

- 10.2 Prior to sample collection the entire assembly (including empty sample impingers) is installed and the flow rate checked at a value near the desired rate. In general flow rates of 100-1000 mL/minute are useful. Flow rates greater than ~1000 mL/minute should not be used because impinger collection efficiency may decrease. Generally calibration is accomplished using a soap bubble flow meter or, calibrated wet test meter connected to the flow exit, assuming the entire system is sealed. ASTM Method D3686 describes an appropriate calibration scheme not requiring a sealed flow system downstream of the pump.
- 10.3 Ideally a dry gas meter is included in the system to record total flow. If a dry gas meter is not available the operator must measure and record the sampling flow rate at the beginning and end of the sampling period to determine sample volume. If the sampling period exceeds two hours the flow rate should be measured at intermediate points during the sampling period. Ideally a rotameter should be included to allow observation of the flow rate without interruption of the sampling process.
- 10.4 To collect an air sample two clean midget impingers are loaded with 10 mL of purified DNPH reagent and 10 mL of isooctane. The impingers are connected in series to the sampling system and sample flow is started. The following parameters are recorded on the data sheet (see Figure 3 for an example): date, sampling location, time, ambient temperature, barometric pressure (if available), relative humidity (if available), dry gas meter reading (if appropriate), flow rate, rotameter setting, DNPH reagent batch number, and dry gas meter and pump identification numbers.
- 10.5 The sampler is allowed to operate for the desired period, with periodic recording of the variables listed above. The total flow should not exceed ~80 liters. The operator must ensure that at least 2-3 mL of isooctane remains in the first impinger at the end of the sampling interval (i.e. for high ambient temperatures lower sampling volumes may be required).

- 10.6 At the end of the sampling period the parameters listed in 10.4 are recorded and the sample flow is stopped. If a dry gas meter is not used the flow rate must be checked at the end of the sampling interval. If the flow rate at the beginning and end of the sampling period differ by more than 15% the sample should be marked as suspect.
- 10.7 Immediately after sampling the impingers are removed from the sampling system. The contents of the first impinger are emptied into a clean 50 mL glass vial having a teflon-lined screw cap. The first impinger is then rinsed with the contents of the second (backup) impinger and the rinse solution is added to the vial. The vial is then capped, sealed with teflon tape and placed in a friction top can containing 1-2 inches of granular charcoal. The samples are stored in the can, refrigerated until analysis.
- 10.8 If a dry gas meter or equivalent total flow indicator is not used the average sample flow rate must be calculated according to the following equation:

$$Q_A = \frac{Q_1 + Q_2 \dots Q_N}{N}$$

where

Q_A = Average flow rate in mL/minute.

$Q_1, Q_2, \dots, Q_N$ = Flow rates determined at the beginning, end, and intermediate points during sampling.

N = Number of points averaged.

- 10.9 The total flow is then calculated using the following equation:

$$V_m = \frac{(T_2 - T_1) Q_A}{1000}$$

V_m = Total volume sampled in liters at measured temperature and pressure

T_2 = Stop time

T_1 = Start time ($T_2 - T_1$ given in minutes)

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11. Sample Analysis

11.1 Sample Preparation

- 11.1.1 The samples are returned to the laboratory in 50 mL screw-capped glass vials. To recover the DNPH derivatives the following procedure is employed.
- 11.1.2 The vials are shaken in a horizontal position on a reciprocating shaker for 10 minutes. The vials are then removed from the shaker and the isooctane layer is removed and placed in a second clean 50 mL screw-capped glass vial using a disposable pipette.
- 11.1.3 The remaining aqueous layer is extracted with 10 mL of 70/30 (V/V) hexane/methylene chloride in the same manner as described in 11.1.2. The organic layer is removed and combined with the isooctane extract.
- 11.1.4 The combined organic extracts are then concentrated to dryness at 40°C under a stream of pure nitrogen. When the sample just reaches dryness the vial is removed from the nitrogen stream and a measured volume (2-5 mL) of methanol is added to the vial. The vial is tightly capped and stored refrigerated until analysis.

11.2 HPLC Analysis

- 11.2.1 The instrument is assembled and calibrated as described in Section 12. Prior to each analysis the detector baseline is checked to ensure stable operation.
- 11.2.2 A 5-25 μ L aliquot of the sample, dissolved in methanol, is drawn into a clean HPLC injection syringe. The sample injection loop is loaded and an injection is made. The data system, if available, is activated simultaneously with the injection and the point of injection is marked on the stripchart recorder.

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- 11.2.3 After approximately one minute, the injection valve is returned to "load" position and the syringe and valve are flushed with methanol in preparation for the next sample analysis.
- 11.2.4 After elution of the last component of interest the acquisition is terminated and the component concentrations are calculated as described in Section 13.
- 11.2.5 After a stable baseline is achieved the system can be used for further sample analyses as described above.
- 11.2.6 If the concentration of a component exceeds the linear range of the instrument the sample should be diluted with methanol, or a smaller volume can be injected onto the HPLC.

12. HPLC Assembly and Calibration

- 12.1 The HPLC system is assembled as shown in Figure 3. The typical chromatographic performance and operating parameters are shown in Figure 4.
- 12.2 Mobile phase is prepared by mixing 800 mL of methanol and 200 mL of reagent water. This mixture is filtered through a 0.22 μ m polyester membrane filter in an all glass and teflon suction filtration apparatus. The filtered mobile phase is degassed by purging with helium gas for 10-15 minutes ($\sim$ 100 mL/minute) or by heating to $\sim$ 60°C for 5-10 minutes in an Erlenmeyer flask covered with a watch glass. A constant back pressure restrictor ($\sim$ 50 psi) or short length (6-12 inches) of 0.01 inch I.D. teflon tubing should be placed after the detector to further eliminate mobile phase outgassing.
- 12.3 The mobile phase is placed in the HPLC solvent reservoir and the pump flow is set at 1 mL/minute and allowed to pump for 20-30 minutes prior to the first analysis. The detector is switched on at least 30 minutes prior to the first analysis and the detector output is displayed on a stripchart recorder or similar output device at a sensitivity of .008

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absorbance units full scale (AUFS). Once a stable baseline is achieved the system is ready for calibration.

- 12.4 Calibration standards are prepared in methanol from the solid DNPH derivatives. Individual stock solutions of ~ 100 mg/L are prepared by dissolving 10 mg of the solid derivative in 100 mL of methanol. These individual solutions are used to prepare calibration standards containing all of the derivatives of interest at concentrations of 0.1 - 10 mg/L, which spans the concentration of interest for most ambient air work.
- 12.5 All calibration runs are performed as described for sample analyses in Section 11. Before initial use the operator should inject a series of calibration standards (at least three levels) spanning the concentration range of interest. Using the UV detector, a linear response range of approximately 0.1 to 10 mg/L should be achieved, for ~ 10 µL injection volumes. Linear response is indicated where a correlation coefficient of a least 0.999 for a linear least squares fit of the data (concentration versus area response) is obtained.
- 12.6 Once linear response has been documented an intermediate concentration standard near the anticipated levels for each component, but at least 10 times the detection limit, should be chosen for daily calibration. The response for the various DNPH components should be within 10% day to day. If greater variability is observed more frequent calibration may be required to ensure that valid results are obtained.
- 12.7 The response for each component in the daily calibration standard is used to calculate a response factor according to the following equation:

$$RF_C = \frac{C_C \times V_I}{R_C}$$

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where

RF_C = response factor for the component of interest in nanograms injected/response unit (usually area counts).

C_C = concentration of component in the daily calibration standard (mg/L).

V_I = volume of calibration standard injected (μ L).

R_C = response for component of interest in calibration standard (area counts).

13. Calculations

- 13.1 The volume of air sampled is often reported uncorrected for atmospheric conditions (i.e. under ambient conditions). However, the value can be adjusted to standard conditions (25°C and 760 mm pressure) using the following equation:

$$V_S = V_m \times \frac{P_A}{760} \times \frac{298}{273 + T_A}$$

where

V_S = total sample volume at 25°C and 760 mm Hg pressure (liters).

V_m = total sample volume under ambient conditions (liters). Calculated in 10.9 or from dry gas meter reading.

P_A = ambient pressure (mmHg).

T_A = ambient temperature (°C).

- 13.2 The concentration of each aldehyde (as the DNPH derivative is calculated for each sample using the following equation:

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$$W_d = RF_c \times R_d \times \frac{V_E}{V_I}$$

where

W_d = total quantity of derivative in the sample (μg).

RF_c = response factor calculated in 12.7

R_d = response for component in sample extract (area counts or other response units).

V_E = final volume of sample extract (mL).

V_I = volume of extract injected onto the HPLC system (μL).

13.3 The concentration of aldehyde in the original sample is calculated from the following equation:

$$C_A = \frac{W_d}{V_m \text{ (or } V_s)} \times \frac{MW_A}{MW_d} \times 1000$$

where

C_A = concentration of aldehyde in the original sample (ng/L).

V_m or V_s are as specified in Section 13.1.

MW_A and MW_d are the molecular weights (g/mole) of the aldehyde and its corresponding DNPH derivative, respectively.

13.4 The aldehyde concentrations can be converted to ppbv using the following equation:

$$C_A(\text{ppbv}) = C_A(\text{ng/L}) \times \frac{24.4}{MW_A}$$

where

$C_A(\text{ng/L})$ is calculated using V_s .

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14. Performance Criteria and Quality Assurance

This section summarizes the quality assurance (QA) measures and provides guidance concerning performance criteria which should be achieved within each laboratory.

14.1 Standard Operating Procedures (SOPs).

- 14.1.1 Each user should generate SOPs describing the following activities as accomplished in their laboratory: 1) assembly, calibration and operation of the sampling system, 2) preparation, purification, storage and handling of DNPH reagent and samples, 3) assembly, calibration and operation of the HPLC system, and 4) all aspects of data recording and processing.
- 14.1.2 SOPs should provide specific stepwise instructions and should be readily available to, and understood by, the laboratory personnel conducting the work.

14.2 HPLC System Performance

- 14.2.1 The general appearance of the HPLC chromatograph should be similar to that shown in Figure 4.
- 14.2.2 The HPLC system efficiency and peak asymmetry factor should be determined in the following manner. A solution of the formaldehyde DNPH derivative corresponding to at least 20 times the detection limit should be injected with the recorder chart sensitivity and speed set to yield a peak approximately 75% of full scale and 1 cm wide at half height. The peak asymmetry factor is determined as shown in Figure 5, and should be between 0.8 and 1.8.

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- 14.2.3 HPLC system efficiency is calculated according to the following equation:

$$N = 5.54 \left(\frac{t_r}{W_{1/2}} \right)$$

where

N = column efficiency, theoretical plates

t_r = retention time of components (seconds)

$W_{1/2}$ = width of component peak at half height (seconds)

A column efficiency of >5,000 should be obtained.

- 14.2.4 Precision of response for replicate HPLC injections should be $\pm 10\%$ or less, day to day, for calibration standards. Precision of retention times should be $\pm 2\%$, on a given day.

14.3 Process Blanks

- 14.3.1 Prior to use a 10 mL aliquot of each batch of DNPH reagent should be analyzed as described in Section 11. In general, formaldehyde levels equivalent to >5 ng/L in a 60 liter sample should be achieved and other aldehyde levels should be <1 ng/L.
- 14.3.2 At least one field blank should be shipped and analyzed with each group of samples. The field blank is treated identically to the samples except that no air is drawn through the reagent. The same performance criteria described in 14.3.1 should be met for process blanks.

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14.4 Method Precision and Accuracy

- 14.4.1 Analysis of replicate samples indicates a precision of ± 15 -20% relative standard deviation can be readily achieved. Each laboratory should collect parallel samples periodically (at least one for each batch of samples) to document their precision in conducting the method.
- 14.4.2 Precision for replicate HPLC injections should be $\pm 10\%$ or better, day to day, for calibration standards.
- 14.4.3 Method accuracy is difficult to assess because of the difficulty in generating accurate gaseous standards. Literature results indicate (1-3) recoveries of 75% or greater are achieved for a broad range of aldehydes. Each laboratory should periodically collect field samples wherein the impinger solution is spiked with a known quantity of the compound of interest, prepared as a dilute methanol solution. Formaldehyde cannot be spiked in this manner and therefore a solution of the DNPH derivative should be used for spiking purposes.
- 14.4.4 Before initial use of the method each laboratory should generate triplicate spiked samples at a minimum of three concentration levels, bracketing the range of interest for each compound. Triplicate nonspiked samples must also be processed. Recoveries of $>70 \pm 20\%$ and blank levels of <5 ng/L for formaldehyde and 1 ng/L for the other compounds (assuming a 60 liter air sample) should be achieved.

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TABLE 1. ALDEHYDES AND KETONES FOR WHICH THE METHOD HAS BEEN EVALUATED

<u>Compound</u>	<u>Molecular Weight</u>		Typical Relative Retention Time (a)
	<u>Derivative</u>	<u>Compound</u>	
Formaldehyde	210	30	1.0
Acetaldehyde	224	44	1.3
Acrolein	236	56	1.6
Propanal	238	58	1.7
Acetone	238	58	1.9(b)
Crotonaldehyde	250	70	2.3
Isobutyraldehyde	252	72	2.4
Methyl Ethyl Ketone	252	72	2.8
Benzaldehyde	286	106	3.2
Pentanal	266	86	3.7
o-Tolualdehyde	300	120	4.8
m-Tolualdehyde	300	120	5.1
p-Tolualdehyde	300	120	5.3
Hexanal	280	100	5.7

(a) Using HPLC conditions shown in Figure 4.
Formaldehyde = 1.0

(b) Acetone background levels in the reagent prevent its determination in most cases.

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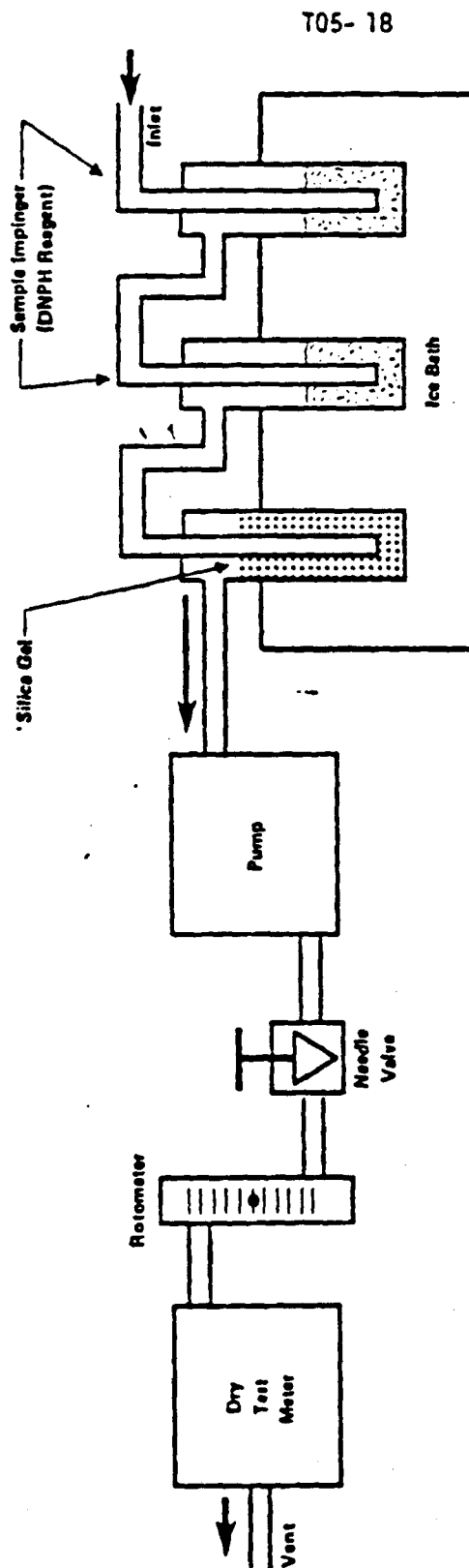


FIGURE 1. TYPICAL SAMPLING SYSTEM

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SAMPLING DATA SHEET
(One Sample Per Data Sheet)

PROJECT: _____

DATE(S) SAMPLED: _____

SITE: _____

TIME PERIOD SAMPLED: _____

LOCATION: _____

OPERATOR: _____

INSTRUMENT MODEL NO: _____

CALIBRATED BY: _____

PUMP SERIAL NO: _____

SAMPLING DATA

Sample Number: _____

Start Time: _____ Stop Time: _____

Time	Dry Gas Meter Reading	Rotameter Reading	Flow Rate, *Q ml/Min	Ambient Temperature °C	Barometric Pressure, mmHg	Relative Humidity, %	Comments
1.							
2.							
3.							
4.							
N.							

Total Volume Data**
 $V_m = (\text{Final} - \text{Initial}) \text{ Dry Gas Meter Reading, or}$

= _____ Liters

 $= \frac{Q_1 + Q_2 + Q_3 \dots Q_N}{N} \times \frac{1}{1000 \times (\text{Sampling Time in Minutes})}$

= _____ Liters

* Flowrate from rotameter or soap bubble calibrator
 (specify which).

** Use data from dry gas meter if available.

FIGURE 2. EXAMPLE SAMPLING DATA SHEET

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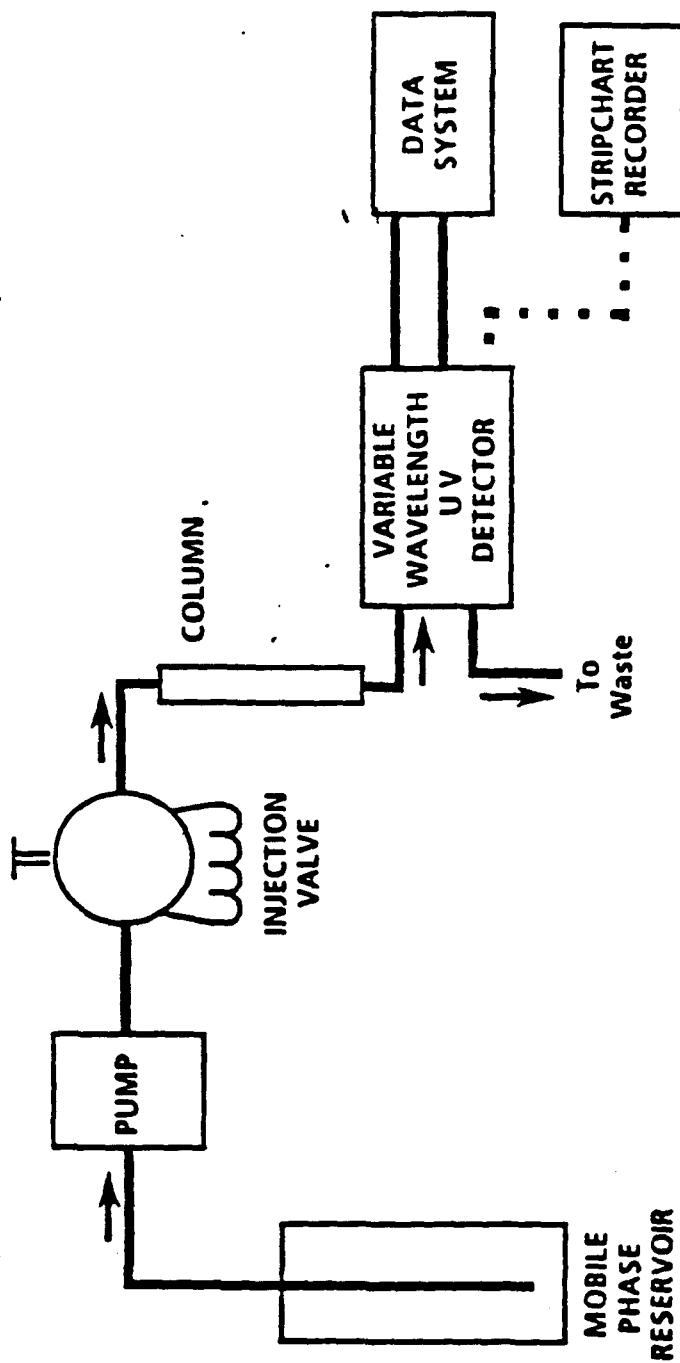


FIGURE 3. TYPICAL HPLC SYSTEM

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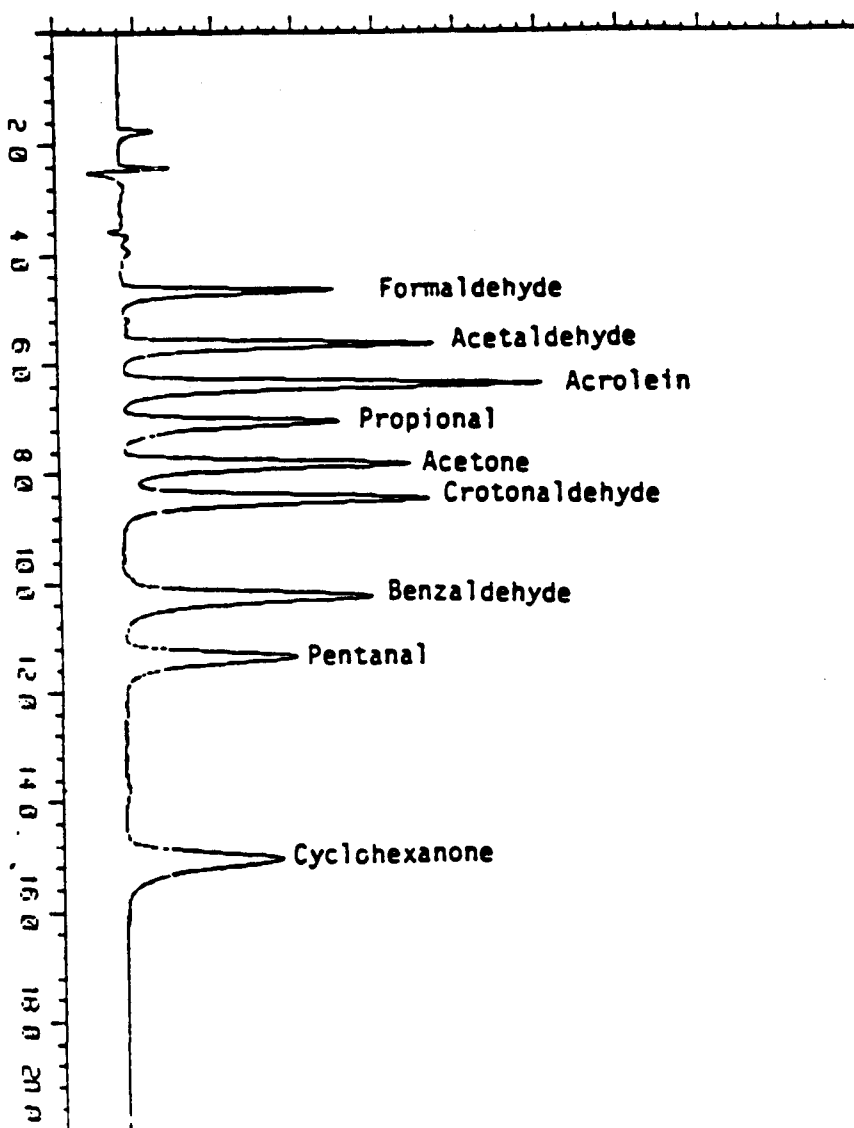


FIGURE 4. TYPICAL HPLC CHROMATOGRAM

Column - Zorbax ODS, 250 x 4.6 mm
Mobile Phase - 80/20 Methanol/H₂O
Flow Rate - 1 mL/Minute
Detector - UV at 370 nm

3. Organic Acids OSHA - 38
Dow Chemical Modifications
(for Formic, Acetic and Acrylic Acids)

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ACRYLIC ACID

Method no.: 28

Matrix: Air

Target concentration: 2 ppm (5.9 mg/m³) see Toxic Effects Section 1.1.2.

Procedure: Samples are collected by drawing a known volume of air through two XAD-8 sampling tubes connected in series. Samples are desorbed with 1/1 methanol/water and analyzed by high performance liquid chromatography (HPLC) using an ultraviolet (UV) detector.

Recommended air volume and sampling rate: 24 L at 0.1 L/min

Detection limit of the overall procedure: 0.014 ppm (0.042 mg/m³)
(Based on the recommended air volume)

Reliable quantitation limit: 0.014 ppm (0.042 mg/m³)

Standard error of estimate at the target concentration: 7.13%
(See Table 4.8.1. and Figure 4.8.1.)

Status of method: A sampling and analytical method which has been subjected to the established evaluation procedures of the Organic Methods Evaluation Branch.

Date: April, 1981

Chemist: Kevin Cummins

Organic Methods Evaluation Branch
OSHA Analytical Laboratory
Salt Lake City, Utah

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1. General Discussion

1.1. Background

1.1.1. History of procedure

A number of analytical methods are reported in the literature for the analysis of acrylic acid. Although a polarographic method has been published, most of these methods involve either gas, liquid, or paper chromatographic techniques (Ref. 5.1.). A direct method of analysis using reverse phase high performance liquid chromatography was developed and used in this study. This method is sensitive, selective, and easy to apply, and it also permits the simultaneous analysis of a number of other acrylate monomers and acrylic acid precursors.

A previous attempt by Brown to use octadecasilane (ODS) based HPLC columns for the analysis of acrylic acid was unsuccessful (Ref. 5.2). It has been recognized in this laboratory for some time that polar molecules of low molecular weight can often be retained and chromatographed in the reverse phase mode using Zorbax ODS packed columns and a high percent of water in the mobile phase. This method, when coupled with an ion suppression technique, proved successful for the retention and separation of acrylic acid. A retention time of approximately six minutes is obtained with a Dupont Zorbax ODS eight-micron, silica packed column and a 96/4, water/acetonitrile mobile phase containing 0.1% by volume of phosphoric acid. The phosphoric acid serves to suppress the ionization of acrylic acid resulting in the retention of the undissociated form of the molecule. Under these conditions acrylic acid is separated from the potential interferences: methacrylic acid, acrylamide, acrolein, acrylonitrile, and acetic acid. Propanoic acid, a saturated precursor of acrylic acid, can be resolved from acrylic acid in a 13 minute analysis at 1 mL/min flow rate using a 0.1% aqueous phosphoric acid mobile base. Acrylic acid, because of its unsaturated nature, is approximately 100 times more sensitive at 210 nm on a weight basis than propanoic acid. This method permits the detection of acrylic acid in the presence of very high levels of propanoic acid.

No published data was found regarding a collection method for acrylic acid from air. In a personal communication, it was reported that silica gel tubes coated with either hydroquinone or *p*-methoxyhydroquinone were being evaluated as a means of sampling acrylic acid in air (Ref. 5.4.). Both of these compounds are commonly used in the acrylic-

acrylate industry to prevent polymerization of a variety of monomeric substances. No decomposition of acrylic acid was observed in evaluations performed at this laboratory using either hydroquinone treated or untreated silica gel tubes. It should be noted, however, that the standard used in this evaluation contained low, unspecified levels of p-methoxyhydroquinone inhibitor.

Further evaluations indicated that some problems with the retention of acrylic acid on SKC silica gel tubes could arise if air sampling is being performed for an extended time in humid atmospheres. No loss of acrylic acid from the front section of a silica gel tube occurred if 80% relative humidity air was sampled for one hour at a 0.1 L/min flow rate. With longer sampling times, a considerable migration from the front section of the sampling tube was observed. When 46.7 ug of acrylic acid in methanol was spiked into an atmosphere ahead of two silica gel tubes mounted in series, and humid air was drawn through the system for four hours at a 0.1 L/min flow rate, only 15% of the total analyte was retained on the front section of the first silica gel tube. (See Backup Data Section 4.9., Table 4.9.)

Differences in retention efficiency between two different lots of SKC silica gel tubes are also apparent from this data. The recently purchased lot 119 silica gel tubes are less effective in retaining acrylic acid in a humid atmosphere than the older SKC silica gel tubes which do not have a lot number designation. (See Backup Data Section 4.9., Table 4.9.) In addition to silica gel, several other solid sorbent materials were determined to be inadequate for sampling acrylic acid. Low desorption efficiencies were obtained for both charcoal and Porapak T sorbents using various ratios of methanol and water to desorb the spiked tubes. XAD-2 and XAD-4, both non-polar, styrene-divinyl benzene copolymers, gave 100% desorption efficiencies using methanol. However, neither of these two sorbents were totally effective in retaining acrylic acid when humid air was sampled. Six XAD-2 tubes retained an average of only 60% of 120 ug acrylic acid spikes when 80% relative humidity air was drawn through each tube for three hours at a 0.1 L/min flow rate. Although more effective in retaining acrylic acid than XAD-2, the higher surface area XAD-4 sorbent still lost an average of 20% of a 327 ug acrylic acid spike when 80% relative humidity air was drawn through duplicate sample tubes at a 0.1 L/min flow rate for 7.5 hours. Further studies on the collection of acrylic acid from air indicated that the solid sorbent, XAD-8, an acrylic ester polymer, was quite effective in collecting and retaining acrylic acid.

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Amounts equivalent to twice the target concentration for a four-hour air sample (327 ug) could be spiked into an atmosphere ahead of the sampling tube and effectively collected and recovered after 80% relative humidity air is drawn through the tube for four hours at 0.1 L/min. No breakthrough onto a second tube mounted in series was observed for acrylic acid collected from a spiked atmosphere, even though 80% relative humidity air was drawn through the system for 8 hours. Similar results were observed when relatively dry laboratory air was sampled. (See Backup Data Section 4.5.)

Although no problems were encountered with the use of XAD-8 in sampling for acrylic acid, it should be noted that there exists a similar polymeric acrylic ester, XAD-7, which because of its higher surface area may be a more effective sampling media for low molecular weight, polar substances. (Ref. 5.5) However, based on the evaluation procedures performed to date, an XAD-8 sorbent packed tube is currently recommended as the sampling media for acrylic acid in air.

1.1.2. Toxic Effects (This section is for information only and should not be taken as the basis of OSHA policy).

Acrylic acid is an acute local irritant. Exposure to its vapors can produce an irritating effect to the skin, eyes, nasal and bronchial passages. (Ref. 5.3.) An exposure of 300 ppm for six hours per day for 20 days resulted in nasal irritation, lethargy, and weight loss in three male and three female rats. A one time, five-hour exposure at saturated conditions (6000 ppm) produced nose and eye irritation, respiratory impairment, and death in one of four exposed rats. (Ref. 5.6.)

A large variability in the LD₅₀ value is reported for both rabbits and mice. LD₅₀ values for a single skin application ranging from 295 mg/kg bw (body weight) to 950 mg/kg bw are reported in rabbits. Oral LD₅₀ values in rats vary from 193 mg/kg bw to 3200 mg/kg bw. (Ref. 5.1.)

In a fetal rat toxicity study conducted by Singh, et al, a dose related increase in the incidences of skeletal abnormalities, reduced birth weights, and resorptions was observed with exposure of pregnant rats to acrylic acid. (Ref. 5.7.) The authors note however, that the effects observed by acrylic acid and several methacrylate esters were not as pronounced as was observed for phthalate ester treated rats in previous studies.

The International Agency for Research in Cancer (IARC) reports that there is no data available regarding the carcinogenic potential of acrylic acid, and recommends study in this area. (Ref. 5.1.)

The recommended target concentration of 2 ppm is based on the results of a recent industry sponsored subchronic-inhalation study of mice and rats. A slight focal degeneration of the olfactory mucosa was observed in a portion of the mice exposed to 5 ppm acrylic acid for 90 days. The 2 ppm level is a suggested TWA exposure limit of the Health and Safety Division of Rohm and Haas. (Ref. 5.8.)

1.1.3. Exposure

Exposure to acrylic acid vapors is primarily confined to production processes since most acrylic acid is used as a precursor in the production of a variety of different acrylates. The alkyl esters of acrylic acid are used to produce a number of products including acrylic fibers, emulsion and solution polymers, and surface coatings. Some of the free acid is used to produce polyacrylic acid, which has industrial uses as a thickener, flocculant, and binder. In 1976 three U.S. companies reported a production of 116.5 million kg of acrylic acid. (Ref. 5.1., 5.3.)

1.1.4. Physical Properties (Ref. 5.9. unless otherwise indicated)

M.W.:	72.06
Solubility:	Miscible in alcohol and ether. Soluble in acetone and benzene.
B.P.:	141°C at 760 mm
Flash Point:	155°F (Ref. 5.10.) Cleveland open cup.
Specific Gravity:	1.05 (20/4°C)
Color:	Clear, colorless (Ref. 5.10.)
Odor:	Pungent, irritating, odor resembling acetic acid. (Ref. 5.10.)
Formula:	$H_2C=CHCOOH$
Synonyms:	Acroleic acid, propenoic acid, ethylene carboxylic acid, propene acid, vinyl formic acid (Ref. 5.11.)

1.2. Limit defining parameters

1.2.1. Detection limit of the analytical procedure

The detection limit of the analytical procedure is 5 ng per injection. This is the amount of analyte which will give a peak whose height is five times the amplitude of the baseline noise. (See Backup Data Section 4.1., Figure 4.2.).

1.2.2. Detection limit of the overall procedure

The detection limit of the overall procedure is 1 μg per sample (0.014 ppm/0.042 mg/m^3). This is the amount of analyte spiked on the sampling device which allows recovery of an amount of analyte equivalent to the detection limit of the analytical procedure. (See backup data section 4.2.)

1.2.3. Reliable quantitation limit

The reliable quantitation limit is 1 μg per sample (0.014 ppm/0.042 mg/m^3). This is the smallest amount of analyte which can be quantitated within the requirements of 75% recovery and 95% confidence limits of $\pm 25\%$. (See Backup Data Section 4.3.)

It must be recognized that the reliable quantitation limit and detection limits reported in the method are based upon optimization of the instrument for the smallest possible amount of analyte. When the target concentration of an analyte is exceptionally higher than these limits, they may not be attainable at the routine operating parameters. In this case, the limits reported on analysis reports will be based on the operating parameters used during the analysis of the samples.

1.2.4. Sensitivity

The sensitivity of the analytical procedure over a concentration range representing 0.5 to 2 times the target concentration based on the recommended air volume is 12,415 area units per $\mu\text{g}/\text{mL}$. The sensitivity is determined by the slope of the calibration curve. (See Backup Data Section 4.4., Figure 4.4.) The sensitivity will vary somewhat with the particular instrument used in the analysis.

1.2.5. Recovery

The average recovery from spiked samples over the range of 0.5 to 2 times the target concentration is 102%. (See Backup Data Section Table 4.7.) The recovery of analyte from the collection medium must be 75% or greater.

1.2.6. Precision (Analytical method only)

The pooled coefficient of variation obtained from eight replicate determinations of analytical standards at 0.5X, 1X and 2X the target concentration is 0.0085. (See Backup Data Section 4.6.)

1.2.7. Precision (Overall Procedure)

The overall procedure must provide results at the target concentration that are $\pm 25\%$ or better at the 95% confidence level. The average precision at the 95% confidence level for the ambient storage tests is $\pm 14\%$. (See Backup Data Section Figure 4.8.1. and Table 4.8.1.) This includes an additional $\pm 5\%$ for sampling error.

1.3. Advantages

1.3.1. The sensitivity of the analytical method permits sampling times as short as 15 minutes.

1.3.2. HPLC analysis of acrylic acid is rapid, direct, and sensitive.

1.3.3. Reanalysis of samples is possible.

1.4. Disadvantages

The method has not been field tested at this time.

2. Sampling Procedure

2.1. Apparatus

2.1.1. A personal sampling pump which can be calibrated to within 5% of the recommended 0.1 L/min flow rate while the sampling tubes are in line.

2.1.2. Glass tubes of 4- to 5-cm length with a 4-mm ID and a 6-mm OD are packed with approximately 100 mg of XAD-8 solid sorbent of 16-50 mesh size. Small silanized glass wool plugs on each end of the tube are used to retain the sorbent. These packed XAD-8 tubes are currently available from the laboratory upon request.

April 6, 1990

Dr. Rafael Moure
University of Lowell

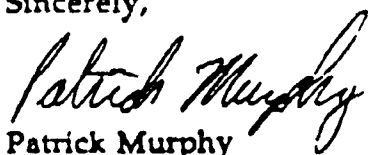
METHOD FOR THE ANALYSIS OF ORGANIC ACIDS IN AIR

Dear Dr. Moure:

This is a brief description of the organic acids analysis method that we discussed on the phone earlier today. Formic, acetic, and acrylic acids can be collected simultaneously on silica gel tubes (700 mg front/300 mg back), with a flow of about 100 mL/min. The acids are then desorbed using de-ionized water (typically 10 mL), with a 1-hour extraction time (we use a flatbed shaker). We have typically seen recoveries in excess of 90%, but we always run some spiked tubes with our samples to confirm the recoveries.

The extraction solvent is then analyzed using high-performance liquid chromatography (HPLC). The column we have found to work the best is an Aminex HPX-87H ion exclusion column (7.8 x 300 mm), which is manufactured by Bio-Rad Laboratories (32 nd Street, Richmond, CA 94804, catalog # 125-0140). The eluent was 0.01 N H₂SO₄ at a flow of 1 mL/min. U.V. detection at 208 nm was used, which was fed into our laboratory data system. Retention times for formic, acetic and acrylic acids were about 8.4, 9.3, and 11.8 minutes, respectively. The limit of detection for formic and acetic acid was about 1 µg/mL in solution, while the LOD for acrylic acid was about 0.1 µg/mL. With a desorption volume of 10 mL and an air sample volume of about 20 L, the corresponding LOD's in air are around 0.2 ppm and 0.02 ppm, respectively. Some representative chromatograms are shown on the next page. If you have any further questions, please do not hesitate to give me a call.

Sincerely,



Patrick Murphy
H&ES Analytical Chemistry
The Dow Chemical Company
1803 Building
Midland, MI 48674
(517) 636-0629

21574151

BFG15455

4. Aerosol Sampling
* Total Dust NIOSH -0600

21574152

BFG15456

FORMULA: The respirable fraction of the dust mass, as specified by the American Conference of Governmental Industrial Hygienists [1]

NUISANCE DUST, RESPIRABLE

METHOD: 0600
ISSUED: 2/15/84

OSHA: 5 mg/m³
NIOSH: no standard
ACGIH: 5 mg/m³

PROPERTIES: Penetrates the non-ciliated portions of the lung; quartz less than 1%

SYNONYMS: boron oxide (CAS #1303-86-2) and nuisance dusts [2], including alumina (CAS #1344-28-1), calcium carbonate (CAS #1317-65-3), cellulose (paper fiber; CAS #9004-34-6), glycerin mist (CAS #56-81-5), limestone (CAS #1317-65-3), etc.

SAMPLING	MEASUREMENT
SAMPLER: CYCLONE + FILTER (10-mm Dorr-Oliver cyclone + tared 5- μ m PVC membrane)	! TECHNIQUE: GRAVIMETRIC (FILTER WEIGHING) ! ! ANALYTE: mass of respirable dust fraction !
FLOW RATE: 1.7 L/min	! BALANCE: 0.01 mg sensitivity or better; use same balance before and after sample collection !
VOL-MIN: 75 L @ 5 mg/m ³ -MAX: 1000 L @ 5 mg/m ³	! ! CALIBRATION: National Bureau of Standards Class M weights !
SHIPMENT: routine	! ! RANGE: 0.3 to 2 mg per sample !
SAMPLE STABILITY: indefinitely	!
BLANKS: 2 to 10 field blanks per set	! ESTIMATED LOD: 0.2 mg per sample !
	! PRECISION: 68 μ g with 0.01-mg sensitivity balance [5] !
ACCURACY	!
RANGE STUDIED: 0.5 to 10 mg/m ³ (lab and field)	!
BIAS: depends on dust size distributions [3]	!
OVERALL PRECISION (s_p): 0.043 to 0.145 (lab); 0.144 to 0.227 (field) [4]	!

APPLICABILITY: The method measures the mass concentration of any non-volatile respirable dust. Besides inert dusts [1], the method is recommended for respirable coal dust, which has an OSHA PEL = 2.4 mg/m³. The method may be biased where the respirable fraction is defined by the British Medical Research Council's criteria or the MRE horizontal elutriator [4].

INTERFERENCES: Larger than respirable particles (over 10 μ m) have been found in some cases by microscopic analysis of cyclone filters. Over-sized particles in the sample are known to be caused by inverting the cyclone assembly. Heavy dust loadings, charged particles, fibers and water-saturated dusts also interfere with the cyclone's size-selective properties.

OTHER METHODS: This method is based on and replaces Sampling Data Sheet #29.02 [6].

2/15/84

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EQUIPMENT:

1. Sampler:

- a. Filter: 37-mm diameter, 5.0- μ m pore size, polyvinyl chloride filter or equivalent hydrophobic membrane filter supported with backup pad in a two-piece, 37-mm cassette filter holder held together by tape or cellulose shrink band.
 - b. Cyclone: 10-mm Dorr-Oliver nylon cyclone.
 - c. Sampling head holder: this holder must keep the cassette, cyclone and coupler together rigidly so that air enters only at the cyclone inlet.
2. Personal sampling pump, 1.7 L/min $\pm$ 5%, with flexible connecting tubing.
NOTE: Pulsation in the pump flow must be within $\pm$ 20% of the mean flow.
 3. Balance, analytical, with sensitivity of at least 0.01 mg. A more sensitive balance will be necessary for substances with PEL's below 1 mg/m³.
 4. Static neutralizer, e.g., Po-210; replace nine months after the production date.
 5. Environmental chamber for balance, e.g., 20 °C $\pm$ 0.3 °C and 50% $\pm$ 5% RH.
 6. Vacuum desiccator.

SPECIAL PRECAUTIONS: None.

PREPARATION OF SAMPLERS BEFORE SAMPLING:

1. Dry filters and backup pads under vacuum in the vacuum desiccator for at least 15 min.
2. Release the vacuum, remove the desiccator cover, and equilibrate the filters in the environmental chamber for at least 1 hr.
3. Number the backup pads with a ballpoint pen and place them, numbered side down, in filter cassette bottom sections.
4. Weigh the filters in the environmental chamber. Record the filter tare weight, W_1 (mg).
 - a. Zero the balance before each weighing;
 - b. Handle the filter with forceps (nylon forceps if further analyses will be done); and
 - c. Pass the filter over an antistatic radiation source. Repeat this step if filter does not release easily from the forceps or if filter attracts balance pan. Static electricity can cause erroneous weight readings.
5. Place the weighed filters on top of the backup pads in the filter cassette bottom sections and allow to stand an additional 8 to 16 hrs in the environmental chamber.
6. Reweigh the filters. If this tare weight differs by more than 0.01 mg from the first tare weight obtained in step 4 above, discard the filter.
NOTE: Insert a rod through the outlet hole of the filter cassette bottom section to raise the backup pad and filter so that the filter can be grasped with forceps.
7. Assemble the filters in the filter cassettes and close firmly so that leakage around the filter will not occur. Place a plug in each opening of the filter cassette. Place a cellulose shrink band around the filter cassette, allow to dry, and mark with the same number as the backup pad.
8. Remove the cyclone's grit cap and vortex finder before use and inspect the cyclone interior. If the inside is visibly scored, discard this cyclone since the dust separation characteristics of the cyclone might be altered. Clean the interior of the cyclone to prevent reentrainment of large particles.
9. Assemble the sampler head. Check alignment of filter holder and cyclone in the sampling head to prevent leakage.

SAMPLING:

10. Calibrate each personal sampling pump to 1.7 L/min with a representative sampler in line.
11. Sample at 1.7 L/min for 45 min to 8 hrs (76 to 816 L). Do not exceed 5 mg dust loading on the filter.

NOTE: Do not allow the sampler assembly to be inverted at any time. Turning the cyclone to anything more than a horizontal orientation may deposit over-sized material from the cyclone body onto the filter.

SAMPLE PREPARATION:

12. Wipe dust from the external surface of the filter cassette with a moist paper towel to minimize contamination. Discard the paper towel.
13. Remove the top and bottom plugs from the filter cassette. Place the filter cassettes in a vacuum desiccator under vacuum for at least 15 min, followed by equilibration for at least 1 hr in the environmental chamber.
14. Remove the filter cassette band, pry open the filter cassette, and remove the filter by inserting a rod in the outlet hole of the filter cassette. Handle the filters very gently by the edge to avoid loss of dust.

NOTE: If the filter sticks to the underside of the cassette top, very gently lift away by using the dull side of a scalpel blade. This must be done carefully or the filter will tear.

CALIBRATION AND QUALITY CONTROL:

15. Zero the microbalance before all weighings. Use the same microbalance for weighing filters before and after sample collection. Calibrate the balance with National Bureau of Standards Class M weights.
16. Take two to four replicate samples for every batch of field samples for quality assurance on the sampling procedures. The set of replicate samples should be exposed to the same dust environment, either in a laboratory dust chamber [7] or in the field [8]. The quality control samples must be taken with the same equipment, procedures and personnel used in the routine field samples. Calculate precision from these replicates and record s_r on control charts. Take corrective action when the precision is out of control [7].

MEASUREMENT:

17. Weigh each filter, including field blanks. Record this post-sampling weight, W_2 (mg), beside its corresponding tare weight. Record anything remarkable about a filter (e.g., visible particles, overloaded, leakage, wet, torn, etc.).

CALCULATIONS:

18. Calculate the concentration of respirable nuisance dust, C (mg/m³), in the air volume sampled, V (L):

$$C = \frac{(W_2 - W_1) + B}{V} \cdot 10^3, \text{ mg/m}^3$$

where: W_1 = tare weight of filter before sampling (mg)

W_2 = post-sampling weight of sample-containing filter (mg)

B = mean change in field blank filter weights between tare and post-sampling (mg) (+ or -).

EVALUATION OF METHOD:

1. Bias. In respirable dust measurements, the bias in a sample is calculated relative to the appropriate respirable dust criterion. The theory for calculating bias is developed by Bartley and Breuer [3]. For this method, the bias, therefore, depends on the ACGIH criterion for respirable dust, the cyclone's penetration curve at 1.7 L/min flow rate, and the size distribution of the ambient dust. Based on the cyclone's penetration curves for non-pulsating flow measured with a monodisperse aerosol by Caplan, Doemeny and Sorenson [9], the bias in this method is shown in Figure 1.

For dust size distributions in the shaded region, the bias in this method lies within the ± 0.10 criterion established by NIOSH for method validation. Bias larger than ± 0.10 would, therefore, be expected for many workplace aerosols, especially those with small mass median diameters. However, bias within ± 0.20 would be expected for dusts with geometric standard deviations greater than 2.0, which is the case in most workplaces.

Bias can also be caused in a cyclone by the pulsation of the personal sampling pump. Bartley, et al. [10] showed that cyclone samples with pulsating flow can have negative bias as large as -0.22 relative to samples with steady flow. The magnitude of the bias depends on the amplitude of the pulsation at the cyclone aperture and the dust size distribution. For pumps with instantaneous flow rates within 20% of the mean, the pulsation bias is less than -0.02 for most dust size distributions encountered in the workplace.

Electric charges on the dust and the cyclone will also cause bias. Briant and Moss [11] have found electrostatic biases as large as -50%, and show that cyclones made with graphite-filled nylon eliminate the problem.

2. Precision. In a recent review [4], the overall cyclone precision is shown to be most sensitive to two factors: the analytical precision and the sampling procedures, particularly the quality control system used in the maintenance and calibration of samplers. Theoretically, the variance for the overall precision is the sum of the variances from the sampling and analysis. The analytical variance depends on the dust loading on the filter. For the dust loading in an 8-hr sample above 1.5 mg/m³, Bowman, et al. [4] find that the empirically determined sampling error dominates this analytical error.

Because of the effects of the environment, precision estimates for dust samplers are much more variable than those reported for gas and vapor sampling. In laboratory tests with 0.01 mg sensitivity balances, the overall precision of a single respirable dust sample has relative standard deviations (s_r) from 0.043 to 0.145 over concentrations ranging from 0.5 to 5 mg/m³. In the laboratory studies where the dust concentrations in the test chamber are more carefully controlled, the estimated s_r is less than 0.091, which is the target precision value for a bias equal to ± 0.10 in the NIOSH validation criteria.

In the field tests with 0.01 mg sensitivity balances, precision estimates range from 0.144 to 0.227 over concentrations ranging from 1 to 10 mg/m³. Whether the larger s_r values in field tests are due to sampler performance or to more inhomogeneous dust concentrations in the field tests cannot be determined from existing data.

REFERENCES:

- [1] TLVs - Threshold Limit Values for Chemical Substances and Physical Agents in the Work Environment with Intended Changes for 1983-84, 38, ACGIH, Cincinnati, OH (1983).
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- [3] Bartley, D. L. and G. M. Breuer. Analysis and Optimization of the Performance of the 10-mm Cyclone, Am. Ind. Hyg. Assoc. J., 43, 520-528 (1982).
- [4] Bowman, J. D., D. L. Bartley, G. M. Breuer and S. A. Shulman. The Accuracy of Sampling Respirable Coal Mine Dust, Draft NIOSH report (1983).
- [5] Parobeck, P., T. F. Tomb, H. Ku and J. Cameron. Measurement Assurance Program for the Weighings of Respirable Coal Mine Dust Samples, J. Qual. Tech., 13, 157 (1981).
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- [8] Breslin, J. A., S. J. Page and R. A. Jankowski. Precision of Personal Sampling of Respirable Dust in Coal Mines, U.S. Bureau of Mines Report of Investigations #8740 (1983).
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- [11] Briant, J. K. and O. R. Moss. The Influence of Electrostatic Charge on the Performance of 10-mm Nylon Cyclones, American Industrial Hygiene Conference (1983).

METHOD WRITTEN BY: Joseph Bowman, Ph.D., CIH, NIOSH/DPSE.

2/15/84

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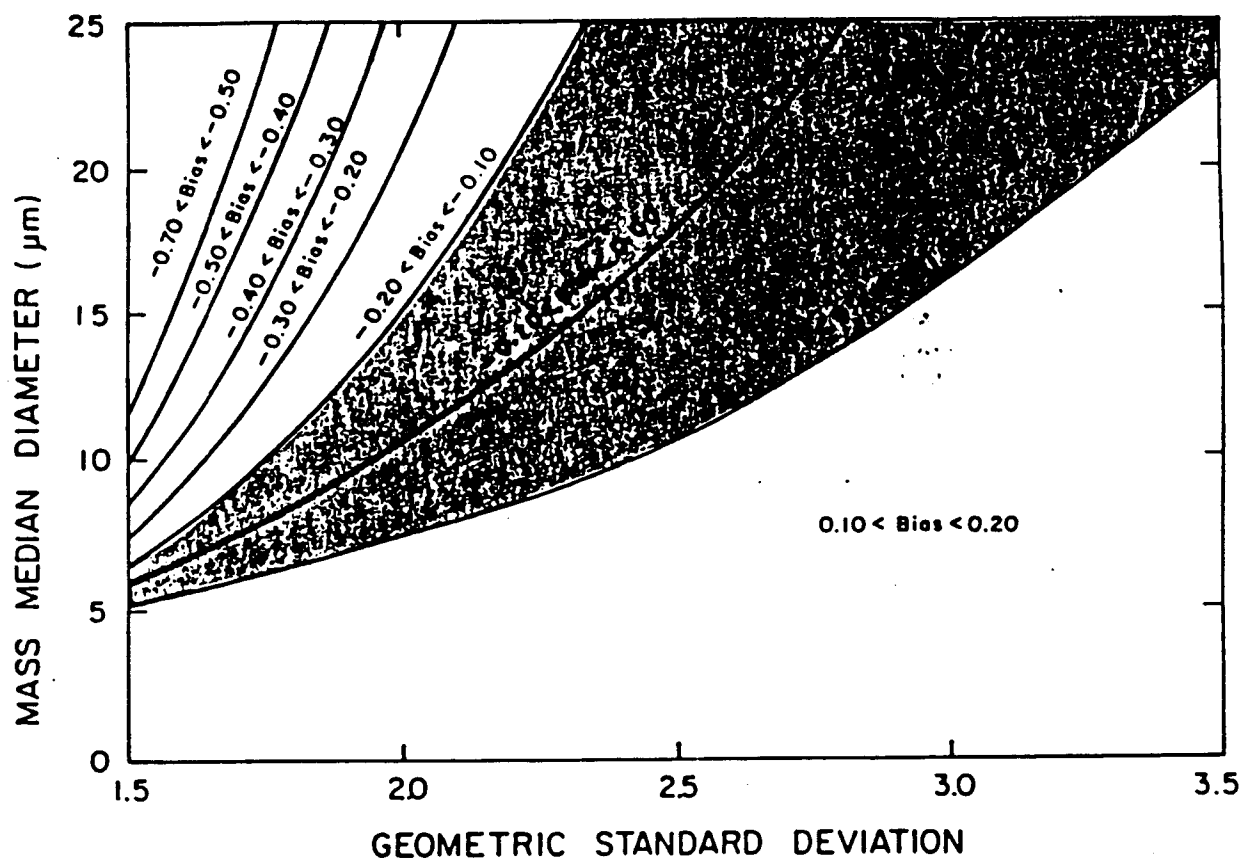


Figure 1. Bias in respirable dust determination.

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4. Aerosol Sampling
* Benzene Soluble Particulate NIOSH - 5023

21574159

BFG15463

COAL TAR PITCH VOLATILES

METHOD: 5023
ISSUED: 5/15/85

OSHA: 0.2 mg/m³ (benzene-solubles)
NIOSH: 0.1 mg/m³/10 hr
(cyclohexane-solubles) [2,3]
ACGIH: 0.2 mg/m³ (benzene solubles) [4]

PROPERTIES: liquid; d ~1.06 g/mL @ 38 °C;
60 to 85% distills @ <355 °C [5];
creosote distills @ 270 to 395 °C [2]

SYNONYMS: benzene-solubles, cyclohexane-solubles, coal tar pitch volatiles (CAS #8007-45-2), creosote from coal tar.

SAMPLING

MEASUREMENT

SAMPLER: FILTER
(2- μ m, 37-mm PTFE membrane)

FLOW RATE: 1 to 4 L/min

VOL-MIN: 500 L @ 0.2 mg/m³
-MAX: 2400 L

SHIPMENT: routine

SAMPLE STABILITY: unknown

FIELD BLANKS: 10% (>2) of samplers

ACCURACY

RANGE STUDIED: not studied

BIAS: unknown

OVERALL PRECISION (s_p): not determined

!TECHNIQUE: GRAVIMETRIC

!ANALYTE: organic-solubles (includes anthracene,
! benzanthracene, benzo(a)pyrene,
! carbazole, chrysene, phenanthrene,
! pyrene and others [1,2,3,4])

!EXTRACTION: benzene, cyclohexane or other
! appropriate solvent;
! ultrasonic 20 min

!CALIBRATION: National Bureau of Standards
! Class M weights

!RANGE: 0.1 to 2 mg per sample

!ESTIMATED LOD: 0.05 mg per sample [6]

```
!PRECISION (sr): 0.02 at 1.35 mg [6];
!               0.23 for blanks [6]
```

APPLICABILITY: The working range is 0.1 to 2 mg/m³ for a 1000-L air sample. The method is useful for air monitoring of coke oven emissions, petroleum combustion products such as diesel emissions, and petroleum asphalt fumes. The method may be applied to bulk samples. The method is non-specific and measures all substances in the sample which are soluble in the solvent selected and which can be desorbed from particulate matter present on the filter.

INTERFERENCES: Changes in temperature or humidity during pre- and post-collection weighing affect accuracy. Losses may occur due to volatilization of collected aerosol during or after sampling.

OTHER METHODS: This method modifies and combines P&CAM 217 [7] and the criteria document method [2].

5/15/85

5023-1

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REAGENTS:

1. Solvent: Benzene,* cyclohexane or other solvent, reagent grade.
2. Dichromic acid cleaning solution.
3. Acetone, reagent grade.
4. Hexane.

*See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: PTFE laminated membrane filter, 2- μ m pore size, 37-mm diameter (Zeflour, Membrana Inc., Pleasanton, CA or equivalent) backed by a gasket (37 mm OD, 32 mm ID) cut from a cellulose support pad in plastic filter holder.
2. Personal sampling pump, 1 to 4 L/min, with flexible connecting tubing.
3. Ultrasonic bath.
4. Microbalance, readable to 1 μ g, with NBS Class M weights.
5. Environmental chamber for balance, e.g., 20 °C $\pm$ 0.3 °C and 50% $\pm$ 5% relative humidity.
6. Weighing cups, PTFE, 2-ml, approximate tare weight 60 mg, in metal rack.
7. Vacuum oven.
NOTE: Keep the interior of the vacuum oven dust-free for maximum sensitivity, reproducibility, and accuracy.
8. Forceps.
9. Test tubes, PTFE-lined, screw cap, 13 mm x 100 mm.*
10. Filter, 0.5- μ m (Millex-SR, Millipore Corp., Bedford, MA or equivalent).
11. Pipets, 1- and 5-ml.*

*Rinse with distilled water, acetone, and hexane; dry.

SPECIAL PRECAUTIONS: Benzene and coal tar pitch volatiles are suspect carcinogens [1,2,3,4].

SAMPLING:

1. Calibrate each sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 1 and 4 L/min for a total sample volume of 500 to 2400 L. Do not exceed a filter loading of ca. 2 mg total particulate.
3. Replace caps in cassette and ship to laboratory.

SAMPLE PREPARATION:

4. Transfer filter carefully using forceps to test tube. Add 5.0 mL solvent via pipet. Cap the tube.
NOTE 1: Cyclohexane is recommended as solvent because of the carcinogenic potential of benzene [2].
NOTE 2: This extraction is also applicable to bulk samples (ground and sieved to ca. 250 μ m). Extract 250 mg bulk sample with 5.0 mL solvent.
5. Place tube upright in beaker containing water to the same level as the liquid in the tube. Place beaker and tube in ultrasonic bath. Sonicate for 20 min.
6. Filter solution through a 0.5- μ m filter into a clean, preweighed weighing cup. Discard the filter.
NOTE: An aliquot of the solution may be taken at this step if other analyses (e.g., polynuclear aromatic hydrocarbons) are to be performed on the sample. Apply the appropriate aliquot factor in calculations.

CALIBRATION AND QUALITY CONTROL:

7. Zero the microbalance on the 1.0 mg range and calibrate per balance manufacturer's directions.
- NOTE: Perform weighings at constant temperature and relative humidity.
8. Process three blank filters through the extraction and measurement procedures.

MEASUREMENT:

9. Transfer via pipet a 1.0-ml aliquot of sample extract to a preweighed weighing cup.
10. Place weighing cup in vacuum oven preheated to 40 °C. Apply vacuum until pressure in the oven is 7 to 27 kPa (50 to 200 mm Hg). Allow solvent to evaporate for 2 hrs. Release vacuum by slowly opening release valve which has an in-line filter to remove room dust.
11. Equilibrate the weighing cup to the temperature and relative humidity of the balance room for at least 30 min. Weigh the weighing cup to the nearest microgram.

CALCULATIONS:

12. Determine the mass of organic-soluble residue found in the sample, W (µg), and in the average media blank, B (µg).
13. Calculate concentration, C, of organic-solubles in the air volume sampled, V (L):

$$C = \frac{(W - B) \cdot 5}{V} \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Several benzene extracts of samples of aluminum reduction plant emissions were combined to give a solution containing 1.35 mg of benzene-soluble material per sample; nine aliquots of this solution gave residue weights with a relative standard deviation of 0.02. Benzene extracts of six blank filters gave residue weights with a relative standard deviation of 0.23 [7].

REFERENCES:

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METHOD REVISED BY: B. R. Belinky, NIOSH/DPSE.

4. Aerosol Sampling
* Lead NIOSH - 7082

21574163

BFG15467

FORMULA: Pb

LEAD

M.W.: 207.19 (Pb); 223.19 (PbO)

METHOD: 7082

ISSUED: 2/15/84

OSHA: 0.05 mg/m³

PROPERTIES: soft metal;

NIOSH: 0.05 mg/m³ [1]

d 11.3 g/cm³; MP 327.5 °C;

ACGIH: 0.15 mg/m³; STEL 0.45 mg/m³

valences +2, +4 in salts

SYNONYMS: vary depending upon the chemical form (elemental lead and lead compounds except alkyl lead); CAS #1317-36-8 (PbO); CAS #7439-92-1 (Pb).

SAMPLING	MEASUREMENT
SAMPLER: FILTER (0.8-µm cellulose ester membrane)	!TECHNIQUE: ATOMIC ABSORPTION, FLAME
FLOW RATE: 1 to 4 L/min	!ANALYTE: lead
VOL-MIN: 200 L @ 0.05 mg/m ³	!ASHING: conc. HNO ₃ , 6 mL; 140 °C
-MAX: 1200 L	!FINAL SOLUTION: 10% HNO ₃ , 10 mL
SHIPMENT: routine	!FLAME: air-acetylene, oxidizing
SAMPLE STABILITY: stable	!WAVELENGTH: 283.3 nm
BLANKS: 2 to 10 field blanks per set	!BACKGROUND CORRECTION: D ₂ or H ₂ lamp
	!CALIBRATION: Pb ⁺⁺ in 10% HNO ₃
	!RANGE: 10 to 200 µg per sample [3,8]
	!ESTIMATED LOD: 2.6 µg per sample [9]
	!PRECISION (s _p): 0.03 [2]
ACCURACY	
RANGE STUDIED: 0.13 to 0.4 mg/m ³ [2]; 0.15 to 1.7 mg/m ³ (fume) [3]	
BIAS: not significant [2]	
OVERALL PRECISION (s _p): 0.072 [2]; 0.068 (fume) [3]	
APPLICABILITY: The working range is 0.025 to 0.5 mg/m ³ for a 400-L air sample. The method is applicable to elemental lead, including Pb fume, and all other aerosols containing lead. This is an elemental analysis, not compound specific. Aliquots of the samples can be analyzed separately for additional elements.	
INTERFERENCES: Use D ₂ or H ₂ continuum background correction to control flame or molecular absorption. High concentrations of calcium, sulfate, carbonate, phosphate, iodide, fluoride, or acetate can be corrected.	
OTHER METHODS: This method combines and replaces P&CAM 173 [8] and S341 [7,9] for lead. Method 7300 (ICP-AES) is an alternate analytical method. Method 7505 is specific for lead sulfide. The following have not been revised: the dithizone method, which appears in P&CAM 102 [4] and the lead criteria document [1]; P&CAM 191 (ASV) [5]; and P&CAM 214 (graphite furnace-AAS) [6].	

2/15/84

7082-1

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REAGENTS:

1. Nitric acid, conc.
2. Nitric acid, 10% (w/v). Add 100 mL conc. HNO_3 to 500 mL water; dilute to 1 L.
3. Hydrogen peroxide, 30% H_2O_2 (w/w), reagent grade.
4. Calibration stock solution, 1000 μg Pb/mL. Commercial standard or dissolve 1.00 g Pb metal in minimum volume of (1+1) HCl and dilute to 1 L with 1% (v/v) HCl. Store in a polyethylene bottle. Stable $\geq$ one year.
5. Air, compressed, filtered.
6. Acetylene.
7. Distilled or deionized water.

EQUIPMENT:

1. Sampler: Cellulose ester filter, 0.8- μm pore size, 37-mm diameter; in cassette filter holder.
2. Personal sampling pump, 1 to 4 L/min, with flexible connecting tubing.
3. Atomic Absorption Spectrophotometer with an air-acetylene burner head.
4. Lead hollow cathode lamp or electrode dischargeless lamp.
5. Regulators, two-stage, for air and acetylene.
6. Beakers, Phillips, 125 mL, or Griffin, 50 mL with watchglass covers.*
7. Volumetric flasks, 10- and 100-mL.*
8. Assorted volumetric pipets as needed.*
9. Hotplate, surface temperature 140° C.
10. Bottles, polyethylene, 100-mL.

*Clean all glassware with conc. nitric acid and rinse thoroughly with distilled or deionized water before use.

SPECIAL PRECAUTIONS: Perform all acid digestions in a fume hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 1 and 4 L/min for up to 8 hrs for TWA measurements. Do not exceed a filter loading of ca. 2 mg total dust.

SAMPLE PREPARATION:

NOTE: The following sample preparation gave quantitative recovery (see EVALUATION OF METHOD) [9]. Steps 4 through 9 of Method 7300 or other quantitative ashing techniques may be substituted, especially if several metals are to be determined on a single filter.

3. Open the cassette filter holders and transfer the samples and blanks to clean beakers.
4. Add 3 mL conc. HNO_3 , and 1 mL 30% H_2O_2 and cover with a watchglass. Start reagent blanks at this step.

NOTE: If PbO_2 is not present in the sample, the 30% H_2O_2 need not be added [3,9].

5. Heat on hotplate (140 °C) until most of the acid has evaporated.
6. Repeat two more times using 2 mL conc. HNO_3 and 1 mL 30% H_2O_2 each time.
7. Heat on 140 °C hotplate until a white ash appears.
8. When sample is dry, rinse the watchglass and walls of the beaker with 3 to 5 mL 10% HNO_3 . Allow the solution to evaporate to dryness.
9. Cool each beaker and dissolve the residues in 1 mL conc. HNO_3 .
10. Transfer the solution quantitatively to a 10-mL volumetric flask and dilute to volume with distilled water.

NOTE: If the concentration (M) of any of the following is expected to exceed the lead concentration (M) by 10-fold or more, add 1 mL 1 M Na_2EDTA to each flask before dilution to volume: CO_3^{2-} , PO_4^{3-} , I^- , F^- , CH_3COO^- . If Ca^{++} or SO_4^{2-} are present in 10-fold excess, make all standards and samples 1% (w/w) in La^{++} [8].

CALIBRATION AND QUALITY CONTROL:

11. Prepare a series of working standards covering the range 1 to 20 $\mu\text{g Pb/mL}$ (1 to 200 $\mu\text{g Pb per sample}$) by adding aliquots of calibration stock solution to 100-mL volumetric flasks. Dilute to volume with 10% HNO_3 . Store the working standards in polyethylene bottles and prepare fresh weekly.
12. Analyze the working standards together with the blanks and samples (steps 17 and 18).
13. Prepare a calibration graph of absorbance vs. solution concentration ($\mu\text{g/mL}$).
14. Aspirate a standard for every 10 samples to check for instrument drift.
15. Check recoveries with at least one spiked media blank per 10 samples.
16. Use method of additions occasionally to check for interferences.

MEASUREMENT:

17. Set spectrophotometer as specified by the manufacturer and to conditions on page 7082-1.

NOTE: An alternate wavelength is 217.0 nm [10]. Analyses at 217.0 nm have slightly greater sensitivity, but poorer signal-to-noise ratio compared to 283.3 nm. Also, non-atomic absorption is significantly greater at 217.0 nm, making the use of D_2 or H_2 continuum background correction mandatory at that wavelength.

18. Aspirate standards, samples, and blanks. Record absorbance readings.

NOTE: If the absorbance values for the samples are above the linear range of the standards, dilute with 10% HNO_3 , reanalyze, and apply the appropriate dilution factor in the calculations.

CALCULATIONS:

19. Using the measured absorbances, calculate the corresponding concentrations ($\mu\text{g/mL}$) of lead in the sample, C_s , and average media blank, C_b , from the calibration graph.
20. Using the solution volumes (mL) of the sample, V_s , and media blanks, V_b , calculate the concentration, C (mg/m^3), of lead in the air volume sampled, V (L):

$$C = \frac{C_s V_s - C_b V_b}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method 5241 [7] was issued on October 24, 1975, and validated over the range 0.13 to 0.4 mg/m^3 for a 180-L air sample, using generated atmospheres of lead nitrate [2]. Recovery in the range 18 to 72 $\mu\text{g Pb per sample}$ was 98%, and collection efficiency of 0.8- μm mixed cellulose ester filters (Millipore Type AA) was 100% for the aerosols. Subsequent studies on analytical recovery of 200 $\mu\text{g Pb per sample}$ gave the results [3,9]:

Species	Digestion Method	Analytical Recovery, %
Pb metal	HNO_3 only	92 ± 4
Pb metal	$\text{HNO}_3 + \text{H}_2\text{O}_2$	103 ± 3
PbO	HNO_3 only	93 ± 4
PbS	HNO_3 only	93 ± 5
PbO ₂	HNO_3 only	82 ± 3
PbO ₂	$\text{HNO}_3 + \text{H}_2\text{O}_2$	100 ± 1
Pb in paint*	HNO_3 only	95 ± 6
Pb in paint*	$\text{HNO}_3 + \text{H}_2\text{O}_2$	95 ± 6

*Standard Reference Material #1579, U.S. National Bureau of Standards.

Additional collection efficiency studies were also done using Gelman GN-4 filters for the collection of Pb fume, which had geometric mean diameter of 0.1 μ m [3]. Mean collection efficiency for 24 sampling runs at flow rates between 0.15 and 4.0 L/min was $>97 \pm 2\%$. Overall precision, s_p , was 0.072 for lead nitrate aerosol [2,7] and 0.068 for Pb fume [3,9].

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METHOD REVISED BY: Mark Millson and R. DeLon Hull, NIOSH/DPSE; S341 originally validated under NIOSH Contract CDC-94-74-45; additional studies under NIOSH Contract 210-79-0058.

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5. Hydrochloric Acid NIOSH - 7903

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INORGANIC ACIDS
Methods Research Branch
Analytical Method

Analyte:	Inorganic acids (Table I)	Method No.:	P&CAM 339
Matrix:	Air	Range:	Table I
Procedure:	Silica gel tube collection, eluent desorption, ion chromatography	Precision:	0.06-0.10
Date Issued:	8/18/81		
Date Revised:		Classification:	D (Operational)

1. Synopsis

- 1.1 A known volume of air is drawn through a silica gel sampling tube to collect the analyte. The samples are desorbed in an aqueous solution of 0.003 M NaHCO_3 /0.0024 M Na_2CO_3 with heat. Solutions of samples and standards are analyzed by means of an ion chromatograph.

2. Working Range, Sensitivity, and Detection Limit

- 2.1 For H_3PO_4 , H_2SO_4 , HNO_3 , and HBr , the working range is based on a 48-L air sample and on a 15-L air sample for HCl . Refer to Table I.
- 2.2 The sensitivity is expressed as μg per sample per mm chart deflection at a conductance setting of 10 μmhos full scale.
- 2.3 With a 10-mL final solution volume and the instrumental parameters stated in the method, the lowest analytically quantifiable level (LAQL) is stated as $\mu\text{g/sample}$ at 10% relative standard deviation. This lower limit may be extended through use of a more sensitive conductivity meter setting.

3. Interferences

- 3.1 Possible interferences in the method are SO_2 for H_2SO_4 and NO_2 for HNO_3 . Their collection potential on silica gel and reduction during desorption have not been investigated.
- 3.2 Chlorine or hypochlorite ion may interfere with chloride up to 50% of its initial concentration, and bromine may give an interference of approximately 30% of its original concentration as determined from spiked samples. The collection potential of these substances on silica gel has not been investigated.

4. Precision and Accuracy

- 4.1 The precision is expressed as percent relative standard deviation for the overall sampling and analytical method over the range stated for each acid (Table I).
- 4.2 The collection efficiencies for each of the acids are based on samples at three concentration levels, 0.2, 1 and 2 times the OSHA permissible exposure limits.

5. Advantages and Disadvantages

- 5.1 The advantage of ion chromatography over other methods is its capability of separating the ions such that each of the acid anions may be identified and measured in a single sample.
- 5.2 The method is specific for the acid anions. Different oxidation states of the acids have different retention times, e.g., NO_2 , NO_3 , SO_3^{2-} , SO_4^{2-} .
- 5.3 The sampling device is a solid sorbent collection tube and involves no liquids.
- 5.4 The sampling device will collect five inorganic acids in both particulate and vaporous forms.
- 5.5 Because identification is based on retention time, interferences may not be easily identified.

6. Apparatus

6.1 Air Sampling Equipment

- 6.1.1 Personal sampling pumps capable of operation at 0.2 L/min and calibrated to an accuracy of $\pm 5\%$ with a representative sampling tube in line.

- 6.1.2 Silica gel tubes. 7-mm o.d./4.8 mm i.d. glass tubes approximately 10 cm in length packed with 400 mg of 20/40 mesh washed silica gel in the front section and 200 mg in the backup section. Polyurethane foam plugs are placed between the sorbent sections and at the end. The front section of silica gel is held in place with a 5-mm diameter plug of thick glass fiber filter.

The silica gel is washed by the following procedure: Approximately a 200-mL volume of silica gel is placed in a 1-L beaker. 500-600 mL of deionized water is added slowly with stirring. When the exothermal reaction has subsided, the silica gel is heated in a 100 °C water bath for approximately 30 minutes with occasional stirring, decanted, and rinsed four to five times with deionized water. It is heated again in deionized water for 15-30 minutes, decanted, and rinsed thoroughly with deionized water. The silica gel is then dried overnight in a 100 °C oven until free flowing. If a blank of the silica gel shows any impurities, the washing procedure is repeated. Approximately 90% of the resulting silica gel will be 20/40 mesh.

- 6.1.3 Barometer.
- 6.1.4 Thermometer.
- 6.1.5 Hygrometer.
- 6.1.6 Stopwatch.
- 6.2 Ion chromatograph with a standard or fast run anion precolumn and separator column, a standard suppressor column, and conductimetric detector (Dionex Corp., Sunnyvale, CA, or equivalent).
- 6.3 Strip chart recorder.
- 6.4 Electronic integrator or some other suitable means of determining peak height (optional).
- 6.5 Centrifuge tubes, 15-mL, graduated.
- 6.6 Micropipettes with disposable tips for preparing standards.
- 6.7 Volumetric flasks, 100-mL and 25-mL or other convenient sizes for preparing standard solutions.
- 6.8 Syringes, 10-mL, polyethylene with luer tip.

6.9 In-line filter holders (Swinnex-type) with 25-mm membrane filters, 0.8 μ m pore size, or Acrodisc in-line filters.

6.10 Parafilm.

6.11 Water bath maintained at 100 °C.

7. Reagents

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

7.1 Deionized, filtered water. Conductivity grade deionized water with specific conductance of 10 μ mho/cm or less is needed for the preparation of eluents and other solutions used in the ion chromatograph. The water must be filtered before use to avoid plugging valves in the chromatograph.

7.2 Silica gel, 3/8 mesh, grade 01, thoroughly washed with deionized water (Sec. 6.1.2).

7.3 Sodium carbonate, Na_2CO_3 .

7.4 Sodium bicarbonate, NaHCO_3 .

7.5 Potassium chloride, KCl .

7.6 Monopotassium phosphate, KH_2PO_4 .

7.7 Potassium sulfate, K_2SO_4 .

7.8 Sodium nitrate, NaNO_3 .

7.9 Sodium bromide, NaBr .

7.10 Stock standard solutions (1000 μ g/mL). Dissolve salt in deionized, filtered water in a 100-mL volumetric flask, and dilute to volume with deionized, filtered water.

7.10.1 Chloride (1000 ppm Cl^-). Dissolve 0.2103 g KCl /100 mL.

7.10.2 Phosphate (1000 ppm PO_4^{3-}). Dissolve 1.433 g KH_2PO_4 /100 mL.

7.10.3 Sulfate (1000 ppm SO_4^{2-}). Dissolve 0.1814 g K_2SO_4 /100 mL.

7.10.4 Nitrate (1000 ppm NO_3^-). Dissolve 0.13707 g NaNO_3 /100 mL.

7.10.5 Bromide (1000 ppm Br⁻). Dissolve 0.1288 g NaBr/100 mL.

7.11 Eluent (0.003 M NaHCO₃/0.0024 M Na₂CO₃). Dissolve 1.008 g NaHCO₃ and 1.0176 g Na₂CO₃ in 4 L of deionized, filtered water.

8. Procedure

8.1 Cleaning of Equipment. Glassware and plasticware should be washed in detergent and thoroughly rinsed with deionized water. Acid cleaning is not recommended.

8.2 Collection and Shipping of Samples

8.2.1 Each personal sampling pump must be calibrated with a representative collection tube in line to assure accurately known sample volumes.

8.2.2 Immediately before sampling, break the ends of the collection tube to provide an opening of at least one half of the internal diameter of the tube.

8.2.3 Insert the tube in the sampling device with the glass fiber filter plug at the inlet. Place tube in a vertical position during sampling to minimize channeling through the sorbent.

8.2.4 Collect the sample at 0.2 Lpm. The air being sampled should not pass through any hose or tubing before entering the collection tube. A sample size of 48-L is recommended.

8.2.5 Record the temperature, relative humidity, and pressure of the air being sampled. If the pressure reading is not available, record the elevation.

8.2.6 After sampling, label the collection tubes appropriately and cap the ends with plastic caps.

8.2.7 With each batch of up to 10 samples submit one blank collection tube which has been subjected to the same handling except that no air has been drawn through it.

8.3 Analysis of Samples

8.3.1 Place the silica gel and glass fiber plug from the front section of the collection tube into a 15-mL graduated centrifuge tube. (The backup section is analyzed separately.)

8.3.2 Add 5-6 mL of eluent solution (Section 7.7) and heat in a 100 °C water bath for 10 minutes. Allow to cool and dilute to a 10-mL volume with eluent. Cover with Parafilm and shake vigorously.

8.3.3 Pour the contents into a 10-mL plastic syringe fitted with an in-line filter and collect the filtrate in a second syringe or autosampler vial.

8.3.4 Inject 100- μ L aliquots of the filtered sample into the ion chromatograph and record the sample identity and instrumental conditions. Typical operating conditions for inorganic acids are:

Eluent: 0.003 M NaHCO₃/0.0024 M Na₂CO₃
Flow Rate: 138 mL/hr (30% pump capacity)
Columns: Standard Anion precolumn
Standard Anion separator
Standard Anion suppressor

Conductivity
Meter Setting: 10 μ mho full scale
Injection Volume: 100 μ L
Recorder Speed: 30 cm/hr.

8.3.5 Measure and record peak height of each peak. The use of peak height is recommended over peak area for ion chromatography.

9. Calibration and Standardization

9.1 From the 1000 μ g/mL acid stock solutions in Section 7.10, prepare mixed working standards in the concentrations of 0.5, 1, 2, 5, 10, 15, and 20 μ g/mL in eluent solution (Section 7.7). The use of eluent eliminates the water dip in the chromatogram which occurs immediately before the elution of the chloride peak. These standards should be prepared fresh weekly and stored in polyethylene bottles.

9.2 With each set of samples analyzed, a complete calibration curve should be constructed. Plot peak height versus concentration.

10. Calculation

10.1 Read the concentration of each sample and blank from the calibration curve obtained in Section 9.2. Calculate the net concentration of each acid anion found

$$C_1 = C_2 - B$$

where: C_1 = acid anion concentration from air sample ($\mu\text{g/mL}$)
 C_2 = total acid anion found on silica gel tube ($\mu\text{g/mL}$)
 B = acid anion concentration from blank ($\mu\text{g/mL}$).

10.2 Calculate the concentration of acid in air sample.

10.2.1 Acid concentration in mg/m^3

$$C_A = \frac{F C_1 D}{V}$$

where: C_A = acid concentration in air (mg/m^3)
 C_1 = anion concentration in solution ($\mu\text{g/mL}$)
 D = final volume of desorbed sample (mL)
 V = volume of air sampled (L)
 F = factor for converting anion to acid.

<u>Acid</u>	<u>F</u>
H_3PO_4	1.032
H_2SO_4	1.021
HNO_3	1.016
HBr	1.0125
HCl	1.028

10.2.2 Vapor-forming acid concentration in ppm. One gram molecular weight of a gas occupies 24.45 L at 25 °C and 760 mm Hg pressure

$$C_B = K \times C_A \times \frac{760 \times T}{298 \times P}$$

where: C_B = acid concentration in air (ppm)
 C_A = acid concentration in air (mg/m^3)
 T = absolute temperature at which the sample was taken ($^{\circ}\text{K} = ^{\circ}\text{C} + 273$)
 P = air pressure at which the sample was taken (mm Hg).

$$K = \frac{\text{vol. acid}}{\text{g-mol. wt. acid}}$$

<u>Acid</u>	<u>K</u>
HNO_3	0.3881
HBr	0.3022
HCl	0.6699

References

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Appendix D
Calibration Sampling Equipment

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APPENDIX D

Calibration of Sampling Equipment

(OSHA Procedure (8), Industrial Hygiene OSHA Technical Manual, 1990)

1. Procedures for Calibration of Pump-Collector Tube System (Organic Vapor Collection) --Using Electronic Bubble Meter Method:

- (1) Allow the pump to run 5 minutes prior to voltage check and calibration.
- (2) Assemble the charcoal tube holder, using the appropriate tube for the sampling method. Compress charcoal tube by using a mechanical press or other means of applying pressure. Use shrink tape around charcoal tube to cover joints and prevent leakage. If a tube adaptor is using , care should be taken to ensure that it does not come in contact with the back-up pad.

NOTE : When calibrating with a bubble meter , the use of tube adaptors can cause moderate to severe pressure drop at high flow rates in the sampling train, which will affect the calibration result . If adaptors are used for sampling , then they should be used when calibrating.

CAUTION: Nylon adapters can restrict air flow due to plugging over time. Stainlesssteel adapters are preferred.

- (3) Connect the collection device, tubing , pump and calibration apparatus as shown in Figure 1 and 2 charcoal tube and cyclone samplers respectively.

- (4) A visual inspection should be made of all Tygon tubing connections.
- (5) Wet the inside of the electronic flow cell with the supplied soap solution by pushing on the button several times.
- (6) Turn on the pump and adjust the pump rotameter, if available, to the appropriate flow rate setting.
- (7) Press the button on the electronic bubble meter. Visually capture a single bubble and electronically time the bubble . The accompanying printer will automatically record the calibration reading in liters per minute.
- (8) Repeat step 7 until two reading are within 5% .
- (9) Repeat the procedures described above for all pumps to be used for sampling. The same charcoal tube may be used for all calibrations involving the same sampling methods.

2. Procedure for Calibration of Pump-Cassette Filter System (Particulate - total dust). --Using Electronic Bubble Meter Method:

- (1) Allow the pump to run 5 minutes prior to voltage check and calibration.
- (2) Assemble the polystyrene cassette filter holder, using the appropriate filter for the sampling method. Compress cassette by using a mechanical press or other means of applying pressure. Use shrink tape around cassette to cover joints and prevent leakage. If a cassette adaptor is using , care should be taken to ensure that it does not come

in contact with the back-up pad.

NOTE : When calibrating with a bubble meter , the use of cassette adaptors can cause moderate to severe pressure drop at high flow rates in the sampling train, which will affect the calibration result . If adaptors are used for sampling , then they should be used when calibrating.

CAUTION: Nylon adapters can restrict air flow due to plugging over time. Stainless steel adapters are preferred.

- (3) Connect the collection device, tubing , pump and calibration apparatus as shown in Figure 1 and 2 cassette and cyclone samplers, respectively.
- (4) A visual inspection should be made of all Tygon tubing connections
- (5) Wet the inside of the electronic flow cell with the supplied soap solution by pushing on the button several times.
- (6) Turn on the pump and adjust the pump rotameter, if available, to the appropriate flow rate setting.
- (7) Press the button on the electronic bubble meter. Visually capture a single bubble and electronically time the bubble . The accompanying printer will automatically record the calibration reading in liters per minute.
- (8) Repeat step 7 until two reading are within 5% .
- (9) Repeat the procedures described above for all pumps to be used for sampling. The same cassette and filter may be used for all calibrations involving the same sampling methods.