T reagent derivative is -0.99 V vs. a saturated calomel electrode. The results of the analysis are read from a calibration curve prepared as described below.

9. Calibration and Standards

9.1 The calibration curve is prepared using standardized 37% formaldehyde solution. The following procedure is used to standardize the 37% formaldehyde solution (Reference 11.3).

9.1.1 Pipet 1 mL of formaldehyde solution "A" into a 250-mL erlenmeyer flask. Into another flask, pipet 1 mL of distilled water. The distilled water serves as the blank.

9.1.2 Add 10 mL of 1% sodium bisulfite and 1 mL of 1% starch solution.

9.1.3 Titrate with 0.1 N iodine to a dark blue color.

9.1.4 Destroy the excess iodine with 0.05 N sodium thiosulfate.

9.1.5 Add 0.01 N iodine until a faint blue end point is reached.

9.1.6 The excess inorganic bisulfite is now completely oxidized to sulfate, and the solution is ready for the assay of the formaldehyde bisulfite addition product.

9.1.7 Chill the flask in an ice bath and add 25 mL of chilled sodium carbonate buffer. Titrate the liberated sulfite with 0.01 N iodine, using a microburette, to a faint blue end point. The amount of iodine added in this step must be accurately measured and recorded.

9.1.8 One mL of 0.0100 N iodine is equivalent to 0.15 mg of formaldehyde. Therefore, since 1 mL of formaldehyde standard solution was titrated, the volume in mL of 0.01 N iodine used in the final titration multiplied by the factor, 0.15, gives the formaldehyde concentration of the standard solution in mg/mL. The factor, 0.15 must be adjusted or determined accordingly on the basis of the exact normality of the iodine solution.

9.2 A series of standards, varying in concentration over the range corresponding to approximately 0.1 to 3 times the OSHA standard for the sample under study, is prepared and analyzed under the same polarographic conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in micrograms/15 mL versus diffusion current. Standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of known day-to-day variations.

9.2.1 Prepare a stock standard solution containing 6.63 mg/mL standardized formaldehyde in deionized water.

9.2.2 From the above stock solution, appropriate aliquots are withdrawn and added to 15 mL of the collection medium. Prepare at least 6 working standards to cover the range of 6-220 micrograms/sample. This range is based on a 18-L sample at the 8-hour time weighted average standard and a 30-minute (5-L) sample for the ceiling standard.

9.2.3 Prepare a standard calibration curve by plotting micrograms/15 mL formaldehyde versus diffusion current.

10. Calculations

10.1 Read the weight, in micrograms, corresponding to each diffusion current from the standard curve. No volume correction is needed, because the standard curve is based on micrograms/15 mL of solution.

10.2 Corrections for the blank must be made for each sample.

$$\text{micrograms} = \text{microgram sample} - \text{microgram blank}$$

where:

microgram sample = micrograms found in sample bubbler
microgram blank = micrograms found in blank bubbler

10.3 For personal sampling pumps with rotameters only, the following volume correction should be made.

$$\text{Corrected Volume} = f \times t \left(\sqrt{\frac{P_1}{P_2} \times \frac{T_2}{T_1}} \right)$$

where:

f = flow rate sampled
t = sampling time
P_1 = pressure during calibration of sampling pump (mm Hg)
P_2 = pressure of air sampled (mm Hg)
T_1 = temperature during calibration of sampling pump (°K)
T_2 = temperature of air sampled (°K)

10.4 The concentration of formaldehyde in the air sampled can be expressed in mg/cu m.

$$\text{mg/cu m} = \text{micrograms/L} = \frac{\text{Corrected micrograms}}{\text{Corrected air volume sampled (L)}}$$

10.5 Another method of expressing concentration is ppm.

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{\text{M.W.}} \times \frac{760}{\text{P}} \times \frac{\text{T} + 273}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (L/mole) at 25°C and 760 mm Hg
M.W. = molecular weight (g/mole) of formaldehyde
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. <u>References</u>

11.1 Documentation of NIOSH Validation Tests, National Institute for Occupational Safety and Health, Cincinnati, Ohio (DHEW-NIOSH-Publication # 77-185), 1977. Available from Superintendent of Documents, U.S. Government Printing Office, Washington, D.C., Order No. 017-033-00231-2.

11.2 Backup Data Report for Formaldehyde, prepared under NIOSH Contract No. 210-76-0123.

11.3 NIOSH Method No. P&CAM 125, Formaldehyde in Air.

Sampling Data Sheet No. S327

September 2, 1977

Substance

Formaldehyde

Standard

8-hour time-weighted average: 3 ppm

Ceiling: 5 ppm

Peak: 10 ppm for 30 minutes

Analytical Method

A known volume of air is drawn through a midget bubbler containing 15 mL of buffered Girard T reagent to trap the formaldehyde present. The formaldehyde is collected and derivatized with the Girard T reagent and measured by polarography. This method was validated over the range of 1.4 - 6.2 ppm at an atmospheric temperature and pressure of 21°C and 759 mm Hg for a 18-L sample, representing an 8-hour time-weighted average collection. This method was also validated over the range of 4.62-19.84 ppm for 30-minute peak samples at an atmospheric temperature and pressure of 21°C and 757 mm Hg.

Sampling Equipment

Sampling equipment includes a calibrated personal sampling pump whose flow rate can be determined accurately (±5%) at the sampling rate and a midget bubbler containing a solution of Girard T reagent buffered at a pH of 4.5. The Girard T reagent should be obtained from the supporting analytical laboratory. The pump can be protected from spillage or splashover by using a second bubbler or an impinger as a trap.

Sample Size

1. At levels corresponding to the 8-hour time-weighted average standard, a sample size of 18 liters is recommended. Sample at a flow rate of 0.2 liter/minute.

2. Levels corresponding to the peak standard should be collected for 30 minutes at a flow rate of 0.2 liter/minute.

Sampling Procedure

1. Pipet 15 mL of Girard T reagent solution into each midget bubbler. Mark the liquid level on the bubbler with a china marker.

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2. The outlet of the midget bubbler is attached to the pump's inlet or a trap which may be used to protect the pump during personal sampling. The trap is a midget impinger or bubbler with the stem broken off which is used to collect spillage. The trap is attached to the pump with a metal holder. The outlet of the trap is connected to the pump by flexible tubing.

3. Air being sampled should not pass through any hose or tubing before entering the midget bubbler.

4. Set the flow rate as accurately as possible using the manufacturer's directions. Record the temperature and pressure of the atmosphere being sampled. If the pressure reading is not available, record the elevation. Also report the type of sampling pump used.

5. Turn the pump on and begin sample collection. Terminate sampling at the predetermined time and record sample flow rate and collection time.

6. The inlet and outlet of the bubbler stem should be sealed by connecting a piece of Teflon tubing between them or inserting Teflon plugs in the inlet and outlet. Do not seal with rubber. The standard taper joint of the bubbler should be taped securely to prevent leakage during shipping. Care should be taken to minimize spillage or loss of sample by evaporation at all times.

7. With each batch of ten samples, submit one bubbler containing 15 mL of the collection medium prepared from the same stock as that used for sample collection. This bubbler must be subjected to exactly the same handling as the samples except that no air is drawn through it. Label this bubbler as the blank.

Special Considerations

1. When other compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

2. Other volatile aldehydes such as acrolein, crotonaldehyde, and benzaldehyde may cause significant interference.

3. The use of polyvinyl tubing preceding the midget bubbler should be kept to a minimum. Products from the tubing may interfere in the analytical method.

4. Do not return the material which is collected in the trap.

Bulk Sample

A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap or equivalent. This sample should not be transported in the same container as the bubblers.

Shipping Instructions

The bubblers should be shipped in a suitable container designed to prevent damage in transit. The samples should be shipped to the laboratory as soon as possible.

Reference

Formaldehyde, NIOSH Method No. S327.

Backup Data Report No. S327

September 2, 1977

Substance:	Formaldehyde
OSHA Standard:	8-hour time-weighted average: 3 ppm Ceiling: 5 ppm Peak: 10 ppm (30 minutes)
Chemical Used for Validation:	37% Solution of formaldehyde Mallinckrodt

General

The procedure for collection and analysis of air samples of formaldehyde is described in NIOSH Method No. S327. Formaldehyde is collected in a midget bubbler containing an aqueous solution of Girard T reagent buffered at a pH of 4.5. Formaldehyde is derivatized with the Girard T reagent, and the formaldehyde-Girard T derivative is analyzed by polarography. This method has been validated for an 18-liter, 8-hour time-weighted average air sample and for a 5.5-liter, 30-minute peak sample using the criteria for validation outlined in Reference 1. Using these criteria, the absolute total error (sampling and analysis) is less than 25% at each of the 8-hour time-weighted average and peak OSHA standard levels 95% of the time.

The protocol for testing this method was:

To analyze 18 samples (6 each at 0.5X, 1X, and 2X the 8-hour time-weighted average OSHA standard) spiked with the appropriate amounts of formaldehyde to represent 18-L air samples.

To analyze 18 samples (6 each at 0.5X, 1X, and 2X the peak OSHA standard) spiked with appropriate amounts of formaldehyde to represent 30-minute sample collection at a flow rate of 0.2 liter/minute.

To analyze 18 samples collected from dynamically generated test atmospheres (6 samples collected at each of 0.5X, 1X, and 2X the 8-hour time-weighted average OSHA standard).

To analyze 18 samples collected from dynamically generated test atmospheres (6 samples collected at each of 0.5X, 1X, and 2X the peak OSHA standard).

To determine the collection efficiency of the midget bubbler containing buffered pH 4.5 Girard T reagent.

To test the storage stability of six collected samples at 1X the 8-hour time-weighted average OSHA standard.

To assess the precision and accuracy of the method for samples collected for the 8-hour time-weighted average and 30-minute peak OSHA standards.

Analysis

A description of the method of analysis is given in NIOSH Method No. S327. Spiked samples were prepared by spiking known amounts of a solution of formaldehyde in water (6.63 micrograms/microliter) into 15 mL of Girard T reagent buffered at a pH of 4.5. Spiked samples were prepared at 0.5X, 1X, and 2X the OSHA standard for both the 8-hour time-weighted average standard and peak standard. The results of the analytical method recoveries are presented in Table S327-5 and Table S327-7.

Sampling and Analysis

A total hydrocarbon analyzer, calibrated with bag standards of methylcyclohexanol at 2X the OSHA standard was used to monitor the generation system and determine the dilution ratios. The system is described in Attachment A. After calibration of the dilution system, generation of test atmospheres of formaldehyde was conducted. A solution of formaldehyde in water (12.13 micrograms/microliter) was introduced into the generation system by a calibrated automated syringe drive system (Harvard infusion/withdrawal pump, Model 950). A 5-mL syringe was filled with the analyte and placed in the syringe drive pump. A 10-in long stainless steel needle was attached to the syringe. The other end of the needle passed through a rubber septum into a heated glass tube maintained at 90°C. The syringe drive pump delivered 34.09 microliters/minute of formaldehyde solution into the tube. The vapor was carried out of the first stage of the generator by a stream of house air and diluted with the appropriate amount of house air to obtain samples at 2X the 8-hour time-weighted average OSHA standard. Dilutions to 1X and 0.5X the OSHA standard levels were made as described in Attachment A. The samples were collected as described in Method S327 using midget bubblers containing 15 mL of buffered solution containing Girard T reagent.

Six samples were collected from each chamber for 97 minutes to obtain 18-L samples. The results of the analyses of these samples are presented in Table S327-6. In addition, the backup bubblers at 2X the 8-hour time-weighted average OSHA standard were analyzed and found to contain less than the limit of detection, which was 0.06 ppm.

An additional six samples were collected at 1X the 8-hour time-weighted average OSHA standard. These samples were used for the storage stability study.

Sample generation was repeated to collect samples at the peak OSHA standard. A solution of formaldehyde in water (36.4 micrograms/microliter) was delivered from a syringe drive pump at a rate of 34.16

microliters/minute. An appropriate amount of air was added to obtain samples at 2X the peak OSHA standard. Dilutions to 1X and 0.5X the OSHA standard were made as described in Attachment A. Six samples at each of 2X, 1X, and 0.5X the peak OSHA standard were collected for 30 minutes at an average flow rate of 0.185 liter/minute. The results of the analyses of these samples are presented in Table S327-8.

Storage Stability

A study was conducted to assess whether formaldehyde would be successfully stored as the formaldehyde-Girard T reagent derivative in midget bubblers for one week after collection. The storage stability samples at 1X the 8-hour time-weighted average OSHA standard were collected at the same time as the samples which were used for validation, using the generation parameters described in the Sampling and Analysis Section. The samples were collected for 97 minutes with an average flow rate of 0.185 liter/minute. The bubblers were capped and stored on the laboratory bench for one week before analysis. The results are presented in Table S327-1.

Table S327-1

Storage Stability Study

	Samples Analyzed Immediately (ppm)	Samples Analyzed After One Week (ppm)
	3.11	3.00
	3.13	3.01
	3.15	2.77
	3.19	2.70
	3.10	3.28
	3.12	3.06
mean	3.13	2.97
std dev	0.03	0.21
CV	0.010	0.071

The criterion for acceptance is that the mean of the six samples stored at room temperature for seven days should be within ±10% of the mean of the set analyzed at the beginning of the storage period. The two means compare within 5.1%; thus, the storage stability is adequate.

Collection Efficiency

Collection efficiency tests were conducted at 6.40 ppm by connecting two midget bubblers in series. Each bubbler contained 15 mL of a solution of Girard T reagent buffered at a pH of 4.5. The test atmosphere was generated as described in the Sampling and Analysis Section. Six samples at 2X the 8-hour time-weighted average OSHA standard were collected. Samples were collected for 97 minutes with an average flow rate of 0.185 liter/minute. The results of the collection efficiency test are presented in Table S327-2.

Table S327-2

Collection Efficiency

μg found first bubbler	μg found backup bubbler	Collection Efficiency
143.1	N.D.*	1.00
138.4	N.D.	1.00
145.1	N.D.	1.00
140.6	N.D.	1.00
141.5	N.D.	1.00
148.1	N.D.	1.00

* N.D. = No formaldehyde was found at a detection limit of 1.1 μg.

The above results demonstrate that formaldehyde is collected efficiently using a single midget bubbler. Since collection efficiency was determined to be 1.00, no correction is needed.

Discussion

The Girard T reagent (N,N,N-trimethyl ammonium acetyl hydrazine) is often used for separation of carbonyl compounds from complex mixtures (Reference 2). The reaction mechanism is similar to that of other carbonyl reagents such as semicarbazide and the phenyl hydrazines. The reaction is reversible, and recovery of the carbonyl compounds is effected by hydrolysis of the derivative by the action of strong acids.

The reaction can be written in the general form:

$$R_2C{=}O \; + \; R'NH_2 \; \overset{H^+}{\rightleftharpoons} \; R_2C{=}NR' \; + \; H_2O$$

where $R'NH_2$ represents the carbonyl reagent such as the Girard T reagent used in the present study. The position of the equilibrium and the reaction rate are functions of the pH of the system. Conant and Bartlett (Reference 3) studied the semicarbazone formation of various carbonyl compounds in aqueous buffer systems and found the reaction to be general acid catalyzed. In another study, the reaction rates of both ketones and aldehydes with Girard T reagent were found to be extremely slow in alkaline medium, but rapid at pH 3.5 (Reference 4). At lower pH, the wet reaction rate decreases since hydrolysis of the derivative occurs at higher acidity.

The buffer concentrations and pH of the sampling system were chosen based upon consideration of the above studies. The concentration of the Girard T reagent in the collection medium represents a 160-fold molar excess over the formaldehyde if 1X the OSHA standard is collected. This excess was used to force the equilibrium of the reaction to the right in the above equation.

Experimental work indicated that the reaction of formaldehyde with the Girard T reagent is complete in 10 minutes when the concentration of the

Girard T reagent is greater than 80 times the concentration of formaldehyde. Formaldehyde is stable in water to allow this 10-minute reaction to take place.

Preliminary experimental work was done at 1X the 8-hour time-weighted average OSHA standard to assess the stability of the formaldehyde-Girard T reagent derivative over time when stored in midget bubblers. Eighteen samples were prepared by spiking 15 mL of buffered Girard T reagent solution with 10 microliters of a solution of formaldehyde in water containing 6.63 micrograms/microliter. Six samples were stored in the dark, and six were stored on the laboratory bench.

Since phenol is known to be present in atmospheres where formaldehyde is present, an experiment was conducted to determine if phenol would present problems in the analytical method or in storage stability. Six samples were spiked with 1.153 mg of phenol. This level corresponds to 3X the OSHA standard for phenol. One sample from each group was analyzed on a daily basis, and recoveries were determined. The results indicate that formaldehyde-Girard T derivative is stable for one week under all test conditions. The results are presented in Table S327-3.

Table S327-3

Stability of Spiked Samples Stored in the Light and in the Dark

Time After Spiking (hours)	Recoveries of Samples Stored on Lab Bench	Recoveries of Samples Stored in the Dark	Recoveries of Samples Spiked with Phenol and Stored on the Lab Bench
25	0.983	0.943	0.996
44	1.018	1.018	1.008
67	0.977	0.972	0.964
100	0.944	0.970	0.952
138	0.965	0.965	0.973
161	0.930	0.974	0.950
mean	0.970	0.974	0.974
std dev	0.031	0.024	0.024
CV	0.032	0.025	0.024

Independent Method

The independent method for determining the concentration of formaldehyde in the generator consisted of calculating the concentrations using the delivery rate of the syringe drive pump, concentration of the water solution of formaldehyde used in the generation, and appropriate dilution factors. The concentration in the generator is given in Table S327-4. These concentrations were compared with the samples taken from the 0.5X, 1X, and 2X chambers.

Table S327-4

Independent Method

	8-Hour Time-Weighted Average Generation	Peak Generation
0.5X	1.435 ppm	4.62 ppm
1X	3.02 ppm	9.72 ppm
2X	6.16 ppm	19.84 ppm

Precision and Accuracy

Statistical procedures and definitions of the terms are described in Reference 5. The precision of the analytical method was assessed for the 8-hour time-weighted average and peak OSHA standards using the data in Tables S327-5 and S327-7, respectively. The pooled Coefficient of Variation ($\overline{CV}_1$) for three sets of analytical samples representing 0.5X, 1X, and 2X the 8-hour time-weighted average and peak OSHA standards was found to be 0.021 and 0.014, respectively.

Precision and accuracy of the total sampling and analytical method was evaluated for the 8-hour time-weighted average and peak OSHA standards using the data in Tables S327-6 and S327-8, respectively, as well as the results obtained from collection efficiency tests and storage stability tests. The pooled Coefficient of Variation ($\overline{CV}_2$) for three sets of samples collected from test atmospheres at the 8-hour time-weighted average and peak OSHA standards was 0.013 and 0.029, respectively. To obtain a measure of the accuracy of the method, the mean value of the concentration found by analysis at each level was compared with the value for the concentration taken. The average recovery (concentration found divided by concentration taken) for all three levels at the 8-hour time-weighted average and peak standards was 103.5% and 98.9%, respectively. The value for the taken concentration was obtained as described under the Independent Method Section. The difference between the taken and found concentrations is considered to result from experimental uncertainties in the value for the taken concentration and does not represent a bias in the method. Further confidence in the accuracy of the tested methods are established by the results of the collection efficiency test and the storage stability test, described above.

The total Coefficients of Variation ($\overline{CV}_T$) for the 8-hour time-weighted average and peak standard are 0.052 and 0.058, respectively.

Table S327-5

Data Sheet: Formaldehyde

8-Hour Time-Weighted Average

Analysis

Level	0.5X			1X			2X	
µg taken	µg found	A.M.R.	µg taken	µg found	A.M.R.	µg taken	µg found	A.M.R.
33.2	33.5	1.009	66.3	66.7	1.006	132.6	133.7	1.008
33.2	33.1	0.997	66.3	65.8	0.992	132.6	133.7	1.008
33.2	32.9	0.991	66.3	63.1	0.952	132.6	133.1	1.004
33.2	32.9	0.991	66.3	64.5	0.973	132.6	130.9	0.987
33.2	32.7	0.985	66.3	62.9	0.949	132.6	131.1	0.989
33.2	33.5	1.009	66.3	60.5	0.913	132.6	132.0	0.995
n =		6			6			6
mean		0.997			0.964			0.998
std dev		0.010			0.033			0.009
CV_1		0.010			0.034			0.009

$\overline{CV}_1$ 0.021

$\overline{CV}_{A+\overline{AMR}}$ 0.023

$$\text{A.M.R.} = \frac{\mu g \text{ found}}{\mu g \text{ taken}}$$

Table S327-6

Data Sheet: Formaldehyde

8-Hour Time-Weighted Average

Sampling and Analysis

Test Level	Found				Taken	
	µg	Liters	mg/cu m	ppm*	ppm	Percent Recovery
0.5X	32.4	17.94	1.806	1.453	1.435	
	33.4	18.04	1.851	1.489	1.435	
	34.2	18.53	1.846	1.485	1.435	
	33.4	18.04	1.851	1.489	1.435	
	32.8	17.85	1.838	1.478	1.435	
	33.0	18.12	1.821	1.465	1.435	
			n = 6			
			mean	1.477		102.9%
			std dev	0.015		
			CV_2	0.010		
1X	73.5	19.01	3.87	3.11	3.02	
	72.4	18.62	3.89	3.13	3.02	
	68.4	17.46	3.92	3.15	3.02	
	66.2	16.68	3.97	3.19	3.02	
	71.0	18.43	3.85	3.10	3.02	
	71.2	18.33	3.88	3.12	3.02	
			n = 6			
			mean	3.13		103.6%
			std dev	0.03		
			CV_2	0.010		
2X	143.1	18.24	7.85	6.31	6.16	
	138.4	16.98	8.15	6.56	6.16	
	145.1	18.53	7.83	6.30	6.16	
	140.6	17.46	8.05	6.47	6.16	
	141.5	17.65	8.02	6.45	6.16	
	148.1	18.82	7.87	6.33	6.16	
			n = 6			
			mean	6.40		103.9%
			std dev	0.11		
$\overline{CV}_2$ 0.013			CV_2	0.017		

*All values have passed the Grubbs' outlier test at the 1% confidence level as described in Reference No. 5.

Table S327-7

Data Sheet: Formaldehyde

Peak

Analysis

Level		0.5X			1X			2X	
	µg taken	µg found	A.M.R.	µg taken	µg found	A.M.R.	µg taken	µg found	A.M.R.
	36.8	36.7	0.997	73.7	72.3	0.981	147.3	147.4	1.001
	36.8	37.5	1.019	73.7	73.1	0.992	147.3	149.0	1.012
	36.8	36.1	0.981	73.7	72.3	0.981	147.3	147.4	1.001
	36.8	37.3	1.014	73.7	72.3	0.981	147.3	146.3	0.993
	36.8	38.4	1.044	73.7	72.5	0.984	147.3	147.4	1.001
	36.8	37.5	1.019	73.7	74.0	1.004	147.3	148.4	1.008
n =			6			6			6
mean			1.012			0.987			1.003
std dev			0.022			0.009			0.007
CV_1			0.022			0.009			0.007

$\overline{CV}_1$ 0.014

$\overline{CV}_{A+\overline{AMR}}$ 0.015

$$\text{A.M.R.} = \frac{\mu g \text{ found}}{\mu g \text{ taken}}$$

Table S327-8

Data Sheet: Formaldehyde

Peak

Sampling and Analysis

Test Level	Found				Taken	
	µg	Liters	mg/cu m	ppm*	ppm	Percent Recovery
0.5X	30.1	5.55	5.42	4.37	4.62	
	30.8	5.58	5.52	4.45	4.62	
	30.6	5.73	5.34	4.31	4.62	
	30.2	5.58	5.41	4.36	4.62	
	29.9	5.52	5.42	4.37	4.62	
	30.1	5.64	5.34	4.31	4.62	
			n = 6			
			mean	4.36		94.4%
			std dev	0.05		
			CV_2	0.011		
1X	58.8	5.16	11.40	9.19	9.72	
	62.2	5.88	10.58	8.53	9.72	
	64.0	5.70	11.23	9.06	9.72	
	60.4	5.34	11.31	9.12	9.72	
	67.3	5.76	11.68	9.42	9.72	
	61.5	5.40	11.39	9.19	9.72	
			n = 6			
			mean	9.08		93.4%
			std dev	0.30		
			CV_2	0.033		
2X	151.6	5.40	28.07	22.64	19.84	
	142.2	5.64	25.21	20.33	19.84	
	144.6	5.46	26.48	21.36	19.84	
	140.7	5.25	26.80	21.61	19.84	
	155.6	5.82	26.74	21.56	19.84	
	157.6	5.73	27.50	22.18	19.84	
			n = 6			
			mean	21.61		108.9%
			std dev	0.79		
$\overline{CV}_2$ 0.029			CV_2	0.037		

*All values have passed the Grubbs' outlier test at the 1% confidence level as described in Reference No. 5.

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1. Contract 210-76-0123, National Institute for Occupational Safety and Health, Division of the Department of Health, Education and Welfare, U. S. Government.

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5. Documentation of NIOSH Validation Tests, National Institute for Occupational Safety and Health, Cincinnati, Ohio (DHEW-NIOSH-Publication # 77-185), 1977. Available from Superintendent of Documents, U. S. Government Printing Office, Washington, D.C., Order No. 017-033-00231-2.

Attachment A

Generation of Test Atmospheres

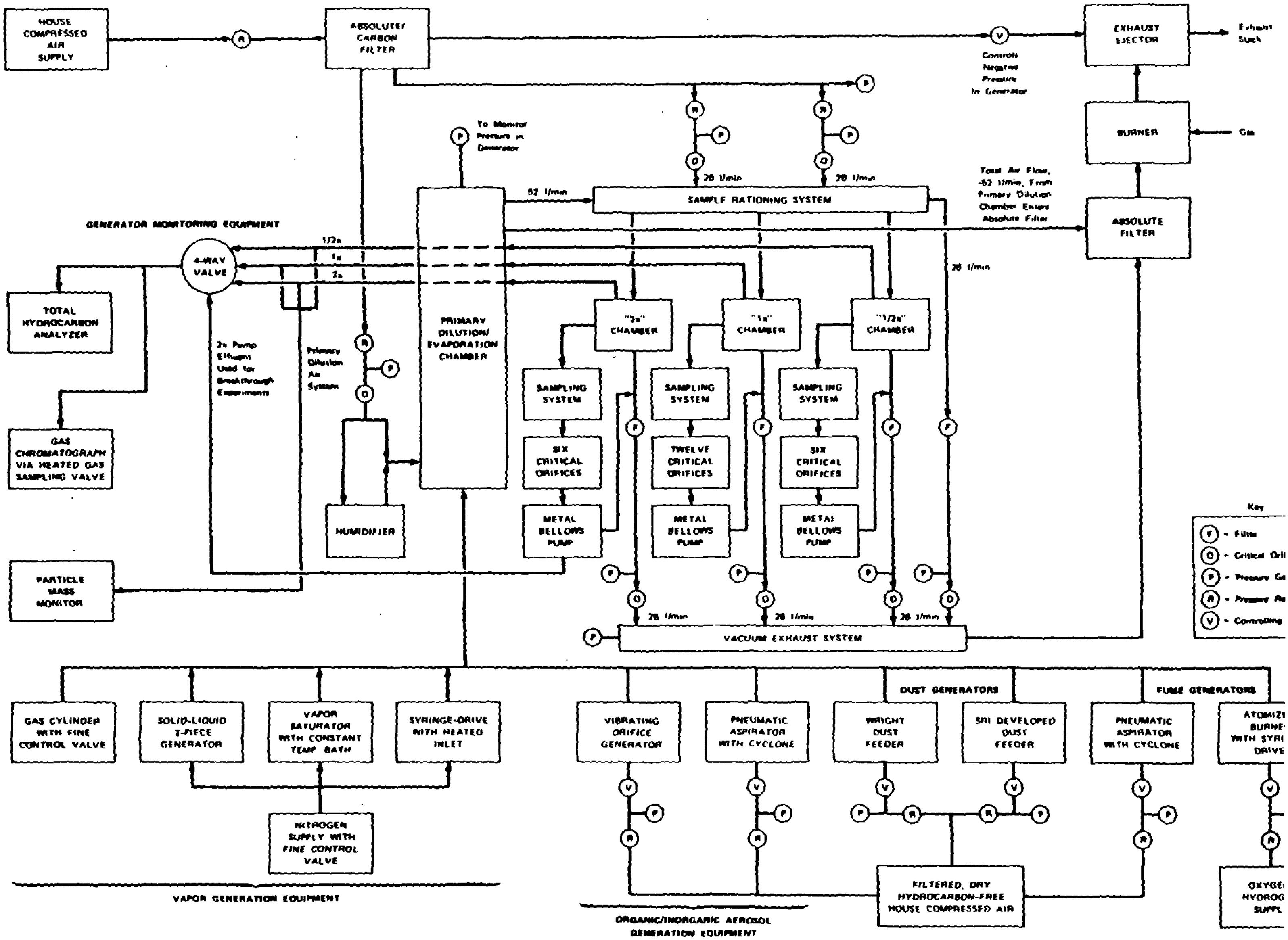
The system for generating and collecting samples of vapor, inorganic/organic particulate, dusts, and fumes consists basically of a sample generator, a mixing and dilution section, and three sampling chambers. Samples are generated at a concentration 2X the OSHA standard, serial dilutions are made to 1X and 0.5X the standard, and samples are collected simultaneously at the three concentrations. A schematic of the generation system and associated components is presented in Figure 1.

The generation system is large enough to be used for polydispersed aerosols as well as for gases and vapors. The primary dilution chamber is 48 inches by 4 inches and may handle air flows up to 400 liters/minute. The large volume dilution chamber is important for several reasons. Even at high air flow rates, the velocity of particles is low to allow complete solvent evaporation in the generation of aerosols. The air velocity is also low enough to avoid impaction on the walls while great enough to prevent particle diffusion to the walls. For these same reasons, the sample rationing system is only 1 inch in diameter and handles a flow of only 52 liters/minute. Gravitational settling is avoided by maintaining a sufficient air velocity.

The sampling cones for the three chambers are 6-inch I.D. at the base (point of sample collection) and narrow to 1-inch I.D. at the point of attachment to the sample rationing system. A constant total air flow of 26 liters/minute through each cone causes a gradual reduction in aerosol velocity toward the point of sample collection. The air velocity at the collection point is 2.4 cm/second.

All portions of the generation system that come in contact with the test atmosphere are constructed of stainless steel or Teflon to avoid any contamination problems. Sections of the generation system at which dilution air is added are constructed such that the incoming air forms a "high-velocity sheath" around the air/analyte mixture that is to be diluted. This sheath serves two functions. The dilution air sheath becomes increasingly less coherent and stable as it moves downstream of its point of entrance and hence is turbulently mixed with air/analyte test atmosphere. At the point of entrance of the dilution air stream, a Venturi effect accelerates the air/analyte mixture to a high velocity. The dilution air sheath also prevents interaction of the accelerated air/analyte stream with the walls of the chamber, thus eliminating a large source of aerosol loss by impaction.

The system being used to generate the initial concentrations of vapor, gas, or particulate is interfaced with the dilution apparatus at the primary dilution chamber. The output of the generator is diluted with the appropriate amount of air to obtain a concentration 2X the OSHA standard. Of the total amount of material generated at the 2X level, a flow of 52 liters/minute enters the rationing system. Under control of a vacuum exhaust orifice, material at the 2X level enters the first sampling chamber at a rate of 26 liters/minute. Downstream of the entrance to the first sampling chamber, dilution air is added (via a critical orifice) at a rate of 26 liters/minute. Thus the flow of material at the 2X level that did not enter the first sampling chamber


HOUSE COMPRESSED AIR SUPPLY
R
ABSOLUTE/ CARBON FILTER
V
Controls Negative Pressure In Generator
EXHAUST EJECTOR
Exhaust Stack
BURNER
Gas
ABSOLUTE FILTER
Total Air Flow, ~52 l/min, From Primary Dilution Chamber Enters Absolute Filter
P
R
O
28 l/min
28 l/min
To Monitor Pressure in Generator
52 l/min
SAMPLE RATIONING SYSTEM
GENERATOR MONITORING EQUIPMENT
4-WAY VALVE
1/2x
1x
2x
TOTAL HYDROCARBON ANALYZER
GAS CHROMATOGRAPH VIA HEATED GAS SAMPLING VALVE
PARTICLE MASS MONITOR
2x Pump Effluent Used for Breakthrough Experiments
Primary Dilution Air System
HUMIDIFIER
PRIMARY DILUTION/ EVAPORATION CHAMBER
"2x" CHAMBER
"1x" CHAMBER
"1/2x" CHAMBER
SAMPLING SYSTEM
SIX CRITICAL ORIFICES
TWELVE CRITICAL ORIFICES
METAL BELLOWS PUMP
F
28 l/min
VACUUM EXHAUST SYSTEM
Key
F - Filter
O - Critical Ori
P - Pressure Ga
R - Pressure Re
V - Controlling
GAS CYLINDER WITH FINE CONTROL VALVE
SOLID-LIQUID 2-PIECE GENERATOR
VAPOR SATURATOR WITH CONSTANT TEMP BATH
SYRINGE-DRIVE WITH HEATED INLET
NITROGEN SUPPLY WITH FINE CONTROL VALVE
VAPOR GENERATION EQUIPMENT
VIBRATING ORIFICE GENERATOR
PNEUMATIC ASPIRATOR WITH CYCLONE
DUST GENERATORS
WRIGHT DUST FEEDER
SRI DEVELOPED DUST FEEDER
FUME GENERATORS
ATOMIZI BURNE WITH SYRI DRIVE
OXYGE HYDROG SUPPL
FILTERED, DRY HYDROCARBON-FREE HOUSE COMPRESSED AIR
ORGANIC/INORGANIC AEROSOL GENERATION EQUIPMENT

S327-A2

(26 liters/minute) is diluted with air at a flow rate of 26 liters/minute to a final concentration of 1X the OSHA standard level. Analyte at the 1X level then enters the second sampling chamber at a rate of 26 liters/minute. The remaining flow, 26 liters/minute is diluted again with air at 26 liters/minute to achieve 0.5X the OSHA standard level. The analyte/air mixture at the 0.5X level is drawn into the third sampling chamber at 26 liters/minute. The remaining material in the rationing system not drawn into the sampling chambers is removed at a rate of 26 liters/minute by the fourth critical orifice in the vacuum exhaust system. This removal of test atmosphere volumes and addition of measured volumes of air thus achieves serial dilutions to 1X and 0.5X the OSHA standard level.

The dilution ratios from chamber to chamber can also be varied by simply changing the amount of dilution air that is added. This is particularly advantageous in generating aerosols, where wall deposition of particles in the rationing system can be offset by changing the rate of addition of dilution air.

The cylindrical section at the base of each sampling chamber contains the fittings necessary to collect samples, using any of a variety of sampling media--solid sorbent tubes, filters, liquid scrubbers, or a combination of these. Six to twelve samples each at three concentration levels can be collected simultaneously. A metal bellows vacuum pump is used for sampling from each chamber. Separate critical flow orifices are used for each sample. Air taken from the chamber during sampling is returned via the sampling pump exhaust line to the chamber outlet line, thus preserving the proper air flows during the time of sampling. The sampling rate therefore does not affect the concentration of material in any of the chambers.

The entire system is maintained at 1-inch water vacuum to prevent toxic materials from escaping into the laboratory. All exhaust air streams (from the vacuum exhaust system and excess from the primary dilution chamber) are fed into a combustion chamber where all toxic materials present are burned before entering the atmosphere.

Hydrogen cyanide

Analyte:	Cyanide ion, CN^-	Method No.	S288
Matrix:		Range:	5.2-21.0 mg/cu m
OSHA Standard:	10 ppm (11 mg/cu m)	Precision ($\overline{CV}_T$):	0.081
Procedure:	Filter/bubbler collection, analysis by cyanide ion selective electrode	Validation Date:	9/2/77

1. Principle of the Method

1.1 A known volume of air is drawn through a filter and midget bubbler containing 0.1N potassium hydroxide. Hydrogen cyanide vapor is collected in its ionized form.

1.2 The filter is used to remove particulate cyanide interference and is discarded. 0.1N potassium hydroxide is used to rinse the bubbler and dilute the sample to a final volume of 25 ml.

1.3 The resulting solution is analyzed by direct potentiometry using a cyanide ion-selective electrode.

2. Range and Sensitivity

2.1 This method was validated over the range of 5.18-20.98 mg/cu m at an atmospheric temperature and pressure of 23°C and 753 mm Hg, using a 12-liter sample.

2.2 The upper limit of the range of the method is dependent on the capacity of the midget bubbler. If higher concentrations than those tested are to be sampled, it is recommended that the sample be diluted to avoid concentrations above 10^{-2} M CN^-.

3. Interferences

3.1 Particulate cyanides will be removed by using a 0.8-micron cellulose ester membrane filter connected in front of the midget bubbler. In humid atmospheres, however, it has been observed that during the collection of particulate cyanide, hydrogen cyanide is liberated (Reference 11.1), therefore, particulate interference is not completely removed. The use of a filter would also eliminate a major proportion of the interferences discussed below.

3.2 Sulfide ion irreversibly poisons the cyanide ion specific electrode and must be removed if found to be present in the sample.

If sulfide is suspected to be present, check for the presence of sulfide ion by touching a drop of sample to a piece of lead acetate paper. The presence of sulfide is indicated by discoloration of the paper.

3.3 Sulfide can be removed by addition of 1 ml of 1 M H_2O_2 and 1 ml of 1 M Na_2SO_3 to sample solutions prior to diluting to volume (Reference 11.2).

3.4 When a drop of liquid no longer discolors a strip of lead acetate paper, remove the solid by filtering the sample through a small plug of glass wool contained in an eye dropper and proceed with the analysis.

3.5 It should also be noted that the cyanide electrode will malfunction if other ions like chloride, iodide and bromide, which form insoluble silver salts, are present in sufficient quantity. Several metal ions are also known to complex with cyanide, such as cadmium, zinc, silver, nickel, cuprous, iron, and mercury. Consult the instruction manual for a list of these ions and also the proper procedure to use when such ions are believed to be present.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total sampling and analytical method in the range of 5.18-20.98 mg/cu m was 0.0813. This value corresponds to a standard deviation of 0.89 mg/cu m at the OSHA standard level. Statistical information can be found in Reference 11.3. Details of the test procedures can be found in Reference 11.4.

4.2 On the average the concentrations obtained in the laboratory validation study at 0.5, 1, and 2X the OSHA standard level were 3.3% lower than the "true" concentrations for 18 samples. Any difference between the "found" and "true" concentrations may not represent a bias in the sampling and analytical method, but rather a random variation from the experimentally determined "true" concentration. Therefore, the Coefficient of Variation is a good measure of the accuracy of the method since the recoveries, storage stability, and collection efficiency were good. Storage stability studies on samples collected from a test atmosphere at a concentration of 10.01 mg/cu m indicate that collected samples are stable for at least one week.

5. Advantages and Disadvantages of the Method

5.1 Collected samples are analyzed by means of a quick and simple method.

5.2 Hydrogen cyanide collected in its ionized form is stable and nonvolatile, making this manner of collection of hydrogen cyanide desirable.

5.3 A disadvantage of the method is the awkwardness in using midget bubblers for collecting personal samples. If the worker's job performance requires much body movement, loss of the collection solution during sampling may occur.

5.4 The bubblers are more difficult to ship than adsorption tubes or filters due to possible breakage and leakage of the bubblers during shipping.

5.5 The precision of the method may be limited by the reproducibility of the pressure drop across the prefilter and bubbler. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one filter/bubbler combination only.

6. Apparatus

6.1 Sampling Equipment. The sampling unit for the collection of personal samples for the determination of cyanide consists of the following components:

6.1.1 Prefilter Unit. The prefilter unit, which is used to remove particulate interferences, consists of a 37-mm diameter cellulose ester membrane filter (Millipore Type AA or equivalent) with a pore size of 0.80 micrometer contained in a 37-mm two-piece filter holder. The filter is supported by a cellulose backup pad.

6.1.2 A glass midget bubbler containing the collecting medium, 0.1N potassium hydroxide.

6.1.3 Personal Sampling Pump. A calibrated personal sampling pump whose flow rate can be determined to an accuracy of 5%. The sampling pump is protected from splashover or water condensation by a second empty bubbler positioned between the exit arm of the first bubbler and the pump.

6.1.4 Potassium Hydroxide, 0.1N. Prepare a sufficient amount for collection of samples.

6.1.5 Double distilled water.

6.1.6 Pipet, 15-ml or other suitable device for adding 0.1N potassium hydroxide to the bubblers.

6.1.7 Thermometer.

6.1.8 Barometer.

6.1.9 Stopwatch.

6.2 Orion 94-06 cyanide ion specific electrode or equivalent.

6.3 Orion 90-20-00 double junction reference electrode or equivalent.

6.4 Orion Model 801 digital pH/mV meter or equivalent.

6.5 Magnetic stirrer and stirring bars.

6.6 Pipets, 1-ml and other convenient sizes.

6.7 Volumetric flasks, 25-ml and other assorted sizes.

6.8 Beakers, 50-ml or other suitable container for potentiometric measurements.

7. Reagents

All reagents used must be ACS reagent grade or better.

7.1 Double distilled water.

7.2 Potassium cyanide.

7.3 Potassium hydroxide, 0.1N. Dissolve 5.6 g potassium hydroxide in distilled water and dilute to 1000 ml.

7.4 Cyanide Standards

7.4.1 Cyanide Standard Stock Solution, 10^{-2} M CN^-. Dissolve 65 mg potassium cyanide in 0.1N potassium hydroxide and dilute to 100 ml with additional 0.1N potassium hydroxide.

7.4.2 Working Standards. Prepare at least 6 working standards to cover the concentration range of interest by proper dilution of the stock standard. Use 0.1N KOH for all dilutions. Prepare these calibration standards fresh daily.

7.5 Lead acetate paper.

7.6 Cadmium carbonate.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water, and dried.

8.2 Calibration of Personal Sampling Pumps. Each personal sampling pump must be calibrated with a representative filter holder, bubbler, and splashover trap in the line to minimize errors associated with uncertainties in the volume sampled.

8.3 Collection and Shipping of Samples

8.3.1 Assemble the filter in the two-piece filter holder and close firmly. The filter is supported by a cellulose backup pad. Secure the filter holder together with tape or shrinkable band.

8.3.2 Pipet 15 ml of 0.1N potassium hydroxide into the first midget bubbler.

8.3.3 Remove the filter holder plugs and attach the outlet of the holder to the inlet arm of the first midget bubbler using a short piece of flexible tubing. The outlet of this bubbler is connected by tubing to the inlet of the trap. The outlet of the trap is connected by a short piece of tubing to the pump's inlet. The trap is in a suitable holder attached to the pump. Liquid which is collected in the trap must never be returned to the first bubbler. The bubblers must be maintained in a vertical position during sampling.

8.3.4 Air being sampled should not pass through any hose or tubing before entering the filter holder.

8.3.5 A sample size of 12 liters is recommended. Sample at a flow rate of 0.2 liter per minute. The flow rate should be known with an accuracy of 5%.

8.3.6 Turn the pump on and begin sample collection. Since it is possible for a filter to become plugged by heavy particulate loading or by the presence of oil mists or other liquids in the air, the pump rotameter should be observed frequently, and the sampling should be terminated at any evidence of a problem.

8.3.7 Terminate sampling at the predetermined time and record sample flow rate, collection time, and ambient temperature and pressure. If pressure reading is not available, record the elevation. Also record the type of sampling pump used.

8.3.8 Remove the bubbler stem and tap the stem gently against the inside wall of the bubbler bottle to recover as much of the sampling solution as possible. Rinse the bubbler stem with 1-2 ml of unused 0.1N potassium hydroxide, and add the wash to the bubbler bottle. Seal the bubbler with a hard, non-reactive stopper (preferably Teflon). Do not seal with rubber. The stoppers on the bubblers should be tightly sealed to prevent leakage during shipping. Repeat this process for the liquid collected in the trap. Do not combine the two solutions in one bubbler bottom. Be sure each bubbler bottom is properly labeled.

8.3.9 Attempt to minimize sample spillage. Do not allow the solution level in the first bubbler to fall below 10 ml. Replace spilled solution with fresh 0.1N potassium hydroxide. If spillage is not evidenced by liquid in the trap or in the tubing, evaporation has probably occurred. Use distilled water to bring the solution volume back up to 15 ml.

8.3.10 The filter should be removed from the filter holder and discarded. The holders should be cleaned and saved for future use.

8.3.11 With each batch of ten samples submit one bubbler containing 15 ml of 0.1N potassium hydroxide prepared from the same stock as that used for sample collection. This bubbler must be subjected to exactly the same handling as the samples except that no air is drawn through it. Label this bubbler as the blank.

8.3.12 Samples should be stored or shipped in containers which prevent exposure to light so that maximum stability is maintained.

8.4 Analysis of Samples

8.4.1 Empty the contents of the bubbler into a 25-ml volumetric flask, using 2 ml of 0.1N potassium hydroxide to rinse the bubbler bottle. Add rinse to the volumetric flask, dilute to 25 ml with 0.1N potassium hydroxide.

8.4.2 Potentiometric Measurements

1. The samples are analyzed by immersing the cyanide ion electrode and reference electrode in the sample solutions and recording the millivolt reading. Both the samples and standards should be stirred while the readings are being taken. The reading should be taken after the meter has stabilized. Follow instrument manufacturer's instruction manual for proper operation and measurement procedures.

2. To obtain the most reliable results, a set of standards should be run both before and after analysis of samples. The standard solutions should be bracket samples of similar responses. A calibration curve is then constructed as given in Section 9.3.

8.4.3 Appropriate bubbler blanks must be analyzed by the same procedure used for the samples.

8.5 Determination of Sample Recovery

8.5.1 Need for Determination. To eliminate any bias in the analytical method for hydrogen cyanide, it is necessary to determine the recovery of the analyte. The analyte recovery should be determined in duplicate over the concentration range of interest. If the recovery of the analyte is less than 95%, the appropriate correction factor should be used to calculate the "true" value.

8.5.2 Procedure for Determining Recovery. A weighed amount of the analyte, preferably equivalent to the concentration found in the sample, is added to 25 ml of 0.1N potassium hydroxide. The solutions are then analyzed as described in Section 8.4. Duplicate determinations should agree within ±5%.

For the validation studies conducted to determine the precision and accuracy of this method, an amount of cyanide equivalent to that present in a 12-liter sample at the selected level was used to determine analytical method recovery. Twenty-five milliliters of 0.1N potassium hydroxide was added by pipet to 18 beakers used for potentiometric measurements. Six beakers were spiked with an amount of cyanide equivalent to 0.5, 1 and 2X the OSHA standard. This was accomplished by taking 20, 40 and 80 μl aliquots of a solution containing 8.21 mg of potassium cyanide per milliliter of 0.1N potassium hydroxide. A parallel blank was also prepared except no sample was added to it. All solutions were then analyzed as in Section 8.4.

The recovery equals the average weight in μg recovered divided by the weight in μg added, or

$$\text{Recovery} = \frac{\text{Average Weight } (\mu g) \text{ Recovered} - \text{Blank } (\mu g)}{\text{Weight } (\mu g) \text{ Added}}$$

The analytical recovery is used to calculate the corrected μg/sample (Section 10.4). If the recovery is greater than 95% no correction should be applied.

9. Calibration and Standards

9.1 Prepare a series of standards equivalent to one-hour collections over the range of 0.1-3 times the OSHA standard (see Section 7.4.2). These standards should be freshly prepared on a daily basis. It is most convenient to express concentration in terms of cyanide molarity. In this way no molecular-weight conversions are needed in calculating hydrogen cyanide concentration.

9.2 The appropriate calibration standards are alternately analyzed with the samples to determine the response factor. This practice will minimize the effect of observed fluctuations or variations in millivolt readingsduring any given day.

9.3 On semilog paper, plot the millivolt readings vs. cyanide ion concentrations of the standards. The cyanide ion concentration in moles per liter is plotted on the log axis.

10. Calculations

10.1 Determine the cyanide ion concentration in terms of moles per liter by using the calibration curve constructed in Section 9.3.

10.2 To calculate the micrograms of hydrogen cyanide collected, the following formula is used:

$$\mu g \text{ Hydrogen Cyanide} = \text{Molarity cyanide ion (Section 10.1)} \times 27.03 \times 10^6 \times 0.025$$

where:

27.03 = molecular weight in grams per mole

0.025 = sample solution volume in liters

10.3 Corrections for the blank must be made for each sample bubbler.

$$\text{Total } \mu g \text{ HCN} = \mu g \text{ sample} - \mu g \text{ blank}$$

where:

µg sample = µg HCN found in sample bubbler

µg blank = µg HCN found in blank bubbler.

10.4 Divide the total µg of HCN by the recovery to obtain the corrected µg HCN/sample.

$$\text{Corrected } \mu g \text{ HCN/sample} = \frac{\text{Total } \mu g \text{ HCN}}{\text{Recovery (Section 8.5.2)}}$$

10.5 For personal sampling pumps with rotameters only, the following volume correction should be made.

$$\text{Corrected Volume} = f \times t\left(\sqrt{\frac{P_1}{P_2} \times \frac{T_2}{T_1}}\right)$$

where:

f = sampling rate

t = sampling time

P_1 = pressure during calibration of sampling pump (mm Hg)

P_2 = pressure of air sampled (mm Hg)

T_1 = temperature during calibration of sampling pump (°K)

T_2 = temperature of air sampled (°K)

10.6 The concentration of the analyte in the air sampled can be expressed in mg per cu m (µg per liter = mg per cu m).

$$\text{mg/cu m} = \frac{\text{Corrected µg HCN (Section 10.4)}}{\text{Sampling Volume (liters)}}$$

10.7 Another method of expressing concentration is ppm.

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{27.03} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
27.03 = molecular weight (g/mole) of hydrogen cyanide
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

11.1 Cyanide (as CN), NIOSH Method No. S250, prepared under NIOSH Contract No. CDC-99-74-45, 1974-1976.

11.2 Technical Services Dept., Orion Research, Cambridge, Mass., personal communication, 1978.

11.3 Documentation of NIOSH Validation Tests, National Institute for Occupational Safety and Health, Cincinnati, Ohio (DHEW-NIOSH-Publication No. 77-185), 1977. Available from Superintendent of Documents, U.S. Government Printing Office, Washington, D.C., Order No. 017-033-00231-2.

11.4 Backup Data Report for Hydrogen Cyanide, No. S288, prepared under NIOSH Contract No. 210-76-0123.

Sampling Data Sheet No. S288
September 2, 1977

Substance

Hydrogen cyanide

Standard

8-hour time-weighted average: 10 ppm (11 mg/cu m)

Analytical Method

A known volume of air is drawn through a mixed cellulose ester membrane filter connected in series with a midget bubbler containing 15 ml of 0.1N potassium hydroxide to trap the hydrogen cyanide present. The filter is used to collect the particulate interferences, and is discarded after sampling. The resulting solution is diluted to 25 ml and analyzed by direct potentiometry using a cyanide ion selective electrode. The method has been validated over the range of 5.2-21.0 mg/cu m for a 12-liter sample at 23°C and 753 mm Hg, atmospheric temperature and pressure.

Sampling Equipment

The following equipment is needed for sampling hydrogen cyanide: a calibrated personal sampling pump whose flow rate can be determined accurately (±5%) at 0.2 liter per minute, a 37-mm, two-piece filter holder held together by tape or shrinkable band, a 37-mm/0.8 micrometer cellulose ester membrane filter connected in series with a midget bubbler, a trap which is a second impinger or bubbler used to protect the pump from spillage, and extra bubbler solution and distilled water.

Sample Size

A sample size of 12 liters is recommended. Sample at a flow rate of 0.2 liter per minute.

Sampling Procedure

1. Assemble the filter in the two-piece filter holder and close firmly. Secure the filter holder together with tape or a shrinkable band. Pipet 15 ml of 0.1N potassium hydroxide into the first bubbler.

2. Remove the holder plugs and attach the outlet of the filter holder to the inlet arm of the midget bubbler using a short piece of flexible tubing. The outlet of this bubbler is connected by tubing to the inlet of the trap. The outlet of the trap is connected by a short piece of tubing to the pump's inlet. The trap is in a suitable impinger holder which is attached to the pump. Liquid collected in the trap must never be returned to the first bubbler.

3. Air being sampled should not pass through any hose or tubing before entering the filter holder.

4. Set the flow rate as accurately as possible using the manufacturer's directions. Record the temperature and pressure of the atmosphere being sampled. If the pressure reading is not available, record the elevation. Also report the type of sampling pump used. Since it is possible for the filter to become plugged by heavy particulate loading or by the presence of oil mists or other liquids in the air, the pump rotameter should be observed frequently, and readjusted as needed. If the rotameter cannot be adjusted to correct a problem, terminate the sampling.

5. After sampling, remove the bubbler stem and tap the stem gently against the inside wall of the bubbler bottle to recover as much of the sampling solution as possible. Rinse the bubbler stem with 1-2 ml of 0.1N potassium hydroxide into the midget bubbler flask. Seal the bubbler with a hard, non-reactive stopper (preferably Teflon). Do not seal with rubber. The stoppers on the bubblers should be tightly sealed to prevent leakage during shipping. Repeat this process for the liquid in the trap. However, do not combine the two solutions.

6. Remove the filter from the filter holder. The filter can be discarded and the holders saved for future use.

7. Carefully record sample identity and all relevant sampling data such as sample flow rate and collection time.

8. Attempt to minimize sample spillage. Do not allow the solution level in the first bubbler to fall below 10 ml. Replace spilled solution with fresh 0.1N potassium hydroxide. If spillage is not evidenced by liquid in the trap or in the tubing, evaporation has probably occurred. Use distilled water to bring the solution volume back up to 15 ml.

9. With each batch of ten samples submit one midget bubbler containing 15 ml of 0.1N potassium hydroxide prepared from the same stock as that used for sample collection. This bubbler must be subjected to exactly the same handling as the samples except that no air is drawn through it. Label this bubbler as the blank.

Special Considerations

1. When other compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample. This is especially important for halides and sulfide which interfere with the cyanide electrode performance and for ions of metals that complex cyanide such as cadmium, zinc, silver, nickel, copper, iron, and mercury.

2. Particulate cyanides will be removed using a 0.8-micron cellulose ester membrane filter connected in front of the midget bubbler. Particulate halides, sulfides and metallic ions will be removed as well.

3. In humid atmospheres collection of cyanide particulate matter has been shown to produce hydrogen cyanide during the sampling process. Therefore, in humid atmospheres the interference from particulate cyanides is not completely removed by placing a filter before the bubbler.

4. Samples should be stored or shipped in containers which prevent exposure to light so that maximum stability is maintained.

5. If a significant amount of hydrogen cyanide is found by the analyst in the trap or if less than 7 ml of solution remains in the bubbler, the sample should be considered invalid.

Shipping Instructions

The bubblers should be shipped in a suitable container designed to prevent damage in transit. The samples should be shipped to the laboratory as soon as possible.

Reference

Hydrogen Cyanide, NIOSH Method No. S288.

Backup Data Report No. S288
September 2, 1977

Substance: Hydrogen cyanide

OSHA Standard: 10 ppm (11 mg/cu m)

Chemical Used for
Validation: Hydrogen cyanide, 0.135% in Nitrogen,
Matheson Gas Products

General Considerations

The method for hydrogen cyanide has been tested in accordance with the various criteria for validation described in Reference 1 and in conformity with the statistical analysis described in Reference 2. The statistical criteria established for this program are related to the present suggested standard for air monitoring accuracy, i.e., the absolute total error (sampling and analysis) should be less than 25% in at least 95% of the samples analyzed at the level of the OSHA standard. In order to satisfy the statistical criteria, a measure of accuracy and precision was established, i.e., overall recovery must be 100 ± 10% and the CV_T of an unbiased method must be less than or equal to 0.105. The fine points of the statistical basis for this program are discussed in Reference 2.

The protocol for validation of a method for hydrogen cyanide consisted of the following experimental studies:

- Evaluation of polytetrafluoroethylene and cellulose ester membrane filters to screen out particulate cyanide interferences,
- Determination of the collection efficiency of the midget bubbler containing 0.1N potassium hydroxide at 2X the OSHA standard,
- Analysis of a total of eighteen samples (six samples at each of the three test levels--0.5, 1, and 2X the OSHA standard) spiked with the appropriate amount of cyanide ion to represent a sample volume equal to 12 liters.
- Analysis of a total of eighteen samples collected from dynamically generated test atmospheres (six samples at each of the three test levels--0,5, 1, and 2X the OSHA standard) for the same sample volume as above,
- Testing of the storage stability of collected samples,
- Assessment of the precision and accuracy of the method.

The details with respect to each of these items are discussed in the following sections. The method tested experimentally and documented in this report has passed all the requirements of this program.

Evaluation of Pre-filters

Polytetrafluoroethylene (PFTE) and mixed cellulose ester (MCE) membrane filters were evaluated for use as pre-filters in removing cyanide salt interferences. Both filters were tested for possible adsorption of hydrogen cyanide in the following experiment. Six samples were collected simultaneously at the OSHA standard using midget bubblers containing 0.1 N KOH. In front of two bubblers, polytetrafluoroethylene filters were inserted. Mixed cellulose ester membrane filters were inserted in front of two others and the remaining two bubblers were allowed to sample directly. The bubblers were analyzed as described in NIOSH Method No. S288 and the results are given below.

Pre-Filter Evaluation

	Pre-Filter		
	MCE	PFTE	None
Avg mg/m^3	10.40	11.74	10.28
Recovery$^+$	0.967	1.091	0.955

$^+$Generator concentration calculated to be 10.76 mg/m^3.

The results given above indicate that either pre-filter tested may be used without grossly affecting the reliability of the sampling and analytical method. It must be emphasized that using a pre-filter will not screen out all interferences from particulate cyanide. Previous experiments (Reference 3) have shown that, while sampling particulate cyanide salts in a humid atmosphere, hydrogen cyanide is produced that passes through a filter and becomes trapped in the bubbler. A filter can therefore only minimize particulate cyanide interference, not eliminate it.

Principle of the Method

The method validated for the analysis of hydrogen cyanide in air is based on collection in midget bubblers containing 15 ml of 0.1N potassium hydroxide, dilution of the sample with 0.1N potassium hydroxide to a final volume of 25 ml, and analysis of the resulting solution by direct potentiometry using a cyanide ion selective electrode. A sample size of 12 liters is recommended.

Analysis

A detailed description of the procedure for analysis, the preparation of analytical samples for determination of recovery and the preparation of calibration standards are given in NIOSH Method No. S288 (Reference 4).

The reliability of the analytical method was tested based on the analysis of eighteen analytical samples. These samples were prepared by spiking 25 ml of 0.1N potassium hydroxide with known aliquots of cyanide ion representing the equivalent of a 12-liter air sample at 0.5, 1, and 2X the OSHA standard.

The data for the full set of eighteen analytical samples are shown in Table S288-1.

Sampling and Analysis

Test atmospheres were generated using the basic system described in Attachments A and B. A cylinder of hydrogen cyanide in nitrogen was used as the source for generation experiments. A reproducible flow of gas from this cylinder, through a regulator and rotameter, was introduced into the system at a calibrated rate. The three sample lines were maintained at measured dilution ratios of 0.244, 0.487 and 1.000 to produce levels 0.5, 1, and 2X the OSHA standard. The actual delivery rate was determined by calibrating both the hydrogen cyanide content of the cylinder used and the rate of its delivery into the dilution/sampling system. The data are given in the section on Independent Method of Verifying Generator Concentration.

The samples were collected as described in NIOSH Method No. S288 using bubblers containing 15 ml of 0.1N potassium hydroxide. Twenty-four samples were collected simultaneously at 0.2 liter per minute for 60 minutes (12 liters). Eighteen samples, six at each of the three test levels, were analyzed after one day, as described in Section 8.4 of NIOSH Method No. S288. The backup bubblers collected at 2X the OSHA standard level were analyzed similarly. The six remaining samples were stored and analyzed after seven days.

The data obtained for the eighteen one-day-old samples are shown in Table S288-2.

Storage Stability

Studies were done to assess the stability of hydrogen cyanide samples upon storage for one week at atmospheric conditions (the samples were kept in the dark, however, to minimize exposure to light). For these studies, six samples collected at the OSHA standard level were stored for seven days, analyzed, and the results compared with the data for six samples collected at the OSHA standard and analyzed after one day. The data for these samples, given in Table S288-3, show that the samples are stable over a seven-day period; the average recovery was 92.4% for the one-day-old samples vs. 92.6% for the seven-day-old samples.

Table S288-1

Data Sheet: Hydrogen Cyanide

Analysis

Level	0.5S			1S			2S	
μg added	μg found	Recovery	μg added	μg found	Recovery	μg added	μg found	Recovery
67.3	64.2	0.954	134.6	141.5	1.051	267.9	291.6	1.088
67.3	67.6	1.004	134.6	137.0	1.018	267.9	272.8	1.018
67.3	66.8	0.993	134.6	131.8	0.979	267.9	267.8	1.000
67.3	67.0	0.996	134.6	121.3	0.901	267.9	293.6	1.096
67.3	69.6	1.034	134.6	127.3	0.946	267.9	292.3	1.091
67.3	67.0	0.996	134.6	136.7	1.016	267.9	295.7	1.104
n =		6			6			6
mean		0.996			0.985			1.066
std dev		0.02562			0.0548			0.0450
CV_1		0.02572			0.0556			0.0422

$\overline{CV}_1$ 0.0429

$\overline{CV}_{AMR}$ 0.0463

Table S288-2

Data Sheet: Hydrogen Cyanide

Sampling and Analysis

Test Level	Found			Taken	Recovery
	µg	Liters	mg/cu m	mg/cu m	
0.5S	57.4	11.43	5.02	5.11	
	60.9	11.79	5.17	5.11	
	62.3	11.79	5.28	5.11	
	63.1	11.73	5.38	5.11	
	58.2	11.49	5.07	5.11	
	77.6	15.12	5.13	5.11	
		n = 6			
		mean	5.18		1.014
		std dev	0.1343		
		CV_2	0.02593		
1S	106.1	11.98	8.86	10.61	
	128.2	12.35	10.38	10.61	
	127.3	12.35	10.31	10.61	
	108.3	12.30	8.80	10.61	
	116.9	12.04	9.71	10.61	
	170.5	15.84	10.76	10.61	
		n = 6			
		mean	9.80		0.924
		std dev	0.826		
		CV_2	0.0843		
2S	247.1	11.85	20.85	21.78	
	*			21.78	
	248.2	11.53	21.53	21.78	
	222.2	11.66	19.06	21.78	
	256.3	12.23	20.96	21.78	
	269.6	11.98	22.50	21.78	
		n = 5			
		mean	20.98		0.963
		std dev	1.257		
		CV_2	0.0599		
		$\overline{CV}_2$	0.0617		

---

*Sample lost.

Table S288-3

Data Sheet: Hydrogen Cyanide

Storage Stability of Collected Samples

Expt. A: Samples Stored 1 Day

Test Level	Found			Taken	Recovery
	µg	Liters	mg/cu m	mg/cu m	
1S	106.1	11.98	8.86	10.61	
	128.2	12.35	10.38	10.61	
	127.3	12.35	10.31	10.61	
	108.3	12.30	8.80	10.61	
	116.9	12.04	9.71	10.61	
	170.5	15.84	10.76	10.61	
		mean	9.80		0.924
		CV_2	0.0843		

Expt. B: Samples Stored 8 Days

1S	123.5	12.36	9.99	10.61	
	109.3	12.74	8.58	10.61	
	112.1	11.79	9.51	10.61	
	157.0	15.27	10.28	10.61	
	131.8	12.04	10.95	10.61	
	129.1	13.31	9.70	10.61	
		mean	9.83		0.926
		CV_2	0.0816		

Collection Efficiency

The collection efficiency of midget bubblers containing 0.1N potassium hydroxide for hydrogen cyanide was determined at a test concentration of 21.85 mg/cu m for a 28-liter sample. Two bubblers containing 15 ml of 0.1N potassium hydroxide were connected in series to each of the six sampling ports at the 2S test level. The contents of the front and backup impingers were analyzed separately. The amount of hydrogen cyanide in the front bubbler relative to the total found in the front and backup bubblers was used as a measure of collection efficiency. The data for six samples, summarized in Table S288-4, show an average collection efficiency of 99.8%.

Independent Method of Verifying Generator Concentration

The concentration of hydrogen cyanide produced within the vapor dilution/sampling system was calculated based on the hydrogen cyanide content of the cylinder used and the calibrated rate at which this gas mixture was delivered to the system. The hydrogen cyanide content of the cylinder was assessed by a bubbler collection of approximately 20 liters of the gas in 50 ml of 0.1N KOH. The flow rate was approximately 2 liters per minute and the volume was calibrated with a dry gas meter placed in line behind the bubbler. The cyanide content was analyzed by the method described in Attachment C. Six collections were made and the data is given below.

ml HCN Found	Liters HCN/N_2 Mixture Collected		HCN Concentration (ppm)
18.44	20.79		887
18.72	21.26		881
17.46	19.84		880
18.25	20.70		882
17.95	20.38		881
18.09	20.57		879
		mean	882
		std dev	2.80
		CV	0.0032

To obtain the hydrogen cyanide concentration within the generator, the flow of the gas mixture into the generator was calibrated by a dry gas meter. Two generation experiments were conducted for the data given in Table S288-2. The first experiment (Experiment A) involved the collection of six samples at 2X the OSHA standard and twelve samples at the OSHA standard for storage stability experiments. The second experiment (Experiment B) was a collection of six samples at 0.5X the OSHA standard. The calibration data for these experiments are given below.

Table S228-4

Data Sheet: Hydrogen Cyanide

Collection Efficiency of Hydrogen Cyanide in 0.1N KOH Midget Bubblers

µg Found					
Front	Backup	Total	Liters	mg/cu m	% Collected in Front
576	1.80	578	28.46	20.24	99.7
582	3.34	585	27.13	21.45	99.5
578	1.30	579	26.98	21.42	99.8
811	0.19	811	33.8	23.99	100.0
651	1.56	653	28.17	23.11	99.7
505	0.02	505	24.17	20.89	100.0

Average Collection Efficiency...... 99.8

Calibration of HCN/N_2 Gas Mixture Delivery Rate (liters per minute)

	Experiment A	Experiment B
	2.379	2.322
	2.362	2.344
	2.358	2.309
	2.374	2.316
	2.354	2.300
	2.355	2.319
mean	2.364	2.318
std dev	0.01044	0.01484
CV	0.00442	0.00640

The following formula gives the delivery rate in mg HCN per minute from the above HCN/N_2 delivery rates in liters per minute:

$$\frac{\text{mg HCN}}{\text{min}} = \left(F \times 0.000882 \times \frac{760}{P} \times \frac{T+273}{298} \times 1.046\right) \div 24.45 \times 27.03$$

where:

F = measured HCN/N_2 flow rate (liters per minute)
0.000882 = HCN content of cylinder gas
P = atmospheric pressure (mm Hg)
T = ambient temperature (°C)
1.046 = correction factor for dry gas meter (calibrated versus spirometer standard)
24.45 = molar volume (ml/mmole)
27.03 = molecular weight of HCN (mg/mmole)

For Experiment A the delivery rate was 2.417 mg HCN/min, and for Experiment B it was 2.360 mg HCN/min. The values under the "Taken" column in Table S288-2 were derived from these injection rates, calibrated main line flow rates of 0.1086 cu m/min, and measured dilution ratios of 1.000 0.487, 0.222 for Experiment A; and a calibrated main line flow of 0.1103 cu m/min and measured dilution ratios of 1.000, 0.520, and 0.244 for Experiment B. In both cases the volume of HCN/N_2 gas mixture delivered to the system was added to the main line flows given above to obtain the final concentration.

Precision and Accuracy

The precision of the method was determined by using the statistical procedures described in Reference 2 and the data in Tables S288-1 and S288-2.

Bartlett's test for homogeneity of variances was applied to the coefficients of variation at 0.5, 1, and 2X the OSHA standard for hydrogen cyanide. The data (Table S288-2) gave a chi squared value of 5.28 indicating that the hypothesis of equal variance is satisfied at p (probability) less than 0.01. Thus, $\overline{CV}_T$ is calculated based on the pooled data.

The precision of the method is expressed in terms of the coefficients of variation for the analytical method, the sampling and analytical method, and the overall method which includes a pump error of 0.05. These values are shown below.

$\overline{CV}_1 = 0.0429$ $\overline{CV}_2 = 0.0617$ $\overline{CV}_T = 0.0813$

The accuracy of the method was determined by comparison of the average value found by analysis of six samples at each of the three test levels with the Taken generator concentration discussed in the preceding section. The data summarized below show good agreement (Found ÷ Taken) with an average of 96.7%.

Test Level	Taken	Found	Agreement (Found ÷ Taken)
0.5S	5.11	5.18	1.014
1S	10.61	9.80	0.924
2S	21.78	20.98	0.963
		Average....	0.967%

The difference between the Taken and Found concentrations may not represent a bias in the sampling and analytical method, but rather a random variation from the experimentally determined "true" concentration. Further confidence in the accuracy of the tested method is established by the results of the collection efficiency test and the storage stability test, described in the appropriate sections.

References

1. Statement of Work, Article 1, Contract No. 210-76-0123, NIOSH Department of Health, Education and Welfare, 4676 Columbia Parkway, Cincinnati, Ohio 45226.
2. Documentation of NIOSH Validation Tests, National Institute of Safety and Health, Cincinnati, Ohio (DHEW-NIOSH-Publication No. 77-185), 1977. Available from Superintendent of Documents, U.S. Government Printing Office, Washington, D.C., Order No. 017-033-00231-2.
3. Cyanide as CN, NIOSH Method No. S250, prepared under NIOSH Contract No. CDC-99-74-45, 1974-1976.
4. Hydrogen Cyanide, NIOSH Method No. S288, prepared under NIOSH Contract No. 210-76-0123 with validation date 10/28/77.

ATTACHMENT A

VAPOR GENERATION

Continuous Direct Injection

Vapor concentrations from liquids are generated by adding known amounts of liquid to the Main Line of the vapor dilution/sampling apparatus. A continuous delivery rate is achieved using a Harvard Model 944 Syringe Drive. The syringe is connected to a 25 G stainless steel needle in the Main Line by a short length of 0.16-cm (1/16-in) O.D. Teflon tubing. If the substance of interest is reactive with the stainless steel needle then the Teflon tubing is placed within the Main Line replacing the needle. When dealing with liquids of low volatility the 25G needle is mounted such that the tip of the needle rests inside a 10-cm length of 8-mm I.D. glass tubing wound with resistance wire. The appropriate amount of current is applied to the heater to assure steady and complete vaporization of the liquid.

Calibration of Syringe Delivery

Preliminary calibrations have been conducted so that the approximate delivery rates of the syringe drive are known at each setting for several syringe sizes. These values are used to set the approximate delivery rate for the specific liquid. The syringe is then filled and connected to a weighing bottle, and the drive is activated for a period of time to allow the actual delivery rate to be determined in mg/min by weighing the amount collected. Sufficient time is allowed to provide a weight change which can be measured reliably and thus enable a precise calibration. Usually 25-800 mg are collected depending on the specific compound being studied.

Calculation of Main Line Concentration

The concentration of the vapor in the main line is calculated from the calibrated syringe delivery rate, mg/min, and the Main Line air flow rate, cu m/min. Thus these two values, each of which can be determined reliably, yield the Main Line concentration directly in the desired units, mg/cu m.

ATTACHMENT B

VAPOR DILUTION/SAMPLING SYSTEM

The vapor generation/dilution system used for the validation studies of several vapors and gases, such as this analyte, is shown schematically in Figure S288-B-1. The system basically consists of a main line air stream to which are added predetermined amounts of various liquids, gases or aerosols to generate the desired vapor concentrations. From the main line, three dilution arms branch off in which the desired multiples 0.5, 1.0 and 2.0 times the OSHA Standard concentration level are established. Six sampling devices are connected in parallel to each of the three dilution lines and are connected via critical flow orifices (CFO's) to the three corresponding vacuum lines.

Air flow rates through the system are established by means of critical flow orifices (CFO's) and flow restrictors. The primary air system derived from the house air compressor is maintained at 20.0 psig. The appropriate orifice diameters are chosen to maintain an air flow of approximately 0.1 cu m/min in the Main Line and an addition of 0.05 cu m/min to each of the dilution lines. The main line is maintained at 8 cm H_2O pressure by means of a needle valve. Appropriate flow restrictor diameters are chosen for the 0.5S, 1S and 2S dilution lines so as to give the desired final concentrations of vapor in air.

The system was designed to generate either 4X or 2X the OSHA Standard concentration in the Main Line. When a 4X level is generated, 0.05 cu m/min of dilution air is added to each dilution line. Orifices are selected so that the 0.5S, 1S and 2S lines have flows equal to approximately 0.007, 0.017 and 0.050 cu m/min respectively of the Main Line concentration added to the dilution air, thus giving the desired final concentrations. Where a Main Line concentration of 2X the OSHA Standard is generated, no dilution air is added to the 2S dilution line--0.017 cu m/min is simply allowed to flow through this line--and 0.050 cu m/min of dilution air is added to the 0.050 cu m/min and 0.017 cu m/min of Main Line mixture admitted to the 1S and 0.5S dilution lines, respectively.

All materials which the vapor may contact before collection are 316 or 304 stainless steel. A glass heater is included where the liquids are added to the main line. Shutoff ball valves are placed in the dilution lines to allow their independent operation and the calibration of air flows. The Main Line has a 2.54-cm (1 in) O.D., and the dilution lines are 1.90-cm (0.75 in) O.D. Diameters were chosen to give turbulent flow with an approximate minimum Reynolds number of 3000.

Air Supply

Air from the house compressor is treated by passing it sequentially through a cotton filter, a silica gel bed, a charcoal bed and a high efficiency glass fiber filter for removal of water, hydrocarbons and particulate. This air is then connected to a manifold containing six takeoff

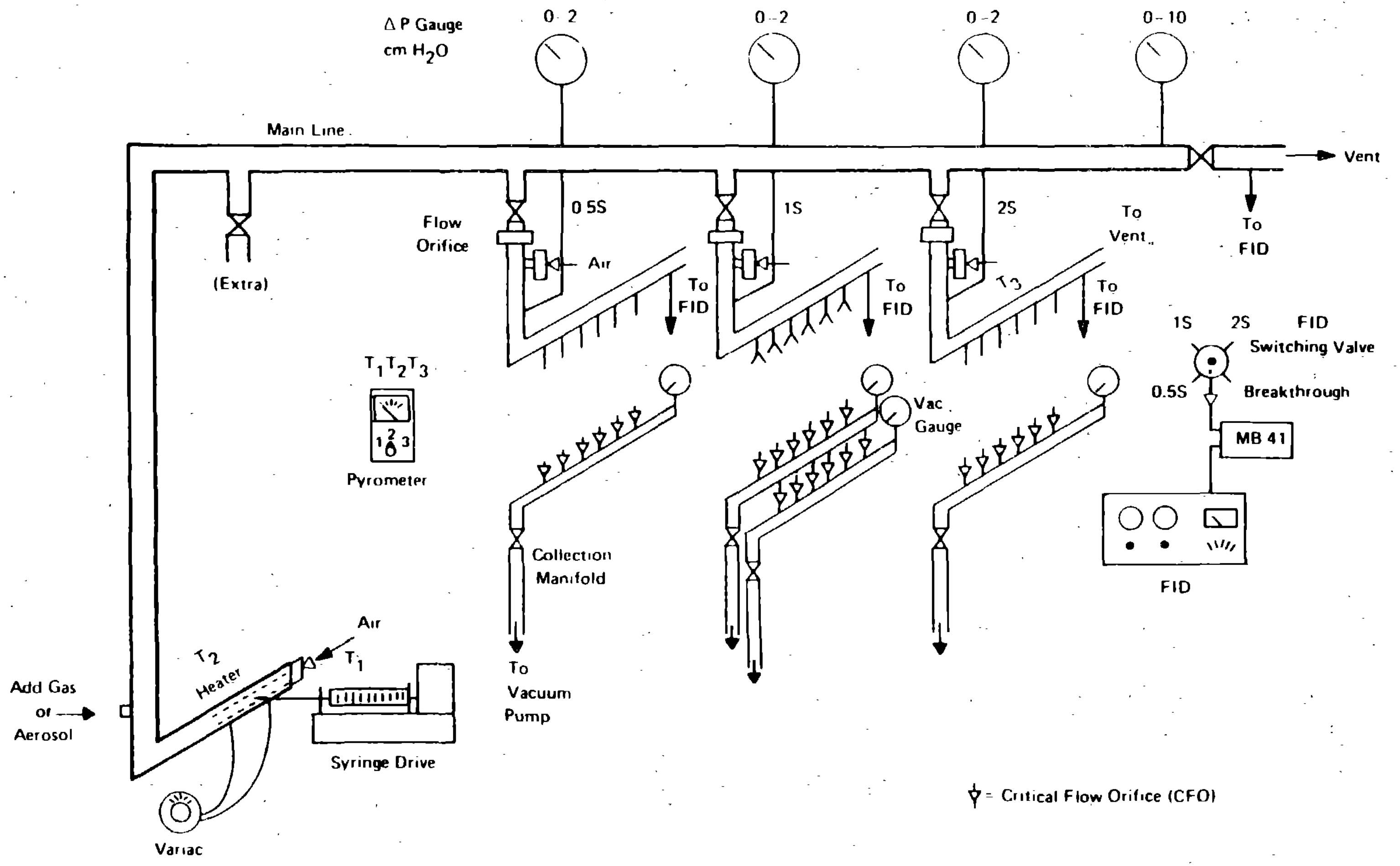


Figure 288-B-1. Vapor Generation/Dilution/Sampling System

ball valves. The pressure (20 psig) at the manifold is maintained with a Nullmatic Moore 40H50 regulator and monitored with an Ashcroft 0-60 psig test gauge. The air supply is used for each of the dilution system connections as well as for the flame ionization detector monitor flame and "zero" air.

Sample Collection Manifold

Sample flow through the sampling devices connected to the dilution lines is established by connecting each device by means of a short piece of flexible tubing to a CFO which is connected to a 1.27 cm (1/2 in) O.D. vacuum manifold. Each dilution line has a separate manifold which derives its vacuum from a Model 0322 Gast vacuum pump. The orifices are jewel orifices pressed into a threaded Teflon rod. One end of the rod is screwed into a tee on the manifold, and the other has a hose tabulation fitting connected to it. The orifice is protected from plugging by means of a piece of 100 mesh stainless steel screen.

Vent System

All excess vapor-laden air is collected via a 3.81-cm (1.5 in) PVC manifolding system where it is passed through a 0.3 x 0.3 x 0.6-M charcoal bed. Flow is established by means of a pressure blower on the exit side of the charcoal bed, and it is vented to the laboratory hood exhaust.

Calibration

Air Flows

Main Line -- The air flow delivered by the Main Line CFO was determined by measurement with a Singer Dry Test Meter. The meter had previously been calibrated with a spirometer primary standard. Using the 0.310-cm diameter orifice at 20 psig air pressure, the flow was found to be 0.1103 cu m/min corrected to 25°C and 760 mm Hg.

Dilution Lines -- The air flow through each of the dilution line CFO's and restrictor orifices was similarly measured with the Dry Test Meter to assure that they met design parameters, but these values did not provide the primary basis for determination of vapor concentration.

Collection CFO's -- Since the flow rate through the sample collection CFO's was lower (0.2 and 1.0 liter per minute) than appropriate for use with the Dry Test Meter, the flow rate of each of these orifices was measured using an SKC soap bubble meter which was independently calibrated by gravimetrically measuring water capacity.

All volume measurements have been referenced to normal temperature and pressure of 25°C and 760 mm Hg.

Dilution Ratios

The concentration of vapor in the dilution lines is determined from the concentration calculated in the Main Line and the dilution ratio determined between the dilution lines and the main line. These dilution ratios were measured by adding a controlled amount of propane gas to the Main Line and then measuring the relative concentration in each of the lines using a Beckman Model 402 heated hydrocarbon analyzer. The procedure was repeated several times and is regularly checked during the program.

In the case where 4X or 2X concentration level conditions were generated, the dilution ratios reported below were observed.

		Relative Concentration		
Case Generated	Main Line	2S	1S	0.5S
4X	1.000	0.5097	0.2557	0.1311
2X	1.000	1.000	0.487	0.244

Each of these sets of values represents a different set of air flow and orifice selection conditions as previously discussed. Point to point comparison of the six sample ports on each manifold showed less than a 1% variation in concentration among them.

Monitors

To provide a ready check on operating conditions, several gauges or monitors have been included in the system. Dwyer Magnehelic gauges monitor the pressure on the Main Line and each of the dilution lines. A 0-10 cm H_2O gauge is used on the Main Line (Setpoint 8 cm) and 0-2 cm H_2O gauges are used for the dilution lines. The purpose of these latter gauges is to provide a check against possible back pressure developing in these lines which would affect the dilution ratios.

The flame ionization detector (FID) is used to determine the time at which the Main Line concentration has reached equilibrium and to monitor the concentration level during breakthrough studies and sample collection.

Breakthrough Studies

A. Low Relative Humidity (Dry Air)

For the measurement of sorbent tube capacity for a given vapor (breakthrough) six sorbent tubes containing only the 100 mg "front half" section of sorbent are connected in parallel to the 2S dilution line and to a 0.635-cm (1/4-in) O.D. stainless steel six-port manifold. Flow through the manifold is controlled by a CFO and is established using a Metal Bellows Corp. Model MB41 pump. Flow through the orifice was

measured as 1.14 liters per minute providing a 0.19-liter per minute flow to each of the tubes. (A separate set of orifice allows a similar determination at a flow rate of 1.0 liter per minute through each tube.) Equal flow through each of the tubes is insured by carefully selecting and/or adjusting packing in the tubes to have an equal pressure drop when precalibrated at a 0.2-liter per minute flow rate.

Once a steady state vapor concentration is established, the 2S concentration level is used to set the 100% point on the hydrocarbon analyzer. Then the valve is switched, and the flow from the breakthrough manifold is passed through the hydrocarbon analyzer and monitored either until 5% of the 2S level is observed or for a period of four hours--whichever occurs first.

B. High Relative Humidity

For the generation of a high relative humidity atmosphere, at least 80% R.H., water vapor is delivered into the generator Main Line via one of the side arms as shown in Figure S288-B-2. A peristaltic pump, Cole-Parmer Masterflex, Model No. 7013, is used to deliver water into a heated copper coil (1/8 in x 10 feet) contained in a tube furnace; the furnace temperature is maintained above 110°C and monitored by a thermocouple and optical pyrometer. Water is delivered at the rate of 1.9 g per minute to blend with the analyte-containing dry air stream flowing at a rate of 0.100 cu m per min to produce an atmosphere of at least 80% R.H. at 25°C and 760 mm Hg.

All other aspects of the breakthrough test procedure are as described above.

Procedure

The overall procedure for a given sample is as follows:

1. Line air flow and dilution ratios are verified.
2. Sample delivery rate is determined by appropriate calibration.
3. Sample is fed into Main Line until vapor concentration equilibrium is established.
4. The breakthrough experiment is performed and subsequent sample collection volumes adjusted if necessary.
5. The four sets of six samples from the three concentration levels are collected simultaneously.

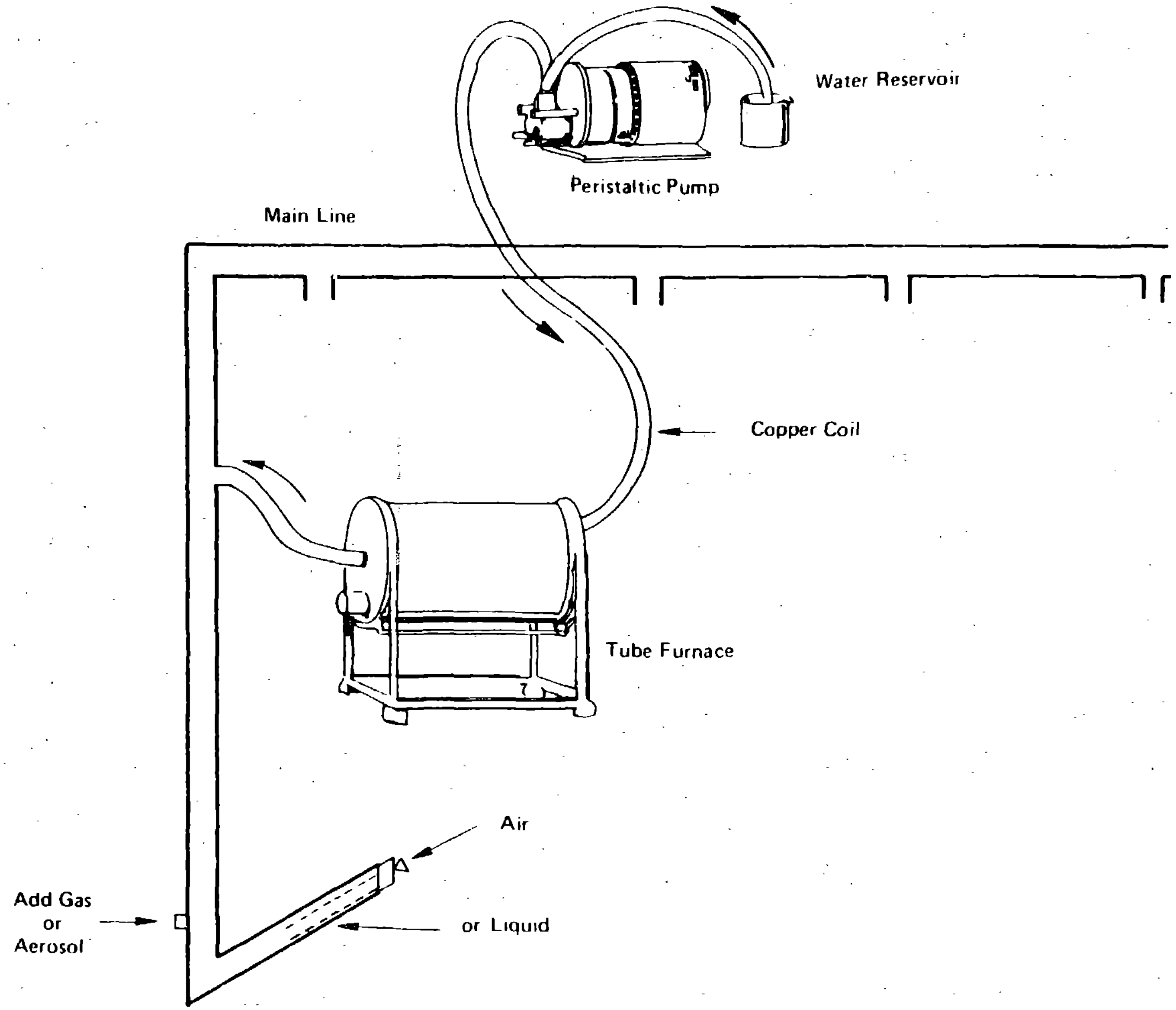


Figure S288-B-2. Generation of High Humidity Atmospheres

ATTACHMENT C

Cyanide (CN^-) Determination

Synopsis

Collection of HCN in 0.1N KOH, addition of excess Ni^{++}, back titration of excess Ni^{++} with EDTA, endpoint detection with Murexide.

Reagents: NH_4OH
0.1 M $NiSO_4$ (1.3143 g $NiSO_4.6H_2O$/500 ml H_2O)
0.1 M EDTA
1 M NH_4Cl (26.75 g/500 ml H_2O)
Indicator: Murexide, 0.5 g Supernatant of saturated aqueous solution--daily fresh

Standardization of $NiSO_4$

Either via nickel glyoxime precipitation, or vs. EDTA (as in analytical method).

Analysis

Pipet into 125 ml Erlenmeyer flask 25 ml $NiSO_4$ solution, 5 ml NH_4Cl solution, 5 ml NH_4OH. Swirl and introduce the solution to be analyzed containing about 20 mg CN^-. Add one drop indicator and back titrate immediately with EDTA. Color change: yellow to violet.

Calculation

1 ml M/100 $NiSO_4 \cong$ 1.0407 mg CN^-

References

1. Schwarzenback - Flaschka: Die Komplexometrische Titration, F. Enke Verlag, Stuttgart 1965, page 221.

2. Hurditz - Flaschka: Die Titration von Cyanid mit Nickellösungen, Z. Anal. Chem. 136, 185 (1952).

Copper Fume

Analyte: Copper

Matrix: Air

OSHA Standard: 0.1 mg/cu m

Procedure: Filter collection, acid digestion, AA

Method No.: S354

Range: 0.05-0.37 mg/cu m in a 480-liter sample

Precision ($\overline{CV}_T$): 0.058

Validation Date: 9/30/77

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1. Synopsis (Reference 11.1)

1.1 A known volume of air is drawn through a mixed cellulose ester membrane filter to collect copper fume.

1.2 The samples are ashed using concentrated nitric acid to destroy the filter and other organic materials in the sample. The copper is taken up in 1% nitric acid.

1.3 The solutions of samples and standards are aspirated into the oxidizing air-acetylene flame of an atomic absorption spectrophotometer (AAS). A hollow cathode lamp for copper is used.

2. Working Range, Sensitivity, and Detection Limit

2.1 This method was validated over the range of 0.0548-0.372 mg/cu m using a 480-liter sample at an atmospheric temperature of 22°C and an atmospheric pressure of 761 mm Hg. Under the conditions of sample size (480 liters), the working range of the method is estimated to be 0.01-0.3 mg/cu m. The method may be extended to higher values by dilution of the solution before AA analysis.

2.2 The sensitivity of the AA analysis as reported by the manufacturer is 0.04 microgram/ml of aqueous solution. This is the concentration of the solution which produces a signal of 1% absorbance.

2.3 The detection limit of the AA analysis as reported by the manufacturer is 0.003 microgram/ml of aqueous standard solution.

3. Interferences

3.1 Any particulate material other than copper fume containing copper or copper salts will result in a high value being reported as copper fume.

3.2 Incomplete digestion of the filter or a high zinc/copper ratio in the atmosphere may lead to depression of the copper absorbance.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV_T}$) for the total analytical and sampling method in the range of 0.0548-0.372 mg/cu m was 0.058. This value corresponds to a 0.006 mg/cu m standard deviation at the OSHA standard level. Statistical information can be found in Reference 11.2. Details of the test procedures can be found in Reference 11.3.

4.2 A collection efficiency of 1.00 was determined for the collecting medium, thus no bias was introduced in the sample collection step, and no correction for collection efficiency is necessary. The Coefficient of Variation is a good measure of the accuracy of the method. Storage stability studies on samples collected from a test atmosphere at a concentration of 0.1181 mg/cu m indicate that collected samples are stable for at least 7 days.

5. Advantages and Disadvantages

The sampling device is small, portable, and involves no liquids. Samples collected on filters are analyzed by means of a quick, instrumental method.

6. Apparatus

6.1 Filter unit: The filter unit consists of a 37-mm diameter, 0.8-micrometer pore size mixed cellulose ester membrane filter supported by a glass fiber backup pad, and an appropriate 37-mm two-piece cassette filter holder.

6.2 Personal Sampling Pump: A calibrated personal sampling pump whose flow can be determined to an accuracy of ±5% at the recommended flow rate.

6.3 Atomic absorption spectrophotometer equipped with an air-acetylene burner head.

6.3.1 Copper hollow cathode lamp.

6.3.2 Oxidant: compressed air.

6.3.3 Fuel: acetylene.

6.3.4 Pressure-reducing valves: A 2-gauge, 2-stage pressure reducing valve and appropriate hose connections are needed for each compressed gas tank.

6.4 Manometer.

6.5 Thermometer.

6.6 Glassware, borosilicate

6.6.1 Phillips beakers: 125 ml.

6.6.2 Watchglass covers.

6.6.3 Pipets of convenient sizes.

6.6.4 Volumetric flasks: 10-ml and other appropriate sizes.

6.7 Polyethylene Bottles

6.7.1 Five 100-ml capacity polyethylene bottles for working atomic absorption standards.

6.7.2 One 1000-ml capacity polyethylene bottle for stock atomic absorption standard.

6.8 Hot Plate: Adjustable thermostatically controlled hot plate capable of reaching 160°C.

7. Reagents

All reagents used must be ACS Reagent Grade or better.

7.1 Water, distilled or deionized.

7.2 Nitric acid, concentrated.

7.3 1% Nitric acid (V/V).

7.4 Aqueous standard stock solutions containing 1000 micrograms/ml of copper (commercially available).

8. Procedure

8.1 Cleaning of Equipment

8.1.1 Before use, all glassware should initially be soaked in a mild detergent solution to remove any residual grease or chemicals.

8.1.2 After initial cleaning, glassware must be cleaned with hot concentrated nitric acid and then rinsed thoroughly with tap water and distilled water, in that order, and then dried.

8.1.3 For glassware which has previously been subjected to the entire cleaning procedure, a nitric acid rinse will be adequate.

8.2 Calibration of Personal Sampling Pumps. Each personal sampling pump must be calibrated with a representative filter cassette in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Assemble the filter in the two-piece filter cassette holder and close firmly to insure that the center ring seals the edge of the filter. The cellulose membrane filter is held in place by a glass fiber backup pad. Secure the cassette holder together with tape or shrinkable band.

8.3.2 Remove the cassette plugs and attach to the personal sampling pump tubing. Clip the cassette to the worker's lapel. The cassette plugs are replaced after sampling.

8.3.3 Air being sampled should not pass through any hose or tubing before entering the filter cassette.

8.3.4 A sample size of 480 liters is recommended. Sample at a flow rate of 2.0 liters per minute. The flow rate should be known with an accuracy of 5%.

8.3.5 Since the filter may become plugged or overloaded as evidenced by caking, the filter and pump's sampling rate should be checked periodically. When the filter becomes overloaded or when the pump's flow rate cannot be adjusted to 2.0 liter/minute, terminate sampling.

8.3.6 Terminate sampling at the predetermined time and record sample flow rate, collection time, and ambient temperature and pressure. If pressure reading is not available, record the elevation. Also record the type of sampling pump used.

8.3.7 With each batch of ten samples, submit one filter from the same lot of filters which was used for sample collection and which is subjected to exactly the same handling as the samples, except that no air is drawn through it. Label this as a blank.

8.3.8 The cassettes in which the samples are collected should be shipped in a suitable container, designed to prevent damage in transit.

8.4 Analysis of Samples

8.4.1 Transfer each sample to a clean 125-ml Phillips beaker.

8.4.2 Wet Ashing. Treat the sample with 10 ml of concentrated nitric acid. Cover each beaker with a watchglass and heat on a hot plate (140-160°C) in a fume hood until most of the acid has evaporated. Add 3 ml more of concentrated nitric acid and repeat the procedure. Evaporate the sample to 0.5 ml. Keep the beakers covered with a watchglass during the entire ashing procedure. When the beakers are cool, rinse the watchglass with 1% nitric acid into the beaker.

8.4.3 Quantitatively transfer the clear solutions to a 10-ml volumetric flask using 1% nitric acid.

8.4.4 Rinse each beaker at least three times with 2-ml portions of 1% nitric acid and quantitatively transfer each rinsing to the solution in the volumetric flask. Dilute all samples to 10 ml with 1% nitric acid.

8.4.5 Aspirate samples (Section 8.4.4) and standard solutions (Section 9.1) into an oxidizing air-acetylene flame and record the absorbance at 324.7 nm. The sample absorbance is proportional to the sample concentration and can be determined from the appropriate calibration curve. When very low concentrations are found in the sample, scale expansion can be used to increase instrument response.

Note: Follow instrument manufacturer's recommendations for specific AAS operating parameters.

8.4.6 Appropriate filter blanks must be analyzed in accordance with the total procedure.

9. Calibration and Standardization

9.1 From the 1000 micrograms/ml stock standard (Section 7.4), prepare at least five working standards to cover the range from 0.5 to 15 micrograms/ml. Prepare all standard solutions in 1% nitric acid and remake each day. Store the standard solutions in 100-ml polyethylene bottles.

9.2 Proceed as in Section 8.4.5.

9.3 Prepare a calibration curve by plotting on linear graph paper the absorbance versus the concentration of each standard in microgram/ml. Standards should be run both before and after the series of samples are analyzed to ensure that conditions have not changed.

10. Calculations

10.1 Read the concentration in micrograms/ml, corresponding to the total absorbance from the calibration curve. The micrograms in each sample equals:

$$\text{micrograms/ml (from curve)} \times 10 \text{ ml} = \text{micrograms Cu/sample}$$

10.2 Corrections for the blank must be made for each sample.

$$\text{microgram} = \text{microgram sample} - \text{microgram blank}$$

where:

microgram sample = microgram found in sample filter
microgram blank = microgram found in blank filter

10.3 For personal sampling pumps with rotameters only, the following air volume correction should be made.

$$\text{Corrected Volume} = f \times t \left(\sqrt{\frac{P_1}{P_2} \times \frac{T_2}{T_1}} \right)$$

where:

f = flow rate sampled
t = sampling time
P_1 = pressure during calibration of sampling pump (mm Hg)
P_2 = pressure of air sampled (mm Hg)
T_1 = temperature during calibration of sampling pump (°K)
T_2 = temperature of air sampled (°K)

10.4 The concentration of copper fume in the air sample can be expressed in mg/cu m (microgram/liter = mg/cu m).

$$\text{mg/cu m} = \frac{\text{microgram (Section 10.2)}}{\text{Air Volume Sampled (liter)}}$$

11. References

11.1 Analytical Methods for Flame Spectrophotometry, Varian Associates, 1972.

11.2 Documentation of NIOSH Validation Tests, National Institute for Occupational Safety and Health, Cincinnati, Ohio (DHEW-NIOSH Publication #77-185), 1977. Available from Superintendent of Documents, U. S. Government Printing Office, Washington, D.C., Order No. 017-033-00231-2.

11.3 Backup Data Report for Copper Fume, prepared under NIOSH Contract No. 210-76-0123.

Sampling Data Sheet No. S354

September 30, 1977

Substance

Copper Fume

Standard

8-hour time-weighted average : 0.1 mg/cu m

Analytical Method

A known volume of air is drawn through a cellulose ester membrane filter to trap the copper fume present. The filter is digested with concentrated nitric acid to destroy the filter and any other organic material. The copper is then taken up in 1% nitric acid and aspirated into an atomic absorption spectrophotometer for determination of concentration. The method has been validated over the range of 0.0548-0.372 mg/cu m using a 480-liter sample at 22°C and 761 mm Hg atmospheric temperature and pressure. A detailed description of the sampling and analytical method is given in the method referenced below.

Sampling Equipment

Sampling equipment includes a calibrated personal sampling pump whose flow can be determined to an accuracy of ±5% at approximately 2.0 liters per minute; a 37-mm two-piece cassette filter holder and a 37-mm/0.8 micrometer mixed cellulose ester membrane filter (MCEF) supported by a cellulose backup pad.

Sample Size

A sample size of 480 liters is recommended. Sample at a flow rate of 2.0 liters per minute.

Sampling Procedure

1. Assemble the filter and two-piece filter cassette and close firmly to insure that the center ring seals the edge of the filter. Examine the holder for a good filter seal. If the cassette will not seal tightly, it should be discarded. Secure the cassette holder together with tape or shrinkable band.

2. Remove the cassette plugs and attach to the personal sampling pump tubing. Clip the cassette to the worker's lapel.

3. Air being sampled should not be passed through any hose or tubing before entering the filter cassette.

4. Set the flow rate as accurately as possible using the manufacturer's directions. Record the temperature and pressure of the atmosphere being sampled. If the pressure reading is not available, record the elevation. Also report the type of sampling pump that is used.

5. Since the filter may become plugged or overloaded as evidenced by caking, the filter and pump's sampling rate should be checked periodically. When the filter becomes overloaded or when the pump's flow rate cannot be adjusted to 2.0 liters per minute, terminate sampling.

6. After termination of sample collection, the cassettes should be firmly sealed with the plugs in both the inlet and outlet.

7. Carefully record sample identity and all relevant sample data such as collection time and sampling flow rate.

8. With each batch of ten samples, submit one filter from the same lot of filters which was used for sample collection and which is subjected to exactly the same handling as the samples except that no air is drawn through it. Label this as a blank.

Special Considerations

1. Incomplete digestion of the filter or a high zinc/copper ratio in the atmosphere may lead to depression of the copper absorbance.

2. Any particulate material other than the fume containing copper or copper salts will also be collected on the filter and analyzed. This will result in a high value being reported as copper fume. If any of these compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

Shipping Instructions

The cassettes in which the samples are collected should be shipped in a suitable container, designed to prevent damage in transit.

Reference

Copper Fume, NIOSH Method No. S354.

Backup Data Report No. S354

September 30, 1977

Substance: Copper Fume

OSHA Standard: 0.1 mg/cu m

Chemicals Used for Validation: Copper metal from Fisher Scientific Company
Copper acetate from Mallickrodt Chemical Works

General

The procedure for collection and analysis of air samples of copper fume is described in NIOSH Method No. S354. This method consists of collection of copper fume on mixed cellulose ester membrane filters (MCEF), wet ashing the filters with concentrated nitric acid, dissolving the copper with concentrated nitric acid, and analysis of the resulting solutions by atomic absorption.

This method has been validated for a 480-liter air sample, using the criteria for validation outlined in Reference 1. Using these criteria, the absolute total error (sampling and analysis) is less than 25% at the OSHA standard 95% of the time.

The protocol for validation of this method was to:

Analyze 18 samples (6 each at 0.5X, 1X, and 2X the OSHA standard) spiked with the appropriate amounts of copper to represent 480-liter air samples.

Analyze 17 samples collected from dynamically generated test atmospheres (6 samples collected at each of 0.5X and 2X the OSHA standard and 5 samples collected at 1X the OSHA standard).

Determine collection efficiency of the MCE filters.

Test the storage stability of six collected samples.

Assess the precision and accuracy of the method.

Details of these procedures are discussed below.

Analysis

A description of the method of analysis is given in NIOSH Method No. S354. The results of the analytical method recovery tests are in Table S354-3 of this report.

Initially, problems were encountered with the analytical method for analyzing copper samples. Significant losses of copper occurred during filter digestion at temperatures over 200°C. It was found that a temperature range of 140-160°C was suitable for filter digestion. Higher temperatures resulted in significant losses of copper.

Sampling and Analysis

Test atmospheres of copper oxide fume were generated for this study. These were generated by thermal decomposition and oxidation of a cupric acetate aerosol. An Environmental Research Corporation (ERC) fluid atomization aerosol generator was used to generate cupric acetate aerosol from a solution containing 5 g of cupric acetate dissolved in water and made up to 1 liter. Oxygen was used to generate the aerosol to assure complete oxidation of the acetate upon its decomposition.

The curpic acetate aerosol/O_2 output from the ERC generator entered a 62-cm long x 2.4-cm I.D. quartz tube. The initial 31 cm of the tube was heated with a tube furnace to approximately 1100°C. The final 31 cm was wrapped in heating tape. The temperature of the gases (at a flow rate of 10.70 liters/minute) leaving the quartz tube was approximately 450°C. (See Figure S354-1).

The average residence time of particles in the furnace, at temperatures of at least 450°C, was 1.7 second. This is ample time to allow decomposition of the cupric acetate and complete oxidation.

The particles enter a dilution chamber through a 18-mm O.D. glass tube which is concentric with a 20-mm I.D. glass tube which delivers the dilution air. Air enters the dilution chamber at a high velocity so that turbulent mixing of the dilution air and aerosol takes place.

The test atmosphere moves from the dilution chamber into the sampling chamber via a 3-way valve (Figure S354-2). The valve, when switched to a bypass mode, allows complete flushing of the sample chamber with room air after a sample run is completed. The stainless steel sampling chamber is the shape of an inverted cone approximately 59 cm high x 15 cm in diameter at the base. The base contains the fittings necessary to hold filter holders. The sampling ports are connected through individual critical flow orifices to a metal bellows pump. The effluent from the sampling pump is added back into the manifold that follows the sampling chamber so the total flow through the sampling cone is not disturbed while samples are being collected.

To achieve the desired concentration levels, the output of the fluid atomization aerosol generator was held constant at 10.70 liters/minute while the dilution air flow rate was changed.

Scanning electron micrographs showed the particles to have a size range of 0.04 to 0.14 micrometers. Samples of the generated material were examined by X-ray diffraction and were found to contain cupric oxide. Crystalline copper metal was not detected.

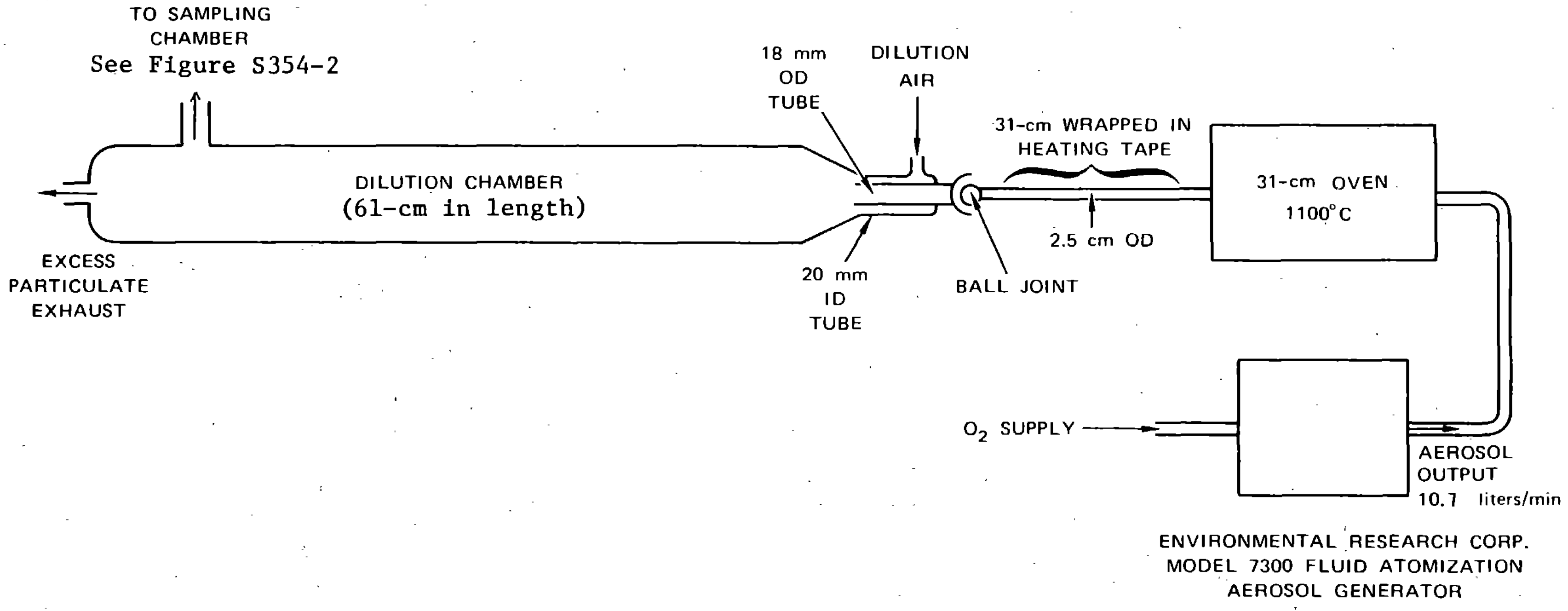

FIGURE S354-1

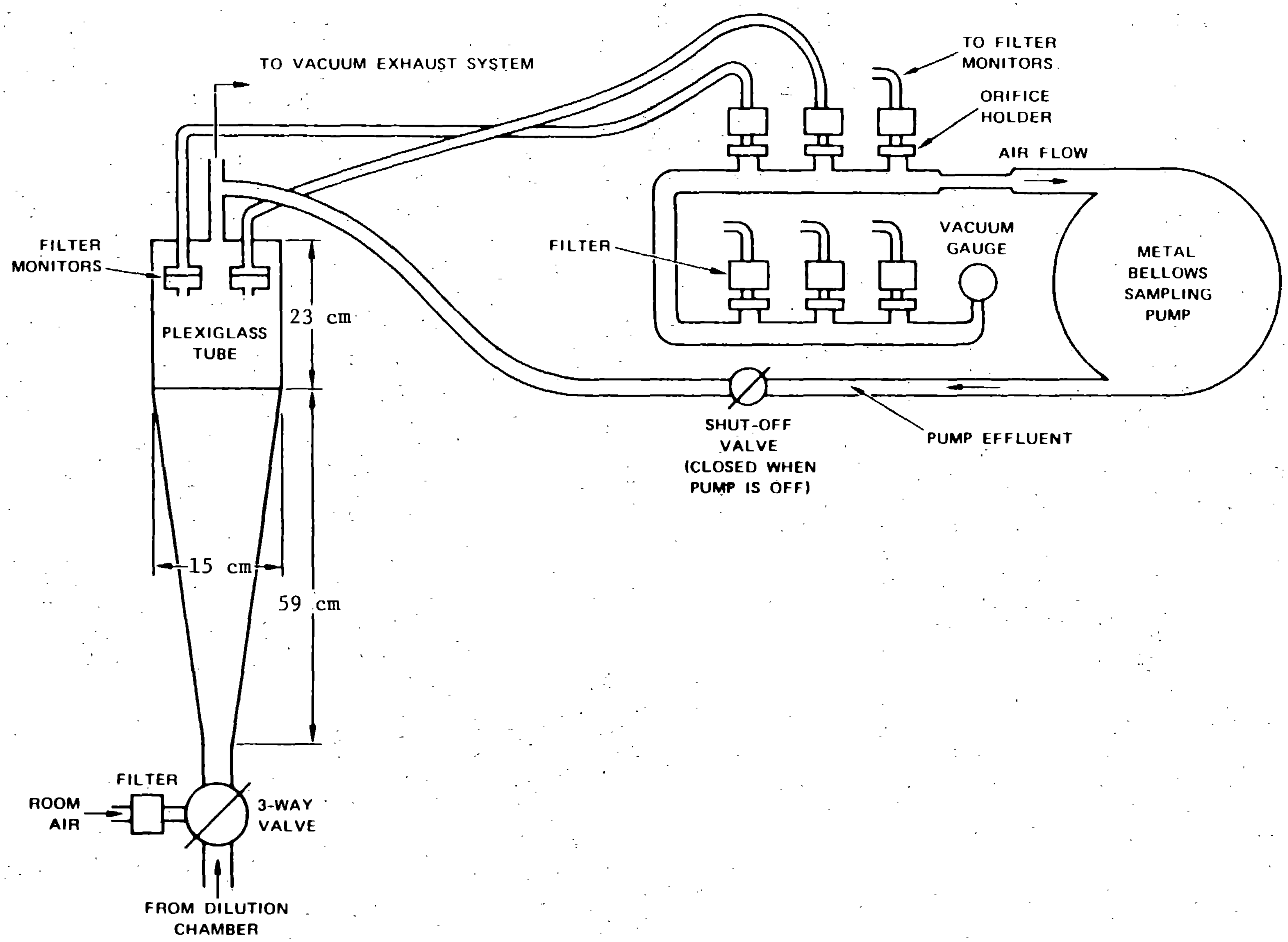

FIGURE S354-2 SAMPLING CHAMBER

Samples were collected for 240 minutes at an average flow rate of 2.0 liters/minute. The results of the Sampling and Analysis experiments are presented in Table S354-4.

Collection Efficiency

Collection efficiency tests were conducted at 0.49 mg/cu m (as determined by analysis of the samples collected by mounting in series two filters in direct contact with each other. The generation conditions described above were used. Samples were collected for 240 minutes at an average flow rate of 2 liters/minute. The results of the collection efficiency test are given in Table S354-1.

Table S354-1

Collection Efficiency Test

micrograms found first filter	micrograms found backup filter	Collection Efficiency
242	0.22	1.00
248	0.22	1.00
248	0.22	1.00
246	0.48	1.00
244	0.15	1.00
238	0.28	1.00

Since collection efficiency was determined to be 1.00 on MCE filters, no correction for collection is needed.

Storage Stability Study

A study was done to assess whether the analyte would be successfully stored for one week after collection. A second set of six samples at 1X the OSHA standard level was collected simultaneously with the 1X samples used in the validation study. The same generation conditions described under the Sampling and Analysis section were used. Samples were collected for 240 minutes at an average flow rate of 2 liters/minute.

The results of the storage stability study are presented in Table S354-2.

Table S354-2

Storage Stability Test

	Sample Analyzed Immediately (mg/cu m)	Samples Analyzed After One Week (mg/cu m)
	0.1198	0.1095
	0.1176	0.1204
	0.1132	0.1179
	0.1204	0.1217
	0.1194	0.1162
		0.1196
mean	0.1181	0.1176
std dev	0.0029	0.0044
CV	0.025	0.037

The criterion for acceptance was that the mean of the six samples stored at room temperature for 7 days should be within ±10% of the mean of the set analyzed at the beginning of the storage period. The two means compare within 0.4%; thus, the storage stability was adequate.

Independent Method

No suitable instrumental method for measuring the concentration of the analyte in the sample generator was available. A separate method of analysis was tested for use as an independent method for determining the concentration in the generator. The neocuproine colorimetric method for copper (Reference 2) did not give satisfactory results for use as an independent method.

During collection of samples for the 2X and 0.5X generations, two additional samples were collected on 37-mm Gelman type AA glass fiber filters. The results for these samples are shown below:

Comparison of Samples Collected on
Glass Fiber Filters and Mixed Cellulose Ester Filters

Concentration (mg/cu m)	
Glass Fiber Filters*	Mixed Cellulose Ester Filters**
0.0548	0.0540
0.372	0.367

* Mean of two samples

** Mean of six samples

Based on this comparison and the results of the collection efficiency test and the storage stability study on collected samples, the assumption that taken and found concentrations were equal is justified.

Precision and Accuracy

The statistical procedures and a definition of the terms are described in Reference 3.

Bartlett's test for homogeneity of variances was applied to the coefficients of variation of 0.5X, 1X, and 2X the OSHA standard for generated samples. The data (Table S354-4) gave a chi squared value of 0.92. Thus, Bartlett's test is passed and it is feasible to pool the coefficients of variation to calculate $\overline{CV}_T$.

The precision of the analytical method was assessed using the data in Table S354-3. The pooled Coefficient of Variation $(\overline{CV}_1)$ for three sets of analytical samples was found to be 0.033.

Precision and accuracy of the total sampling and analytical method were evaluated using the data in Table S354-4 and the results from the storage stability and collection efficiency tests. The pooled Coefficient of Variation $(\overline{CV}_2)$ for the three sets of samples collected from test atmospheres is 0.025.

The total Coefficient of Variation $(\overline{CV}_T)$ is 0.058.

Table S354-3

Data Sheet: Copper Fume

Analysis

Level	0.5X			1X			2X	
µg taken	µg found	A.M.R.	µg taken	µg found	A.M.R.	µg taken	µg found	A.M.R.
24.0	23.6	0.983	48.0	47.2	0.983	98.0	98.8	1.008
24.0	23.8	0.992	48.0	47.2	0.983	98.0	101.0	1.031
24.0	21.7	0.904	48.0	46.6	0.971	98.0	98.1	1.001
24.0	22.5	0.938	48.0	48.1	1.002	98.0	106.5	1.087
24.0	24.5	1.021	48.0	47.2	0.983	98.0	95.6	0.976
24.0	23.6	0.983	48.0	48.1	1.002	98.0	99.0	1.010

n =	6	6	6
mean	0.970	0.987	1.019
std dev	0.042	0.012	0.038
CV_1	0.043	0.012	0.037

$\overline{CV}_1$ 0.033

$\overline{CV}_{A+\overline{AMR}}$ 0.036

A.M.R. = Analytical Method Recovery = $\frac{\text{micrograms found}}{\text{micrograms taken}}$

Based on these data, no correction for Analytical Method Recovery is needed.

Table S354-4

Data Sheet: Copper Fume

Sampling and Analysis

Test Level	Found		
	micrograms	Liters	mg/cu m*
0.5X	24.6	480	0.0512
	25.5	478	0.0533
	25.9	470	0.0551
	26.4	475	0.0556
	26.0	473	0.0550
	25.8	478	0.0540
		n = 6	
		mean	0.0540
		std dev	0.0016
		CV_2	0.030
1X	57.5	480	0.1198
	56.2	478	0.1176
	53.2	470	0.1132
	57.2	475	0.1204
	56.5	473	0.1194
	Sample was lost.		
		n = 5	
		mean	0.1181
		std dev	0.0029
		CV_2	0.025
2X	170.0	480	0.354
	174.0	475	0.366
	175.0	473	0.370
	176.0	478	0.368
	178.0	473	0.376
	176.0	475	0.370
		n = 6	
		mean	0.367
		std dev	0.007
$\overline{CV}_2$ 0.025		CV_2	0.019

* All values have passed the Grubbs' outlier test at the 1% confidence level as described in Reference No. 3.

References

1. Contract 210-76-0123, National Institute for Occupational Safety and Health, Division of the Department of Health, Education, and Welfare, U.S. Government.

2. Welcher, F.J., Standard Methods of Chemical Analysis, Vol. II, Part A, 6th ed., D. Van Nostrand Company, Inc., Princeton, N.J., 1310.

3. Documentation of NIOSH Validation Tests, National Institute for Occupational Safety and Health, Cincinnati, Ohio (DHEW-NIOSH Publication #77-185), 1977. Available from Superintendent of Documents, U.S. Government Printing Office, Washington, D.C., Order No. 017-033-00231-2.

4. Friedman and Horstman, "Method for Generation of Metallic Oxide Aerosols," *Amer. Ind. Hyg. Assoc. J.*, 35, 12, (1974), 825-831.

Nitrogen Dioxide

Analyte:	Nitrite ion, NO_2^-	Method No.:	S320
Matrix:	Air	Range:	3.1 - 11.5 ppm
OSHA Standard:	5 ppm (9 mg/cu m)	Precision ($\overline{CV}_T$):	0.063
Procedure:	Collection on TEA-coated molecular sieve, desorption with TEA, spectrophotometric analysis	Validation Date:	10/28/77

1. Synopsis

A known volume of air is drawn through a sampling tube containing 400 mg triethanolamine-impregnated molecular sieve followed by a backup section of 200 mg triethanolamine-impregnated molecular sieve. Both triethanolamine-impregnated molecular sieve sections in each tube are transferred to flasks, and the nitrogen dioxide is desorbed with an aqueous triethanolamine solution. An aliquot is treated with hydrogen peroxide, sulfanilamide and N-(1-naphthyl)ethylenediamine dihydrochloride and the reacted nitrite ion is measured spectrophotometrically.

2. Working Range, Sensitivity and Detection Limit

2.1 This method was validated over the range of 3.07-11.49 ppm using a 3.9-liter sample volume. This method is capable of measuring much smaller amounts, since the collection and desorption efficiency has been shown to be adequate at levels of approximately 0.5 ppm NO_2 (Reference 11.1).

2.2 The upper limit of the sampling and analytical method is dependent on the adsorptive capacity of the triethanolamine-impregnated molecular sieve section. Breakthrough is defined as the time that the effluent concentration from the collection tube reaches 5% of the concentration in the test gas mixture. When an atmosphere at 84% relative humidity containing 11.59 ppm NO_2 was sampled at 0.064 liter per minute, 5% breakthrough was not observed after 180 minutes. By comparison with data in reference 11.1, it is expected that breakthrough will occur after three hours (capacity = 90 μL NO_2) at a concentration of 30 ppm NO_2. The sample size recommended is less than two-thirds the 5% breakthrough capacity to minimize the probability of overloading the sampling tube.

2.3 At levels in excess of 4X the OSHA standard, the treated sample must be diluted so that absorbance is in the linear portion of the standard curve.

2.4 The detection limit under the prescribed sampling and analytical conditions is approximately 0.10 ppm NO_2.

3. Interferences

3.1 Sampling 50 ppm (2X the OSHA standard for NO) nitric oxide interferent on triethanolamine-impregnated molecular sieve is observed to correspond to less than 0.19 ppm NO_2 and can thus be ignored (Reference 11.1).

3.2 Any compound which is collected on triethanolamine-impregnated molecular sieve <u>and</u> which reacts with the colorimetric reagents may act as a positive or negative interference. If such an interference exists, its impact must be determined by independent analysis.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total sampling and analytical method in the range of 3.07-11.49 ppm was 0.0630. This value corresponds to a 0.315 ppm standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures may be found in References 11.2 and 11.3.

4.2 In validation experiments, this method was found to be capable of coming within ±25% of the "true value" on the average of 95% of the time over the validation range. The concentrations obtained at 0.5, 1 and 2 times the OSHA environmental limit were 2.0% lower than the dynamically generated test concentrations (n=18). The desorption efficiency/analytical method recovery was determined to be 1.047 for a collector loading of 11.82 µL. In storage stability studies the mean of samples analyzed after seven days were within 9.2% of the mean of samples analyzed immediately after collection. Experiments performed in the validation study are described in Reference 11.3.

A serious bias is possible if the stoichiometric factor for conversion of nitrogen dioxide (gas) to nitrite ion (0.63) is not correct. Several authors have reported values from 0.5-0.9. The value determined by Blacker (Reference 11.4) under similar experimental conditions is 0.63. No recovery correction should be applied to the final result.

5. Advantages and Disadvantages

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal due to the analytical specificity which has been corroborated by years of experimentation by many authors.

5.2 One disadvantage of the method is that the amount of sample that can be taken is limited by the number of milligrams that the tube will hold before overloading. When the amount of nitrogen dioxide found on the backup TEA tube exceeds 25% of that found on the front tube, the probability of sample loss exists.

5.3 The sampling tubes are analyzed by a somewhat tedious spectrophotometric method which utilizes a readily available visible spectrophotometer.

5.4 Both adsorbent sections must be analyzed since some breakthrough (<1%) does occur at 2X the OSHA standard level.

5.5 A somewhat uncertain stoichiometric factor (0.63) is used in calculation of concentration.

5.6 The precision of the method is affected by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

6.1 Sampling Equipment

6.1.1 A calibrated personal sampling pump whose flow can be determined within ±5% at the recommended flow rate of 50 milliliters per minute. The pump must be calibrated with a sampling tube in line.

6.1.2 Sampling Tubes. The sampling tube consists of a glass tube, flame-sealed at both ends, with a 7-mm O.D. and a 5-mm I.D., packed with two sections of triethanolamine-impregnated Type 13X, 30-40 mesh molecular sieve. The two sections include a front adsorbing section containing 400 mg and a backup section containing 200 mg. The two sections are separated by a 2-mm portion of silylated glass wool. A 3-mm portion of silylated glass wool is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the adsorbing section.

The triethanolamine-impregnated molecular sieve can be prepared as follows: Add 25 g triethanolamine to a 250-mL beaker; add 4 g gylcerol, 50 mL acetone and sufficient distilled water to bring up to 100 mL. To the mixture add about 50 mL Type 13X, 30-40 mesh molecular sieve. Stir and let stand in a covered beaker for about 30 minutes. Decant the excess liquid and transfer the molecular sieve to a porcelain pan which is then placed under a heating lamp until most of the moisture has evaporated. Complete the drying in an oven at 110°C for one hour. The sorbent should be free flowing. Store in a closed glass container.

6.1.3 Barometer.

6.1.4 Thermometer.

6.1.5 Stopwatch.

6.2 A spectrophotometer capable of measuring absorbance or transmittance at 540 nm.

6.3 Two matched 1-cm silica cells.

6.4 Volumetric flasks, 50-mL and other convenient sizes.

6.5 Beakers, 100-mL.

6.6 Pipets, 1, 5 and 10-mL and other convenient sizes to make standard dilutions.

6.7 Balance.

7. Reagents

Wherever possible, reagents should be ACS reagent grade or better.

7.1 Liquid Absorber. Prepare by dissolving 15.0 g triethanolamine in approximately 500 mL distilled water, adding 0.5 mL n-butanol, and diluting to 1 liter.

7.2 Hydrogen Peroxide Solution 0.02% (v/v). Prepare by diluting 0.2 mL, 30% hydrogen peroxide to 250 mL with distilled water.

7.3 Sulfanilamide Solution. Prepare by dissolving 10 g sulfanilamide in 400 mL distilled water, adding 25 mL concentrated phosphoric acid and diluting to 500 mL.

7.4 NEDA Solution. Prepare by dissolving 0.5 g N-(1-naphthyl)-ethylenediamine dihydrochloride in distilled water and diluting to 500 mL.

7.5 Stock Nitrite Solution, 100 ppm NO_2^-. Prepare by dissolving 0.1500 g sodium nitrite in 1 liter of water.

7.6 Working Nitrite Solution, 2 ppm NO_2^-. Prepare by diluting 2 mL of the stock nitrite solution to 100 mL with absorbing solution.

8. Procedure

8.1 Cleaning of Equipment

8.1.1 Before use, all glassware should be initially soaked in a mild detergent to remove any residual grease or chemicals.

8.1.2 After initial cleaning, the glassware should be thoroughly rinsed with warm tap water, 6 M nitric acid, tap water, distilled water, in that order, and then dried.

8.2 Calibration of Personal Sampling Pumps. Each personal pump must be calibrated with a representative sampling tube in the line. The tube is described in Section 6.2. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Immediately before sampling, break the two ends of the sampling tube to provide an opening of at least one-half of the internal diameter of the tube (5 mm).

8.3.2 The tube should be placed in a vertical direction during sampling to minimize channeling through the sorbent.

8.3.3 Air being sampled should not be passed through any hose or tubing before entering the tube.

8.3.4 A sample size of 3.0 liters is recommended. Sample at a known flow rate of 0.05 liter per minute for 60 minutes. The flow rate should be known with accuracy of at least ±5%.

8.3.5 The temperature and pressure of the atmosphere being sampled should be recorded. If the pressure reading is not available, record the elevation.

8.3.6 The exposed tube should be labeled appropriately and capped with supplied plastic caps.

8.3.7 With each batch of five or fewer samples, submit one sampling tube which had been handled in the same manner as the sample tubes (break, seal, transport), except that no air is sampled through this tube. This tube should be labeled as blank.

8.3.8 Capped sampling tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In order to facilitate removal of the sorbent, the broken ends of each tube are widened with tweezers. The glass wool is removed carefully and discarded, making sure that no sorbent is lost in the process. Both triethanolamine-impregnated molecular sieve sections are transferred to 50-mL volumetric flasks. These two sections are analyzed separately.

8.4.2 Extraction of the Sample. Prior to analysis, liquid absorber is added to the flask to bring the volume to 50 mL. The flask is shaken vigorously for about 30 seconds and the solids allowed to settle.

A blank is prepared similarly with a TEA/molecular sieve section of an unexposed sampling tube.

8.4.3 Spectrophotometer Operation. Turn on the spectrophotometer and allow sufficient time for warmup. Follow the instrument manufacturer's recommendations for specific operating parameters. Adjust the wavelength to 540 nm and set the zero and 100% transmittance scale using a 1-cm cell filled with distilled water. Check these settings prior to making any measurement to check on instrument drift.

8.4.4 Analytical Procedure

1. Pipet 10 mL of the extracted sample into a 50-mL volumetric flask.
2. Add 1.0 mL 0.02% hydrogen peroxide solution, 10.0 mL sulfamilamide solution, and 1.4 mL NEDA solution with thorough mixing after each addition.
3. Allow ten minutes for complete color development.
4. Transfer some of the sample into a 1-cm absorption cell.
5. Measure the absorbance or transmittance at 540 nm using a reagent blank to set zero absorbance.

9. Calibration and Standards

A series of standards varying in concentration over the range of interest is prepared and analyzed under the same conditions and during the same time period as the unknown samples. It is convenient to express concentration of standards in terms of µg per 10 mL since 10 mL aliquots of samples are analyzed. A calibration curve is established by plotting absorbance versus concentration in µg per 10 mL.

9.1 Using freshly prepared working nitrite solution, prepare at least five calibration standards in absorbing solution to cover a nitrite concentration range of 1 to 18 µg nitrite per 10 mL.

9.2 Prepare these standards fresh daily by appropriate dilution of the working nitrite solution using absorbing solution for all dilutions. A reagent blank containing no nitrite should also be prepared.

10. Calculations

10.1 Correction for the sample blank (obtained by extraction and analysis of the sampling tube marked "blank") must be made for each sample.

$$\text{Abs}_{\text{corr}} = \text{Abs}_{\text{sample}} - \text{Abs}_{\text{sample blank}}$$

10.2 Read the amount of nitrite ion, in µg NO_2 (ion) per 10 mL, corresponding to the Abs_{corr} from the standard curve.

10.3 Multiply the amount of nitrite ion per 10 mL by the factor shown below to obtain the µL NO_2 (gas) per 50 mL (total sample) at 25°C and 760 mm Hg.

$$\mu\text{L NO}_2\text{ (gas) in sample} = \mu\text{g NO}_2^-/10\text{ mL} \times \frac{5}{1.88 \times 0.63}$$

where:

$$1\ \mu\text{L NO}_2\text{ (gas)} = 1.88\ \mu\text{g NO}_2\text{ (gas) at 25°C and 760 mm Hg}$$

$$1\ \mu\text{g NO}_2\text{ (gas)} = 0.63\ \mu\text{g NO}_2^- \equiv \text{"Stoichiometric Factor"}$$

10.4 Determine the volume of air sampled at ambient conditions in liters based on the appropriate information, such as flow rate in liters per minute multiplied by sampling time. If a pump using a rotameter for flow rate control was used for sample collection, a pressure and temperature correction must be made for the indicated flow rate. The expression for this correction is:

$$\text{Corrected Volume} = f \times t \left(\sqrt{\frac{P_1}{P_2} \times \frac{T_2}{T_1}} \right)$$

where:

f = sampling flow rate

t = sampling time

P_1 = pressure during calibration of sampling pump (mm Hg)

P_2 = pressure of air sampled (mm Hg)

T_1 = temperature during calibration of sampling pump (°K)

T_2 = temperature of air sampled (°K)

10.5 The concentration of analyte in the air sampled can be expressed in ppm (at standard conditions of 25°C and 760 mm Hg).

$$\text{ppm } NO_2 = \frac{\mu L\ NO_2 \text{ (gas) (see Section 10.3)}}{\text{Air volume sampled (liters)} \times \frac{P}{760} \times \frac{298}{T + 273}}$$

Another method of expressing concentration is mg/cu m.

$$\text{mg/cu m} = \text{ppm} \times \frac{46.01}{24.45}$$

where:

P = pressure (mm Hg) of air sampled

T = temperature (°C) of air sampled

760 = standard pressure (mm Hg)

298 = standard temperature (°C)

24.45 = molar volume (liter/mole) of air at 25°C and 760 mm Hg

46.01 = molecular weight of nitrogen dioxide

11. References

11.1 M.A. Willey, C. McCammon, Jr., and L. Doemeny, Am. Ind. Hyg. Assoc. J., 38, 358 (1977).

11.2 Documentation of NIOSH Validation Tests, National Institute for Occupational Safety and Health, Cincinnati, Ohio (DHEW-

NIOSH-Publication No. 77-185), 1977. Available from Superintendent of Documents, Washington, D.C., Order No. 017-033-00231-2.

11.3 Backup Data Report S320 for Nitrogen Dioxide, prepared under NIOSH Contract No. 210-76-0123.

11.4 J. H. Blacker, *Am. Ind. Hyg. Assoc. J.*, *34*, 390 (1973).

Sampling Data Sheet No. S320
October 28, 1977

Substance

Nitrogen Dioxide

Standard

Time-weighted average: 5 ppm (9 mg/cu m)

Analytical Method

A known volume of air is drawn through a sampling tube containing triethanolamine-impregnated molecular sieve to collect the nitrogen dioxide. The nitrogen dioxide is desorbed with a triethanolamine solution and an aliquot treated with hydrogen peroxide, sulfanilamide and N-(1-naphthyl)ethylenediamine dihydrochloride. The reacted nitrite ion is measured spectrophotometrically at 540 nm. The method has been validated over the range of 3.074-11.49 ppm for a 3.9-liter sample at 19°C and 758 mm Hg atmospheric temperature and pressure.

Sampling Equipment

The sampling equipment needed consists of a sampling tube containing triethanolamine-impregnated molecular sieve and a personal sampling pump calibrated with a representative sampling tube in the line. The pump flow rate should be determined accurately, ±5%, at 0.050 liter per minute. A suitable tube holder should be used to protect the worker from the sharp edges of the glass sampling tube.

The sampling tube used to collect the sample consists of a glass tube flame-sealed at both ends, with a 7-mm OD and a 5-mm ID, packed with a 400-mg section of triethanolamine-impregnated molecular sieve and a backup section of 200-mg triethanolamine-impregnated molecular sieve. Sections are separated by glass wool.

The triethanolamine-impregnated molecular sieve can be prepared as follows: Add 25 g triethanolamine to a 250-mL beaker; add 4 g glycerol, 50 mL of acetone and sufficient distilled water to bring up to 100 mL. To the mixture add about 50 mL Type 13X, 30-40 mesh molecular sieve. Stir and let stand in a covered beaker for about 30 minutes. Decant the excess liquid and transfer the molecular sieve to a porcelain pan which is then placed under a heating lamp until most of the moisture has evaporated. Complete the drying in an oven at 110°C for one hour. The sorbent should be free flowing. Store in a closed glass container.

Sample Size

A sample size of 3.0 liters is recommended. Sample at a flow rate of 0.050 liter per minute for 60 minutes.

Sampling Procedure

1. Immediately before sampling, the ends of the tubes should be broken so as to provide openings approximately one-half the internal diameter of the tubes.

2. The sampling tube should be placed in a vertical position during sampling to avoid channeling and subsequent premature breakthrough of the analyte.

3. Air being sampled should not be passed through any hose or tubing before entering the front section of the sampling tube.

4. A low flow rate pump is used. Set the flow rate as accurately as possible using the manufacturer's directions. Record all the necessary information to determine flow rate or volume and also record the initial and final sampling time. Record the temperature and pressure of the atmosphere being sampled. If pressure reading is not available, record the elevation.

5. The sampling tubes should be labeled properly and capped with the supplied plastic caps immediately after sampling.

6. One sampling tube should be handled in the same manner as the sample tubes (break, seal, and transport), except for the taking of an air sample. This tube should be labeled as a blank. Submit one blank for every batch of five or fewer samples.

Special Considerations

1. Where two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

2. Due to the high resistance of the sampling tube, this sampling method places a heavy load on the sampling pump. Therefore, no more than eight hours of sampling should be done without first fully recharging the battery.

Shipping Instructions

Capped sampling tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

Reference

Nitrogen Dioxide, NIOSH Method No. S320.

Backup Data Report No. S320

October 28, 1977

Substance: Nitrogen Dioxide

OSHA Standard: 5 ppm (9 mg/cu m)

Chemical Used for Validation: Nitrogen Dioxide, 1020 ppm, Scott Specialty Gas, Inc.

General Considerations

The method for nitrogen dioxide (NO_2) has been tested in accordance with the various criteria for validation described in References 1 and 2 and in conformity with the statistical analysis described in Reference 2. The statistical criteria established for this program are related to the present suggested standard for air monitoring accuracy, i.e., the absolute total error (sampling and analysis) should be less than 25% in at least 95% of the samples analyzed at the level of the OSHA standard. In order to satisfy the statistical criteria, a measure of accuracy and precision was established, i.e., overall recovery must be 100 ± 10% and CV_T must be less than or equal to 0.105. The fine points of statistical basis for this program are discussed in Reference 2.

The protocol for validation of a method for nitrogen dioxide consisted of the following experimental studies:

- Determination of the breakthrough capacity of triethanolamine (TEA)-impregnated molecular sieve at high relative humidity,
- Analysis of a set of eighteen analytical samples (six samples at each of the three test levels), prepared by drawing known amounts of nitrogen dioxide in nitrogen through TEA-impregnated molecular sieve to collect the equivalent of 3.9 liters at 0.5, 1 and 2X the OSHA standard,
- Analysis of a set of eighteen samples (six samples at each of the test levels) collected from a dynamically generated test atmosphere to represent 60 minute samples (3.9 liters) at 0.5, 1 and 2X the OSHA standard,
- Independent verification of the concentration of a set of six samples collected from a dynamically generated test atmosphere

at the OSHA standard level,

- Testing of the storage stability of collected samples,
- Assessment of the precision and accuracy of the method,

The details with respect to each of these items are discussed in the following sections. The method tested experimentally and documented in this report has passed all the requirements of the program.

It is important to note two considerations that critically affect the accuracy of the validation experiments discussed in the following sections. Firstly, it should be understood that the choice of the stoichiometric factor, which relates the amount of NO_2 gas collected on the sorbent tube to the amount of analyte (i.e. nitrite ion, NO_2^-) measured colorimetrically, is based on previous experimental data (References 3 and 4). The stoichiometry of the reaction of NO_2 (g) in triethanolamine to yield nitrite ion and nitrate ion has been observed to be a function of the concentration of NO_2. At high concentrations the factor approaches 0.5, with equimolar amounts of nitrite and nitrate being produced. At concentrations in the range of interest in this validation (1-10 ppm NO_2), the factor increases to an observed maximum of about 0.79. For the data of Blacker (Reference 4), the mean value for the stoichiometric factor at the concentrations of interest is 0.63. Rather than attempting to resolve the cause of this variability, a stoichiometric factor of 0.63 has been assumed. It should be noted that this value was found to be consistent with the experimental data in the nitric oxide validation study (Reference 5). It will be noted that this stoichiometric factor is somewhat less satisfactory (but still acceptable) in this nitrogen dioxide validation study. Secondly, it should be pointed out that, since previous experimental evidence indicates that NO_2 gas calibration standards are not stable over long storage periods, the concentration of both the 4.81 ppm and 1020 ppm NO_2 standards provided and calibrated by Scott Specialty Gas were independently verified during the validation experiments. They were verified by collection of known volumes of the gases in bubblers filled with triethanolamine solution. The independent verification data is included in the following sections in a manner consistent with the actual time of analysis.

Principle of the Method

The method validated for the analysis of nitrogen dioxide in air is based on the work of Willey _et al_ (Reference 5). It involves collection on 400 mg of triethanolamine-impregnated molecular sieve, desorption with a triethanolamine absorbing solution, and analysis of the resulting nitrite ion by spectrophotometry. The sample is collected at a flow rate of about 50 mL/minute for a sampling duration of 60 minutes.

Analysis

A detailed description of the procedure for analysis, preparation of sample collection devices and the preparation of calibration standards is given in NIOSH Method No. S320 (Reference 6).

The reliability of the analytical method was tested, based on analysis of eighteen samples. The analytical samples were prepared by drawing a 4.81 ppm NO_2 gas standard through sampling tubes at 65 mL/min for 35, 70 and 140 minutes to represent the equivalent of a 4-liter sample at 0.5, 1 and 2X the OSHA standard, respectively.

The front and backup TEA/molecular sieve sections were treated with triethanolamine solution so as to desorb the NO_2. An aliquot of the resulting solution was treated with hydrogen peroxide, sulfanilamide and N-(1-naphthyl)ethylenediamine dihydrochloride. Spectrophotometric analysis was done with a Perkin-Elmer Coleman 55 Spectrophotometer at 540 nm using a treated blank to zero the instrument. The absorbance was observed to be directly proportional to the nitrite ion concentration in the sample. Appropriate standard solutions, prepared from a 100-ppm nitrite stock standard, were analyzed on the same day as the samples. The data for the full set of eighteen analytical samples are shown in Table S320-1.

Understanding that the stability of NO_2 gas in a cylinder is known to be a problem, the 4.81 ppm NO_2 standard was calibrated by drawing the gas through six bubblers containing TEA absorbing solution at 61.8 mL/min for 60 minutes. The resulting solution was diluted to 50 mL with additional absorbing solution and an aliquot analyzed by the same techniques as for the sorbent tubes.

This calibration technique indicated a concentration of 4.54 ppm NO_2. If this value is used the recovery values are increased to those shown in Table S320-2.

The mean recovery based on 4.81 ppm NO_2 is 0.996 while that based on 4.54 ppm NO_2 is 1.055. The difference between these recoveries is discussed further in the section on Independent Verification of Generator Concentration.

Table S320-1

Data Sheet: Nitrogen Dioxide

Analysis

(Based on 4.81 ppm)

Level	0.5S			1S			2S	
μL added	μL found	Recovery	μL added	μL found	Recovery	μL added	μL found	Recovery
11.17	10.22	0.915	22.34	22.69	1.016	44.7	47.3	1.058
10.92	10.03	0.918	21.84	21.76	0.996	43.6	46.8	1.073
11.01	9.66	0.877	22.04	21.39	0.970	44.0	47.2	1.073
10.78	9.95	0.923	21.57	21.10	0.978	43.1	46.4	1.076
10.74	9.95	0.926	21.46	20.55	0.958	42.9	46.5	1.084
10.41	9.95	0.956	20.83	21.92	1.052	41.6	44.7	1.074
n =		6			6			6
mean		0.919			0.995			1.073
std dev		0.02536			0.0346			0.00844
CV_1		0.02760			0.0348			0.00786

$\overline{CV}_1$ 0.02605

$\overline{CV}_{A+\overline{DE}}$ 0.02814

Table S320-2

Data Sheet: Nitrogen Dioxide

Analysis

(Based on 4.54 ppm)

Level	0.5S			1S			2S	
μL added	μL found	Recovery	μL added	μL found	Recovery	μL added	μL found	Recovery
10.55	10.22	0.969	21.10	22.69	1.075	42.2	47.3	1.121
10.31	10.03	0.973	20.62	21.76	1.055	41.2	46.8	1.136
10.40	9.66	0.929	20.81	21.39	1.028	41.6	47.2	1.135
10.18	9.95	0.977	20.37	21.10	1.036	40.7	46.4	1.140
10.14	9.95	0.981	20.27	20.55	1.014	40.5	46.5	1.148
9.83	9.95	1.012	19.67	21.92	1.114	39.3	44.7	1.137

	0.5S	1S	2S
n =	6	6	6
mean	0.974	1.054	1.136
std dev	0.02665	0.0364	0.00879
CV_1	0.02736	0.0345	0.00774

$\overline{CV}$ 0.02581

$\overline{CV}_{A+\overline{DE}}$ 0.02788

Breakthrough Tests

Breakthrough is defined as the time at which the effluent concentration from the collection tube is 5% of the concentration in the test gas mixture. The criterion for acceptance of sampling tube capacity is that the volume of air that has passed through the tube at the time of breakthrough must be at least 1.5 times the volume of air that would be passed through the tube during collection of a full sample, when the substance of interest in the test atmosphere is at 2X the OSHA standard level.

Breakthrough experiments were done in a test atmosphere of 83-84% relative humidity. The procedure for determining breakthrough of NO_2 consisted of (1) generating a test atmosphere of NO_2 at a concentration of 11.59 ppm (measured with six bubblers containing triethanolamine absorbing solution), (2) placing two sampling tubes (containing 400 mg TEA/molecular sieve) in series to act as a primary collector and a breakthrough monitor, (3) collecting six samples at a flow rate of 65 mL/min for various times from 15 to 180 minutes, and (4) analyzing the TEA/molecular sieve sections of each set of sampling tubes.

The tests were conducted at an atmospheric temperature of 19.8°C and an atmospheric pressure of 758.9 mm Hg. The analytical data for the six tubes are shown in Table S320-3. There was a measurable breakthrough after 60 minutes (1.0%) and the breakthrough after 180 minutes was 2.4%. Since the breakthrough in a volume of 4.5 liters (1.5 times the recommended collection volume) was only about 1.4%, the 400 mg TEA/molecular sieve tubes were used throughout the method validation procedure. This choice would permit the possible use of the three-section NO sampling tubes as an alternative sampling device and makes it unnecessary to use a larger sampling tube with a higher pressure drop.

It is recommended that a sampling rate of 50 mL/min and sampling time of 60 minutes for collection of a 3.0 L sample be used for field collection of NO_2.

Sampling and Analysis

Test atmospheres were generated using the vapor dilution system described in Attachment A. A steady stream of 1020 ppm NO_2 in nitrogen was delivered from a gas cylinder via a calibrated rotameter at a flow rate of approximately 1.0 liter per minute into a dry air stream flowing at a rate of 0.105 cu m per minute. The three sample lines were maintained at dilution ratios of 0.233, 0.501 and 1.000 to produce 0.5, 1 and 2X the OSHA standard test levels. The delivery rate of the nitrogen dioxide was determined by

Table S320-3

Breakthrough Analysis of NO_2 Sampling Tube

Collection Time (Minutes)	Volume (Liters)	ppm NO_2		Breakthrough (%)
		Collection Tube	Breakthrough Tube	
15	0.938	11.22	< 0.05	< 0.4
30	1.926	11.50	< 0.05	< 0.4
60	3.89	11.32	0.11	1.0
90	5.74	11.23	0.13	1.1
120	7.85	11.22	0.22	1.9
180	11.81	11.14	0.28	2.4

ppm taken = 11.59 ppm NO_2

calibrating the rotameter using a soap-bubble flow meter. Six samples were collected simultaneously at each test level at a flow rate of 65 mL/min for 60 minutes (3.9 liters). The samples were analyzed as described in Section 8.4 of NIOSH Method No. S320.

As with all NO_2 generation experiments, the 1S dilution arm was monitored with a calibrated Energetic Sciences "Enolyzer". It was observed immediately that the calculated generator concentration (10.16 ppm) based on the measured flow from the 1020 ppm NO_2 calibration gas and the main line was much different than that indicated by the "Enolyzer" (12.6 ppm). Since the stability of NO_2 gas is known to be poor, it was decided to utilize the "Enolyzer" values as the "taken" concentrations in all calculations. This of course necessitated that another method be used for independent verification of the generator concentration.

The data obtained for these eighteen samples are shown in Table S320-4.

Storage Stability

Studies were done to assess the stability of nitrogen dioxide samples upon storage for twelve days at atmospheric conditions. Twelve samples, representative of the OSHA standard level, were collected simultaneously from the vapor generator. The generator concentration (6.09 ppm NO_2) was independently measured with an "Enolyzer". Six samples were analyzed one day after collection and the other six samples were stored and analyzed twelve days after collection. The comparative data given in Table S320-5 indicate that the samples are stable over the twelve-day period. The average value found for nitrogen dioxide was 5.99 ppm for the one-day-old samples versus 6.54 ppm for the twelve-day-old samples; a recovery of 109.2%. It is felt that the true recovery is somewhat nearer to 100% than is indicated by the data since the 5.02 ppm value in Table S320-5 lowers the one-day mean considerably. However, the value is not low enough to be excluded based on Grubb's test for outliers. It is also apparent that migration from the front section to the backup sorbent section during storage is negligible.

Independent Verification of Generator Concentration

As noted previously, attempts to establish the generator concentration of nitrogen dioxide by determining the gas delivery rate and the dilution air flow at the main line and dilution lines were unsuccessful. In order to measure the generator concentration during experiments, it was therefore necessary to monitor the generator with a calibrated Energetic Sciences Enolyzer Model 7100. As noted in the analysis section, the Enolyzer was calibrated with

Table S320-4

Data Sheet: Nitrogen Dioxide Sampling and Analysis

Test Level	Found			Taken	
	µL	Liters	ppm	ppm	Recovery
0.5S	12.36	3.78	3.27	2.937	
	11.24	3.59	3.13	2.937	
	11.90	4.02	2.960	2.937	
	12.18	4.09	2.978	2.937	
	* 8.64	4.15	2.082	2.937	
	11.43	3.77	3.03	2.937	
		n = 6			
		mean	3.074		
		std dev	0.1282		
		CV_2	0.0417		1.047
1S	24.46	3.92	6.24	6.30	
	23.90	3.83	6.24	6.30	
	23.43	3.86	6.07	6.30	
	23.06	3.78	6.10	6.30	
	23.62	3.76	6.28	6.30	
	22.51	3.65	6.16	6.30	
		n = 6			
		mean	6.18		0.981
		std dev	0.0850		
		CV_2	0.01375		
2S	41.4	3.68	11.25	12.60	
	44.7	3.78	11.82	12.60	
	45.0	3.82	11.78	12.60	
	44.7	3.76	11.89	12.60	
	41.6	3.85	10.80	12.60	
	44.0	3.86	11.40	12.60	
		n = 6			
		mean	11.49		0.912
		std dev	0.423		
		CV_2	0.0368		
		$\overline{CV_2}$	0.0324		

* This value excluded from statistical analysis.

Table S320-5

Data Sheet: Nitrogen Dioxide
Stability of Generated/Collected NO_2 Samples

Samples Stored 1 Day			Samples Stored 12 Days		
μL NO_2 Found	Liters	ppm	μL NO_2 Found	Liters	ppm
Front Section			**Front Section**		
24.92	3.78	6.59	25.39	3.92	6.48
22.14	3.59	6.17	25.58	3.83	6.68
23.43	4.02	5.83	25.58	3.86	6.63
26.14	4.09	6.39	26.87	3.78	7.11
20.83	4.15	5.02	24.83	3.76	6.60
22.32	3.77	5.92	21.02	3.65	5.76
	n = 6			n = 6	
	mean	5.99		mean	6.54
	std dev	0.552		std dev	0.440
	CV	0.0922		CV	0.0673
Backup Section			**Backup Section**		
< 0.1024	3.78	< 0.02709	0.1767	3.92	0.0451
< 0.1024	3.59	< 0.02852	0.1024	3.83	0.02674
< 0.1024	4.02	< 0.02547	< 0.1024	3.86	< 0.02653
< 0.1024	4.09	< 0.02504	< 0.1024	3.78	< 0.02709
< 0.1024	4.15	< 0.02467	< 0.1024	3.76	< 0.02723
< 0.1024	3.77	< 0.02716	< 0.1024	3.65	< 0.02805

a 4.81 ppm NO_2 gas standard (Scott Gas) whose concentration was independently measured by drawing 3.7 liters of the gas through each of six bubblers filled with 15 mL triethanolamine absorbing solution at a flow rate of 61.8 mL/min and then analyzing an aliquot by the spectrophotometric procedure used for the sampling tubes. The results of this calibration are shown in Table S320-6.

At least six Enolyzer measurements of generator concentration in the 1S dilution arm were made during sample generation/collection. The "taken" data shown in Table S320-4 were obtained from the Enolyzer and calculated based on measured dilution ratios of the vapor generator. In order to verify the 1S arm generator concentration as determined by the Enolyzer, six bubbler samples and six sampling tube samples were collected at the same time as six Enolyzer measurements were made during a separate generation experiment. The data shown in Table S320-7 compare the generator concentrations based on the three independent measurement techniques as well as the concentration calculated based on the calibration of the 1020 ppm Scott Specialty Gas, Inc. NO_2 gas cylinder and calibrated flow devices.

The data show that with the exception of the Scott Gas Calibration which was made on 7/21/77, the concentrations agree within ± 10% as shown below.

Method	ppm NO_2		Agreement
	Taken	Found	(Found ÷ Taken)
Scott Gas Calibration	6.10	5.09	0.834
Bubbler	6.10	5.82	0.954
Sampling Tube	6.10	5.99	0.982

Precision and Accuracy

The precision of the method was determined by using the statistical procedures described in Reference 2 and the data in Tables S320-1 and S320-4.

Bartlett's test for homogeneity of variances of 0.5, 1 and 2X the OSHA standard for sampling and analysis was applied to the data for nitrogen dioxide. The data (Table S320-4) give a chi-squared value of 4.85. This chi-squared value indicates that it is feasible to pool the coefficients of variation. Thus $\overline{CV}_T$ is calculated based on the pooled data.

Table S320-6

Calibration of NO_2 Compressed Gas Cylinder*

Bubbler No.	Found		
	µL NO_2	Liters	ppm
1	15.99	3.89	4.11
2	17.76	3.68	4.83
3	16.46	3.76	4.38
4	16.27	3.73	4.36
5	17.95	3.74	4.80
6	16.55	3.46	4.78

n = 6

mean	4.54
std dev	0.301
CV	0.0663

---

* Original calibration by Scott Specialty Gas, Inc., October 17, 1977, indicated a concentration of 4.81 ppm NO_2.

Table S320-7

Independent Verification of Generator Concentration

	ppm NO_2			
	ppm Taken: Enolyzer	ppm:* Scott Gas Calibration	ppm: Bubbler	ppm Found: Sampling Tube
	6.14	5.09	5.69	6.59
	6.04	5.09	5.80	6.17
	6.10	5.09	5.90	5.83
	6.18	5.09	5.99	6.39
	6.02	5.09	5.29	5.02
	6.09	5.09	6.23	5.92
mean	6.10	5.09	5.82	5.99
std dev	0.0599	-	0.317	0.552
CV	0.00982	-	0.0545	0.0922

---

*Based on rotameter calibration, not independent measurements.

The precision of the method is expressed in terms of the coefficients of variation for the analytical method, the sampling and analysis method, and the overall method which includes a pump error of 0.05. These values are shown below:

$\overline{CV}_1 = 0.02581$ $\overline{CV}_2 = 0.0368$ $\overline{CV}_T = 0.0630$

The experimentally determined $\overline{CV}_T$ value is a good estimate not only of the precision but also of the accuracy of the method. This assumption is suggested by the data for the set of six samples described in the section on Independent Verification and other data collected during generation of NO_2. The differences between the taken and found concentrations described in the Independent Verification section of this report are considered to result from experimental uncertainties and uncertainties in the stoichiometric factor (0.63) used for all calculations. The work by Blacker (Reference 5) and Gold (Reference 6) indicate that this factor varies according to the concentration of NO_2 collected in the range from 3-10 ppm NO_2. Attempts were made to rationalize the differences in recovery observed at 0.5, 1 and 2S levels in the Analysis set and Sampling and Analysis set, but the fact that the trends are opposite in these two sets of data made this impossible. It is felt, however, that further understanding of the mechanism of the nitrogen dioxide/triethanolamine reaction will resolve this problem in the future. Of course, if the NO_2 standard is lowered to 1 ppm in the future, it will require confirmation of the stoichiometric factors at this level. The fact that smaller differences in recovery of NO at levels of 12.5, 25 and 50 ppm were observed (Reference 7) during method validation may confirm Gold's observation that the stoichiometric factor does not vary significantly for air concentrations of NO_2 greater than 10 ppm.

Further confidence in the accuracy of the tested method is established by the results of the collection efficiency test and storage stability test, described in the appropriate sections.

References

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2. Documentation of NIOSH Validation Tests, National Institute of Occupational Safety and Health, Cincinnati, Ohio (DHEW-NIOSH-Publication No. 77-185), 1977. Available from Superintendent of Documents, U.S. Government Printing Office, Washington, D. C., Order No. 017-033-00231-2.

3. M. A. Willey, C. McCammon, Jr. and L. Doemeny, Am. Ind. Hyg. Assoc. J., 38, 358 (1977).

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ATTACHMENT A

VAPOR DILUTION/SAMPLING SYSTEM

The vapor generation/dilution system used for the validation studies of several vapors and gases, such as this analyte, is shown schematically in Figure S320-A-1. The system basically consists of a main line air stream to which are added predetermined amounts of various liquids, gases or aerosols to generate the desired vapor concentrations. From the main line, three dilution arms branch off in which the desired multiples 0.5, 1.0 and 2.0 times the OSHA Standard concentration level are established. Six sampling devices are connected in parallel to the 0.5S dilution line and six to the 2S dilution line; twelve sampling devices are connected to the 1S dilution line. All these devices are connected via critical flow orifices (CFO's) to the corresponding vacuum lines.

Air flow rates through the system are established by means of critical flow orifices (CFO's) and flow restrictors. The primary air system derived from the house air compressor is maintained at 20.0 psig. The appropriate orifice diameters are chosen to maintain an air flow of approximately 0.1 cu m/min in the Main Line and an addition of 0.05 cu m/min to each of the dilution lines. The main line is maintained at 8 cm H_2O pressure by means of a needle valve. Appropriate flow restrictor diameters are chosen for the 0.5S, 1S and 2S dilution lines so as to give the desired final concentrations of vapor in air.

The system was designed to generate either 4X or 2X the OSHA Standard concentration in the Main Line. When a 4X level is generated, 0.05 cu m/min of dilution air is added to each dilution line. Orifices are selected so that the 0.5S, 1S and 2S lines have flows equal to approximately 0.007, 0.017 and 0.050 cu m/min respectively of the Main Line concentration added to the dilution air, thus giving the desired final concentrations. Where a Main Line concentration of 2X the OSHA Standard is generated, no dilution air is added to the 2S dilution line--0.017 cu m/min is simply allowed to flow through this line--and 0.050 cu m/min of dilution air is added to the 0.050 cu m/min and 0.017 cu m/min of Main Line mixture admitted to the 1S and 0.5S dilution lines, respectively.

All materials which the vapor may contact before collection are 316 or 304 stainless steel. A glass heater is included where the liquids are added to the main line. Shutoff ball valves are placed in the dilution lines to allow their independent operation and the calibration of air flows. The Main Line has a 2.54-cm (1 in) O.D., and the dilution lines are 1.90-cm (0.75 in) O.D. Diameters were chosen to give turbulent flow with an approximate minimum Reynolds number of 3000.

Air Supply

Air from the house compressor is treated by passing it sequentially through a cotton filter, a silica gel bed, a charcoal bed and a high efficiency glass fiber filter for removal of water, hydrocarbons and particulate. This air is then connected to a manifold containing six takeoff

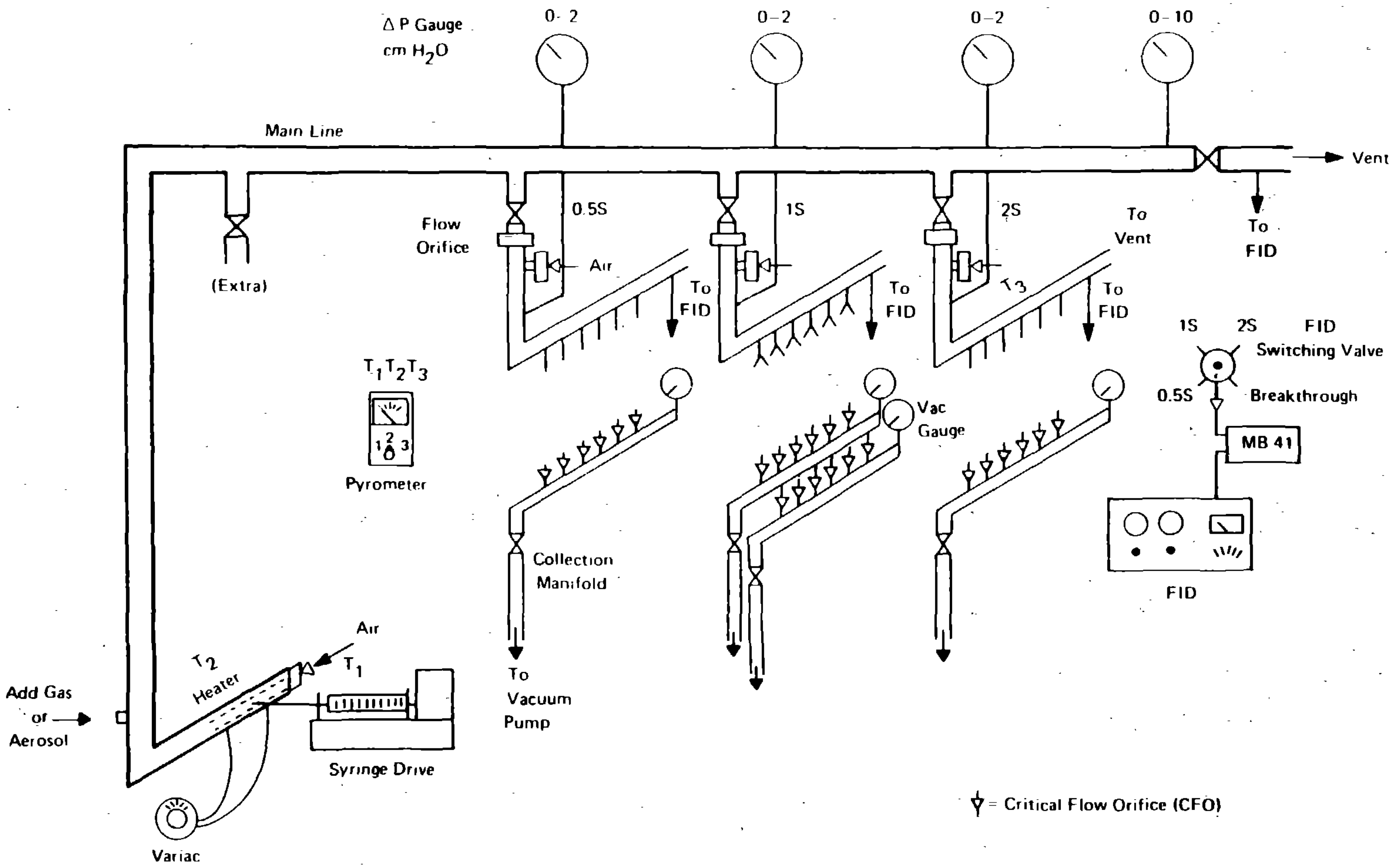

Figure S320-A-1. Vapor Generation/Dilution/Sampling System

ball valves. The pressure (20 psig) at the manifold is maintained with a Nullmatic Moore 40H50 regulator and monitored with an Ashcroft 0-60 psig test gauge. The air supply is used for each of the dilution system connections as well as for the flame ionization detector monitor flame and "zero" air.

Sample Collection Manifold

Sample flow through the sampling devices connected to the dilution lines is established by connecting each device by means of a short piece of flexible tubing to a CFO which is connected to a 1.27 cm (1/2 in) O.D. vacuum manifold. Each dilution line has a separate manifold which derives its vacuum from a Model 0322 Gast vacuum pump. The orifices are jewel orifices pressed into a threaded Teflon rod. One end of the rod is screwed into a tee on the manifold, and the other has a hose tabulation fitting connected to it. The orifice is protected from plugging by means of a piece of 100 mesh stainless steel screen.

Vent System

All excess vapor-laden air is collected via a 3.81-cm (1.5 in) PVC manifolding system where it is passed through a 0.3 x 0.3 x 0.6-M charcoal bed. Flow is established by means of a pressure blower on the exit side of the charcoal bed, and it is vented to the laboratory hood exhaust.

Calibration

Air Flows

Main Line -- The air flow delivered by the Main Line CFO was determined by measurement with a Singer Dry Test Meter. The meter had previously been calibrated with a spirometer primary standard. Using the 0.310-cm diameter orifice at 20 psig air pressure, the flow was found to be 0.1086 cu m/min corrected to 25°C and 760 mm Hg.

Dilution Lines -- The air flow through each of the dilution line CFO's and restrictor orifices was similarly measured with the Dry Test Meter to assure that they met design parameters, but these values did not provide the primary basis for determination of vapor concentration.

Collection CFO's -- Since the flow rate through the sample collection CFO's was lower (0.2 and 1.0 liter per minute) than appropriate for use with the Dry Test Meter, the flow rate of each of these orifices was measured using an SKC soap bubble meter which was independently calibrated by gravimetrically measuring water capacity.

All volume measurements have been referenced to normal temperature and pressure of 25°C and 760 mm Hg.

Dilution Ratios

The concentration of vapor in the dilution lines is determined from the concentration calculated in the Main Line and the dilution ratio determined between the dilution lines and the main line. These dilution ratios were measured by adding a controlled amount of propane gas to the Main Line and then measuring the relative concentration in each of the lines using a Beckman Model 402 heated hydrocarbon analyzer. The procedure was repeated several times and is regularly checked during the program.

In the case where 4X or 2X concentration level conditions were generated, the dilution ratios reported below were observed.

		Relative Concentration		
Case Generated	Main Line	2S	1S	0.5S
4X	1.000	0.5097	0.2557	0.1311
2X	1.000	1.000	0.499	0.227

Each of these sets of values represents a different set of air flow and orifice selection conditions as previously discussed. Point to point comparison of the six sample ports on each manifold showed less than a 1% variation in concentration among them.

Monitors

To provide a ready check on operating conditions, several gauges or monitors have been included in the system. Dwyer Magnehelic gauges monitor the pressure on the Main Line and each of the dilution lines. A 0-10 cm H_2O gauge is used on the Main Line (Setpoint 8 cm) and 0-2 cm H_2O gauges are used for the dilution lines. The purpose of these latter gauges is to provide a check against possible back pressure developing in these lines which would affect the dilution ratios.

The flame ionization detector (FID) is used to determine the time at which the Main Line concentration has reached equilibrium and to monitor the concentration level during breakthrough studies and sample collection.

Breakthrough Studies

A. Low Relative Humidity (Dry Air)

For the measurement of sorbent tube capacity for a given vapor (breakthrough) six sorbent tubes containing only the 100 mg "front half" section of sorbent are connected in parallel to the 2S dilution line and to a 0.635-cm (1/4-in) O.D. stainless steel six-port manifold. Flow through the manifold is controlled by a CFO and is established using a Metal Bellows Corp. Model MB41 pump. Flow through the orifice was

measured as 1.14 liters per minute providing a 0.19-liter per minute flow to each of the tubes. (A separate set of orifice allows a similar determination at a flow rate of 1.0 liter per minute through each tube.) Equal flow through each of the tubes is insured by carefully selecting and/or adjusting packing in the tubes to have an equal pressure drop when precalibrated at a 0.2-liter per minute flow rate.

Once a steady state vapor concentration is established, the 2S concentration level is used to set the 100% point on the hydrocarbon analyzer. Then the valve is switched, and the flow from the breakthrough manifold is passed through the hydrocarbon analyzer and monitored either until 5% of the 2S level is observed or for a period of four hours--whichever occurs first.

B. High Relative Humidity

For the generation of a high relative humidity atmosphere, at least 80% R.H., water vapor is delivered into the generator Main Line via one of the side arms as shown in Figure S320-A-2. A peristaltic pump, Cole-Parmer Masterflex, Model No. 7013, is used to deliver water into a heated copper coil (1/8 in x 10 feet) contained in a tube furnace; the furnace temperature is maintained above 110°C and monitored by a thermocouple and optical pyrometer. Water is delivered at the rate of 1.9 g per minute to blend with the analyte-containing dry air stream flowing at a rate of 0.100 cu m per min to produce an atmosphere of at least 80% R.H. at 25°C and 760 mm Hg.

All other aspects of the breakthrough test procedure are as described above.

Procedure

The overall procedure for a given sample is as follows:

1. Line air flow and dilution ratios are verified.
2. Sample delivery rate is determined by appropriate calibration.
3. Sample is fed into Main Line until vapor concentration equilibrium is established.
4. The breakthrough experiment is performed and subsequent sample collection volumes adjusted if necessary.
5. The four sets of six samples from the three concentration levels are collected simultaneously.

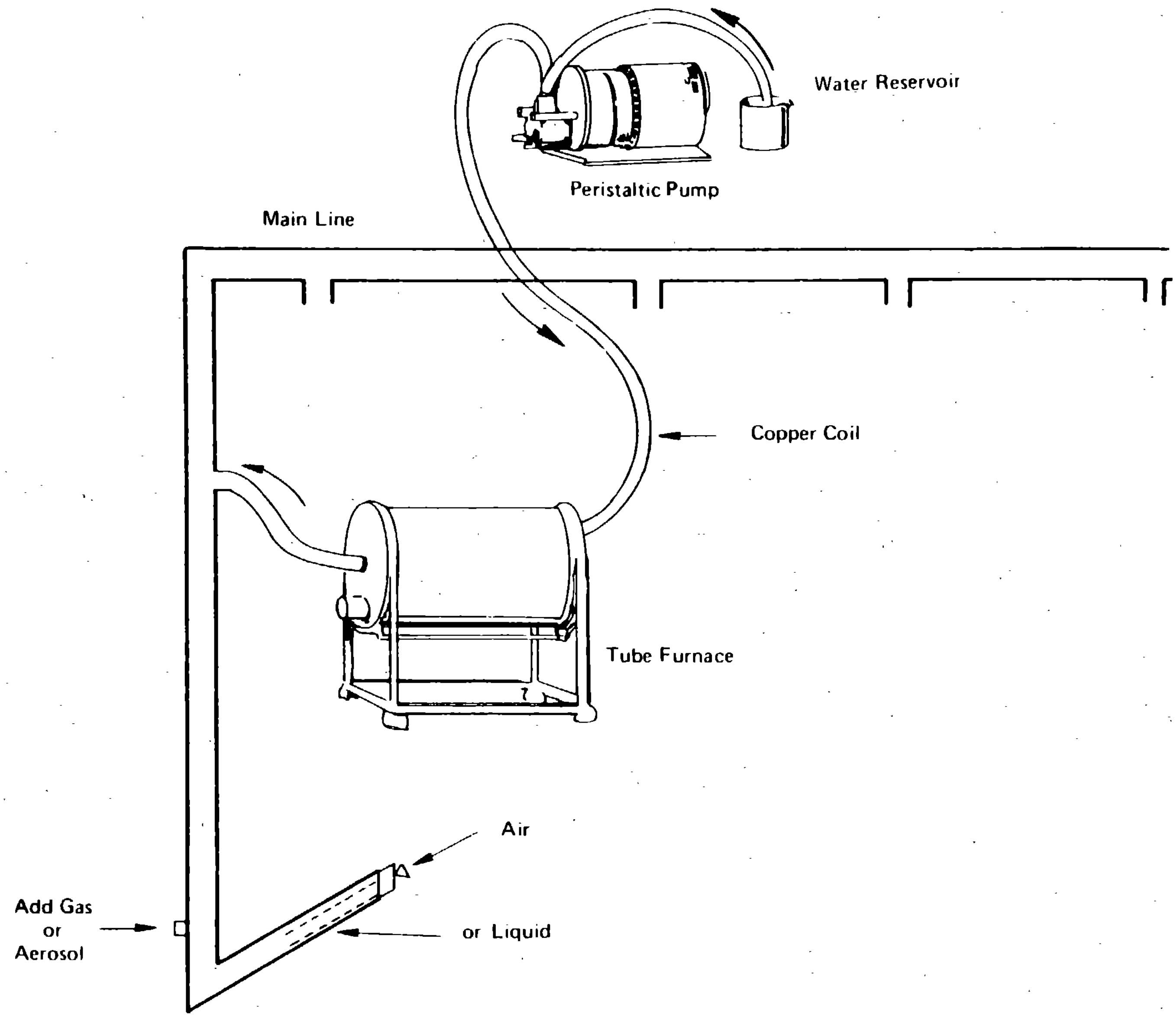

Figure S320-A-2. Generation of High Humidity Atmospheres

Phosphorus (Yellow)

Analyte:	Phosphorus (yellow)	Method No.:	S334
Matrix:	Air	Range:	0.056-0.244 mg/cu m
OSHA Standard:	0.1 mg/cu m	Precision (CV_T):	0.090
Procedure:	Collection on Tenax-GC, extraction with xylene, GC/FPD.	Validation Date:	11/25/77

1. Principle of the Method

1.1 A known volume of air is drawn through a tube containing Tenax-GC resin to trap the phosphorus vapors present. The tube consists of 100 mg of 35/60 mesh Tenax-GC held in place by two pieces of silylated glass wool followed by a 50-mg backup section.

1.2 The phosphorus is extracted from the Tenax-GC resin using a known amount of xylene.

1.3 An aliquot of the extracted sample is analyzed by injection into a gas chromatograph equipped with a phosphorus specific flame photometric detector. The area of the resulting peak is determined and compared with areas obtained from the injection of standards.

2. Range and Sensitivity

2.1 This method was validated over the range of 0.056-0.244 mg/cu m at an atmospheric temperature of 23°C and atmospheric pressure of 763 mm Hg using a 12-liter sample volume. This sample volume is less than two-thirds of the 5% breakthrough capacity determined at >85% relative humidity when sampling a test atmosphere at 3X the OSHA standard. This method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the capacity of the sorbent tube and stability of the analyte. The method is capable of measuring concentrations higher than noted in Section 2.1, provided the capacity is adequate and desorption of the analyte is performed with a larger volume of xylene to bring the concentration of phosphorus in the extract to a level less than 5 μg/ml.

3. Interferences

3.1 When two or more phosphorus compounds are known or suspected to be present in the air, such information, including their suspected identifies, should be transmitted with the sample.

3.2 It must be emphasized that any phosphorus compund which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered as proof of chemical identity.

3.3 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range 0.056-0.244 was 0.0901. This value corresponds to a 0.009 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in References 11.1 and 11.2.

4.2 On the average, the concentration obtained at the OSHA standard level using the overall sampling and analysis procedure was 2.1% higher than the average taken concentration for a limited number of laboratory experiments. Any difference between the found and taken concentrations may not represent a bias in the sampling and analytical method but rather a random variation from the experimentally determined taken ("true") concentration. In addition, samples collected at a concentration of 0.1028 mg/cu m were found to be stable for at least seven days.

5. Advantages and Disadvantages

5.1 The sampling device is small, portable and involves no liquids.

5.2 Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The collected samples are analyzed by means of a quick, instrumental method.

5.3 The precision of the method is affected by the reproducibility of the pressure drop across the tube. This drop will affect the flow rate and cause the volume to be imprecise, since the pump is usually calibrated for only one tube.

5.4 The amount of sample which can be taken is limited by the capacity that the tube will hold before overloading. When an atmosphere containing 0.31 mg/cu m of phosphorus at 85% relative humidity was sampled at 0.2 liter per minute, 0.2% breakthrough was observed after 240 minutes of sampling (capacity is at least 45 liters or 13.9 μg). The sample size recommended is less than 5% breakthrough capacity at 85% relative humidity for a test atmosphere of 3X the OSHA standard to minimize the probability of overloading the sampling tube.

6. Apparatus

6.1 Sampling Equipment. The sampling unit for the solid sorbent collection method consists of the following components:

6.1.1 A calibrated personal sampling pump suitable for sampling at 0.2 liter per minute for 60 minutes. The pump must be accurate to within ±5% at the recommended flow rate. The pump must be calibrated with a representative sorbent tube in line.

6.1.2 Sampling Tubes. Glass tube with both ends flame sealed (8-cm long with 8-mm O.D. and 6-mm I.D.) containing two sections of Tenax-GC (35/60 mesh, Applied Science Laboratories, Inc.). The absorbing section contains 100 mg of resin, the backup section, 50 mg. Small wads of silylated glass wool are placed in front of the absorbing section, between the two sections, and at the end of the backup section. Since the pressure drop across the tube must be less than 25 mm of Hg at a flow rate of 1 liter per minute, it is necessary to avoid overpacking with glass wool.

6.1.3 Thermometer.

6.1.4 Barometer.

6.1.5 Stopwatch.

6.2 Gas chromatograph with a phosphorus specific flame photometric detector.

6.3 Column (1.82 m x 6.35 m O.D. x 2 mm I.D. glass) packed with 3% OV-101 on 80/100 mesh Supelcoport.

6.4 An electronic integrator or some other suitable method for measuring peak areas.

6.5 Sample containers with Teflon-lined caps, 2-ml.

6.6 Microliter syringes, 10-microliter and other convenient sizes for making standards and taking sample aliquots for dilution.

6.7 Pipets, 1-ml and other convenient sizes.

6.8 Volumetric flasks, 10-ml and other convenient sizes for making standard solutions.

6.9 Glove box.

7. Reagents

All reagents must be ACS reagent grade or better.

7.1 Phosphorus (yellow), stored under distilled water.

7.2 Xylene, mixture of ortho-, meta-, and para-isomers.

7.3 Acetone.

7.4 Hydrogen, prepurified.

7.5 Air, filtered, compressed.

7.6 Helium, dried.

7.7 Nitrogen, dried

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent-washed and thoroughly rinsed with tap water and distilled water.

8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative sorbent tube in line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Immediately before sampling, break the two ends of the tube to provide an opening of at least one half of the internal diameter of the tube (3-mm).

8.3.2 The section containing 50 mg of resin is used as a backup and should be positioned nearest to the sampling pump.

8.3.3 The sampling tube should be placed in a vertical direction during sampling to minimize channeling through the sorbent.

8.3.4 Air being sampled should not be passed through any hose or tubing before entering the tube.

8.3.5 A sample size of 12 liters is recommended. Sample at a flow rate 0.2 liter per minute for 60 minutes. The flow rate should be known with an accuracy of at least ±5%.

8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If the pressure reading is not available, record the elevation.

8.3.7 The sorbent tube should be labeled appropriately and capped with supplied plastic caps. Under no circumstances should rubber caps be used.

8.3.8 With each batch of ten samples, submit one sorbent tube which had been handled in the same manner as the sample tubes (break, seal, transport), except that no air is sampled through this tube. This tube should be labeled as blank.

8.3.9 Capped sorbent tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each sorbent tube is scored with a file and broken open. The glass wool is removed with care, making sure that a minimal amount of resin is lost in the process. The resin in the front 100-mg section is then transferred to a 2-ml vial. The second 50-mg section is transferred to another vial. The two sections are analyzed separately.

8.4.2 Desorption of the Sample. Prior to analysis, 1 ml of mixed xylene is pipetted into each vial containing the sorbent. The desorption is carried out for 30 minutes at room temperature with occasional swirling during this period.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 50 ml/min (40 psig) helium carrier gas flow.
2. 35 ml/min (40 psig) hydrogen gas flow to detector.
3. 220 ml/min (60 psig) air flow to detector.
4. 200°C injector temperature.
5. 200°C detector temperature.
6. 80°C column temperature.

8.4.4 Injection of Sample. A 5-microliter aliquot of the sample solution is injected into the gas chromatograph. The solvent flush method or other suitable alternative can be used provided that duplicate injections of a solution agree well. No more than a 3% difference in area is to be expected.

8.4.5 Measurement of Area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed in Section 9.

8.5 Determination of Desorption Efficiency

8.5.1 Importance of Determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of Tenax-GC to another. Thus, it is necessary to determine the percentage of the specific compound that is removed in the desorption process for the particular batch of resin used for sample collection and over the concentration range of interest.

8.5.2 Preparation of Analytical Samples for Desorption Efficiency Determination. The desorption efficiency must be determined over the sample concentration range of interest. In order to determine the sample concentration range which should be tested, the collected samples are analyzed first and then the analytical samples are prepared based on the relative amount of phosphorus found in the samples. The desorption efficiency must be determined at least in duplicate for each concentration level of phosphorus found in the samples. Duplicate determination should agree within ±5%.

For the validation studies conducted to determine the precision and accuracy of this method, an amount of the analyte equivalent to that present in a 12-liter sample at the selected level was used to determine the analytical method recovery. Six vials at each of the three levels (0.5 1 and 2X the OSHA standard) containing 100 mg of sorbent were spiked with 2, 4 and 8 μl aliquots of a solution of phosphorus in xylenes (0.296 mg/ml). A parallel blank was also prepared except that no sample was added to it. All samples were then analyzed as described in Section 8.4.

The sample recovery equals the average weight in μg recovered from the sorbent divided by the weight in μg added to the sorbent, or

$$\text{D.E.} = \frac{\text{Average Weight } (\mu g) \text{ recovered} - \text{Blank } (\mu g)}{\text{Weight } (\mu g) \text{ added}}$$

The desorption efficiency may be dependent on the amount of phosphorus collected on the resin. Plot the desorption efficiency versus weight of phosphorus found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of µg per ml of xylene because the samples are prepared in this amount of solvent. The standard solutions are prepared by the appropriate dilution of a stock solution made by dissolving an acetone washed and dried piece of phosphorus (yellow) into a pre-tared 10-ml volumetric flask containing 5 ml of xylene under a nitrogen or other inert gas atmosphere in a glove box. The amount of phosphorus added is determined from the difference in weight, and the flask is then made up to volume. A series of standards varying in concentration over the range of interest is prepared and analyzed using the same GC conditions and during the same time period as the unknown samples in order to minimize the effect of variations in FPD response. A calibration curve is established by plotting concentration in µg per ml versus peak area.

10. Calculations

10.1 Read the weight, in µg, corresponding to each peak area from the standard curve. No volume corrections are needed because the standard curve is based on µg per one ml and the volume of sample injected is identical to the volume of the standards injected.

10.2 Correction for the blank must be made for each sample.

$$\mu g = \mu g \text{ sample} - \mu g \text{ blank}$$

where:

µg sample = µg found in sample solution
µg blank = µg found in blank solution

10.3 Divide the total weight by the desorption efficiency to obtain the corrected µg per sample

$$\text{Corrected } \mu g/\text{sample} = \frac{\text{Weight in } \mu g \text{ (Front Section)}}{\text{D.E.}}$$

10.4 Add the amounts present in the front and backup sections for the same sample to determine the total weight in the sample.

10.5 Determine the volume of air sampled at ambient conditions in liters based on the appropriate information, such as flow rate in liters per minute multiplied by sampling time. If a pump using a rotameter for flow rate control was used for sample collection, a pressure and temperature correction must be made for the indicated flow rate. The expression for this correction is

$$\text{Corrected volume} = f \times t \left(\sqrt{\frac{P_1}{P_2} \times \frac{T_2}{T_1}}\right)$$

where:

f = sample flow rate

t = sampling time

P_1 = pressure during calibration of sampling pump (mm Hg)

P_2 = pressure of air samples (mm Hg)

T_1 = temperature during calibration of sampling pumps (°K)

T_2 = temperature of air sampled (°K)

10.6 The concentration of the analyte in the air sampled can be expressed in mg/cu m which is numerically equal to μg/liter.

$$\text{mg/cu m} = \frac{\text{Corrected μg (Section 10.3)}}{\text{Air Volume Sampled (liters)}}$$

Another method of expressing concentration is ppm (corrected to standard conditions of 25°C and 760 mm Hg).

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{30.97} \times \frac{760}{P} \times \frac{(T + 273)}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
30.97 = atomic weight of phosphorus
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

11.1 Documentation of NIOSH Validation Tests, National Insitute for Occupational Safety and Health, Cincinnati, Ohio (DHEW-NIOSH-Publication No. 77-185), 1977. Available from Superintendant of Documents, U. S. Government Printing Office, Washington, D. C., Order No. 757-057/6708.

11.2 Backup Data Report for Phosphorus, No. S334, prepared under NIOSH Contract No. 210-76-0123.

Sampling Data Sheet No. S334

November 25, 1977

Substance

Phosphorus (yellow)

Standard

8-hour time-weighted average: 0.1 mg/cu m

Analytical Method

A known volume of air is drawn through a tube filled with Tenax-GC to trap the phosphorus vapor. The phosphorus is extracted from the resin using xylene. An aliquot of this extract is injected into a gas chromatograph equipped with a flame photometric detector. This method has been validated over the range of 0.056-0.244 mg/cu m for a 12-liter sample at 23°C and 763 mm Hg atmospheric temperature and pressure.

Sampling Equipment

The sampling equipment needed consists of a Tenax-GC resin sampling tube and a personal sampling pump calibrated with a representative resin tube in the line. The pump flow rate should be determined accurately, ±5%, at 0.2 liter per minute. A suitable tube holder should be used to protect the worker from the sharp edges of the glass sampling tube.

The resin tube used to collect the sample consists of a glass tube flame sealed at both ends, 10-cm long with an 8-mm O.D. and a 6-mm I.D., packed with two sections of 35/60-mesh Tenax-GC resin. The two sections include a front section containing 100 mg of resin and a backup section containing 50 mg. The two sections are separated by a plug of silylated glass wool and both the inlet and outlet ends of the tube are plugged with silylated glass wool. The pressure drop across the tube must be less than 25 mm of mercury at a flow rate of 1 liter per minute.

Sample Size

A sample size of 12 liters is recommended. Sample at a flow rate of 0.2 liter per minute or less. Do not sample at flow rates less than 0.01 liter per minute.

Sampling Procedure

1. Immediately before sampling, the ends of the tube should be broken so as to provide an opening approximately one-half the internal diameter of the tube (3-mm).

2. The section containing 50 mg of resin is used as a backup and should be positioned nearest the sampling pump. The resin tube

series should be placed in a vertical position during sampling to avoid channeling and subsequent premature breakthrough of the analyte.

3. Air being sampled should not be passed through any hose or tubing before entering the Tenax-GC tube.

4. A low flow rate pump is used. Set the flow rate as accurately as possiable using the manufacturer's directions. Record all the necessary information to determine the flow rate or volume and also record the initial and final sampling time. Record the temperature and pressure of the atmosphere being sampled. If pressure reading is not available, record the elevation.

5. The Tenax-GC tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

6. One resin tube should be handled in the same manner as the sample tubes (break, seal, and transport), except for the taking of an air sample. This tube should be labeled as a blank. Submit one blank for every batch of 10 samples.

7. Unused, capped sampling tubes should accompany the samples. These tubes are used in desorption efficiency studies in conjunction with these samples, because desorption efficiency can vary from one batch of resin to another. Record the batch number of the resin used.

Special Considerations

When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

Bulk Samples

A bulk sample of the suspected compound should be submitted to the laboratory in a glass container with a Teflon-lined cap. Label of the bulk sample should match air samples for identification purposes.

Shipping Instructions

Capped Tenax-GC tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping. Do not transport, mail or ship the bulk sample in the same container as the sample or blank tube.

Reference

Phosphorus (yellow), NIOSH Method No. S334.

Backup Data Report No. S334

November 25, 1977

Substance: Phosphorus (yellow)

OSHA Standard: 0.1 mg/cu m (0.079 ppm)

Chemical Used for Validation: Phosphorus (yellow), 5/8" sticks, Fisher Scientific

General Considerations

The method for phosphorus (yellow) has been tested in accordance with the various criteria for validation described in Reference 1 and in conformity with the statistical analysis described in Reference 2. The statistical criteria established for this program are related to the present suggested standard for air monitoring accuracy, i.e. the absolute total error (sampling and analysis) should be less than 25% in at least 95% of the samples analyzed at the level of the OSHA standard. In order to satisfy the statistical criteria, a measure of accuracy and precision was established, i.e., overall recovery must be 100 ± 10% and the $\overline{CV}_T$ of an unbiased method must be less than or equal to 0.105. The fine points of the statistical basis for this program are discussed in Reference 2.

The protocol for validation of a method for phosphorus (yellow) consisted of the following experimental studies:

- Analysis of a total of 18 samples (six samples at each of the three test levels--0.5, 1 and 2X the OSHA standard) spiked with the appropriate amount of phosphorus to represent a sample volume of 12 liters;
- Analysis of a total of 18 samples collected from dynamically generated test atmospheres (six samples at each of the three test levels--0.5, 1 and 2X the OSHA standard) for the same sample volume as above;
- Verification of the collection efficiency at a high relative humidity at 2.8X the OSHA standard;
- Testing of the storage stability of collected samples;
- Assessment of the precision and accuracy of the method.

The details with respect to each of these items are discussed in the following appropriate sections. The method tested experimentally and documented in this report has passed all the requirements of this program.

Development of Analtical Method

Based on the results of previous work on elemental phosphorus (Reference 3), the analytical method chosen was gas chromatography using a phosphorus specific flame photometric detector. A detailed description of the procedure for analysis and the preparation of standards is given in NIOSH Method No. S334 (Reference 4). The calibration curve for phosphorus in xylene exhibited good linearity over the working range of 0.3-4.0 μg/ml (correlation coefficient of 0.9998). Initial experiments were directed at determining the suitability of XAD-2 (Rohm and Haas Co.) as a solid sorbent to check on the storability of the analyte on this material. The data obtained for the analytical method recovery, storage stability of spiked samples and collection efficiency (both in dry and 85% RH atmospheres) for tubes containing 100 mg of XAD-2 are given in Tables S334-1 through S334-3. These data indicate an average analytical method recovery of 95.2%, loss of 1.8% after 20 days' storage at room temperature of spiked samples, and an average collection efficiency of 98.1% for a 46-liter sample in a dry atmosphere. However, the collection efficiency in an atmosphere of 85% RH was only 80-90%. This low collection efficiency made XAD-2 unacceptable as a collection resin.

The method developed for phosphorus (yellow) involves collection on Tenax-GC (Enka N.V., The Netherlands). As described below, in the appropriate section, the large decrease in breakthrough volume observed for phosphorus on XAD-2 in the presence of high humidity was not observed for Tenax-GC.

Principle of the Method

The method validated for the analysis of phosphorus (yellow) in air is based on collection using Tenax-GC, desorption using 1 ml of mixed xylenes (ortho-, meta- and para- isomers), and analysis of the resulting solution by gas chromatography with a phosphorus specific flame photometric detector. A sample size of 12 liters is recommended.

Analysis

The details of the equipment and instruments used for the analysis and the general approach used are described in Attachment A.

A detailed description of the procedure for analysis, the preparation of analytical samples for determination of recovery and the preparation of calibration standards are given in NIOSH Method No. S334 (Reference 4). The reliability of the analytical method was tested based on the analysis of 18 analytical samples. These samples were prepared by spiking 100 mg of Tenax-GC with known aliquots of a solution of phosphorus in mixed xylenes representing the equivalent of a 12-liter sample at 0.5, 1 and 2X the OSHA standard. The data for the full set of 18 analytical samples are shown in Table S334-4. The average analytical method recovery found was 97.9%.

Table S334-1

Data Sheet: Phosphorus (yellow)
XAD-2 Collection Tubes

Analysis

Level	1S			2S			4S		
	µg added	µg found	DE*	µg added	µg found	DE*	µg added	µg found	DE*
	1.200	1.140	0.950	2.400	2.270	0.946	4.80	4.61	0.960
	1.200	1.100	0.917	2.400	2.210	0.921	4.80	4.84	1.008
	1.200	1.140	0.950	2.400	2.270	0.946	4.80	4.66	0.971
		mean	0.939			0.938			0.980

*Desorption Efficiency

Table S334-2

Data Sheet: Phosphorus (yellow)

Storage Stability of Spiked XAD-2 Samples

Expt. A: Samples Stored 1 Day

μg added	μg found	Recovery*
2.400	2.270	0.946
2.400	2.210	0.921
2.400	2.270	0.946
	mean	0.938

Expt. B: Samples Stored 20 Days at Room Temperature

2.400	2.130	0.888
2.400	2.330	0.971
2.400	2.160	0.900
	mean	0.920

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* μg(found) ÷ μg(added)

Table S334-3

Data Sheet: Phosphorus (yellow)

Collecton Efficiency on XAD-2

Expt. A: Dry Atmosphere

Test Level*	Volume Sampled (liters)	-----µg found-------			% Collected in front
		Front	Backup	Total	
1S	48.0	6.05	0.100	6.15	98.4
	45.6	6.16	0.160	6.32	97.5
	44.4	5.87	0.100	5.97	98.3
		Average Collection Efficiency			98.1

Expt. B: 85% RH Atmosphere

Test Level*	Volume Sampled (liters)	Front	Backup	Total	% Collected in front
3S	23.04	6.00	0.680	6.68	89.8
	27.45	7.10	0.970	8.07	88.0
	34.9	9.10	1.020	10.12	89.9
	47.9	12.05	1.600	13.65	88.3
	45.6	13.20	3.480	16.68	79.1
	57.6	16.10	3.650	19.75	81.5

* Determined from total µg found and volume sampled.

Table S334-4

Data Sheet: Phosphorus (yellow) Analysis

Level	0.5S			1S			2S		
	µg added	µg found	Recovery	µg added	µg found	Recovery	µg added	µg found	Recovery
	0.592	0.549	0.927	1.184	1.109	0.937	2.384	2.420	1.015
	0.592	0.551	0.931	1.184	1.131	0.955	2.384	2.440	1.023
	0.592	0.562	0.949	1.184	1.175	0.992	2.384	2.390	1.003
	0.592	0.546	0.922	1.184	1.178	0.995	2.384	2.401	1.007
	0.592	0.595	1.005	1.184	1.166	0.985	2.384	2.449	1.027
	0.592	0.570	0.963	1.184	1.136	0.959	2.384	2.429	1.019
n =			6			6			6
mean			0.950			0.971			1.016
std dev			0.0312			0.0235			0.0093
CV_1			0.0328			0.0242			0.0091

$\overline{CV}_1$ 0.0241

$\overline{CV}_{A+\overline{DE}}$ 0.0260

Sampling and Analysis

Test atmosphere samples were generated using the basic system described in Attachments B and C. A steady stream of a solution of phosphorus (11.1 mg/ml) in tetralin was delivered via a calibrated syringe drive at a rate of 0.00159 mg/min to a dry air stream flowing at a rate of 0.108 cu m/min. The syringe was connected directly to the generation equipment by means of a small piece of Teflon tubing. Although a steady concentration of phosphorus vapor was produced using this technique, the conversion of the added amount of phosphorus in solution to phosphorus vapor was not quantitative (see Independent Method of Verifying Generator Concentration) and the test level generated was determined independently using impingers filled with xylene.

The samples were collected as described in NIOSH Method No. S334 using a tube which consisted of front (100 mg) and backup (50 mg) sections of Tenax-GC. Eighteen samples were collected simultaneously at 0.2 liter per minute for 60 minutes (12 liters). The eighteen samples, six at each of the three test levels, were analyzed after one day as described in Section 8.4 of NIOSH Method No. S334. The data obtained for the 18 one-day-old samples are shown in Table S334-5. Recovery corrections were applied to the samples (although the recoveries were above 95%) since a trend of low recoveries at the lower levels was observed for both the analytical samples and the generated samples.

Storage Stability

Studies were conducted to assess the stability of phosphorus (yellow) samples collected on Tenax-GC and stored for seven days at ambient conditions. For these studies, 12 samples were collected simultaneously at 1X the OSHA standard. Six samples were analyzed after one-day storage and the other six analyzed after seven-day storage. The data for these samples, given in Table S334-6, show an acceptable loss of 5.5% over a seven-day period; the average recovery was 96.3% for the one-day-old samples vs. 91.0% for the seven-day-old samples.

Collection Efficiency and Breakthrough Tests

Breakthrough studies were conducted at a test concentration of 0.311 mg/cu m (3.11S) in an atmosphere of 85% relative humidity. These tests were performed using front and backup sections (containing 100 mg and 50 mg of Tenax-GC, respectively) separated by a wad of silylated glass wool. Samples were taken after 2, 2.5, 3.0, 3.5 and 4 hours of collection at 0.2 liter per minute and both sections analyzed as described previously. The results obtained from these experiments are presented in Table S334-7. These data indicate that breakthrough did not occur in 240 minutes of sampling.

The collection efficiency of the Tenax-GC was also determined at a test level of 0.14 mg/cu m (1.4S) in a dry atmosphere. These experiments

Table S334-5

Data Sheet: Phosphorus (yellow)

Sampling and Analysis

		Found			Taken*	
Test Level	μg	μg+	Liters	mg/cu m+	mg/cu m	Recovery
0.5S	0.760	0.800	15.48	0.0517	0.0524	
	0.695	0.732	12.48	0.0586	0.0524	
	0.728	0.766	12.80	0.0599	0.0524	
	0.759	0.799	14.34	0.0557	0.0524	
	0.850	0.895	14.87	0.0602	0.0524	
	0.620	0.653	13.27	0.0492	0.0524	
			n = 6			
			mean	0.0559		1.067
			std dev	0.00457		
			CV_2	0.0817		
1S	1.650	1.699	12.86	0.1321	0.1151	
	1.485	1.529	12.26	0.1247	0.1151	
	1.400	1.442	12.19	0.1182	0.1151	
	1.645	1.694	15.28	0.1109	0.1151	
	1.475	1.519	12.73	0.1194	0.1151	
	1.524	1.570	13.00	0.1207	0.1151	
			n = 6			
			mean	0.1210		1.051
			std dev	0.00706		
			CV_2	0.0583		
2S	3.28	3.23	14.81	0.2180	0.2307	
	3.16	3.11	12.53	0.2482	0.2307	
	3.18	3.15	12.19	0.2508	0.2307	
	2.720	2.677	12.11	0.2211	0.2307	
	3.42	3.37	12.93	0.2603	0.2307	
	3.54	3.48	13.33	0.2614	0.2307	
			n = 6			
			mean	0.2443		1.059
			std dev	0.0197		
			CV_2	0.0806		
			$\overline{CV}_2$	0.0743		

---

* Data obtained by collection in impingers. See Independent Method for Verifying Generator Concentration.

\+ Corrected for desorption efficiency.

Table S334-6

Data Sheet: Phosphorus (yellow)

Storage Stability of Collected Samples

Expt. A: Samples Stored 1 Day

Test Level	Found				Taken*	
	µg	µg^{+}	Liters	mg/cu m	mg/cu m	Recovery
1S	1.069	1.101	11.34	0.0971	0.1028	
	1.261	1.299	11.64	0.1116	0.1028	
	1.151	1.185	11.58	0.1024	0.1028	
	1.163	1.198	11.64	0.1029	0.1028	
	1.413	1.455	14.40	0.1011	0.1028	
	0.959	0.988	9.72	0.1016	0.1028	
			mean	0.1028		1.000
			CV$_2$	0.0465		

Expt. B: Samples Stored 7 Days

1S	0.944	0.972	10.52	0.0924	0.1028	
	1.142	1.176	10.98	0.1071	0.1028	
	0.945	0.973	10.92	0.0891	0.1028	
	1.291	1.330	13.68	0.0972	0.1028	
	1.051	1.082	11.40	0.0949	0.1028	
	1.100	1.133	11.64	0.0973	0.1028	
			mean	0.0963	(0.964)	0.937
			CV$_2$	0.0636		

*Data obtained by collection in impingers. See Independent Method for Verifying Generator Concentration.

+Corrected for desorption efficiency.

Table S334-7

Data Sheet: Phosphorus (yellow)

Expt. A: Breakthrough Data at 85% RH (0.2 liter per minute)

Level	Sampling Time (hrs)	Volume (liters)	µg Found+ Front	Backup	Total	% Collected in Front
3S	2	26.6	7.70	N.D.	7.70	100*
	2.5	28.0	7.90	N.D.	7.90	100*
	3.0	32.8	10.10	N.D.	10.10	100*
	3.5	38.6	13.00	0.01	13.01	99.9
	4.0	46.3	15.60	0.03	15.60	99.8

Expt. B: Collection Efficiency in Dry Air (0.2 liter per minute)

1S	4.0	48.0	7.00	N.D.	7.00	100*
		45.6	6.50	N.D.	6.50	100*
		43.2	6.08	N.D.	6.08	100*
					Average	100*

N.D. Not Detectable. Detection limit is estimated at 0.005 µg.

* Based on the detection limit the collection efficiency is at least 99.9%.

\+ Not corrected for desorption efficiency.

were conducted in a similar manner to the breakthrough studies except that samples were taken only after four hours of collection at 0.2 liter per minute. These results (also presented in Table S334-7) indicate an average collection efficiency of at least 99.9%.

Migration Studies

Studies were conducted to determine if any migration of phosphorus occurred from the front to the backup sections of the Tenax-GC tube during storage for seven days. These experiements were conducted with the samples used to determine the storage stability of phosphorus on Tenax-GC. The results showed that for all six samples where the front section contained 0.944-1.291 μg of phosphorus, the backup section contained less than 0.005 μg of phosphorus (the detection limit). Thus based on this data the amount migrated during the seven days storage period was less than 0.5%.

Generation Difficulties

The generation of a predetermined test atmosphere of phosphorus was hampered by the lack of agreement of the expected level calculated by the amount of phosphorus added to the generator and the level found using impingers or Tenax-GC sorbent tubes. This lack of agreement is illustrated by the data given in Table S334-8.

Table S334-8

Comparison of the Phosphorus Levels Obtained in the Generator To Those Predicted

Predicted Level[a] (mg/cu m)	Found Level[b] (mg/cu m)	Yield (%)
0.223	0.142 (2.0 hrs)[c]	63.7
0.164	0.103 (2.0 hrs)	62.8
0.349	0.280 (2.0 hrs)	80.2
	0.315 (2.5 hrs)	90.3
	0.305 (3.0 hrs)	87.4
	0.326 (4.0 hrs)	93.4
0.163	0.115 (1.0 hrs)	70.6
	0.106 (2.0 hrs)	65.0
	0.115 (3.0 hrs)	70.6

[a] Calculated using the calibrated syringe addition rate and the known concentration of phosphorus in the tetraline solution.

[b] Determined from analyses of impinger solutions and Tenax-GC tubes.

[c] Values in parentheses are number of hours generator was in operation.

Although the percent yield varied from generation to generation, the level produced in a single generation experiment was relatively constant over a period of at least 4 hours (see above). The possibility that the discrepancy arose due to some of the phosphorus being oxidized and converted to the particulate phase was checked by comparing data for collection in impingers preceded by a mixed cellulose ester filter (Millipore AA) to those without any prior filter. The results of this experiment are given in Table S334-9.

Table S334-9

Comparison of Filtered and Unfiltered Phosphorus Air Samples*

Volume (liters)	µg found	Concentration (mg/cu m)
(Samples passed through AA filters prior to collection)		
25.80	9.00	0.349
25.27	8.50	0.336
30.32	11.05	0.364
	Average:	0.350
(Samples collected directly in impingers)		
25.67	9.05	0.353
24.47	8.50	0.347
25.14	10.05	0.400
24.11	8.87	0.368
24.87	9.25	0.372
29.35	9.00	0.307
	Average:	0.358

*The nine samples were collected simultaneously.

These data indicate that no particulate matter was present in the test atmosphere and therefore that none was being collected by the xylene impingers.

These generator difficulties were compensated for in the method validation by use of an independent method for determining generator concentration. This method is described in the following section.

Independent Method for Determining Generator Concentrations

The method used to determine the phosphorus concentration in the test atmospheres generated was collection of the vapor at 0.2 liter per minute in impingers containing 20 ml of mixed xylenes and analysis using gas chromatography with a flame photometric detector. The collection efficiency of this method was determined at a test concentration of 0.37 mg/cu m for an average sample volume of 25 liters. These data are presented in Table S334-10 and indicate a collection efficiency of at least 97.7%.

Table S334-10

Collection Efficiency of Phosphorus in Mixed Xylene Impingers*

Volume Collected (liters)	-- µg Found ---		% Collected in Front
	Front	Backup	
27.7	10.05	N.D.	100**
22.2	9.05	N.D.	100
22.9	8.50	N.D.	100
25.7	8.88	N.D.	100
26.6	9.25	N.D.	100
23.8	9.00	N.D.	100
		Average Collection Efficiency	100**

N.D. = Not Detectable. Detection limit is 0.25 µg.

* Average flow rate - 0.2 liter per minute.

** The average collection efficiency is at least 97.7% based on the detection limit and average µg of phosphorus found in the front impinger.

The test atmosphere concentrations of phosphorus were derived from the amount of phosphorus collected in the impingers and assuming a collection efficiency of 100%. The data used to derive the generator concentrations in all the experiments are presented in Table S334-11.

Precision and Accuracy

The precision of the method was determined by using the statistical procedures described in Reference 2 and the data in Tables S334-4 and S334-5.

Bartlett's test for homogeneity of variances was applied to the coefficients of variation at 0.5, 1 and 2X the OSHA standard for phosphorus (yellow). The data (Table S334-5) give a chi squared value of 6.34,

Table S334-11

Data Sheet: Phosphorus (yellow)

Taken Phosphorus Concentrations Based on Impinger Collection Data

Liters	µg Phosphorus Found	Test Concentration mg/cu m
(Data for Storage Stability Set)		
13.86	1.330	0.0960
11.10	1.210	0.1090
11.46	1.273	0.1111
12.84	1.223	0.0952
13.32	1.437	0.1079
11.88	1.163	0.0979
	n = 6	
	mean	0.1028
	std dev	0.0072
	CV	0.0700
(Data for Generated Set)[a]		
16.08	1.826	0.1136
13.00	1.467	0.1128
12.93	1.397	0.1080
13.00	1.513	0.1164
12.73	1.545	0.1214
12.66	1.500	0.1185
	n = 6	
	mean	0.1151
	std dev	0.00471
	CV	0.0409

[a] This data was taken at the 1S dilution arm. The dilution ratios of 1.000:0.499:0.227 for the 2S:1S:0.5S dilution arms were used in calculating the "taken" concentrations of 0.0524 and 0.2307 mg/cu m given for the 0.5S and 2S levels shown in Table S334-5.

indicating that the hypothesis of equal variance is satisfied at p (probability) less than 0.01. Thus, $\overline{CV}_T$ is calculated based on the pooled data.

The precision of the method is expressed in terms of the coefficients of variation for the analytical method, the sampling and analytical method, and the overall method which includes a pump error of 0.05. These values are shown below.

$$\overline{CV}_1 = 0.0241 \qquad \overline{CV}_2 = 0.0743 \qquad \overline{CV}_T = 0.0901$$

The accuracy of the method was determined by comparison of the average value found by analysis of six samples at each of the three test levels with the Taken generator concentration discussed in the preceding section. The data summaried in Table S334-12 show good agreement (Found ÷ Taken) with an average of 102.0%.

Table S334-12

Comparison of Taken vs. Found Concentrations

Test Level	Taken (mg/cu m)	Found (mg/cu m)	Agreement (Found ÷ Taken)
0.5S	0.0524	0.0559	1.067
1.0S	0.1157	0.1210	1.051
2.0S	0.2307	0.2443	1.058
1.0S	0.1028	0.1028	1.000
		Mean:	1.042

The difference between the Taken and Found concentrations may not represent a bias in the sampling and analytical method, but rather a random variation from the experimentally determined "true" concentration. Further confidence in the accuracy of the tested method is established by the results of the collection efficiency test and the storage stability test, described in the appropriate sections.

References

1. Statement of Work, Article 1, Contract No. 210-76-0123, NIOSH Department of Health, Education and Welfare, 4676 Columbia Parkway, Cincinnati, Ohio 45226.

2. Documentation of NIOSH Validation Tests, National Institute for Occupational Safety and Health, Cincinnati, Ohio (DHEW-NIOSH-Publication No. 77-185), 1977. Available from Superintendant of Documents, U.S. Government Printing Office, Washington, D. C. Order No. 757-057/6708.

3. Barrett, W.J. and Dillon, H.K. "Development of Methods for Determination of Elemental Phosphorus and Phosphine in Air," Final Report for Contract Number 210-75-0047, Southern Research Institute, January 1977.

4. Phosphorus (yellow) NIOSH Method No. S334 prepared under NIOSH Contract No. 210-76-0123 with validation date 11/25/77.

ATTACHMENT A

GAS CHROMATOGRAPHY ANALYTICAL PROCEDURE

Equipment

The equipment used for the gas chromatography (GC) methods consists of a Varian 2700 Series Gas Chromatograph, a Varian Model 8000 automatic sample injector and a Spectra Physics System 1 computing integrator.

The Varian 2700 is a dual column unit equipped with a flame ionization detector and a photoionization detector (Hnu Systems, Inc.). The unit can be set for isothermal or for linear temperature program operation, either manually or automatically.

The Model 8000 automatic sample injector is mounted horizontally on the Varian 2700 and can readily be moved to align with either of the two injection ports. The autosampler has a rotating carousel module which can hold 60 sample vials (2 ml glass vials with screw tops and Teflon-lined septa), an injector module with an adjustable side-arm syringe pneumatically actuated by compressed dry nitrogen, and a control unit which permits total automation in a closed loop form with a computer. For this program, the syringe injector has been set to deliver 5 microliters of sample solution. The unit has been tested to verify that sample to sample cross-contamination does not occur and that the reproducibility of the sample injection is adequate. Periodic checks have been carried out on six or twelve repetitive injections of a standard solution in carbon disulfide and the observed standard deviation of the integrated peak areas is never greater than 2.5%.

All peak area measurements were done with the System 1 computing integrator. The operating parameters of the unit can readily be optimized to suit the particular chromatograms, i.e., both narrow and broad peaks are properly integrated; tailing peaks and peaks eluting at the tail end of a peak can be detected, and appropriate baseline is readily established; a cluster of peaks can be integrated together as a total mass. System 1 also has the capability to calculate sample concentration directly once the calibration factor has been determined.

Approach

The internal standard method (relative area measurements) has been used for this program not only because of its inherently better reproducibility than the external standard method (absolute area measurements) but also as a safeguard against any problems that could arise during the periods of unattended overnight operation. Such problems include detector response variations and the partial clogging of the sample injector loop which can give rise to variability in sample size injections. These clogging effects are caused by the very fine solid sorbent particles which remain suspended in the solution.

A comparative study of the reproducibility of the absolute area and the relative area measurements was performed using sec-butyl acetate (1.5 mg/ml) and undecane as internal standard. The precision of 12 successive determinations was 1.7% based on absolute areas and 0.4% using relative areas.

The choice of an internal standard has been restricted to those compounds which present minimal adsorption losses on the specific solid sorbent used. Experiments have been run to verify adsorption losses by determining the integrated areas of analyte and internal standard in a calibration solution and comparing these areas with the respective areas obtained when 1.0 ml (or other appropriate volume) aliquots of the same calibration solution are added to the appropriate amounts of solid sorbent. (Use the same weight of solid sorbent as that used for sampling.) The ideal internal standard is one which does not show any significant decrease in area due to the solid sorbent addition; this phenomenon is dependent on the interactive characteristics of the internal standard, the solid sorbent and the desorption solvent.

ATTACHMENT B

VAPOR DILUTION/SAMPLING SYSTEM

The vapor generation/dilution system used for the validation studies of several vapors and gases, such as this analyte, is shown schematically in Figure S344-B-1. The system basically consists of a main line air stream to which are added predetermined amounts of various liquids, gases or aerosols to generate the desired vapor concentrations. From the main line, three dilution arms branch off in which the desired multiples 0.5, 1.0 and 2.0 times the OSHA Standard concentration level are established. Six sampling devices are connected in parallel to each of the three dilution lines and are connected via critical flow orifices (CFO's) to the three corresponding vacuum lines.

Air flow rates through the system are established by means of critical flow orifices (CFO's) and flow restrictors. The primary air system derived from the house air compressor is maintained at 20.0 psig. The appropriate orifice diameters are chosen to maintain an air flow of approximately 0.1 cu m/min in the Main Line and an addition of 0.05 cu m/min to each of the dilution lines. The main line is maintained at 8 cm H_2O pressure by means of a needle valve. Appropriate flow restrictor diameters are chosen for the 0.5S, 1S and 2S dilution lines so as to give the desired final concentrations of vapor in air.

The system was designed to generate either 4X or 2X the OSHA Standard concentration in the Main Line. When a 4X level is generated, 0.05 cu m/min of dilution air is added to each dilution line. Orifices are selected so that the 0.5S, 1S and 2S lines have flows equal to approximately 0.007, 0.017 and 0.050 cu m/min respectively of the Main Line concentration added to the dilution air, thus giving the desired final concentrations. Where a Main Line concentration of 2X the OSHA Standard is generated, no dilution air is added to the 2S dilution line--0.017 cu m/min is simply allowed to flow through this line--and 0.050 cu m/min of dilution air is added to the 0.050 cu m/min and 0.017 cu m/min of Main Line mixture admitted to the 1S and 0.5S dilution lines, respectively.

All materials which the vapor may contact before collection are 316 or 304 stainless steel. A glass heater is included where the liquids are added to the main line. Shutoff ball valves are placed in the dilution lines to allow their independent operation and the calibration of air flows. The Main Line has a 2.54-cm (1 in) O.D., and the dilution lines are 1.90-cm (0.75 in) O.D. Diameters were chosen to give turbulent flow with an approximate minimum Reynolds number of 3000.

Air Supply

Air from the house compressor is treated by passing it sequentially through a cotton filter, a silica gel bed, a charcoal bed and a high efficiency glass fiber filter for removal of water, hydrocarbons and particulate. This air is then connected to a manifold containing six takeoff

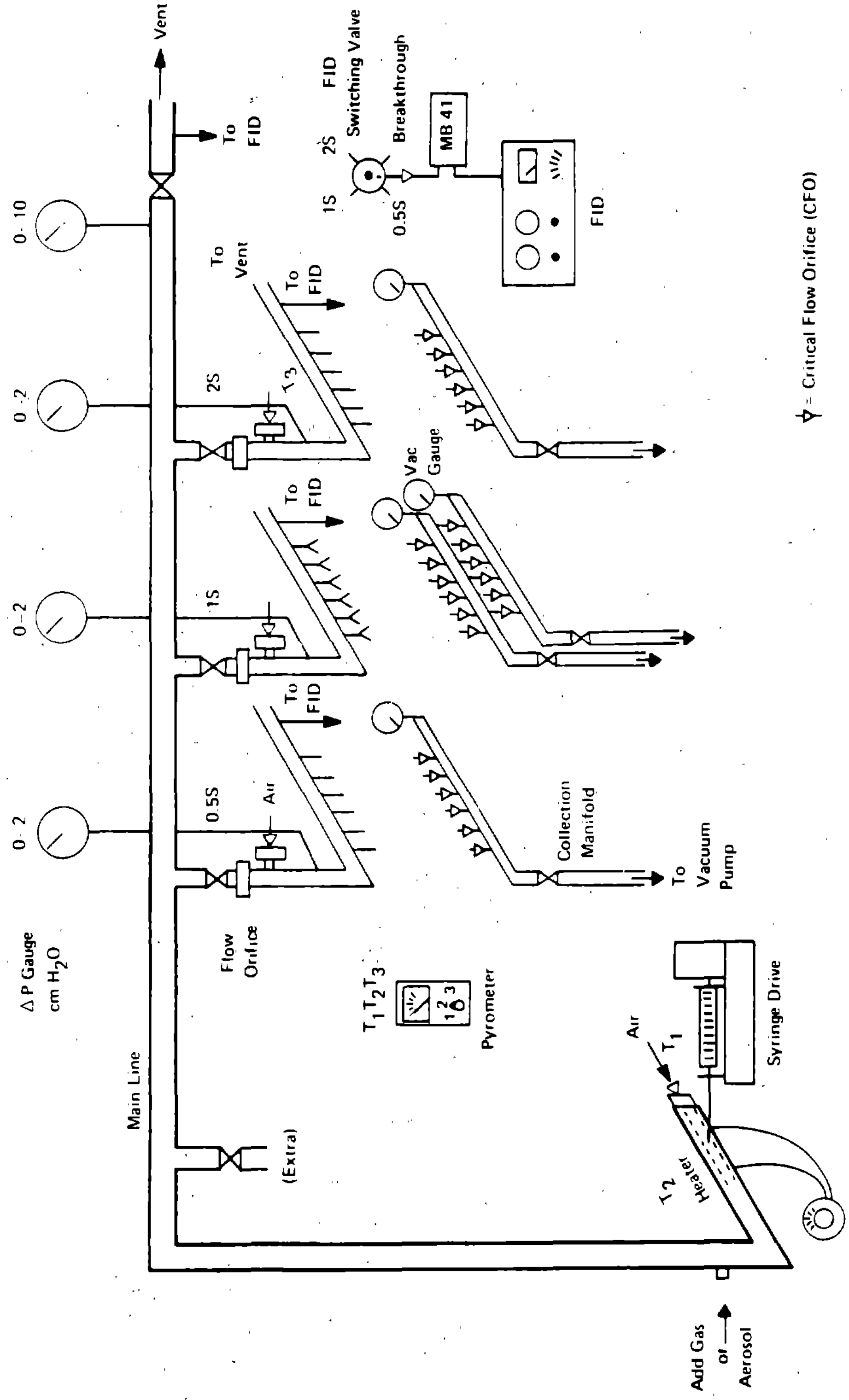

Figure S334-B-1 Vapor Generation/Dilution/Sampling System

ball valves. The pressure (20 psig) at the manifold is maintained with a Nullmatic Moore 40H50 regulator and monitored with an Ashcroft 0-60 psig test gauge. The air supply is used for each of the dilution system connections as well as for the flame ionization detector monitor flame and "zero" air.

Sample Collection Manifold

Sample flow through the sampling devices connected to the dilution lines is established by connecting each device by means of a short piece of flexible tubing to a CFO which is connected to a 1.27 cm (1/2 in) O.D. vacuum manifold. Each dilution line has a separate manifold which derives its vacuum from a Model 0322 Gast vacuum pump. The orifices are jewel orifices pressed into a threaded Teflon rod. One end of the rod is screwed into a tee on the manifold, and the other has a hose tabulation fitting connected to it. The orifice is protected from plugging by means of a piece of 100 mesh stainless steel screen.

Vent System

All excess vapor-laden air is collected via a 3.81-cm (1.5 in) PVC manifolding system where it is passed through a 0.3 x 0.3 x 0.6-M charcoal bed. Flow is established by means of a pressure blower on the exit side of the charcoal bed, and it is vented to the laboratory hood exhaust.

Calibration

Air Flows

Main Line -- The air flow delivered by the Main Line CFO was determined by measurement with a Singer Dry Test Meter. The meter had previously been calibrated with a spirometer primary standard. Using the 0.310-cm diameter orifice at 20 psig air pressure, the flow was found to be 0.1086 cu m/min corrected to 25°C and 760 mm Hg.

Dilution Lines -- The air flow through each of the dilution line CFO's and restrictor orifices was similarly measured with the Dry Test Meter to assure that they met design parameters, but these values did not provide the primary basis for determination of vapor concentration.

Collection CFO's -- Since the flow rate through the sample collection CFO's was lower (0.2 and 1.0 liter per minute) than appropriate for use with the Dry Test Meter, the flow rate of each of these orifices was measured using an SKC soap bubble meter which was independently calibrated by gravimetrically measuring water capacity.

All volume measurements have been referenced to normal temperature and pressure of 25°C and 760 mm Hg.

Dilution Ratios

The concentration of vapor in the dilution lines is determined from the concentration calculated in the Main Line and the dilution ratio determined between the dilution lines and the main line. These dilution ratios were measured by adding a controlled amount of propane gas to the Main Line and then measuring the relative concentration in each of the lines using a Beckman Model 402 heated hydrocarbon analyzer. The procedure was repeated several times and is regularly checked during the program.

In the case where 4X or 2X concentration level conditions were generated, the dilution ratios reported below were observed.

		Relative Concentration		
Case Generated	Main Line	2S	1S	0.5S
4X	1.000	0.5097	0.2557	0.1311
2X	1.000	1.000	0.499	0.227

Each of these sets of values represents a different set of air flow and orifice selection conditions as previously discussed. Point to point comparison of the six sample ports on each manifold showed less than a 1% variation in concentration among them.

Monitors

To provide a ready check on operating conditions, several gauges or monitors have been included in the system. Dwyer Magnehelic gauges monitor the pressure on the Main Line and each of the dilution lines. A 0-10 cm H_2O gauge is used on the Main Line (Setpoint 8 cm) and 0-2 cm H_2O gauges are used for the dilution lines. The purpose of these latter gauges is to provide a check against possible back pressure developing in these lines which would affect the dilution ratios.

The flame ionization detector (FID) is used to determine the time at which the Main Line concentration has reached equilibrium and to monitor the concentration level during breakthrough studies and sample collection.

Breakthrough Studies

A. Low Relative Humidity (Dry Air)

For the measurement of sorbent tube capacity for a given vapor (breakthrough) six sorbent tubes containing only the 100 mg "front half" section of sorbent are connected in parallel to the 2S dilution line and to a 0.635-cm (1/4-in) O.D. stainless steel six-port manifold. Flow through the manifold is controlled by a CFO and is established using a Metal Bellows Corp. Model MB41 pump. Flow through the orifice was

measured as 1.14 liters per minute providing a 0.19-liter per minute flow to each of the tubes. (A separate set of orifice allows a similar determination at a flow rate of 1.0 liter per minute through each tube.) Equal flow through each of the tubes is insured by carefully selecting and/or adjusting packing in the tubes to have an equal pressure drop when precalibrated at a 0.2-liter per minute flow rate.

Once a steady state vapor concentration is established, the 2S concentration level is used to set the 100% point on the hydrocarbon analyzer. Then the valve is switched, and the flow from the breakthrough manifold is passed through the hydrocarbon analyzer and monitored either until 5% of the 2S level is observed or for a period of four hours--whichever occurs first.

B. High Relative Humidity

For the generation of a high relative humidity atmosphere, at least 80% R.H., water vapor is delivered into the generator Main Line via one of the side arms as shown in Figure S334-B-2. A peristaltic pump, Cole-Parmer Masterflex, Model No. 7013, is used to deliver water into a heated copper coil (1/8 in x 10 feet) contained in a tube furnace; the furnace temperature is maintained above 110°C and monitored by a thermocouple and optical pyrometer. Water is delivered at the rate of 1.9 g per minute to blend with the analyte-containing dry air stream flowing at a rate of 0.100 cu m per min to produce an atmosphere of at least 80% R.H. at 25°C and 760 mm Hg.

All other aspects of the breakthrough test procedure are as described above.

Procedure

The overall procedure for a given sample is as follows:

1. Line air flow and dilution ratios are verified.

2. Sample delivery rate is determined by appropriate calibration.

3. Sample is fed into Main Line until vapor concentration equilibrium is established.

4. The breakthrough experiment is performed and subsequent sample collection volumes adjusted if necessary.

5. The four sets of six samples from the three concentration levels are collected simultaneously.

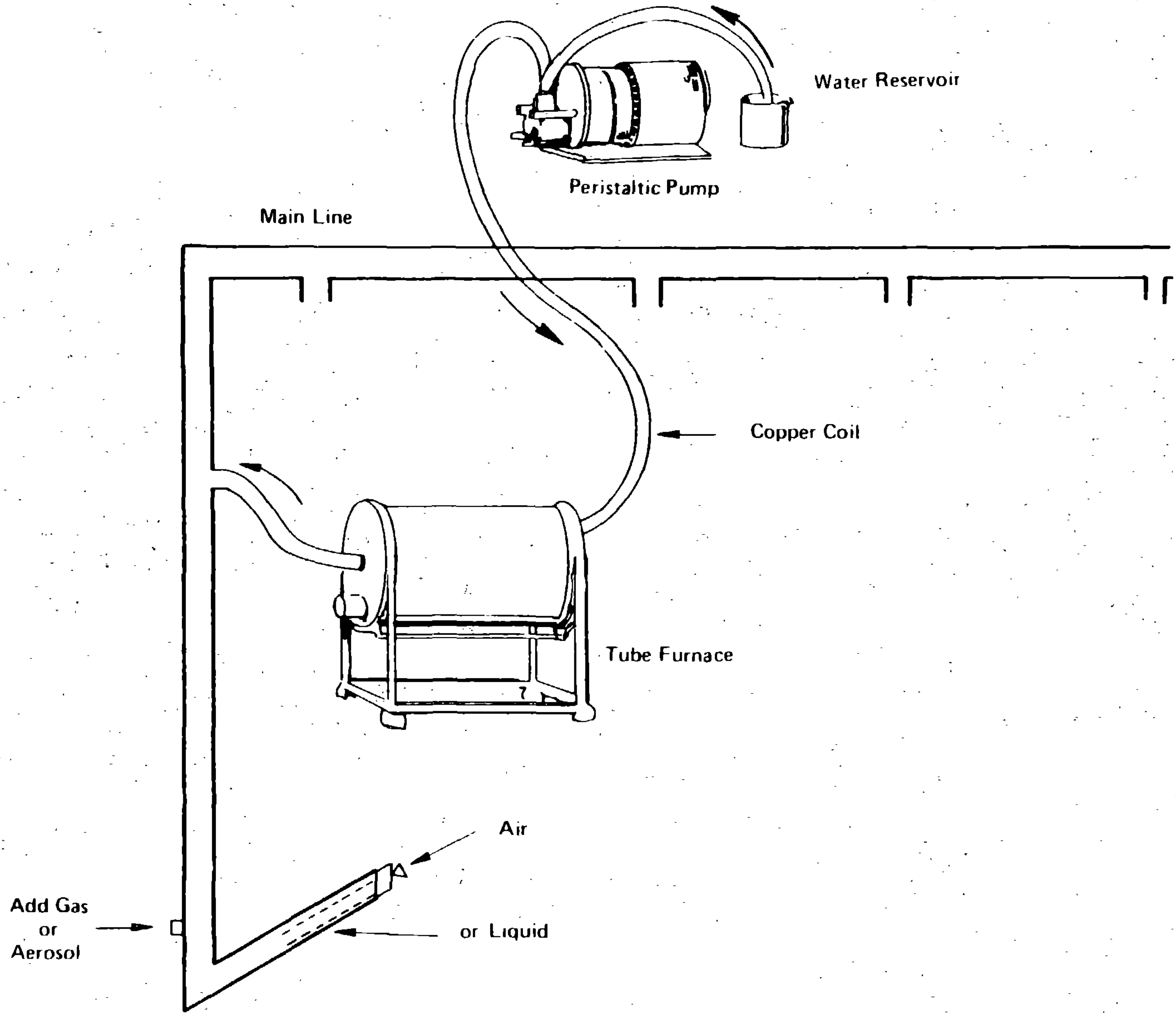

Figure S334-B-2 Generation of High Humidity Atmospheres

ATTACHMENT C

VAPOR GENERATION

Continuous Direct Injection

Vapor concentrations from liquids are generated by adding known amounts of liquid to the Main Line of the vapor dilution/sampling apparatus. A continuous delivery rate is achieved using a Harvard Model 944 Syringe Drive. The syringe is connected to a 25 G stainless steel needle in the Main Line by a short length of 0.16-cm (1/16-in) O.D. Teflon tubing. If the substance of interest is reactive with the stainless steel needle then the Teflon tubing is placed within the Main Line replacing the needle. When dealing with liquids of low volatility the 25G needle is mounted such that the tip of the needle rests inside a 10-cm length of 8-mm I.D. glass tubing wound with resistance wire. The appropriate amount of current is applied to the heater to assure steady and complete vaporization of the liquid.

Calibration of Syringe Delivery

Preliminary calibrations have been conducted so that the approximate delivery rates of the syringe drive are known at each setting for several syringe sizes. These values are used to set the approximate delivery rate for the specific liquid. The syringe is then filled and connected to a weighing bottle, and the drive is activated for a period of time to allow the actual delivery rate to be determined in mg/min by weighing the amount collected. Sufficient time is allowed to provide a weight change which can be measured reliably and thus enable a precise calibration. Usually 25-800 mg are collected depending on the specific compound being studied.

Methoxychlor

Analyte:	Methoxychlor	Method No.:	S371
Matrix:	Air	Range:	7.7-31 mg/cu m in a 100-L sample
OSHA Standard:	15 mg/cu m	Precision ($\overline{CV}_T$):	0.054
Procedure:	**Filter collection, iso-octane extraction, GC, electrolytic conductivity detection**	Validation Date:	12/23/77

1. Synopsis

1.1 A known volume of air is drawn through a glass fiber filter to collect particulate matter containing methoxychlor.

1.2 Methoxychlor is extracted from the filter with iso-octane, and the sample is analyzed by gas chromatography using ECD.

2. Working Range Sensitivity, and Detection Limit

2.1 This method was validated over the range of 7.7-31 mg/cu m at an atmospheric temperature of 23°C and atmospheric pressure of 761 mm Hg, using a 100-liter sample.

2.2 The upper limit of the range of the method depends on the capacity of the glass fiber filter. If higher concentrations than those tested are to be sampled, smaller volumes should be used.

3. Interferences

3.1 When interfering compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

3.2 Any compound that has the same retention time as methoxychlor at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered proof of chemical identity.

3.3 Technical formulations usually contain 6-12% of the o,p' isomer of methoxychlor. Gas chromatographic conditions should be adjusted so the isomers are separated.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV_T}$) for the total analytical and sampling method in the range of 7.7-31 mg/cu m was 0.054 for 18 samples collected from test atmospheres. This value corresponds to a 0.81 mg/cu m standard deviation at the OSHA standard level. Statistical information can be found in Reference 11.1. Details of the test procedures are found in Reference 11.2.

4.2 On the average, the concentrations obtained in the laboratory validation study at 0.5X, 1X, and 2X the OSHA standard level were 0.3% higher than the "true" concentrations for 18 samples. Any difference between the "found" and "true" concentrations may not represent a bias in the sampling and analytical method, but rather a random variation from the experimentally determined "true" concentration. The Coefficient of Variation is a good measure of the accuracy of the method since the recoveries, collection efficiency of the filter, and storage stability were good and would not contribute to a bias in a determined concentration. Storage stability studies on samples collected from a test atmosphere at a concentration of 15.36 mg/cu m indicate that collected samples are stable for at least 7 days. The mean of samples analyzed immediately versus the mean of samples analyzed after 7 days of collection compare within 5%.

5. Advantages and Disadvantages

5.1 The sampling device is small, portable, and involves no liquids. Samples collected on filters are analyzed by means of a quick, instrumental method.

5.2 The analytical method is selective for halogenated compounds.

6. Apparatus

6.1 Filter Unit: The filter unit consists of a 37-mm diameter glass fiber filter (Gelman Type A/E or equivalent) and a polystyrene 37-mm two-piece cassette filter holder. The filter is held in the two-piece filter holder supported by a backup pad. The filter must be free of organic binders. Filter holders made of Tenite should not be used.

6.2 Personal Sampling Pump: A calibrated personal sampling pump whose flow can be determined within 5% at the recommended flow rate. Each personal sampling pump must be calibrated with a representative filter cassette in the line to minimize errors associated with uncertainties in the volume sampled.

6.3 Manometer.

6.4 Thermometer.

6.5 Scintillation vials: 20-mL, with Teflon-lined caps, or equivalent.

6.6 Gas chromatograph equipped with an electrolytic conductivity detector.

6.7 Column (5.5-m long x 4-mm I.D. glass) packed with 5% SE-30 on Chromosorb W.

6.8 An electronic integrator or some other suitable method for measuring peak areas.

6.9 Tweezers.

6.10 Microliter syringes: 25-microliter.

6.11 Volumetric flasks: Convenient sizes for preparing standard solutions.

6.12 Pipets: Convenient sizes for preparing standard solutions, and 15-mL pipets for measuring the extraction medium.

7. Reagents

Whenever possible, reagents should be ACS reagent grade or better.

7.1 Methoxychlor.

7.2 Iso-octane.

7.3 Helium, purified.

7.4 Hydrogen, prepurified.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis as well as the scintillation vials should be detergent washed and thoroughly rinsed with tap water and distilled water, and dried.

8.2 Collection and Shipping of Samples

8.2.1 Assemble the filter in the two-piece filter cassette holder and close firmly. The filter is supported by a backup pad.

8.2.2 Remove the cassette plugs and attach the cassette to the personal sampling pump tubing. Clip the cassette to the worker's lapel.

8.2.3 Air being sampled should not pass through any hose or tubing before entering the filter cassette.

8.2.4 A sample size of 100 liters is recommended. Sample at a flow rate of 1.5 liter/minute. The flow rate should be known with an accuracy of 5%.

8.2.5 Turn the pump on and begin sample collection. Since it is possible for a filter to become plugged by heavy particulate loading of greater than 2 mg of dust per sample or by the presence of oil mists or other liquids in the air, the rotameter should be observed frequently, and sampling should be terminated at any evidence of a problem.

8.2.6 Terminate sampling at the predetermined time and record ambient temperature and pressure, sample flow rate, and collection time. If pressure reading is not available, record the elevation.

8.2.7 Cap each end of the filter cassette firmly.

8.2.8 Record the sample identity and all relevant sampling data.

8.2.9 The filter cassettes in which the samples are collected should be shipped in a suitable container, designed to prevent damage in transit.

8.2.10 With each batch of ten samples, submit one filter from the same lot of filters used for sample collection. This filter must be subjected to exactly the same handling as the samples except that no air is drawn through it. Label this filter as a blank.

8.2.11 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the collected samples.

8.3 Analysis of Samples

8.3.1 Each sample is analyzed separately.

8.3.2 Remove the glass fiber filter from the cassette filter holder and place it in a clean scintillation vial. Care must be taken to handle the filter with clean tweezers.

8.3.3 Pipet 15 mL of iso-octane into each vial. Swirl the contents in each vial occasionally for a period of 15 minutes.

8.3.4 Appropriate filter blanks must be analyzed at the same time as the samples.

8.3.5 GC Conditions. The typical operating conditions for the gas chromatograph are:

80 mL/minute helium carrier gas flow
80 mL/minute hydrogen flow through pyrolysis tube of the detector
225°C column temperature
250°C injector temperature
250°C transfer block temperature
820°C furnace temperature

The retention time of the p,p' isomer of methoxychlor is 6.0 minutes. The o,p' isomer will elute before the p,p' isomer.

8.3.6 Injection. The first step in the analysis is to inject the sample into the gas chromatograph. To eliminate difficulties arising from blow back or evaporation of solvent within the syringe needle, a solvent flush injection technique should be used. A 25-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe, the needle is removed from the solvent, and the plunger is pulled back about 1.0 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 15-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and before injection, the plunger is pulled back 2.0 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 14.9-15.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

Since a 15-microliter aliquot is likely to cause malfunction of the electrolytic conductivity cell, the valve should be opened when injection is made and should be closed after the solvent (iso-octane) has been vented and before the analyte is eluted. Under the conditions above (Section 8.3.5), it was found that 3.0 minutes was adequate to elute the solvent.

8.3.7 The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and results are read from a standard curve prepared as discussed below.

9. Calibration and Standardization

A series of standards varying in concentration over the range corresponding to approximately 0.1 to 3 times the OSHA standard for the sample under study, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg methoxychlor/15 mL versus peak area. Note: Since no internal standard is used in this method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of known day-to-day variations and variations during the same day of the electrolytic conductivity response.

9.1 Prepare several stock standard solutions of methoxychlor in iso-octane.

9.2 From the above stock solutions, appropriate aliquots are withdrawn and dilutions are made in iso-octane. Prepare at least 5 working standards to cover the range of 0.15-4.5 mg/15 mL. This range is based on a 100-liter sample.

9.3 Prepare a standard calibration curve by plotting concentration of methoxychlor in mg/15 mL versus peak area.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume correction is needed, because the standard curve is based on mg/15 mL of iso-octane and the volume of sample injected is identical to the volume of the standards injected.

10.2 A correction for the blank must be made for each sample.

$$\text{mg} = \text{mg sample} - \text{mg blank}$$

where:

mg sample = mg found in sample filter

mg blank = mg found in blank filter

10.3 For personal sampling pumps with rotameters only, the following volume correction should be made.

$$\text{Corrected Volume} = f \times t \left(\sqrt{\frac{P_1}{P_2} \times \frac{T_2}{T_1}} \right)$$

where:

f = flow rate sampled

t = sampling time

P_1 = pressure during calibration of sampling pump (mm Hg)

P_2 = pressure of air sampled (mm Hg)

T_1 = temperature during calibration of sampling pump (°K)

T_2 = temperature of air sampled (°K)

10.4 The concentration of methoxychlor in the air sample can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{mg (Section 10.2)} \times 1000 \text{ (liters/cu m)}}{\text{Corr. Air Volume Sampled (liters) (Section 10.3)}}$$

11. References

11.1 Documentation of NIOSH Validation Tests, National Institute for Occupational Safety and Health, Cincinnati, Ohio (DHEW-NIOSH Publication #77-185), 1977. Available from Superintendent of Documents, U.S. Government Printing Office, Washington, D.C., Order No. 017-033-00231-2.

11.2 Backup Data Report for Methoxychlor, prepared under NIOSH Contract No. 210-76-0123.

Sampling Data Sheet No. S371

December 23, 1977

Substance

Methoxychlor

Standard

8-hour time-weighted average: 15 mg/cu m

Analytical Method

A known volume of air is drawn through a glass fiber filter to trap methoxychlor. Methoxychlor is extracted from the filter with iso-octane, and the sample is separated and analyzed using a gas chromatograph equipped with an electrolytic conductivity detector. The method has been validated over the range of 7.7-31 mg/cu m for a 100-liter sample at 23°C and 761 mm Hg atmospheric temperature and pressure. Details of the sampling and analytical method are given in the method referenced below.

Sampling Equipment

Sampling equipment includes a calibrated personal sampling pump whose flow can be determined accurately ($\pm 5\%$) between 1-1.5 liter/minute, a 37-mm two-piece cassette filter holder held together by tape or shrinkable band, and a 37-mm diameter glass fiber filter. The filter must be free of organic binders. The filter holder should be made of polystyrene. Do not use filter holders made of Tenite.

Sample Size

A sample size of 100 liters is recommended. Sample at a flow rate of 1.5 liter/minute.

Sampling Procedure

1. Assemble the filter and two-piece filter cassette and close firmly. Examine the holder for a good filter seal. The filter is supported by a backup pad. If the cassette will not seal tightly, it should be discarded. Secure the cassette holder together with tape or shrinkable band.

2. Remove the cassette plugs and attach the cassette to the personal sampling pump tubing. Clip the cassette to the worker's lapel.

3. Air being sampled should not be passed through any hose or tubing before entering the filter cassette.

4. Set the flow rate as accurately as possible using the manufacturer's directions. Record the temperature and pressure of the atmosphere being sampled. If the pressure reading is not available, record the elevation. Also report the type of sampling pump used. Since it is possible for the filter to become plugged by particulate loading of greater than 2 mg of dust per sample or by the presence of oil mists or other liquids in the air, the rotameter should be observed frequently, and the flow rates readjusted as needed. If the flow rate cannot be adjusted to correct the problem, terminate sampling.

5. After sampling, cap each end of the filter cassette firmly.

6. Record sample identity and all relevant sample data such as sample flow rate and collection time.

7. With each batch of ten samples, submit one filter from the same lot of filters used for sample collection. This filter must be subjected to exactly the same handling as the samples except that no air is drawn through it. Label this filter as a blank.

Special Considerations

1. When interfering compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

2. Technical formulations usually contain 6-12% of the o,p' isomer of methoxychlor, which may cause an interference in the analytical method.

Bulk Samples

A bulk sample of the methoxychlor should be submitted to the laboratory in a glass container with a Teflon-lined cap. Label of the bulk sample should match air samples for identification purposes.

Shipping Instructions

The cassettes in which the samples are collected should be shipped in a suitable container designed to prevent damage in transit. Never transport, mail, or ship the bulk sample in the same container as the sample or blank tube.

Reference

Methoxychlor, NIOSH Method No. S371.

Backup Data Report No. S371

December 23, 1977

Substance:	Methoxychlor
OSHA Standard:	15 mg/cu m
Chemicals Used for Validation:	Methoxychlor, 99% from Alltech Associates (for preparing standards and spiked samples for analytical method validation). Methoxychlor 2EC, emulsifiable liquid, from Niagra Chemical Division of FMC (for generation of test atmospheres)

General

The procedure for collection and analysis of air samples of methoxychlor is described in NIOSH Method No. S371. This method consists of collection of the sample on glass fiber filters, extraction with iso-octane, and analysis of the resulting solution by gas chromatography.

This method has been tested for validity for a 100-liter air sample, using the criteria for validation outlined in Reference 1. Using these criteria, the absolute total error (sampling and analysis) is less than 25% at the OSHA standard level 95% of the time.

The protocol for validation of this method was to:

Analyze 18 samples (6 each at 0.5X, 1X, and 2X the OSHA standard) spiked with the appropriate amounts of methoxychlor to represent 100-liter air samples.

Analyze 18 samples collected from dynamically generated test atmospheres (6 samples collected at each of 0.5X, 1X, and 2X the OSHA standard).

Determine collection efficiency of the glass fiber filters.

Test the storage stability of six collected samples.

Assess the precision and accuracy of the method.

Details of these procedures are discussed below.

Analysis

A description of the method of analysis is given in NIOSH Method No. S371. The results of the analytical method recovery tests are in Table S371-4.

The appropriate aliquot (20, 40, and 80 microliters) of a 37.5 mg/ml solution of methoxychlor in acetone was added to 37-mm Gelman Type AE glass fiber filters. Methoxychlor was extracted from the filter with iso-octane and analyzed by gas chromatography using an electrolytic conductivity detector.

The sensitivity of the method for the instrumental conditions used during the validation study of a 200 microgram/ml standard resulted in a peak whose height was 60% of full scale when the detector bridge attenuation was 4 and the electronic integrator attenuation was 64.

The detection limit of the analytical method is estimated to be less than 50 ng, corresponding to a 15-microliter aliquot of a 3.3 nanogram/microliter standard.

Sampling and Analysis

Samples of methoxychlor in air were generated by the procedure described in Attachments A and B and collected as described in Method No. S371. The results of the sampling and analysis experiments are presented in Table S371-5.

A 22 g/liter solution of methoxychlor in toluene was used in the aspiration system for the generation of methoxychlor. To obtain the desired concentration, a set of generation conditions were chosen, and 15-minute samples from the 2X chamber were collected and analyzed. The results of the analyses were used to determine the conditions necessary to obtain the required concentration. When the desired concentration was reached, six samples were collected simultaneously each at the 2X, 1X, and 0.5X levels. Six additional samples were collected at the 1X level for storage stability tests.

The estimated average size of the particles was less than 1 micron diameter.

Samples were collected for 72 minutes at a flow rate of approximately 1.4 liters per minute.

Collection Efficiency

Collection efficiency tests were conducted at 30.9 mg/cu m (as determined by the independent method). The samples were collected using a glass fiber filter connected in series to a backup filter and midget bubbler. The bubbler contained 10 ml of iso-octane. The generation conditions used were the same as described under the Sampling and Analysis Section. Samples were collected for 72 minutes at a flow rate of approximately 1.4 liters per minute. The results of the collection efficiency tests are presented in Table S371-1.

Table S371-1

Collection Efficiency Tests

mg found in front filter	mg found in second filter	mg found in midget bubbler	Collection Efficiency
2.896	N.D.**	N.D.**	1.00
2.851	N.D.	N.D.	1.00
2.908	N.D.	N.D.	1.00
2.957	N.D.	N.D.	1.00
2.926	N.D.	N.D.	1.00
2.938	N.D.	N.D.	1.00

** N.D. = Not detected. Detection limit was 0.050 mg/filter.

From the above data, no correction for collection efficiency is necessary.

Storage Stability

A storage stability test was conducted to assess whether methoxychlor could be successfully stored for at least a week after collection. Twelve samples were collected simultaneously at 1X the OSHA standard. (The actual concentration was 15.36 mg/cu m as determined by the independent method). The generation conditions described under the Sampling and Analysis Section were used. The samples were collected for 72 minutes at an average flow rate of 1.4 liter per minute. Six samples were analyzed 3 days after collection of samples. The remaining six samples were analyzed 10 days after collection of the samples. All filters were stored in filter cassettes until the samples were analyzed. The results of the storage stability test are presented in Table S371-2.

Table S371-2

Storage Stability Test

	Stored 3 days mg/cu m	Stored 10 days mg/cu m
	15.52	14.50
	15.41	14.82
	15.83	15.43
	15.92	15.29
	16.09	15.16
	15.80	14.81
mean	15.76	15.00
std dev	.25	.35
CV	0.016	0.023

The criterion for acceptance was that the mean of the six samples stored at room temperature for seven days should be ±10% of the mean of the samples at the beginning of the storage period. The two means in the above table compare within 5%; thus, the storage stability was adequate.

Independent Method

An independent method of measuring the concentration of methoxychlor was conducted so that the results from the validated method could be compared. For this method, samples were collected on mixed cellulose ester membrane filters (37-mm diameter, 0.8 micrometer pore size). The test atmosphere was generated from a 22 g/liter solution of methoxychlor in toluene, and samples were collected for 72 minutes at an average flow rate of 1.4 liters per minute. These samples were analyzed by extracting the filters with iso-octane and by analyzing by gc using an electrolytic conductivity detector. The concentration of methoxychlor found using the independent method at the three generated levels are given in Table S371-3.

Table S371-3

Independent Method

Level	mg found	Liters		mg/cu m
2X	2.94	94.4		31.1
	2.96	96.0		30.8
	2.98	96.3		30.9
			mean	30.9
1X	1.568	102.4		15.31
	1.580	102.5		15.42
			mean	15.36
0.5X	0.830	105.9		7.84
	0.785	103.9		7.56
			mean	7.70

Precision and Accuracy

The statistical procedures and a definition of the terms used are described in Reference 2.

Bartlett's test for homogeneity of variances was applied to the coefficients of variation of 0.5X, 1X, and 2X the OSHA standard for generated samples. The data (Table S371-5) gave a chi squared value of 2.71. Thus, Bartlett's test is passed and it is feasible to pool the coefficients of variation to calculate $\overline{CV}_T$.

The precision of the analytical method was assessed using the data in Table S371-4. The pooled Coefficient of Variation ($\overline{CV}_1$) for three sets of analytical samples was found to be 0.017.

Precision and accuracy of the total sampling and analytical method was evaluated using the data in Table S371-5 and the results from the storage stability and collection efficiency tests. The pooled Coefficient of Variation ($\overline{CV}_2$) for the three sets of samples collected from test atmospheres is 0.020.

Confidence in the accuracy of the tested method is established by the results of the collection efficiency test and the storage stability test, described above.

The total Coefficient of Variation ($\overline{CV}_T$) is 0.054.

Table S374-4

Data Sheet: Methoxychlor

Analysis

Level	0.5X			1X			2X		
	mg taken	mg found	A.M.R.	mg taken	mg found	A.M.R.	mg taken	mg found	A.M.R.
	0.749	0.699	0.933	1.498	1.458	0.973	2.997	2.921	0.975
	0.749	0.704	0.940	1.498	1.473	0.983	2.997	2.974	0.992
	0.749	0.720	0.961	1.498	1.423	0.950	2.997	3.039	1.014
	0.749	0.727	0.971	1.498	1.487	0.993	2.997	2.987	0.997
	0.749	0.727	0.971	1.498	1.513	1.010	2.997	2.981	0.995
	0.749	0.725	0.968	1.498	1.481	0.989	2.997	2.942	0.982
n =			6			6			6
mean			0.957			0.983			0.992
std dev			0.017			0.020			0.013
CV_1			0.018			0.020			0.013

$\overline{CV}_1$ 0.017

$CV_{A+\overline{AMR}}$ 0.018

$$\text{A.M.R.} = \text{Analytical Method Recovery} = \frac{\text{mg found}}{\text{mg taken}}$$

Table S371-5

Data Sheet: Methoxychlor

Sampling and Analysis

Test Level	Found mg	Found Liters	Found mg/cu m*	Taken mg/cu m	Recovery (%)
0.5X	0.828	107.5	7.70	7.70	
	0.826	105.9	7.80	7.70	
	0.839	105.1	7.98	7.70	
	0.795	102.2	7.78	7.70	
	0.793	107.3	7.39	7.70	
	0.798	105.9	7.54	7.70	
		n =	6		100.0
		mean	7.70		
		std dev	0.21		
		CV_2	0.027		
1X	1.656	106.7	15.52	15.36	
	1.621	105.2	15.41	15.36	
	1.678	106.0	15.83	15.36	
	1.653	103.8	15.92	15.36	
	1.717	106.7	16.09	15.36	
	1.716	108.6	15.80	15.36	
		n =	6		102.6
		mean	15.76		
		std dev	0.25		
		CV_2	0.016		
2X	2.896	94.0	30.8	30.9	
	2.851	95.9	29.7	30.9	
	2.908	95.9	30.3	30.9	
	2.957	97.1	30.5	30.9	
	2.926	96.3	30.4	30.9	
	2.938	96.0	30.6	30.9	
		n =	6		98.4
		mean	30.4		
		std dev	0.4		
$\overline{CV}_2$ 0.020		CV_2	0.013		

*All values have passed the Grubbs' outlier test at the 1% confidence level as described in Reference No. 2.

References

1. Contract 210-76-0123, National Institute for Occupational Safety and Health, Division of the Department of Health, Education and Welfare, U. S. Government.

2. Documentation of NIOSH Validation Tests, National Institute for Occupational Safety and Health, Cincinnati, Ohio (DHEW-NIOSH-Publication No. 77-185), 1977. Available from Superintendent of Documents, U. S. Government Printing Office, Washington, D.C., Order No. 017-033-00231-2.

Attachment A

Generation of Organic Particulates

Test atmospheres of organic particulates are generated by an aspiration/spray-dry technique. The aerosol generation system consists of a fluid aspirator, an impactor, a cyclone and a mixing chamber where solvent evaporates from the aerosol droplets. Several different aspirators are available.

Aerosols are produced by atomization of a solution of the analyte in a suitable solvent. Larger particles of atomized material are removed by impaction of the droplets on the walls of the vessel; all particles with diameters greater than two microns are removed by passing the aerosol through a cyclone.

The remaining droplets are mixed with solvent-free air in the mixing chamber. The residence time in the mixing chamber is sufficient for solvent evaporation to occur.

Generation of aerosols at the desired concentration is accomplished by adjusting the grams of analyte per liter of solvent and/or the flow of air through the aspirator and the amount of primary dilution air.

Attachment B

Generation of Test Atmospheres

The system for generating and collecting samples of vapor, inorganic/organic particulate, dusts, and fumes consists basically of a sample generator, a mixing and dilution section, and three sampling chambers. Samples are generated at a concentration 2X the OSHA standard, serial dilutions are made to 1X and 0.5X the standard, and samples are collected simultaneously at the three concentrations. A schematic of the generation system and associated components is presented in Figure 1.

The generation system is large enough to be used for polydispersed aerosols as well as for gases and vapors. The primary dilution chamber is 48 inches by 4 inches and may handle air flows up to 400 liters/minute. The large volume dilution chamber is important for several reasons. Even at high air flow rates, the velocity of particles is low to allow complete solvent evaporation in the generation of aerosols. The air velocity is also low enough to avoid impaction on the walls while great enough to prevent particle diffusion to the walls. For these same reasons, the sample rationing system is only 1 inch in diameter and handles a flow of only 52 liters/minute. Gravitational settling is avoided by maintaining a sufficient air velocity.

The sampling cones for the three chambers are 6-inch I.D. at the base (point of sample collection) and narrow to 1-inch I.D. at the point of attachment to the sample rationing system. A constant total air flow of 26 liters/minute through each cone causes a gradual reduction in aerosol velocity toward the point of sample collection. The air velocity at the collection point is 2.4 cm/sec. Isokinetic sampling is not attempted here since sampling will not be done in this manner in the field.

All portions of the generation system that come in contact with the test atmosphere are constructed of stainless steel or Teflon to avoid any contamination problems. Sections of the generation system at which dilution air is added are constructed such that incoming air forms a "high-velocity sheath" around the air/analyte mixture that is to be diluted. This sheath serves two functions. The dilution air sheath becomes increasingly less coherent and stable as it moves downstream of its point of entrance and hence is turbulently mixed with air/analyte test atmosphere. At the point of entrance of the dilution air stream, a Venturi effect accelerates the air/analyte mixture to a high velocity. The dilution air sheath also prevents interaction of the accelerated air/analyte stream with the walls of the chamber, thus eliminating a large source of aerosol loss by impaction.

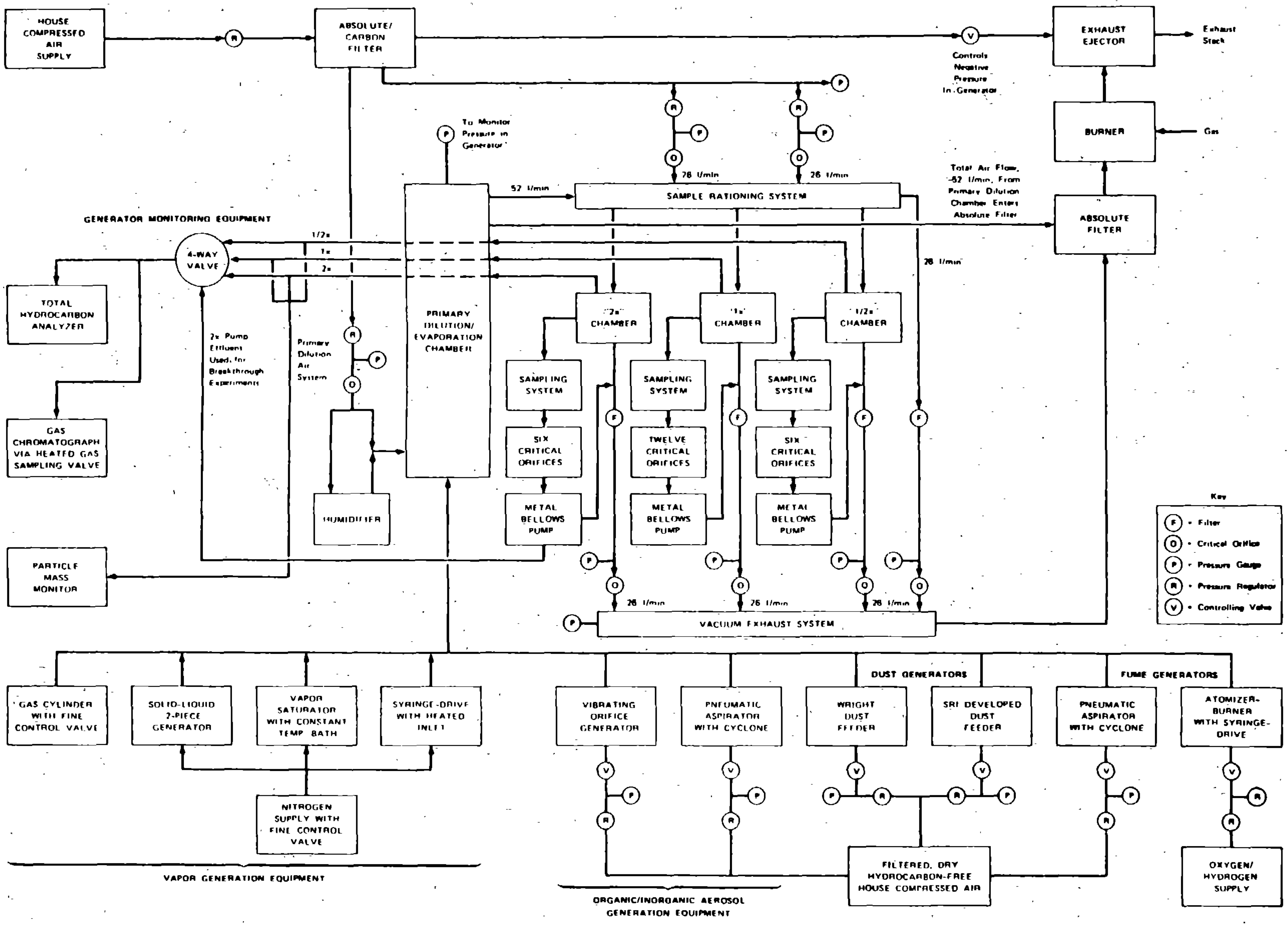

FIGURE S371-B1 SCHEMATIC OF SAMPLE GENERATION FACILITIES

The system being used to generate the initial concentrations of vapor, gas, or particulate is interfaced with the dilution apparatus at the primary dilution chamber. The output of the generator is diluted with the appropriate amount of air to obtain a concentration 2X the OSHA standard. Of the total amount of material generated at the 2X level, a flow of 52 liters/minute enters the rationing system. Under control of a vacuum exhaust orifice, material at the 2X level enters the first sampling chamber at a rate of 26 liters/minute. Downstream of the entrance to the first sampling chamber, dilution air is added (via a critical orifice) at a rate of 26 liters/minute. Thus, the flow of material at the 2X level that did not enter the first sampling chamber (26 liters/minute) is diluted with air at a flow rate of 26 liters/minute to a final concentration of 1X the OSHA level. Analyte at the 1X level then enters the second sampling chamber at a rate of 26 liters/minute. The remaining flow, 26 liters/minute, is diluted again with air at 26 liters/minute to achieve 0.5X the OSHA standard level. The analyte/air mixture at the 0.5X level is drawn into the third sampling chamber at 26 liters/minute. The remaining material in the rationing system not drawn into the sampling chambers is removed at a rate of 26 liters/minute by the fourth critical orifice in the vacuum exhaust system. This removal of test atmosphere volumes and addition of measured volumes of air thus achieves serial dilutions to 1X and 0.5X the OSHA standard level.

The dilution ratios from chamber to chamber can also be varied by simply changing the amount of dilution air that is added. This is particularly advantageous in generating aerosols, where wall deposition of particles in the rationing system can be offset by changing the rate of addition of dilution air.

The cylindrical section at the base of each sampling chamber contains the fittings necessary to collect samples, using any of a variety of sampling media--solid sorbent tubes, filters, liquid scrubbers, or a combination of these. Six to twelve samples each at three concentration levels can be collected simultaneously. A metal bellows vacuum pump is used for sampling from each chamber. Separate critical flow orifices are used for each sample. Air taken from the chamber during sampling is returned via the sampling pump exhaust line to the chamber outlet line, thus preserving the proper air flows during the time of sampling. The sampling rate therefore does not affect the concentration of material in any of the chambers.

The entire system is maintained at 1-inch water vacuum to prevent toxic materials from escaping into the laboratory. All exhaust air streams (from the vacuum exhaust system and excess from the primary dilution chamber) are fed into a combustion chamber where all toxic materials present are burned before entering the atmosphere.

Methylcyclohexanol*

Analyte:	Methylcyclohexanol	Method No.:	S374
Matrix:	Air	Range:	215-920 mg/cu m in a 12-L sample
OSHA Standard:	100 ppm (470 mg/cu m)	Precision ($\overline{CV}_T$):	0.063
Procedure:	Adsorption on charcoal, desorption with methylene chloride, GC	Validation Date:	1/20/78

1. Synopsis

1.1 A known volume of air is drawn through a tube containing activated coconut charcoal to trap methylcyclohexanol (Reference 11.1).

1.2 Methylcyclohexanol is desorbed from the charcoal with methylene chloride, and the sample is analyzed by gas chromatography.

2. Working Range, Sensitivity, and Detection Limit

2.1 This method was validated over the range of 215-920 mg/cu m at an atmospheric temperature of 25.5°C and atmospheric pressure of 761 mm Hg, using a 12-liter sample. This sample size is based on the capacity of the charcoal to collect vapors of methylcyclohexanol in air. The method may be capable of measuring smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method depends on the adsorptive capacity of the charcoal. This capacity may vary with the concentrations of methylcyclohexanol and other substances in the air. Breakthrough is defined as the time that the effluent concentration from the collection tube (containing 100 mg of charcoal) reaches 5% of the concentration in the test gas mixture. A breakthrough test was conducted at a concentration of 942 mg/cu m and 85% relative humidity. Breakthrough occurred in 116 minutes at an average sampling rate of 0.190 liter/minute. This corresponds to a breakthrough capacity of 20.8 mg and volume of 22.4 liters.

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* 50:50 mixture of the meta and para isomers of methylcyclohexanol

3. Interferences

3.1 When other compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

3.2 Any compound that has the same retention time as methylcyclohexanol at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered proof of chemical identity.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 215-920 mg/cu m was 0.063. This value corresponds to a 30 mg/cu m standard deviation at the OSHA standard level. Statistical information can be found in Reference 11.2. Details of the test procedures are found in Reference 11.3.

4.2 The Coefficient of Variation is a good measure of the accuracy of the method. Experiments performed in validation studies are described in Reference 11.3. In these experiments the desorption efficiency was greater than 0.919 for a loading of 2.710-11.31 mg on the sorbent. A correction was applied for this recovery. On the average the concentrations obtained at 0.5X, 1X, and 2X the OSHA standard level were 2.9% higher than the "true" concentration for 17 samples collected from dynamically generated test atmospheres. This difference does not represent a bias in the method, but rather a random variation from the experimentally determined "true" concentration. Storage stability studies indicated that the mean concentration of samples analyzed after 7 days compared within 0.2% to the mean concentration of samples analyzed immediately after collection. Thus, there are no known uncorrected sources of bias in the method.

5. Advantages and Disadvantages

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those that occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method.

5.2 One disadvantage of the method is that the amount of sample that can be taken is limited by the number of milligrams that the tube will hold before overloading. When the amount of methylcyclohexanol found on the backup section of the charcoal tube exceeds 25% of that found on the front section, the probability of sample loss exists.

5.3 The precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for using one tube only.

6. Apparatus

6.1 Personal Sampling Pump: A calibrated personal sampling pump whose flow rate can be determined within 5% at the recommended flow rate. Each personal sampling pump must be calibrated with a representative charcoal tube in the line to minimize errors associated with uncertainties in the volume sampled.

6.2 Charcoal Tubes. Glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing two sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The adsorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the adsorbing section. The pressure drop across the tube must be less than 1 inch of mercury at a flow rate of 0.2 liter/minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (12 ft x 1/8 in stainless steel) packed with 10% FFAP on 80/100 mesh Chromosorb W.

6.5 An electronic integrator or some other suitable method of determining peak areas.

6.6 Sample Containers: Two-milliliter glass sample containers with glass stoppers or Teflon caps.

6.7 Microliter Syringes: 10-microliter and other convenient sizes for preparing standards.

6.8 Pipets: Delivery type, 1.0-mL and other convenient sizes.

6.9 Volumetric Flasks: 10-mL and other convenient sizes for preparing standard solutions.

6.10 Stopwatch.

6.11 Manometer.

7. Reagents

Whenever possible, reagents should be ACS reagent grade or better.

7.1 m-Methylcyclohexanol.

7.2 p-Methylcyclohexanol.

7.3 Methylene chloride.

7.4 Methylcyclohexanol Stock Standard Solution. Prepare a standard solution of a 50:50 mixture of the m- and p-isomers of methylcyclohexanol.

7.5 Nitrogen, purified.

7.6 Hydrogen, prepurified.

7.7 Air, filtered, compressed.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed, thoroughly rinsed with tap water and distilled water, and dried.

8.2 Collection and Shipping of Samples

8.2.1 Immediately before sampling, break the ends of the charcoal tube to provide an opening at least one-half the internal diameter of the tube. All tubes must be from the same manufacturer's lot.

8.2.2 The smaller section of charcoal is used as a backup and should be positioned nearer the sampling pump.

8.2.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

8.2.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.

8.2.5 A sample size of 12 liters is recommended. Sample at a known flow rate of 0.01-0.2 liter/minute. Record the sampling time flow rate, and type of sampling pump used.

8.2.6 The temperature, pressure, and relative humidity of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.

8.2.7 The charcoal tube should be capped with plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.2.8 With each batch of ten samples, submit one tube from the same lot of tubes used for sample collection. This tube must be subjected to exactly the same handling as the samples except that no air is drawn through it. This tube should be labeled as the blank. A minimum of 18 extra charcoal tubes should be shipped for desorption efficiency determinations.

8.2.9 Capped tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.2.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the collected samples.

8.3 Analysis of Samples

8.3.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 2-mL stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another sample container vial. These two sections are analyzed separately.

8.3.2 Desorption of Samples. Prior to analysis, 1.0 mL of methylene chloride is pipetted into each sample container. Desorption should be done for 20 minutes. Tests indicated that this is adequate if the sample is agitated occasionally during this period. The sample vials should be capped as soon as the solvent is added to minimize volatilization. All work with methylene chloride should be performed in a hood.

8.3.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

60 mL/min (60 psig) nitrogen carrier gas flow
50 mL/min (24 psig) hydrogen gas flow to detector
500 mL/min (50 psig) air flow to detector
230°C injector temperature
230°C detector manifold temperature
140°C column temperature

A single peak for the meta and para isomers of methylcyclohexanol will be observed. A retention time of 5-6 minutes is to be expected for a mixture of the meta and para isomers of methylcyclohexanol under these conditions and using the column recommended in Section 6.4.

The method was validated for a mixture of the meta and para isomers of methylcyclohexanol. However, the response characteristics of the flame ionization detector and desorption efficiencies of the ortho isomer were found to be similar to the mixture of the meta and para isomers. Ortho-methylcyclohexanol elutes before the meta/para isomers and may appear as a shoulder peak in front of the meta/para peak. If this occurs, it may be necessary to alter chromatographic conditions to either merge the two peaks or separate them; this will be dependent on the concentraiton of the ortho isomer.

8.3.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or evaporation of solvent within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

8.3.5 The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and results are read from a standard curve prepared as discussed below.

8.4 Determination of Desorption Efficiency

8.4.1 The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine the fraction of the specific compound that is removed in the desorption process for a particular batch of charcoal.

8.4.2 Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 64-mm, 4-mm I.D. glass tube, flame sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of a 50:50 mixture of the meta and para isomers of methylcyclohexanol is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm. The density of methylcyclohexanol is 0.914 at 20°C. The amount injected is equivalent to that present in a 12-liter air sample at the selected level.

Six tubes at each of three levels (0.5X, 1X, and 2X the OSHA standard) are prepared in this manner and allowed to stand for at least overnight to assure complete adsorption of the methylcyclohexanol onto the charcoal. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of methylcyclohexanol into 1.0 mL of methylene chloride with the same syringe used in the preparation of the samples. These are analyzed with the samples. These standards are used to confirm the calibration of the gas chromatograph.

The desorption efficiency (D.E.) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

$$\text{D.E.} = \frac{\text{Average Weight recovered (mg) - Blank (mg)}}{\text{Weight added (mg)}}$$

The desorption efficiency is dependent on the amount of methylcyclohexanol collected on the charcoal. Plot the desorption efficiency versus weight of methylcyclohexanol found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standardization

A series of standards, varying in concentration over the range corresponding to approximately 0.1 to 3 times the OSHA standard for the sample under study, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg/1.0 mL versus peak area. Note: Since no internal standard is used in this method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of known day-to-day variations and variations during the same day of the FID response.

9.1 From the stock standard solution (Section 7.4), appropriate aliquots are withdrawn and dilutions are made in methylene chloride. Prepare at least 5 working standards to cover the range of 0.56-16.8 mg/mL. This range is based on a 12-liter sample.

9.2 Analyze the standards as per Section 8.3.

9.3 Prepare a standard calibration curve by plotting concentration of methylcyclohexanol in mg/1.0 mL versus peak area.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed because the standard curve is based on mg/1.0 mL methylene chloride and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

$$\text{mg} = \text{mg sample} - \text{mg blank}$$

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where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the weights found in the front and backup sections to determine the total weight of the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.4.2) for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{DE}}$$

10.5 For personal sampling pumps with rotameters only, the following correction should be made.

$$\text{Corrected Volume} = f \times t \left(\sqrt{\frac{P_1}{P_2} \times \frac{T_2}{T_1}}\right)$$

where:

f = flow rate sampled

t = sampling time

P_1 = pressure during calibration of sampling pump (mm Hg)

P_2 = pressure of air sampled (mm Hg)

T_1 = temperature during calibration of sampling pump (°K)

T_2 = temperature of air sampled (°K)

10.6 The concentration methylcyclohexanol in the air sampled can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4)} \times 1000 \text{ (liters/cu m)}}{\text{Corrected air volume sampled (liters) (Section 10.5)}}$$

10.7 Another method of expressing concentration is ppm.

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{\text{M.W.}} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (L/mole) at 25°C and 760 mm Hg
M.W. = molecular weight (g/mole) of methylcyclohexanol
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

11.1 White, L.D., et al., "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31, 225, (1970).

11.2 Documentation of NIOSH Validation Tests, National Institute for Occupational Safety and Health, Cincinnati, Ohio (DHEW-NIOSH Publication #77-185), 1977. Available from Superintendent of Documents, U. S. Government Printing Office, Washington, D.C., Order No. 017-033-00231-2.

11.3 Backup Data Report for Methylcyclohexanol, prepared under NIOSH Contract No. 210-76-0123.

Sampling Data Sheet No. S374

January 20, 1978

Substance

Methylcyclohexanol*

Standard

8-hour time-weighted average: 100 ppm (470 mg/cu m)

Analytical Method

A known volume of air is drawn through a tube containing activated coconut charcoal to trap methylcyclohexanol vapors present. The methylcyclohexanol is desorbed from the charcoal with methylene chloride, and the sample is separated and analyzed using a gas chromatograph with a flame ionization detector. The method has been validated over the range of 215-920 mg/cu m for a 12-liter sample at 25.5°C and 761 mm Hg atmospheric temperature and pressure. A detailed description of the sampling and analytical method is given in the method referenced below.

Sampling Equipment

Sampling equipment includes a calibrated personal sampling pump whose flow can be determined accurately (±5%) at 0.2 liter/minute. A charcoal tube (7-cm long with a 6-mm O.D. and a 4-mm I.D.), containing two sections of 20/40 mesh activated coconut charcoal separated by a 2-mm portion of urethane foam, is used to collect the samples. The front section of the tube contains 100 mg of charcoal, and the back section contains 50 mg.

Sample Size

A sample size of 12 liters is recommended. Sample at a known flow rate of 0.01-0.2 liter/minute.

Sampling Procedure

1. Immediately before sampling, the ends of the charcoal tube should be broken so as to provide an opening at least one-half the internal diameter of the tube. All tubes must be from the same manufacturer's lot.
2. The smaller section of charcoal is used as a backup and should be positioned nearer the sampling pump. The charcoal tube should be

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* 50:50 mixture of the meta and para isomers of methylcyclohexanol.

placed in a vertical position during sampling to avoid channeling and subsequent premature breakthrough of methylcyclohexanol.

3. Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.

4. Set the flow rate as accurately as possible using the manufacturer's directions. Record the temperature, relative humidity, and pressure of the atmosphere being sampled. If the pressure reading is not available, record the elevation. Also report the type of sampling pump that is used.

5. The charcoal tubes should be capped individually with plastic caps immediately after sampling. Masking tape is the only suitable substitute for sealing the tubes. Under no circumstances should rubber caps be used.

6. With each batch of ten samples, submit one charcoal tube from the same lot of tubes used for sample collection. This tube must be subjected to exactly the same handling as the samples except that no air is drawn through it. Label this tube as a blank. Information on the batch number of the charcoal must be supplied. A minimum of 18 extra charcoal tubes should be shipped for desorption efficiency determinations.

Special Considerations

1. When other compounds are known or suspected to be present in the air, such information, including their suspected identities should be transmitted with the sample.

2. Due to the high resistance of the charcoal tube, this sampling method places a heavy load on the sampling pump. Therefore, no more than eight hours of sampling should be done without first fully recharging the battery.

3. The volume recommended is based on high humidity breakthrough tests. If condensation of water occurs in the tube, the substance will not be trapped quantitatively.

Bulk Sample

A bulk sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap.

Shipping Instructions

Capped charcoal tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping. Never transport, mail, or ship the bulk sample in the same container as the sample or blank tube.

Reference

Methylcyclohexanol, NIOSH Method No. S374.

Backup Data Report No. S374

January 20, 1978

Substance: Methylcyclohexanol*

OSHA Standard: 100 ppm (470 mg/cu m)

Chemicals Used for Validation: m-Methylcyclohexanol and p-methylcyclohexanol, 99% Aldrich Chemical Company

General

The procedure for collection and analysis of air samples of methylcyclohexanol is described in NIOSH Method No. S374. This method consists of collection of the sample on activated coconut charcoal, desorption with methylene chloride, and analysis of the resulting solution by gas chromatography.

This method has been tested for validity for a 12-liter air sample, using the criteria for validation outlined in Reference 1. Using these criteria, the absolute total error (sampling and analysis) is less than 25% at the OSHA standard 95% of the time.

The protocol used for testing this method was to:

Analyze 18 samples (6 each at 0.5X, 1X, and 2X the OSHA standard) spiked with the appropriate amounts of methylcyclohexanol to represent 12-liter air samples.

Analyze 18 samples collected from dynamically generated test atmospheres (6 samples collected at each of 0.5X, 1X, and 2X the OSHA standard).

Test the breakthrough capacity of activated coconut charcoal at high relative humidity.

Test the storage stability of six collected samples.

Assess the precision and accuracy of the method.

Details of these procedures are discussed below.

Analysis

A description of the method of analysis is given in NIOSH Method No. S374. The desorption efficiency must be at least 75% for a loading

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* 50:50 mixture of the meta and para isomers of methylcyclohexanol.

equivalent to a collection at the OSHA standard. The results of the desorption efficiency tests are in Table S374-4 of this report. A 50:50 mixture of the meta and para isomers of methylcyclohexanol was used in the desorption efficiency tests.

The sensitivity of the method for the instrumental conditions used during the validation study of a 11.2 mg/mL standard resulted in a peak whose height was 2/3 of full scale when the detector bridge attenuation was 64 and the electronic integrator attenuation was 16.

The detection limit of the analytical method is estimated to be less than 80 ng, corresponding to a 5-microliter injection aliquot of a 16 micrograms/mL standard.

Sampling and Analysis

Test atmospheres of a 50:50 mixture of the meta and para isomers of methylcyclohexanol were generated using the vapor generator described in Attachment A. The generator was submerged in a thermostated water bath. The vapor was carried out of the first stage of the generator by a stream of nitrogen. It was diluted with air immediately downstream from the heated zone to obtain 2X the OSHA standard. Dilutions to 1X and 0.5X the OSHA standard were made as described in Attachment B. A total hydrocarbon analyzer, which was calibrated with bag standards, was used to monitor the stability of the concentration of methylcyclohexanol in each of the test chambers. The samples were collected as described in Method S374 using sampling tubes packed with activated coconut charcoal, SKC Lot 105.

Six samples were collected from each chamber for 60 minutes at an average flow rate of 0.2 liter/minute to obtain 12-liter air samples. An additional six samples were collected at 1X the OSHA standard and were used for storage stability tests. The results of the analyses of the samples used for the validation study are in Table S374-5.

In addition, the backup sections of the sampling tubes at the 2X level were analyzed and found to contain less than the limit of detection, which was estimated at 2.0 mg/cu m.

Storage Stability Study

A study was done to assess whether methylcyclohexanol can be successfully stored for one week after collection. A second set of six samples at 1X the OSHA standard was collected at the same time as the samples that were used for immediate analysis. Samples were collected for 60 minutes at an average flow rate of 0.2 liter/minute. These sample tubes were capped and stored on the laboratory bench for one week before analysis. The results are presented in Table S374-1.

Table S374-1

Storage Stability Study

	Samples Stored One Day After Generation (mg/cu m)	Samples Stored for Eight Days After Generation (mg/cu m)
	452	448
	448	449
	431	452
	473	465
	451	430
	472	471
mean	454	453
std dev	15	14
CV	0.034	0.032

The criterion for acceptance was that the mean of the six samples stored at room temperature for one week should be within ±10% of the mean of the set analyzed at the beginning of the storage period. The two means compare within 0.2%; thus, the storage stability was adequate.

Breakthrough Tests

A breakthrough test was performed at a relative humidity of 85%. Details of the method of generating atmosphere containing high relative humidities are given in Attachment C. The test atmosphere was generated using the apparatus described in Attachment A.

Breakthrough is defined as the time that the effluent concentration from the collection tube (containing 100 mg of charcoal) reaches 5% of the concentration in the test gas mixture.

The breakthrough time was measured by testing in parallel six sampling tubes, each containing 100 mg of charcoal. The tubes were placed in the sample generation apparatus. The test atmosphere was caused to flow through each tube at the flow rates to be used during sample collection. Sampling flow rates were regulated with the use of 0.006-inch orifices for a rate of 0.19 liter/minute. The orifices were connected to a manifold, which was evacuated to about 24 inches of Hg using a metal bellows pump. This pump was selected, because it does not leak and is constructed entirely of stainless steel; therefore, it will not alter the composition of the test atmosphere.

A total hydrocarbon analyzer, which was calibrated with bag standards, was used to monitor the concentration of the generator during the breakthrough test.

Breakthrough occurred in 116 minutes at an average sampling rate of 0.19 liter/minute and concentration of 942 mg/cu m. This corresponds to a breakthrough capacity of 20.8 mg.

Discussion

Several experiments were performed with the 1-, 2-, 3-, and 4-isomers of methylcyclohexanol. A calibration curve was prepared for each isomer. Each curve was found to be linear in the range of 0.8-16 mg/mL in methylene chloride. Elution times were found to be.

	Seconds
1-methylcyclohexanol	210
2-methylcyclohexanol	290
3-methylcyclohexanol	334
4-methylcyclohexanol	327

A mixture of the 2, 3, and 4 isomers yielded two peaks which were not resolved. It was decided that a 50:50 mixture of the meta and para isomers be used in the validation study (References 2,3). Reference 3 describes the commercial product as a mixture of the meta and para isomers. Chromatographic conditions were established so that these isomers would elute as a single peak. If the field sample contains a significant amount of the ortho isomer, the chromatographic conditions may have to be altered to achieve a better degree of precision.

Desorption efficiency tests were performed using the meta, para, and ortho isomers of methylcyclohexanol. Three microliters of each isomer was spiked onto 100 mg of charcoal. The samples were desorbed with 1 mL of methylene chloride. The results are presented in Table S374-2.

Table S374-2

Desorption Efficiency for o-, m-, and p-
Isomers of Methylcyclohexanol

Ortho			Meta			Para		
mg taken	mg found	D.E.	mg taken	mg found	D.E.	mg taken	mg found	D.E.
2.76	2.62	0.949	2.71	2.50	0.922	2.71	2.55	0.941
2.76	2.58	0.935	2.71	2.56	0.945	2.71	2.59	0.956
2.76	2.52	0.913	2.71	2.55	0.941	2.71	2.56	0.945
2.76	2.60	0.942	2.71	2.57	0.948	2.71	2.54	0.937
2.76	2.63	0.953	2.71	2.54	0.937	2.71	2.56	0.945
2.76	2.66	0.964	2.71	2.48	0.915	2.71	2.34	0.863
mean		0.943			0.935			0.931
std dev		0.018			0.013			0.034
CV		0.019			0.014			0.036

The above results show that the desorption efficiencies of the three isomers of methylcyclohexanol agree.

Independent Method

The concentration of methylcyclohexanol in each test chamber of the generator was monitored during generation with a total hydrocarbon analyzer which was calibrated with bag standards prepared at the 2X level. The 2X bag standards were prepared by combining 10 microliters of a 50:50 mixture of the meta and para isomers of methylcyclohexanol with air at a flow rate of 0.91 liter/minute for 636 seconds at 25.5°C and 761 mm Hg in a Tedlar plastic bag to give a concentration of 934 mg/cu m. The data are summarized in Table S374-3.

Table S374-3

Sample Generator Data: Methylcyclohexanol

Hydrocarbon Analyzer Chart Readings

	2X Bags	2X Chamber	1X Chamber	0.5X Chamber
	78.8	77.8	38.3	18.1
	80.8	79.8	38.8	18.8
	82.3	80.8	39.8	18.8
mean	80.6	79.5	39.0	18.6
mg/cu m	934	921	452	215

Precision and Accuracy

The statistical procedures and a definition of the terms used are described in Reference 4.

Bartlett's test for homogeneity of variances was applied to the coefficients of variation of 0.5X, 1X, and 2X the OSHA standard for generated samples. The data (Table S374-5) gave a chi squared value of 2.11. Thus, Bartlett's test is passed and it is feasible to pool the coefficients of variation to calculate $\overline{CV}_T$.

The precision of the analytical method was assessed using the data in Table S374-4. The pooled Coefficient of Variation ($\overline{CV}_1$) for three sets of analytical samples was found to be 0.018.

Precision and accuracy of the total sampling and analytical method was evaluated using the data in Table S374-5 and the results obtained from breakthrough tests and storage stability tests. The pooled Coefficient of Variation ($\overline{CV}_2$) for the three sets of samples collected from test atmospheres is 0.038. To obtain a measure of the accuracy of the method, the mean value of the concentration found by analysis at each level was compared with the value for the concentration taken.

The average recovery (concentration found divided by concentration taken) for all three levels was 102.9%. The value for the taken concentration was obtained as described under the Independent Method Section. The difference between the taken and found concentrations is considered to result from experimental uncertainties in the value for the taken concentration and does not represent a bias in the method. Further confidence in the accuracy of the tested method is established by the results of the breakthrough test and the storage stability test, described above.

The total Coefficient of Variation $(\overline{CV}_T)$ is 0.063.

Table S374-4

Data Sheet: Methylcyclohexanol*

Analysis

Level	0.5X			1X			2X	
mg taken	mg found	D.E.	mg taken	mg found	D.E.	mg taken	mg found	D.E.
2.710	2.613	0.964	5.61	5.14	0.916	11.31	10.71	0.947
2.710	2.480	0.915	5.61	5.22	0.930	11.31	10.76	0.951
2.710	2.542	0.938	5.61	5.22	0.930	11.31	10.88	0.962
2.710	2.458	0.907	5.61	5.23	0.932	11.31	10.81	0.956
2.710	2.426	0.895	5.61	5.24	0.934	11.31	11.01	0.973
2.710	2.426	0.895	5.61	5.25	0.936	11.31	10.83	0.958

	0.5X	1X	2X
n =	6	6	6
mean	0.919	0.930	0.958
std dev	0.027	0.007	0.009
CV_1	0.029	0.008	0.009

$\overline{CV}_1$ 0.018

$\overline{CV}_{A+\overline{DE}}$ 0.019

The equation D.E. = $0.945 - e^{-1.434 \times \text{mg found}}$ was used to calculate corr. mg in the Sampling and Analysis table. A program for the use of this equation is given in Reference 5. This equation should only be used for samples in the range of 0.5X to 2X the OSHA standard.

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* 50:50 mixture of the meta and para isomers of methylcyclohexanol.

Table S374-5

Data Sheet: Methylcyclohexanol*

Sampling and Analysis

Test Level	Found				Taken	Percent Recovery
	mg	Corr mg	Liters	mg/cu m**	mg/cu m	
	2.170	2.411	11.46	210.4	215	
	2.434	2.660	11.40	233.3	215	
	2.322	2.554	11.80	216.4	215	
	2.497	2.723	11.40	238.9	215	
	2.462	2.688	11.64	230.9	215	
	Sample was lost.					
			n = 5			
			mean	226.0		105.1
			std dev	12.0		
			CV_2	0.053		
	4.84	5.13	11.34	452	452	
	4.95	5.24	11.70	448	452	
	4.81	5.10	11.82	431	452	
	5.04	5.34	11.28	473	452	
	5.03	5.33	11.82	451	452	
	5.21	5.52	11.70	472	452	
			n = 6			
			mean	454		100.4
			std dev	16		
			CV_2	0.035		
	9.71	10.28	11.04	931	921	
	10.74	11.36	12.18	933	921	
	9.87	10.44	10.86	961	921	
	9.94	10.52	11.28	933	921	
	10.36	10.96	11.46	956	921	
	10.94	11.58	11.64	995	921	
			n = 6			
			mean	952		103.4
			std dev	25		
$\overline{CV}_2$ 0.038			CV_2	0.026		

* 50:50 mixture of the meta and para isomers of methylcyclohexanol.

** All values have passed the Grubbs' outlier test at the 1% confidence level as described in Reference No. 4.

References

1. Contract 210-76-0123, National Institute for Occupational Safety and Health, Division of the Department of Health, Education and Welfare, U. S. Government.

2. Failure Report No. S374 for Methylcyclohexanol, prepared under NIOSH Contract No. CDC-99-74-45.

3. F. A. Patty, Industrial Hygiene and Toxicology, Vol. II, 2nd Ed., Interscience, N. Y., 1963.

4. Documentation of NIOSH Validation Tests, National Institute for Occupational Safety and Health, Cincinnati, Ohio (DHEW-NIOSH Publication #77-185), 1977. Available from Superintendent of Documents, U. S. Government Printing Office, Washington, D.C., Order No. 017-033-00231-2.

5. Sampson, Paul, "Non-Linear Least Squares," Biomedical Computer Programs, W. J. Dixon, Ed., p. 387, (University of California Press, Los Angeles, California, 1973).

Attachment A

Vapor Generation System

Test atmospheres of organic vapors can be generated with an apparatus described in Reference No. 1, which describes a method for measuring liquid vapor pressure.

The vapor generator was adapted from the apparatus described in Reference No. 1. A schematic diagram of this vapor generator is shown in Figures S374-1 and S374-2. The vapor generator consists of two sections--a generating section (Figure S374-1) and a diluting section (Figure S374-2) which are connected by a ground glass joint.

The generating section (Figure S374-1) consists of a pyrex glass tube which is 2.4 cm in diameter and 19.5 cm long. A coarse glass frit is sealed in the bottom of the tube. The bottom of this tube is connected to a 7-mm O.D. glass tube which is bent 180° and extends up until it is nearly as high as the larger tube. The sample, which may be either a liquid or low melting solid, is introduced into the large tube. This part of the apparatus is immersed in a thermostated bath with the analyte level below the bath level. Nitrogen gas is introduced through the small tube and passes through the frit. The small bubbles, which form at the frit, rise through the liquid and become saturated or nearly saturated with the vapor of the liquid. The bath temperature and the flow of nitrogen determine the actual amount of vapor generated. Increasing either the nitrogen flow or the bath temperature, increases the amount of vapor generated.

The diluting section (Figure S374-2) of the vapor generator consists of a pyrex glass tube which is 2.4 cm in diameter and 13 cm high. The dilution air is introduced through a 7-mm O.D. glass tube connected to the side of the diluting tube. Sufficient air is added to dilute the vapor in nitrogen to the desired concentration. Vapor saturation of the air stream must not be exceeded to produce a well-mixed stream.*

The equations given in Reference No. 1 can be used to determine the approximate vapor concentration in the saturated nitrogen stream. The actual concentration of the vapor in each chamber in the generator should be measured using either a Beckman Model 402 total hydrocarbon analyzer or a gas chromatograph. Bag standards are used to calibrate the instrument used.

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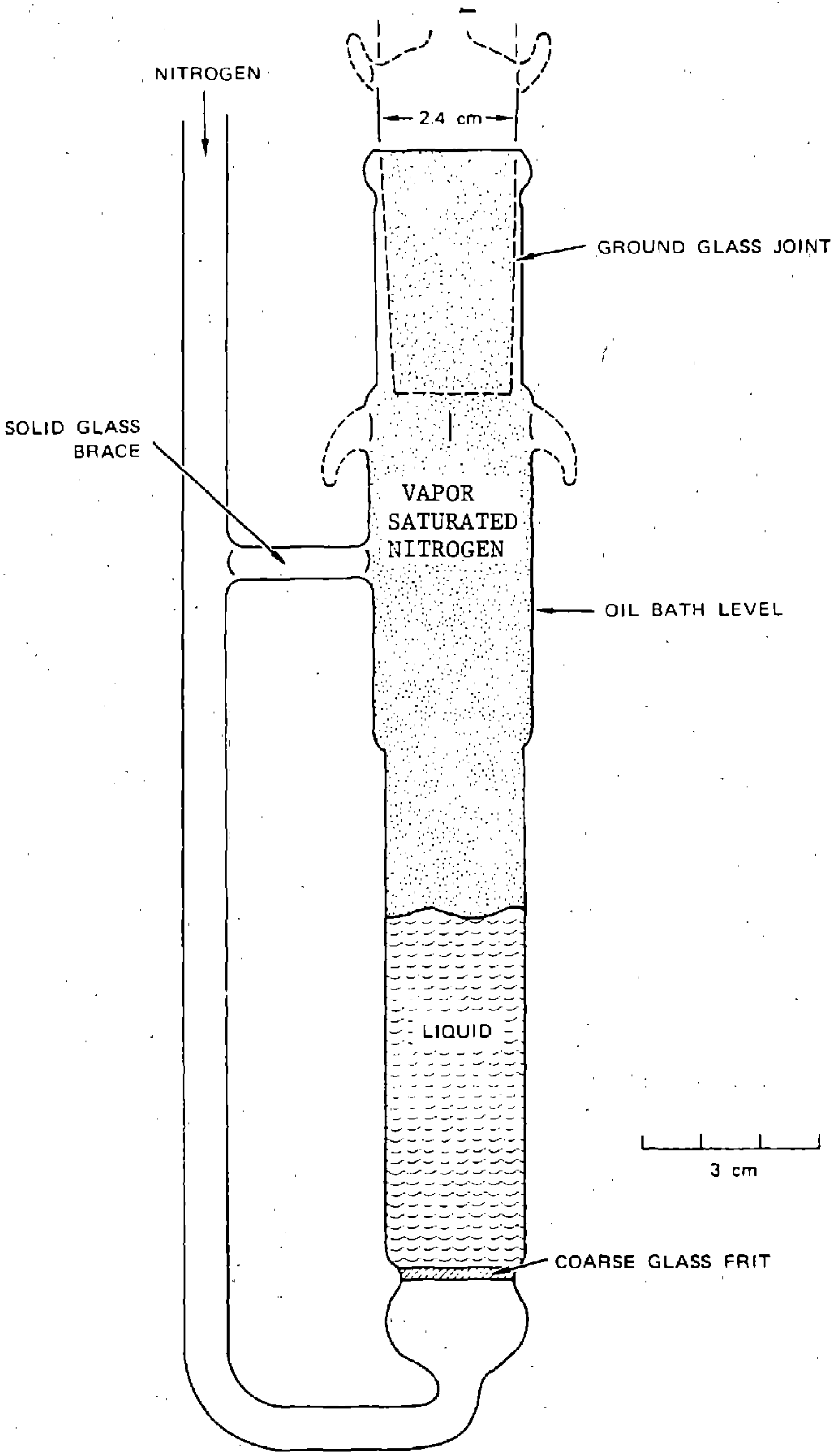
1. Physical Methods of Chemistry, Part V, A. Weissberger and B. W. Rossiter, eds., (John Wiley & Sons, 1971), 61-66.

*If the vapor saturation concentration is exceeded, particles will be formed in the cool air stream.



NOTE Apparatus is immersed in a thermostated bath.

FIGURE S374-A1 VAPOR GENERATOR (generating section)

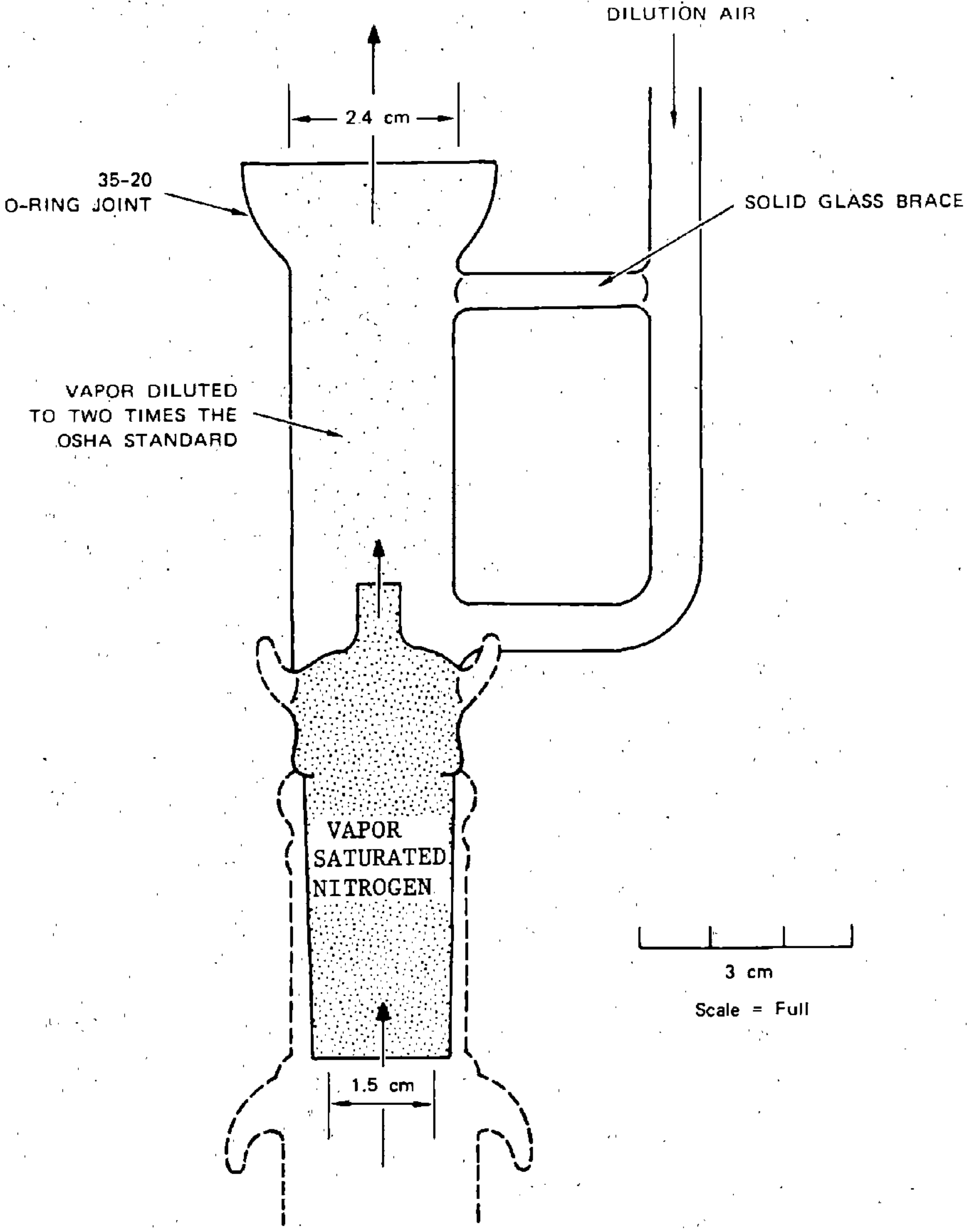


FIGURE S374-A2 VAPOR GENERATOR (diluting section)

Attachment B

Generation of Test Atmospheres

The system for generating and collecting samples of vapor, inorganic/organic particulate, dusts, and fumes consists basically of a sample generator, a mixing and dilution section, and three sampling chambers. Samples are generated at a concentration 2X the OSHA standard, serial dilutions are made to 1X and 0.5X the standard, and samples are collected simultaneously at the three concentrations. A schematic of the generation system and associated components is presented in Figure 1.

The generation system is large enough to be used for polydispersed aerosols as well as for gases and vapors. The primary dilution chamber is 48 inches by 4 inches and may handle air flows up to 400 liters/minute. The large volume dilution chamber is important for several reasons. Even at high air flow rates, the velocity of particles is low to allow complete solvent evaporation in the generation of aerosols. The air velocity is also low enough to avoid impaction on the walls while great enough to prevent particle diffusion to the walls. For these same reasons, the sample rationing system is only 1 inch in diameter and handles a flow of only 52 liters/minute. Gravitational settling is avoided by maintaining a sufficient air velocity.

The sampling cones for the three chambers are 6-inch I.D. at the base (point of sample collection) and narrow to 1-inch I.D. at the point of attachment to the sample rationing system. A constant total air flow of 26 liters/minute through each cone causes a gradual reduction in aerosol velocity toward the point of sample collection. The air velocity at the collection point is 2.4 cm/second.

All portions of the generation system that come in contact with the test atmosphere are constructed of stainless steel or Teflon to avoid any contamination problems. Sections of the generation system at which dilution air is added are constructed such the incoming air forms a "high-velocity sheath" around the air/analyte mixture that is to be diluted. This sheath serves two functions. The dilution air sheath becomes increasingly less coherent and stable as it moves downstream of its point of entrance and hence is turbulently mixed with air/analyte test atmosphere. At the point of entrance of the dilution air stream, a Venturi effect accelerates the air/analyte mixture to a high velocity. The dilution air sheath also prevents interaction of the accelerated air/analyte stream with the walls of the chamber, thus eliminating a large source of aerosol loss by impaction.

The system being used to generate the initial concentrations of vapor, gas, or particulate is interfaced with the dilution apparatus at the primary dilution chamber. The output of the generator is diluted with the appropriate amount of air to obtain a concentration 2X the OSHA standard. Of the total amount of material generated at the 2X level, a flow of 52 liters/minute enters the rationing system. Under control of a vacuum exhaust orifice, material at the 2X level enters the first sampling chamber at a rate of 26 liters/minute. Downstream of the entrance to the first sampling chamber, dilution air is added (via a critical orifice) at a rate of 26 liters/minute. Thus the flow of material at the 2X level that did not enter the first sampling chamber

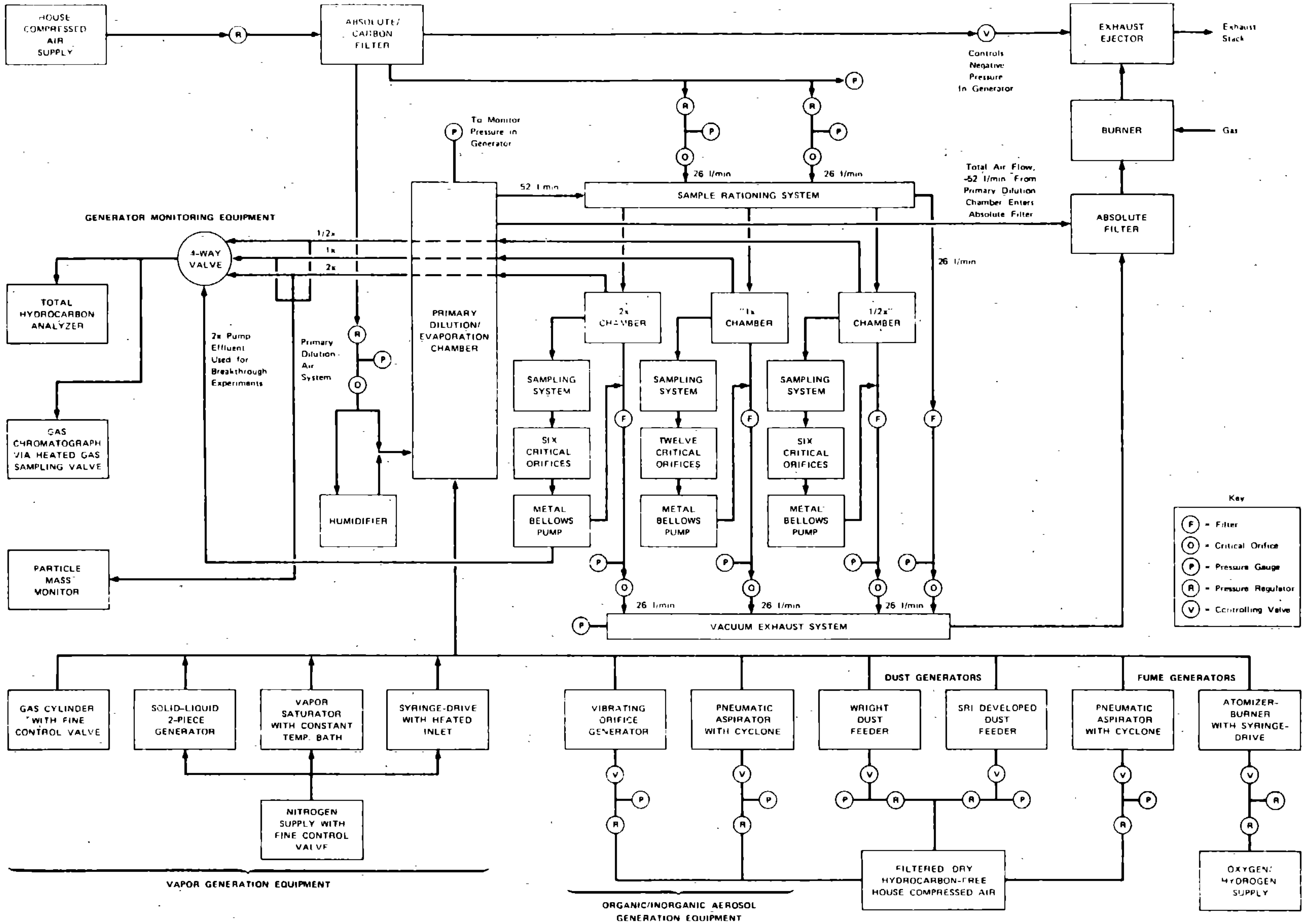


FIGURE S374-B1 SCHEMATIC OF SAMPLE GENERATION FACILITIES

(26 liters/minute) is diluted with air at a flow rate of 26 liters/minute to a final concentration of 1X the OSHA standard level. Analyte at the 1X level then enters the second sampling chamber at a rate of 26 liters/minute. The remaining flow, 26 liters/minute is diluted again with air at 26 liters/minute to achieve 0.5X the OSHA standard level. The analyte/air mixture at the 0.5X level is drawn into the third sampling chamber at 26 liters/minute. The remaining material in the rationing system not drawn into the sampling chambers is removed at a rate of 26 liters/minute by the fourth critical orifice in the vacuum exhaust system. This removal of test atmosphere volumes and addition of measured volumes of air thus achieves serial dilutions to 1X and 0.5X the OSHA standard level.

The dilution ratios from chamber to chamber can also be varied by simply changing the amount of dilution air that is added. This is particularly advantageous in generating aerosols, where wall deposition of particles in the rationing system can be offset by changing the rate of addition of dilution air.

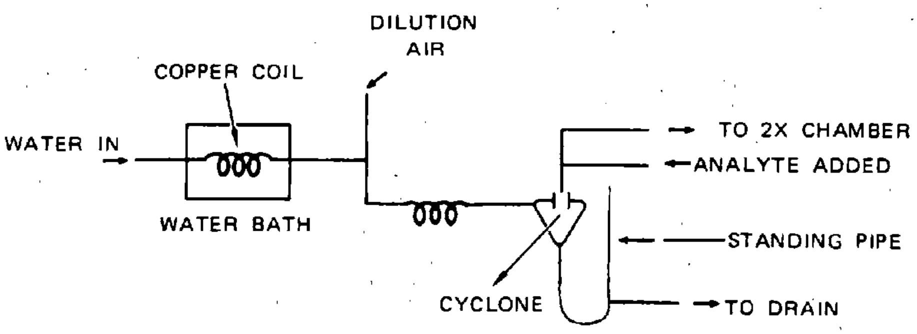
The cylindrical section at the base of each sampling chamber contains the fittings necessary to collect samples, using any of a variety of sampling media--solid sorbent tubes, filters, liquid scrubbers, or a combination of these. Six to twelve samples each at three concentration levels can be collected simultaneously. A metal bellows vacuum pump is used for sampling from each chamber. Separate critical flow orifices are used for each sample. Air taken from the chamber during sampling is returned via the sampling pump exhaust line to the chamber outlet line, thus preserving the proper air flows during the time of sampling. The sampling rate therefore does not affect the concentration of material in any of the chambers.

The entire system is maintained at 1-inch water vacuum to prevent toxic materials from escaping into the laboratory. All exhaust air streams (from the vacuum exhaust system and excess from the primary dilution chamber) are fed into a combustion chamber where all toxic materials present are burned before entering the atmosphere.

Attachment C

Generation of Known Humidity Test Atmospheres

A diagram of the apparatus used for generating high humidity atmospheres is shown below.



A regulated flow of tap water at approximately 15°C flows through a copper coil contained in a thermostated water bath. After emerging from the water bath it enters a 5-foot length of 5/16-inch Tygon tubing. The dilution air is introduced into this same tubing and becomes water saturated at the temperature of the bath. This water-air mixture passes into a cyclone, where excess water is removed from the air stream and drains from the bottom of the cyclone. The U-shaped tube and standing pipe provide a water seal at the bottom of the cyclone to prevent loss of air by this route. The humid air passes through the top of the cyclone. A controlled flow of the analyte enters the air stream at the outlet of the cyclone at a rate such that the 2X concentration is obtained.

The temperature of the water bath is kept 1°C lower than the temperature of the room. Thus, the air is saturated with water vapor at the lower temperature and reaches a relative humidity of less than 100% as it warms to room temperature after leaving the cyclone.

The relative humidity of the air in the sampling chamber is measured by the dry and wet bulb thermometer method. A flow of 32 liters/minute of the test atmosphere is drawn from the sampling chamber over the thermometers.

To ensure that a sufficiently high flow rate of air passes over the thermometers to give an accurate measurement, both thermometers are enclosed in glass tubing with an internal diameter of 11 mm.

From the readings of the relative temperatures of these two thermometers, the relative humidity at the temperature of the dry thermometer is found by consulting relative humidity tables.