50272-101

REPORT DOCUMENTATION PAGE	1. REPORT NO.	2.	3. PB84-243245

4. Title and Subtitle
Ten NIOSH-Analytical Methods - Formic Acid

5. Report Date
79/04/00

6.

7. Author(s)
Anonymous

8. Performing Organization Rept. No.

9. Performing Organization Name and Address
Division of Physical Sciences and Engineering, NIOSH, U.S. Department of Health and Human Services, Cincinnati, Ohio

10. Project/Task/Work Unit No.

11. Contract(C) or Grant(G) No.
(C)
(G)

12. Sponsoring Organization Name and Address
Same as box 9.

13. Type of Report & Period Covered

14.

15. Supplementary Notes

16. Abstract (Limit: 200 words)

The NIOSH validated method for the determination of formic-acid (64186) is presented. Twenty four liters of air (flow rate at 0.05 to 0.20 liters per minute) are drawn through two glass tubes connected in series containing 60/80 mesh Chromosorb 103 to trap formic-acid vapors. The contents of each tube are transferred to a 20 milliliter (ml) container and the sample is desorbed with 10ml deionized water. The desorbant is injected into an ion chromatograph equipped with an electrolytic conductivity detector. The height of the sample peak is measured. The concentration of formic-acid in the sample is determined by reference to a calibration curve obtained by analyzing standards having concentrations of 0.1 to 3 times the OSHA standard of 9 milligrams per cubic meter (mg/m3). Sample tubes are stored and analyzed immediately or 7 days after collection. Average sample concentrations after 7 days are 91.5 percent of the average concentration found immediately after collection. The useful range is 4.4 to 21.6mg/m3 formic-acid with a standard deviation of 0.7mg/m3. The detection limit is estimated to be 2 micrograms formic-acid per sample tube.

17. Document Analysis a. Descriptors

b. Identifiers/Open-Ended Terms
NIOSH-Publication, NIOSH-Author, NIOSH-Analytical-Method, Analytical-Method, Standards, Sampling, Standards-Completion-Program, SCP, Set-7, Chromatographic-analysis

c. COSATI Field/Group

18. Availability Statement:

19. Security Class (This Report)

21. No. of Pages
29

20. Security Class (This Page)

22. Price

Formic Acid

Analyte:	Formate Ion	Method No.:	S173
Matrix:	Air	Range:	4.4-21.6 mg/cu m
OSHA Standard:	5 ppm (9 mg/cu m)	Precision ($\overline{CV}_T$):	0.073
Procedure:	Adsorption on Chromosorb 103, desorption with deionized water, ion chromatography/electrolytic conductivity detection	Validation Date:	5/12/78

1. Synopsis

1.1 A known volume of air is drawn through two glass tubes connected in series containing Chromosorb 103 to trap formic acid vapors. A Teflon prefilter is connected in front of the Chromosorb 103 tubes to remove interfering formate salts.

1.2 Formic acid is desorbed from the Chromosorb 103 with deionized water and the sample is analyzed by ion chromatography using electrolytic conductivity detection.

2. Working Range, Sensitivity, and Detection Limit

2.1 This method was validated over the range of 4.4-21.6 mg/cu m at an atmospheric temperature of 23°C and atmospheric pressure of 759 mm Hg, using a 24-liter sample. 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 Chromosorb 103. This capacity may vary with the concentrations of formic acid and other substances in the air. Breakthrough is defined as the time that the effluent concentration from the collection tube (containing 50 mg of Chromosorb 103) reaches 5% of the concentration in the test gas mixture. Breakthrough did not occur after sampling for 302 minutes at an average sampling rate of 0.18 liter/minute and relative humidity of 85% and temperature of 22°C. The breakthrough test was conducted at a concentration of 25 mg/cu m.

2.3 The sensitivity of the method for the instrumental conditions used during the validation study was 7 μmho/cm/μg formate ion. In other words, a 100-microliter injection of a 22 microgram/mL solution of formic acid gave a peak whose height was 50% of full scale on a 1-volt recorder when the ion chromatograph was set on range 30 μmho/cm.

2.4 The detection limit of the analytical method is estimated to be 2 micrograms formic acid/sample tube. This corresponds to a 100-microliter aliquot of a 0.2 microgram/mL standard.

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 the formate ion at the operating conditions described in this method is an interference. Retention time data cannot be considered proof of chemical identity.

3.3 Formate esters may interfere only if collected by the sorbent and subsequently hydrolyzed to formic acid.

3.4 A Teflon prefilter is connected in front of the sampling tubes to remove formate salts which may interfere in the analysis of formic acid.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 4.4-21.6 mg/cu m was 0.073. This value corresponds to a 0.7 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 In validation experiments, this method was found to be capable of coming within ±25% of the "true value" on the average 95% of the time over the validation range. The concentrations obtained at 0.5X, 1X, and 2X the OSHA environmental limit averaged 3.8% lower than the dynamically generated test concentrations (n=16). The desorption efficiency was determined to be 1.002 for a collector loading of 106.4 micrograms. In storage stability studies, the mean of samples analyzed after 7 days were within 8.5% of the mean of samples analyzed immediately after collection. Experiments performed in the validation study are described in Reference 11.2.

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 or by use of the prefilter in front of the collection tubes. 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 formic acid found on the backup Chromosorb 103 tube exceeds 25% of that found on the front tube, 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 one set of tubes 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 is needed. Each personal sampling pump must be calibrated with a representative prefilter, front and backup Chromosorb 103 tube in the line to minimize errors associated with uncertainties in the volume sampled.

6.2 Prefilter Unit. The prefilter unit is used to collect interfering formate salts. It consists of a 13-mm filter holder and a 13-mm diameter/5-micrometer pore size Teflon filter.

6.3 Chromosorb 103 Tubes. Glass tube with both ends unsealed, 7-cm long with a 6-mm O.D. and a 4-mm I.D., containing 60/80 mesh Chromosorb 103*. The tube contains 50 mg of Chromosorb 103. A plug of silylated glass wool is placed at each end of the tube to retain the sorbent. Two tubes connected in series with a short piece of polyvinyl chloride tubing are used for sampling. The pressure drop across the prefilter and tubes must be less than 1 inch of mercury at a flow rate of 0.2 liter/minute.

Immediately prior to packing, the empty glass tubes should be rinsed with acetone and dried to eliminate the problem of Chromosorb 103 adhering to the walls of the glass tubes. The tubes are capped with plastic caps at each end.

6.4 Ion chromatograph** equipped with a 100-microliter sample loop and an electrolytic conductivity detector.

6.5 Columns: 3-mm I.D. x 150-mm long anion precolumn; 3-mm I.D. x 500-mm long anion analytical column; 6-mm I.D. x 250-mm long anion suppressor column.**

---

* Chromosorb 103 is a polymeric gas chromatographic column packing material which is manufactured by Johns-Manville Corp., Ken-Caryl Ranch, Denver, Colorado.

** Dionex Corp., Model 10 or 14, 1228 Titan Way, Sunnyvale, CA.

6.6 Filtration unit for protection of the anion analytical column from particulate contamination: 13-mm diameter/0.8 micrometer pore size cellulose ester membrane filter and holder.

6.7 Syringes: 10-mL with luer-lock or luer-slip connection.

6.8 Scintillation Vials: 20 mL.

6.9 Volumetric Flasks: Convenient sizes for preparing standard solutions.

6.10 Volumetric Pipets: Convenient sizes for preparing standard solutions.

6.11 Ruler with mm graduations.

6.12 Stopwatch.

6.13 Manometer.

6.14 Thermometer.

7. Reagents

Whenever possible, all reagents used must be ACS reagent grade or better.

7.1 Acetone.

7.2 Formic acid, 88%.

7.3 Sodium formate. This reagent is used to standardize the formic acid stock solution. Sodium formate should be dried in an oven at approximately 110°C for 4 hours and stored in a desiccator.

7.3.1 Prepare a stock solution containing 1.503 g sodium formate/liter deionized water. This solution contains 995 micrograms formate ion/mL.

7.3.2 From the stock solution prepare at least 3 working standards in the range of 9.95-39.8 µg/mL formate ion.

7.3.3 Analyze the working standards as described in Sections 8.3.3-8.3.8.

7.3.4 Prepare a standard calibration curve by plotting concentration of formate ion in µg/mL versus peak height. This curve is used to determine the concentration of the formic acid stock solution.

7.4 Deionized water.

7.5 Dioxane.

7.6 Formic acid stock solution (1.074 mg/mL formic acid in water). Add 1 mL of 88% formic acid to a 100-mL volumetric flask and make to volume with deionized water. This solution must be prepared fresh daily. To accurately determine the concentration of this solution, analyze this solution as described in Sections 8.3.3-8.3.8. Read the concentration from the calibration curve prepared in Section 7.3.4.

7.7 Formic acid solution for determining desorption efficiency (27 mg/mL formic acid in dioxane). Pipet 6 mL of 88% formic acid into a 125-mL volumetric flask and make to volume with dioxane. Prepare fresh daily.

Note: All standards must be prepared fresh daily. Loss of formic acid was observed after 24 hours. Pipetting below the liquid level of the standard will minimize loss of formic acid from evaporation. If loss of formic acid is suspected, the formic acid standard should be standardized against sodium formate as described above.

7.8 Ion chromatograph eluant, 0.0025 M $Na_2B_4O_7 \cdot 10\ H_2O$. Add 3.82 g $Na_2B_4O_7 \cdot 10\ H_2O$ to 4 liters of deionized water. Dissolve the salt, then filter to remove particles which are greater than 1 micrometer.

7.9 0.1 M $Na_2B_4O_7 \cdot 10\ H_2O$. Add 145 g $Na_2B_4O_7 \cdot 10\ H_2O$ to 4 liters of deionized water. Filter the solution to remove particles greater than 1 micrometer. This is used to clean the analytical column.

8. Procedure

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

8.2 Collection and Shipping of Samples

8.2.1 Immediately before sampling, remove the caps from the ends of the Chromosorb 103 tubes. All tubes must be packed with Chromosorb 103 from the same manufacturer's lot.

8.2.2 Two tubes connected in series are used for sample collection. The tubes are connected with a short piece of polyvinyl chloride tubing. The shortest length of tubing compatible with maintaining a leak-free connection should be used. The tube nearest the sampling pump is the backup tube. A prefilter is connected in front of the sampling train to remove interfering formate salts.

8.2.3 The tubes should be placed in a vertical direction during sampling to minimize channeling through the Chromosorb 103.

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

8.2.5 A sample size of 24 liters is recommended. Set the flow rate as accurately as possible using the manufacturer's directions. Sample at a flow rate between 0.05 and 0.2 liter/minute. Do not sample at a flow rate less than 0.05 liter/minute. Record 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 Chromosorb 103 tubes should be separated and capped individually with plastic caps immediately after sampling. Under no circumstances should rubber caps be used. Each set of tubes should be marked to identify the front Chromosorb 103 tube with the corresponding backup Chromosorb 103 tube. The prefilter should be removed from the filter cassette and discarded. The filter cassettes should be cleaned and saved for future use.

8.2.8 With each batch or partial batch of ten samples, submit one set of tubes (two Chromosorb 103 tubes) from the same lot of tubes used for sample collection. These tubes must be subjected to exactly the same handling as the samples except that no air is drawn through them. Label these tubes as the blanks.

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 or equivalent. This sample should not be transported in the same container as the Chromosorb 103 tubes. A minimum of 18 extra Chromosorb 103 tubes should be provided for desorption efficiency determinations.

8.3 Analysis of Samples

8.3.1 Desorption of Formic Acid. Remove the plastic caps from both ends of the front Chromosorb 103 tube and transfer the entire contents of the tube to a 20-mL scintillation vial. This is accomplished by pushing the contents out of the tube with a clean glass rod. Pipet 10 mL of deionized water through the empty tube into the vial. Cap the vial.

The backup Chromosorb 103 tube should be handled in a similar manner, using a separate vial. The two samples are analyzed separately.

8.3.2 Shake the sample vigorously. Desorption is complete in 5 minutes. Analyses should be completed the same day the formic acid is desorbed.

8.3.3 Ion Chromatograph Conditions. The typical operating conditions for the ion chromatograph are:

Column Temperature: Ambient
Pump: 25% of total capacity
Column Pressure: 400 psig
Flow Rate: 165 mL/hr
Mobile Phase: 0.0025 M $Na_2B_4O_7 \cdot 10\ H_2O$

8.3.4 Filtration and Injection. The sample is drawn into a 10-mL syringe. The filtration unit with filter is attached to the syringe and about 1 mL of the sample is flushed through the sample loop of the ion chromatograph. The sample is then injected onto the ion exchange columns. The syringe and filter unit should be rinsed with deionized water between injections. The filter should be changed when the pressure required to expel the sample through the filter unit increases.

8.3.5 The columns are flushed with 0.1 M $Na_2B_4O_7 \cdot 10\ H_2O$ for one minute after the formate ion has eluted. This procedure removes later eluting ions quickly from the column. The eluting solvent is then replaced with the normal 0.0025 M $Na_2B_4O_7 \cdot 10\ H_2O$ solution. The ion chromatograph is ready for the next sample when a baseline is reestablished.

8.3.6 The peak height of the sample peak is measured in mm with a ruler and the results are read from a standard curve prepared as discussed in Section 9. It is not recommended to quantitate sample peaks using an electronic area integrator. The output of the ion chromatograph is not compatible with most electronic integrators and reproducible results cannot be obtained.

8.3.7 Concentration levels that exceed the range of the calibration curve should be diluted appropriately.

8.3.8 Sample blanks must be analyzed following the same procedure as that used for the samples.

8.4 Determination of Desorption Efficiency

8.4.1 The desorption efficiency of a particular compound may vary from one laboratory to another and also from one batch of Chromosorb 103 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 Chromosorb 103.

8.4.2 Chromosorb 103 sample tubes, prepared as described in Section 6.3 are used to determine desorption efficiency. The Chromosorb 103 must be from the same batch as that used in obtaining the samples. A known amount of a dioxane solution of formic acid containing 27 mg/mL (Section 7.7) is injected

directly into the Chromosorb 103 with a microliter syringe, and the tube is capped with plastic caps. The amount injected is equivalent to that present in a 24-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 formic acid onto the Chromosorb 103. 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 8.3.

8.4.3 To prepare standards at each level, add approximately 7 mL of deionized water to each of three 10-mL volumetric flasks. Deliver 2, 4, and 8 microliters of the 27 micrograms/mL stock solution to each flask under the surface of the water, then bring the volume to 10 mL.

8.4.4 The desorption efficiency (D.E.) equals the average weight in micrograms recovered from the tube divided by the weight in micrograms added to the tube, or

$$\text{D.E.} = \frac{\text{Average weight recovered } (\mu g) - \text{Blank } (\mu g)}{\text{Weight added } (\mu g)}$$

The desorption efficiency may be dependent on the amount of formic acid collected on the Chromosorb 103. Plot the desorption efficiency versus weight of formic acid found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standardization

9.1 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 ion chromatograph conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in micrograms/10 mL versus peak height. 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.

9.2 From the stock standard solution of formic acid in deionized water (Section 7.6), appropriate aliquots are withdrawn and dilutions are made in deionized water. Prepare at least 5 working standards to cover the range of 20-650 micrograms/10 mL. This range is based on a 24-liter sample.

9.3 Analyze the standards as described in Section 8.3.

9.4 Prepare a standard calibration curve by plotting concentration of formic acid in micrograms/10 mL versus peak height.

10. Calculations

10.1 Read the weight, in micrograms, corresponding to each peak height from the standard curve. No volume corrections are needed because the standard curve is based on micrograms/10 mL deionized water 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.

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

where:

μg sample = μg found in front sample tube

μg blank = μg found in front blank tube

A similar procedure is followed for the backup tubes.

10.3 Add the weights found in the front and backup tubes to determine the total weight of the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.4.4) for the amount found in the front tube. Divide the total weight by this desorption efficiency to obtain the corrected micrograms/sample.

$$\text{Corrected micrograms/sample} = \frac{\text{Total weight}}{\text{D.E.}}$$

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 (liters/min)

t = sampling time (min)

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 formic acid in the air sampled can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{Corrected } \mu g \text{ (Section 10.4)}}{\text{Corrected air volume sampled (liters) (Section 10.5)}}$$

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 (liters/mole) at 25°C and 760 mm Hg
M.W.	=	molecular weight (g/mole) of formic acid
760	=	standard pressure (mm Hg)
298	=	standard temperature (°K)

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 Formic Acid, prepared under NIOSH Contract No. 210-76-0123.

Sampling Data Sheet No. S173

May 12, 1978

Substance

Formic Acid

Standard

8-hour time-weighted average: 5 ppm (9 mg/cu m)

Analytical Method

A known volume of air is drawn through two glass tubes connected in series containing 60/80 mesh Chromosorb 103 to trap the formic acid vapors present. A Teflon prefilter is connected in front of the Chromosorb 103 tubes to remove interfering formate salts. Formic acid is desorbed from the Chromosorb 103 with deionized water, and the sample is separated and analyzed using an ion chromatograph with an electrolytic conductivity detector. The method has been validated over the range of 4.4-21.6 mg/cu m for a 24-liter sample at 23°C and 759 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%) in the range of 0.05 to 0.20 liter/minute. The sample tube (7 cm long with a 6-mm O.D. and 4-mm I.D.), is packed with 50 mg of 60/80 mesh Chromosorb 103. Two tubes connected in series are used to collect samples. Immediately prior to packing, the empty glass tubes should be acetone rinsed and dried to eliminate the problem of Chromosorb 103 adhering to the walls of the glass tubes. A prefilter unit is used to collect interfering formate salts. It consists of a 13-mm filter holder and a 13-mm diameter/5-micrometer pore size Teflon filter.

Sample Size

A sample size of 24 liters is recommended. Sample at a flow rate between 0.05 and 0.20 liter/minute. Do not sample at a flow rate less than 0.05 liter/minute.

Sampling Procedure

1. Immediately before sampling, remove the caps from the ends of the tube. All tubes must contain Chromosorb 103 from the same manufacturer's lot.

2. Two tubes connected in series are used for sample collection. The tubes are connected with a short piece of polyvinyl chloride tubing. The shortest length of tubing compatible with maintaining a leak-free connection should be used. The tube nearest the sampling pump is the backup tube. A prefilter is connected in front of the sampling train to remove interfering formate salts.

3. The tubes should be placed in a vertical position during sampling to avoid channeling and subsequent premature breakthrough of formic acid.

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

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. The Chromosorb 103 tubes should be separated and capped individually with plastic caps immediately after sampling. Under no circumstances should rubber caps be used. Each set of tubes should be marked to identify the front Chromosorb 103 tube with the corresponding backup Chromosorb 103 tube. The prefilter should be removed from the filter cassette with tweezers and discarded. The filter cassettes should be cleaned and saved for future use.

7. With each batch or partial batch of ten samples, submit one set of tubes (two Chromosorb 103 tubes) from the same lot of tubes used for sample collection. These tubes must be subjected to exactly the same handling as the samples except that no air is drawn through them. These tubes should be labeled as the blanks. Information on the batch number of the Chromosorb 103 must be supplied. A minimum of 18 extra Chromosorb 103 tubes should be provided 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 Chromosorb 103 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. Reduction in sample volume due to high humidity should not be needed.

Bulk Samples

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

Shipping Instructions

Capped Chromosorb 103 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

Formic Acid, NIOSH Method No. S173.

Backup Data Report No. S173

May 12, 1978

Substance: Formic Acid

OSHA Standard: 5 ppm (9 mg/cu m)

Chemical Used for Validation: Formic Acid, 88%
J. T. Baker Chemical Company

General

The procedure for collection and analysis of air samples of formic acid is described in NIOSH Method No. S173. This method consists of collection of the sample on Chromosorb 103, desorption with deionized water, and analysis of the resulting solution by ion chromatography.

This method has been tested for validity for a 24-liter air sample using the criteria for validation outlined in Reference 1. Using these criteria, the absolute total error (sampling and analysis) should be 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 formic acid to represent 24-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 the breakthrough capacity of Chromosorb 103 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. S173. The results of the desorption efficiency tests are in Table S173-5. Chromosorb 103, Lot 43, was used in the validation study.

A known amount of solution containing formic acid in dioxane (27 mg/mL) was used to prepare spiked samples of formic acid on Chromosorb 103. Six samples at each of three levels (0.5X, 1X, and 2X the OSHA standard) were prepared to represent 24-liter air samples. Dioxane was selected as the solvent for the spiking solution, because formic acid had adequate solubility in dioxane and dioxane does not affect the Chromosorb 103. An inert solvent such as hexane was not used, because formic acid is not soluble in hexane.

The sensitivity of the method for the instrumental conditions used during the validation study was 7 μmho/cm/μg formate ion. In other words, a 100-microliter injection of a 22 microgram/mL solution of formic acid gave a peak whose height was 50% of full scale on a 1-volt recorder when the ion chromatograph was set on range 30 μmho/cm.

The detection limit of the analytical method is estimated to be 2 micrograms formic acid/sample tube. This corresponds to a 100-microliter aliquot of a 0.2 microgram/mL standard.

Sampling and Analysis

Test atmospheres of formic acid in air were generated with an automated syringe drive system (Harvard infusion/withdrawal pump, Model 950). A 2-mL syringe was filled with the analyte and placed in the syringe drive pump. A 15-in long stainless steel needle, attached to the syringe, passed through a rubber septum which entered into a heated glass tube. The tube was packed with glass wool to provide a large surface area. The vapor was carried out of the first stage of the generator by a stream of nitrogen. It was diluted with air immediately downstream to obtain a formic acid concentration of 2X the OSHA standard. Dilutions to 1X and 0.5X the OSHA standard were made as described in Attachment A. The samples were collected as described in Method S173 using two sampling tubes connected in series each containing 50 mg of Chromosorb 103. A Teflon filter preceeded the sampling train during collection of the test samples. The concentration of formic acid vapor in the test chambers was determined by the independent method described below.

Six samples were collected from each chamber for 133 minutes at an average flow rate of 0.18 liter/minute to obtain a 24-liter air sample. An additional six samples were collected at 1X the OSHA standard for a storage stability test. The results of the analyses of the samples used for the validation are in Table S173-6.

In addition, the backup sampling tubes at 2X the OSHA standard were analyzed and found to contain less than the limit of detection which was estimated at 2 micrograms.

Storage Stability Study

A study was done to assess whether formic acid 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 collected for immediate analysis. Samples were collected for 133

minutes at an average flow rate of 0.18 liter/minute. These sample tubes were capped and stored on the laboratory bench for one week before analysis. The results are presented in Table S173-1.

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 8.5%; thus, the storage stability was adequate.

Table S173-1

Storage Stability Study

Samples Analyzed Immediately (mg/cu m)	Samples Analyzed After One Week (mg/cu m)
10.83	9.99
10.62	10.91
11.75	10.36
12.60	9.87
10.31	10.29
	10.22
mean 11.22	10.27
std dev 0.94	0.36
CV 0.084	0.035

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 B. The test atmosphere was generated using the syringe drive system described earlier.

Breakthrough is defined as the time that the effluent concentration from the collection tube (containing 50 mg of Chromosorb 103) reaches 5% of the concentration in the test gas mixture.

The breakthrough time was measured by testing 20 sampling tubes in parallel, each containing 50 mg of Chromosorb 103 followed by a backup tube containing 50 mg of Chromosorb 103. The tubes were placed in the sample generation apparatus. The test atmosphere was sampled through each set of tubes at the flow rate of 0.18 liter/minute. After the start of the test, a sample tube and corresponding backup tube was analyzed approximately every 20 minutes. No formic acid was detected in the backup tubes. The data collected during the breakthrough test is presented in Table S173-2.

Breakthrough did not occur when the average sampling rate was 0.18 liter/minute and the relative humidity was 85%. The concentration tested was 22 mg/cu m.

Table S173-2

Breakthrough Test

Time (min)	Micrograms Formic Acid Collected in Front Tube	Micrograms Formic Acid Collected in Backup Tube
20	73.3	N.D.*
60	283.1	N.D.
100	425	N.D.
120	532	N.D.
140	621	N.D.
160	730	N.D.
180	742	N.D.
200	844	N.D.
220	922	N.D.
240	850	N.D.
260	991	N.D.
300	1086	N.D.

*N.D. = Not detected at a detection limit of 2 micrograms.

Discussion

A number of analytical methods for formic acid were considered. Formic acid can be measured by oxidizing or reducing it and then measuring the products or the amount of reagent consumed. Another method relies on the distillation of a chloroform-formic acid azeotrope to separate formic acid from higher carboxylic acids. Formic acid is then determined by a potentiometric titration with sodium hydroxide. These methods suffer from interferences and have relatively high detection limits. Gas chromatography has been used to measure formic acid both directly and as various derivatives. Direct analysis poses the problems of corrosion of metal surfaces and of high detection limits with a flame ionization detector. Derivatives of formic acid eliminate corrosion and have lower detection limits on a flame ionization detector. However, derivatization lengthens analysis time, may require special equipment, and is not always quantitative (References 2-4).

Ion chromatography has been used to measure formic acid as formate ion. A major problem in this type of analysis has been detection of the species of interest. One approach for compounds with low uv absorbance, such as formic acid, has been to saturate a reverse phase liquid chromatographic column with a uv absorbing counter ion then to pair this ion with the analyte ion to achieve acceptable detection limits (Reference 5).

Another approach is to separate the ions of interest on a conventional ion exchange column and then detect them by conductivity (Reference 6). High concentrations of eluting solvent ions, that present interferences with a conductivity detector, are removed or converted to a weakly ionized species. This is done by use of a suppressor column placed between the analytical column and the detector. Ion chromatography

using a conductivity detector was selected for the analysis of formic acid.

Quantitation of formic acid was done by peak height measurements. Initially an electronic integrator was used to measure peak area. However, the integrator was not successful in reproducibly integrating the formate ion peak due to a negative peak which preceeded the formate ion peak. Peak height measurements were more precise.

Several methods for the collection of formic acid vapor were investigated. Formic acid can be collected in a bubbler containing a basic aqueous solution such as sodium hydroxide (Reference 7). However, hydroxide was found to interfere in the analysis by ion chromatography. Water was also investigated for collecting formic acid. It was found that formic acid solutions in water were unstable, decaying about 5% after one day.

Several solid sorbents were tested for desorption efficiency and sample stability. Samples containing approximately 100 mg of each sorbent was spiked with an amount of formic acid that represented a 12-liter sample at 2X the OSHA standard. Separate spiked samples were allowed to equilibrate for 5 minutes, 1 day, and 2 days before analysis. The samples were then desorbed with deionized water and analyzed by ion chromatography. The results of these tests are presented in Table S173-3.

Table S173-3

Desorption Efficiencies of Formic Acid From Several Solid Sorbents

		5 min		1 day		2 days	
Sorbent	µg taken	µg found	D.E.	µg found	D.E.	µg found	D.E.
Charcoal 105 (Three 3-mL water extracts)	213.2	212.7	0.998	194.7	0.913	178.2	0.836
Carbosieve B (One 10-mL water extract)	213.2	120.9	0.567	-	-	-	-
Chromosorb 103 (One 10-mL water extract)	213.2	215.6	1.011	212.6	0.997	217.4 218.8	1.020 1.026

Based upon these results, further tests were conducted with the Chromosorb 103.

Analysis of Chromosorb 103 blanks revealed an interference with the same retention time as the formate ion. The sorbent was not cleaned before use, because precleaning the sorbent would remove the species responsible for sorption of the formic acid. In order to reduce the relative amount of interference to an acceptable level, the sample size was increased from 12 to 24 liters, and the amount of Chromosorb 103 in the

collection tube was reduced from 100 mg to 50 mg. Under these conditions, the Chromosorb 103 used in the validation study gave a blank interference that was 10% of the amount collected at 0.5X the OSHA standard. This was equivalent to 10 micrograms of formic acid per sample.

Carbonate and bicarbonate ions are present in the extract of Chromosorb 103 and appear as two long retention time peaks. They must be eluted from the columns or they will appear as interferences in later analyses. To remove these ions it has been recommended in the validated method that the columns be flushed with 0.1 M $Na_2B_4O_7 \cdot 10\ H_2O$ for one minute after the formate ion has eluted. The eluting solvent is then replaced with the normal 0.0025 M $Na_2B_4O_7 \cdot 10\ H_2O$ solution.

Two sampling tubes connected in series rather than a single tube (containing two sections of Chromosorb 103) were used to collect formic acid. It is difficult to remove Chromosorb 103 from the sampling tube because of the very fine particles. Because of this it would be difficult to separate the two sections of Chromosorb 103 well during analysis if only a single tube were used for sampling. It was therefore decided to collect formic acid using two tubes in series to solve the separation problem. The entire contents of a single tube was transferred to a vial by pushing out the sorbent and glass wool plugs in the tube with a glass rod. In this way the glass wool plugs sweep the walls of the tube removing any adhering Chromosorb 103. Desorption is accomplished by adding 10 mL of deionized water via the empty tube into the vial containing the Chromosorb 103.

Independent Method

The concentration of formic acid in the generator was determined by collecting formic acid in a midget bubbler containing 15 mL of deionized water at 0.5X, 1X, and 2X the OSHA standard. Backup bubblers were used at the 2X level. The collected samples were analyzed by ion chromatography. The backup bubbler at the 2X level was found to contain 7.32% of the total formic acid collected, and a correction for collection efficiency was made on the concentrations at the 0.5X and 1X levels.

The results of the independent method are presented in Table S173-4.

Table S173-4

Independent Method

Level	Micrograms Formic Acid	Corr. Micrograms Formic Acid*	Volume (liters)	mg/cu m
0.5X	815	879	197.9	4.44
	779	840	191.1	4.40
	809	873	196.3	4.45
			mean	4.43
1X	2018	2177	193.7	11.24
	1877	2025	194.3	10.42
			mean	10.83

	Micrograms Front Bubbler	Micrograms Backup Bubbler	Volume (liters)	mg/cu m
2X	4060	269.6	197.7	21.90
	3810	312	199.5	20.66
	4120	296.0	198.7	22.22
			mean	21.59

* Based upon a collection of 0.927.

Precision and Accuracy

The statistical procedures and a definition of the terms used are described in Reference 8.

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 S173-6) gave a chi squared value of 7.21. 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 S173-5. The pooled Coefficient of Variation ($\overline{CV}_1$) for three sets of analytical samples was found to be 0.026.

Precision and accuracy of the total sampling and analytical method was evaluated using the data in Table S173-6 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 0.052. 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 96.2%. 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 0.073.

Table S173-5

Data Sheet: Formic Acid

Analysis

Level	0.5X			1X			2X	
µg taken	µg found	D.E.*	µg taken	µg found	D.E.	µg taken	µg found	D.E.
106.4	105.8	0.994	212.8	211.6	0.994	426	435	1.021
106.4	104.6	0.983	212.8	209.8	0.986	426	444	1.042
106.4	111.8	1.051	212.8	221.2	1.040	426	444	1.042
106.4	102.2	0.961	212.8	215.4	1.012	426	433	1.016
106.4	108.4	1.019	212.8	219.2	1.030	426	434	1.019
Sample was lost.			212.8	217.0	1.020	426	421	0.988
n =		5			6			6
mean		1.002			1.014			1.021
std dev		0.035			0.021			0.020
CV_1		0.035			0.021			0.020

$\overline{CV}_1$ 0.026

$\overline{CV}_{A+\overline{DE}}$ 0.028

* D.E. = Desorption Efficiency = $\frac{\mu g \text{ found}}{\mu g \text{ taken}}$

No correction for desorption efficiency was made.

Table S173-6

Data Sheet: Formic Acid

Sampling and Analysis

Test Level	Found			Taken	Percent Recovery
	µg	Liters	mg/cu m	mg/cu m	
0.5X	119.1	23.71	5.02*	4.43**	
	104.7	25.53	4.10	4.43	
	98.5	23.85	4.13	4.43	
	96.0	23.91	4.02	4.43	
	96.9	23.87	4.06	4.43	
	107.4	24.71	4.35	4.43	
		n = 5			
		mean	4.13		93.2
		std dev	0.13		
		CV_2	0.031		
1X	258.1	23.83	10.83	10.83**	
	264.0	24.87	10.62	10.83	
	290.4	24.71	11.75	10.83	
	314.0	24.93	12.60	10.83	
	266.8	25.88	10.31	10.83	
	Sample was lost.				
		n = 5			
		mean	11.22		103.6
		std dev	0.94		
		CV_2	0.084		
2X	477	24.09	19.80	21.59	
	491	25.07	19.58	21.59	
	474	24.09	19.68	21.59	
	467	24.27	19.24	21.59	
	497	24.09	20.63	21.59	
	474	23.68	20.02	21.59	
		n = 6			
		mean	19.82		91.8
		std dev	0.47		
$\overline{CV}_2$ 0.052		CV_2	0.024		

* This value did not pass the Grubbs' outlier test at the 1% significance level as described in Reference No. 8, and it was not used in the statistical treatment of data.

** Corrected for a collection efficiency of 0.927.

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. Peters, D. G., et al., Chemical Separation and Measurements, Philadelphia: W.B. Saunders Co., (1974), 316-321.

3. Grant, W. M., "Colorimetric Microdetermination of Formic Acid Based on Reduction to Formaldehyde," Anal. Chem., 20, (1948), 267.

4. Failure Report No. S173 for Formic Acid, prepared under NIOSH Contract No. CDC-99-74-45.

5. Eksborg, S., et al., "Ion-Pair Chromatography of Organic Compounds," J. of Chrom., 83, (1973), 99-110.

6. Small, H., et al., "Novel Ion Exchange Chromatographic Method Using Conductimetric Detection," Anal. Chem., 47, (1975), 1801-9.

7. Smallwood, A.W., "Analysis of Formic Acid in Air Samples," Amer. Ind. Hyg. Assoc. J., 39, (1978), 151-3.

8. 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.

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

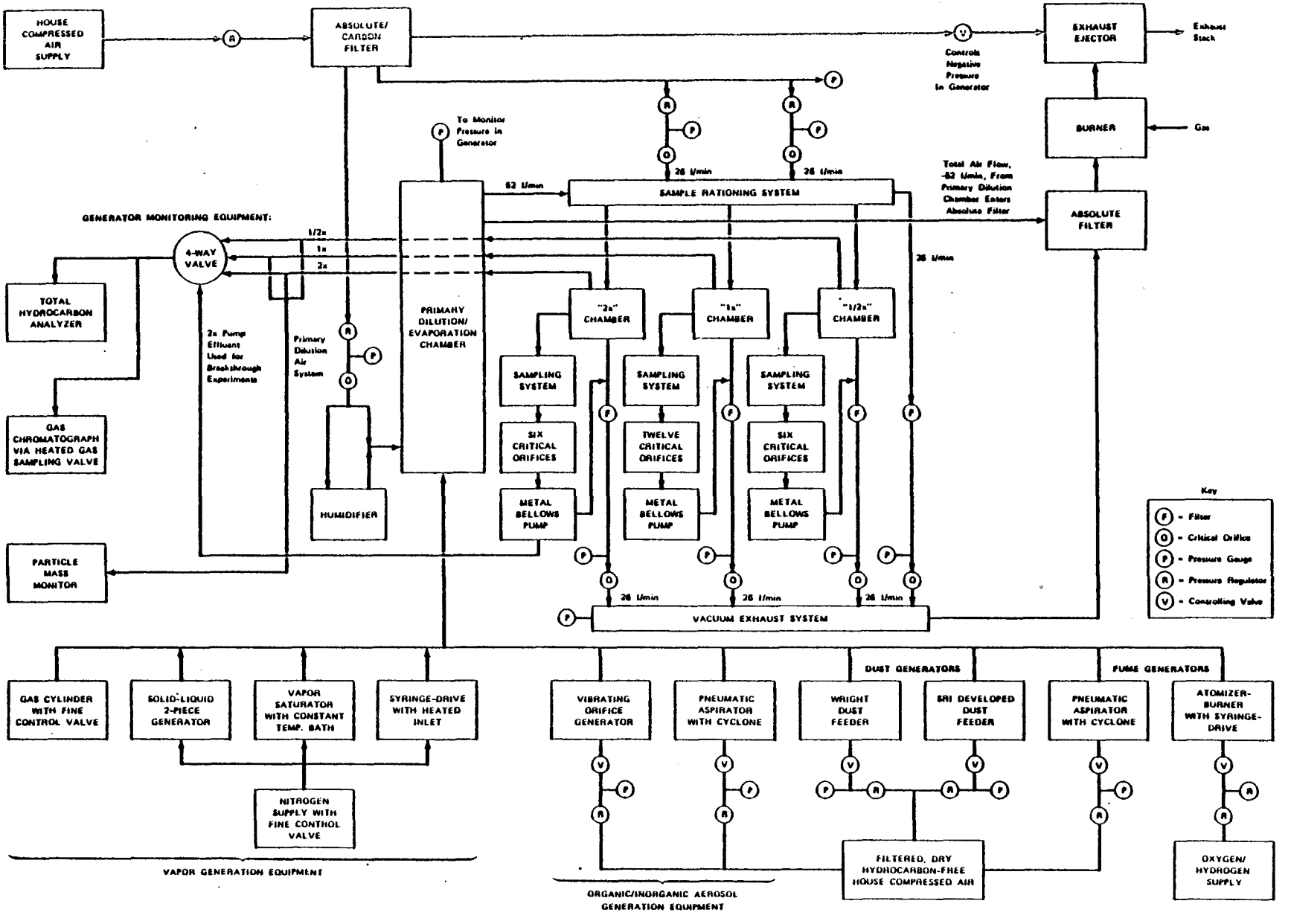


FIGURE S173-A1 SCHEMATIC OF SAMPLE GENERATION FACILITIES

S173-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.

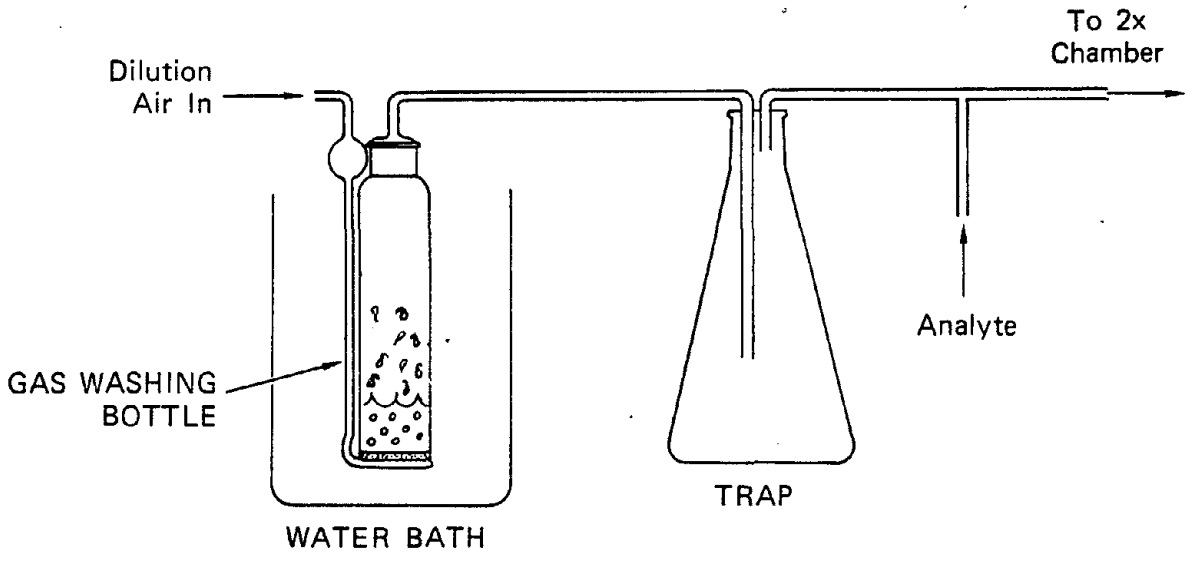
The cylindrical section at the base of each sampling chamber contains the fittings necessary to collect samples, using any of a variety of sampling media--solid sorbent tubes, filters, liquid scrubbers, or a combination of these. Six to twelve samples each at three concentration levels can be collected 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.

Attachment B

Generation of Test Atmospheres of Known Humidity

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



Dilution air is passed through a 500-mL gas washing bottle (bubbler with diffuser) containing about 150 mL of deionized water. The bottle is maintained in a temperature controlled water bath. The humidified air passes through a trap and is then mixed with the analyte to obtain a test atmosphere concentration at 2X the OSHA standard.

The temperature of the water bath is adjusted so that a test atmosphere relative humidity of at least 80% is maintained. The temperature setting is dependent upon the flow and temperature of the incoming dilution air.

The relative humidity of the air in the sampling chamber is measured by the dry and wet bulb thermometer method. A flow of 25 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.