Sodium Hydroxide

Analyte:	Sodium Hydroxide	Method No.:	S381
Matrix:	Air	Range:	0.75 - 3.9 mg/cu m
OSHA Standard:	2 mg/cu m	Precision: ($\overline{CV}_T$):	0.062
Procedure:	Filter Collection, extraction with aqueous acid, back titration with sodium hydroxide	Validation Date:	7/8/77

1. Principle of the Method

1.1 A known volume of air is drawn through a polytetrafluorethylene filter to trap the sodium hydroxide aerosol present.

1.2 The sodium hydroxide collected is extracted from the filter by addition of a known amount of excess hydrochloric acid and the resultant solution purged with a stream of nitrogen gas.

1.3 The excess hydrochloric acid is titrated with a standard solution of sodium hydroxide under a nitrogen atmosphere.

1.4 The amount of sodium hydroxide collected is calculated from the difference between the known amount of acid added and the amount of acid remaining after extraction of the filter.

2. Range and Sensitivity

2.1 This method was validated over the range of 0.758-3.88 mg/cu m at an atmospheric temperature and pressure of 23°C and 758 mm Hg, using a 360-liter sample. For a sample size of 360 liters, the working range of the method is estimated to be 0.4-5.4 mg/cu m.

2.2 The method may be extended to higher concentrations by addition of larger aliquots of standard hydrochloric acid. The detection limit of the analytical method is estimated to be 28 µg of sodium hydroxide or 7×10^{-4} mmoles of alkalinity.

3. Interferences

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

3.2 It must be emphasized that the method determines total alkalinity present in particulate form and thus is not specific to sodium hydroxide.

3.3 If the titration curve obtained in the analysis is not one of a titration of a strong acid with a strong base then the presence of an interfering species is indicated and the results should be confirmed by an alternate method of analysis.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 0.758 - 3.88 mg/cu m was 0.0622. This value corresponds to a 0.124 mg/cu m standard deviation at the OSHA standard level. Statistical information can be found in Reference 10.1. Details of the test procedures are found in Reference 10.2.

4.2 A collection efficiency of at least 99.0% was determined for the collection medium; thus, no significant bias was introduced in the sample collection step. There was also no bias in the analytical method -- the average recovery from the filters was 99.7%. In addition, the samples were found to be stable when stored on the filters for seven days. Thus, $\overline{CV}_T$ is a satisfactory measure of both accuracy and precision of the sampling and analytical method.

5. Advantages and Disadvantages of the Method

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

5.2 The method measures the toxic species, alkalinity, and is free from interference of other non-alkaline sodium compounds.

5.3 The method is not specific for sodium hydroxide but measures total alkalinity and the presence of any other alkaline species will present an interference.

5.4 Interference by carbon dioxide during collection has been minimized by virtue of the back titration used in the analytical procedure.

6. Apparatus

6.1 Sampling Equipment. The sampling unit for the collection of personal air samples for the determination of aerosols has the following components:

6.1.1 Filter. The filter unit consists of the filter medium (Section 6.2) and 37-mm 3-piece cassette filter holder.

6.1.2 Personal Sampling Pump. A calibrated personal sampling pump whose flow can be determined to an accuracy of ±5% at the recommended flow rate is needed. The pump must be calibrated with a representative filter holder and filter in the line.

6.1.3 Thermometer.

6.1.4 Barometer.

6.1.5 Stopwatch.

6.2 A polytetrafluoroethylene (PTFE-Fluoropore) membrane filter, 1.0 micrometer pore size and 37-mm diameter. The filter is supported in the three-piece cassette by a cellulose backup pad.

6.3 Titration Assembly

6.3.1 A pH meter equipped with pH electrodes and a recorder (recommended chart drive of 1.5 inches per minute).

6.3.2 A titration vessel made from a 175-ml ointment jar (2.5 inches diameter) with two 5/8-inch holes drilled in the cap for the pH electrodes and two 3/8-inch holes for other inlets.

6.3.3 A constant feed syringe drive and syringe (recommended delivery rate of 1 ml per minute).

6.3.4 Magnetic stirrer and bar.

6.3.5 Glass rod, 5-mm diameter and 15-cm long.

6.3.6 Blunt-end Stainless Steel Needle, 10-cm long.

In the assembled apparatus the titration vessel contains the stirrer bar, solution to be titrated, the pH electrodes, nitrogen purge inlet and automatic syringe drive inlet all inserted through the cap and immersed in the solution. The vessel is positioned on top of the magnetic stirrer.

6.4 Pipets, 5 and 10 ml.

6.5 Balance, capacity of 1.000-100.000 g.

6.6 Ruler, graduated in millimeters.

6.7 Volumetric flasks, 100 and 1000 ml.

6.8 Glass bottle, 1 liter equipped with a stopper containing a trap filled with a suitable CO_2 absorbing material (recommended for storage of dilute sodium hydroxide solution).

6.9 Graduated Cylinder, 100 ml.

7. Reagents

All reagents used must be ACS Reagent Grade or better.

7.1 Distilled water.

7.2 Standard stock hydrochloric acid solution, 0.1N.

7.3 Standard dilute hydrochloric acid, 0.01N. Prepare by diluting 10 ml of the stock solution into 100 ml.

7.4 Stock sodium hydroxide solution, 0.1N.

7.5 Working sodium hydroxide solution, 0.01N. Prepare by dilution of stock with distilled water through which nitrogen has been passed for 30 minutes.

7.6 Nitrogen gas.

7.7 Standard Buffer Solutions, pH 4 and pH 7.

8. Procedure

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

8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative filter cassette in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples.

8.3.1 Assemble the filter in the three-piece filter cassette holder and close firmly to insure that the center ring seals the edge of the filter. The PTFE membrane filter is supported by a cellulose backup pad and the filter holder is held together by plastic tape or a shrinkable cellulose band. If the filter does not lay flat on the backup pad and the middle piece of the filter holder does not fit snugly into the bottom piece of the filter holder, sample leakage will occur around the filter. A piece of flexible tubing is used to connect the filter holder to the pump.

8.3.2 Clip the cassette to the worker's lapel. Air being sampled should not be passed through any hose or tubing before entering the filter cassette.

8.3.3 A sample size of 360 liters is recommended. Sample at a flow rate of 1.5 liters per minute for 4 hours. The flow rate should be known with an accuracy of at least ±5%.

8.3.4 Turn the pump on and begin sample collection. Since it is possible for filters to become plugged by heavy partic-

ulate loading or by the presence of oil mists or other liquids in the air, the pump rotameter should be observed frequently, and the sampling should be terminated at any evidence of a problem.

8.3.5 Terminate sampling at the predetermined time and note sample flow rate, collection time and ambient temperature and pressure. If pressure reading is unavailable, record the elevation. Replace filter plugs.

8.3.6 Blank. With each batch of ten samples submit one filter from the same lot of filters which was used for sample collection and which is subjected to the same handling as for the samples except that no air is drawn through it. Label this as a blank.

8.3.7 Shipping. The filter cassettes should be plugged and shipped in a suitable container, designed to prevent damage in transit.

8.4 Analysis of Samples

8.4.1 Set the pH recorder with the pH 4 and 7 buffers so that the range between pH 3 and 10 is recorded.

8.4.2 Add 75 ml of distilled water to the titration vessel.

8.4.3 Open the cassette filter holder and carefully remove the PTFE membrane filter from the holder and cellulose backup pad with the aid of appropriate tweezers. Transfer the filter to the titration vessel with the collection side face down. Place the end of a glass rod in the center of the filter to maintain it completely below the liquid surface during the complete analytical procedure. Replace the titration vessel cover and place the pH electrode in place.

8.4.4 Pipet 5 ml of 0.01N hydrochloric acid into the vessel, start the magnet stirrer and a nitrogen purge of the solution.

8.4.5 After 15 minutes have passed, titrate the solution with 0.01N sodium hydroxide while maintaining a nitrogen purge in the system. Initiate the syringe drive at a known position on the chart recorder paper so that the amount of NaOH added may be determined from the distance elapsed to the inflection point of the titration curve.

8.4.6 Appropriate filter blanks should be analyzed by the same procedure used for the samples.

8.5 Calibration of Syringe Drive and Chart Recorder

8.5.1 The syringe drive must be calibrated so that the volume

of sodium hydroxide added can be known accurately. Fill the syringe with the titrating solution and connect the delivery tube to a weighing bottle which has been pretared. Activate the syringe drive for a period of time sufficient to allow the delivery rate in grams/min to be determined by weighing the amount of liquid collected.

8.5.2 Determine the syringe delivery rate in ml/min by converting the grams/min to volume/min using the density of the solution at the appropriate temperature.

8.5.3 Calibrate the chart speed on the recorder and accurately determine the speed (in mm/minute).

8.5.4 Using the calibrated syringe delivery rate and the recorder chart speed calculate the volume per mm on the chart paper.

ml per mm = ml per minute/mm per minute

8.6 Determination of Sample Recovery

8.6.1 Need for Determination. To eliminate any bias in the analytical method, it is necessary to determine the recovery of the compound from the collection device. The sample recovery should be determined in duplicate and should cover the concentration ranges of interest. If the recovery is less than 95%, the appropriate correction factor should be used to calculate the true value.

8.6.2 Procedure for Determining Recovery. An aliquot of a standard solution containing a known amount of the analyte, preferably equivalent to the sample concentration expected is added to a representative PTFE membrane filter and air dried. The analyte is then recovered from the filter and analyzed as described in Section 8.4. Duplicate determinations should agree within ±5%.

For the validation study conducted to determine the precision and accuracy of this method, an amount of the analyte equivalent to that present in a 360-liter sample at the selected level has been used for the recovery studies. Six filters at each of the three levels (0.5, 1.0 and 2.0X the OSHA standard) were spiked accordingly by adding an aliquot of a solution of sodium hydroxide in methanol containing known amounts of alkalinity. A parallel blank filter was also treated in the same manner except that no sample was added to it. All the filters were then extracted and analyzed as described in Section 8.4. The average recovery value obtained was 0.997.

The sample recovery equals the average weight in µg recovered from the filter divided by the weight in µg added to the filter, or

$$\text{Recovery} = \frac{\text{Average Weight (µg) recovered}}{\text{Weight (µg) added}}$$

8.7 Standardization of the Titrating Solution

8.7.1 The sodium hydroxide titrating solution is standardized against the standard 0.0100N hydrochloric acid prepared by dilution of standard 0.1N hydrochloric acid.

8.7.2 The standarization is carried out according to the procedure described in Section 8.4 except for addition of a sample or a blank filter. The standardization is carried out in triplicate. The normality of sodium hydroxide is calculated as follows:

$$\text{Normality of sodium hydroxide} = \frac{\text{(Normality of hydrochloric acid) x (Volume of hydrochloric acid added)}}{\text{(mm on chart) x (ml/mm for chart)}}$$

9. Calculations

9.1 Determine the volume of sodium hydroxide needed to neutralize the excess hydrochloric acid present by multiplying the distance (in mm) elapsed from the initiation of the syringe drive to the endpoint in the titration by the conversion of ml per mm or:

Volume of sodium hydroxide needed (ml) = mm to endpoint x ml/mm

9.2 The amount of sodium hydroxide (alkalinity) present on the filter is determined from the difference between the amount of hydrochloric acid added and the amount of sodium hydroxide needed in the back titration, or:

mmoles of sodium hydroxide present = (Volume of hydrochloric acid added (ml) x Normality of hydrochloric acid)

- (Volume of sodium hydroxide added (ml) x Normality of sodium hydroxide)

The amount of sodium hydroxide present is calculated using the molecular weight:

µg sodium hydroxide sample = mmoles of sodium hydroxide present x 40,000.

9.3 Correction for the blank must be made for each sample.

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

where:

μg sample = μg found in sample filter

μg blank = μg found in blank filter

9.4 Divide the total weight by the recovery to obtain the corrected μg sample.

$$\text{Corrected } \mu g/\text{sample} = \frac{\text{Total Weight } (\mu g)}{\text{Recovery (Section 8.6)}}$$

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

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

where:

f = sampling flow rate

t = sampling time

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

P_2 = pressure of air sampled (mm Hg)

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

T_2 = temperature of air sampled (°K)

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

$$\text{mg/cu m} = \frac{\text{Corrected } \mu g \text{ (Section 9.4)}}{\text{Volume of Air Sampled in Liters (Section 9.5)}}$$

10. References

10.1 Memoranda, Kenneth A. Busch (Chief, Statistical Service, DLCD), to Deputy Director, DLCD, dated 1/6/77, 11/8/77, subject: Statistical Protocol for Analysis of Data from Contract CDC-99-74-45.

10.2 S381 Backup Data Report for Sodium Hydroxide, prepared under NIOSH Contract No. 210-76-0123, 7/8/77.

Sampling Data Sheet No. S381
July 8, 1977

Substance

Sodium Hydroxide, NaOH

Standard

8-hour time-weighted average: 2 mg/cu m

Analytical Method

A known volume of air is drawn through a polytetrafluoroethylene membrane filter to trap the sodium hydroxide particulate present. The sample filters are placed in water containing a known amount of excess hydrochloric acid. The amount of analyte present is determined by back titration of the remaining excess hydrochloric acid with standard sodium hydroxide. The method has been validated over the concentration range of 0.76-3.88 mg/cu m for a 360-liter sample at 23°C and 758 mm Hg atmospheric temperature and pressure.

Sampling Equipment

The following items are needed: a calibrated personal sampling pump whose flow rate can be determined to an accuracy of ± 5% at a flow rate of 1.5 liters per minute; a 37-mm two or three-piece filter holder held together by stretchable tape or shrinkable band; and a 37-mm diameter, 1.0 micrometer pore size polytetrafluoroethylene (PTFE) membrane filter supported by a cellulose backup pad.

Sample Size

A sample volume of 360 liters is recommended. Sample at a flow rate of 1.5 liters per minute.

Sample Procedure

1. Assemble the filter and three-piece filter cassette and close firmly to insure that the center ring seals the edge of the filter. Examine the holder for a good filter seal. If the cassette will not seal tightly, it should be discarded. Secure the cassette holder together with tape or shrinkable band.

2. Remove the cassette plugs and attach to the personal sampling pump tubing. Clip the cassette to the worker's lapel.

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

4. Set the flow rate as accurately as possible using the manufacturer's directions. Record all the necessary information to determine flow rate or volume and record also the initial and final sampling time. Record the temperature and pressure of the atmosphere being sampled. If the pressure reading is not available, record the elevation. The pump rotameter should be observed frequently, and readjusted as needed. If the flow rate cannot be adjusted to correct a problem, terminate the sampling.

5. Collected sample cassettes should be firmly sealed with plugs in both the inlet and outlet.

6. Carefully record sample identity and all relevant sample data.

7. Blank. With each batch of samples, submit one filter which is subjected to exactly the same handling as for the samples except that no air is drawn through it. Label this as a blank. Submit one blank for every ten samples.

Special Considerations

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

2. This method does not distinguish between sodium hydroxide and other alkaline species such as sodium carbonate and sodium bicarbonate.

Shipping Instructions

The cassettes in which the samples are collected should be shipped in a suitable container, designed to prevent damage in transit.

Reference

Sodium Hydroxide, NaOH, NIOSH Method No. S381.

Backup Data Report No. S381
July 8, 1977

Substance: Sodium Hydroxide, NaOH

OSHA Standard: 2 mg/cu m

Chemicals Used for Validation:
Sodium Hydroxide, NaOH, Certified
Electrolytic Pellets, Fisher
Hydrochloric Acid Solution, 0.100N, Titrisol
Standard Solution, E. Merck
Sodium Hydroxide Solution 0.100N, Tritrisol
Standard Solution, E. Merck

General Considerations

The method for sodium hydroxide has been tested in accordance with the various criteria for validation described in Reference 1 and in conformity with the statistical analysis described in Reference 2. The statistical criteria established for this program are related to the present suggested standard for air monitoring accuracy, i.e., the method should read to within ±25% of the true value at the statistical confidence level of 95% over the range of 0.5 to 2X the OSHA standard. In order to satisfy the statistical criteria, a measure of accuracy and precision was established, i.e., overall recovery must be 100 ±10% and $\overline{CV}_T$ must be less than or equal to 0.105. The fine points of the statistical basis for this program are discussed in Reference 2. The protocol for validation of the method for sodium hydroxide, NaOH, consisted of the following experimental studies:

- Analysis of a set of 18 analytical samples (6 samples at each of three test levels) prepared by adding known aliquots of a methanolic solution of sodium hydroxide to 37-mm diameter/1.0 micrometer pore size polytetrafluoroethylene (Fluoropore or PTFE) membrane filters,

- Testing the storage stability of six samples spiked with an amount of sodium hydroxide equivalent to a 360-liter collection at the OSHA standard level,

- Determination of the accuracy of the method for collected samples by comparison of the data obtained by titration to that obtained from analysis of sodium using atomic absorption,

- Testing the response of the analytical method to sodium carbonate, the expected major interference,

- Evaluation of the collection efficiency of sodium hydroxide on Fluoropore (PTFE) filters,

- Analysis of 18 samples (6 samples at each of the three test levels-- 0.5, 1 and 2X the OSHA standard) collected from dynamically generated test atmospheres,

- Testing the storage stability of collected samples,

- Assessing the precision and accuracy of the method.

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

Principle of the Method

The method validated for the analysis of sodium hydroxide in air is based on collection using a Fluoropore membrane filter, extraction of the alkalinity using a known excess of hydrochloric acid and an electrometric titration of the remaining excess acid with standard sodium hydroxide using an automatic feed microburet assembly. An air sample size of 360 liters is recommended. The method determines total alkalinity but all the data in this report are expressed as NaOH alkalinity.

Analysis

A detailed description of the procedure for analysis, and the preparation of analytical samples for the determination of sample recovery are given in NIOSH Method No. S381 (Reference 3).

The reliability of the analytical method was tested, based on the analysis of 18 filter samples. The analytical samples were prepared by spiking 37-mm Fluoropore filters with known aliquots of a solution of sodium hydroxide in methanol (1.052N) and allowing the solvent to evaporate overnight. The aliquots added contained, respectively, 379, 757 and 1466 micrograms of NaOH. The sample containing filters were placed in the titration vessel of the apparatus shown in Figure S381-1 filled with 75 ml of distilled water. An Orion Research Model 801A pH meter equipped with an Esterline Angus AZUG Recorder was used along with a Sargent Model C Automatic Constant Rate Buret. A glass rod was used to maintain the filter totally immersed in the solution and to prevent it from floating and covering an electrode surface during the titration. An aliquot of standard hydrochloric acid (5 ml of 0.0100N) was added to neutralize all the alkalinity and to reduce the pH of the solution to below 4. A nitrogen flow of approximately 1.5 liters per minute for 15 minutes was introduced via a blunt end stainless steel needle to purge out any dissolved CO_2. The remaining acidity was titrated with a standard sodium hydroxide solution (0.0106N) using a rate of addition of 0.998 ml/minute. The endpoint of the titration was determined electrometrically. In all cases the observed titration curve was identical to that expected for titration for a strong acid with a strong base and there was no indication as to the presence of any weakly acidic or basic species. A blank Fluoropore filter carried through the method yielded no available alkalinity. The

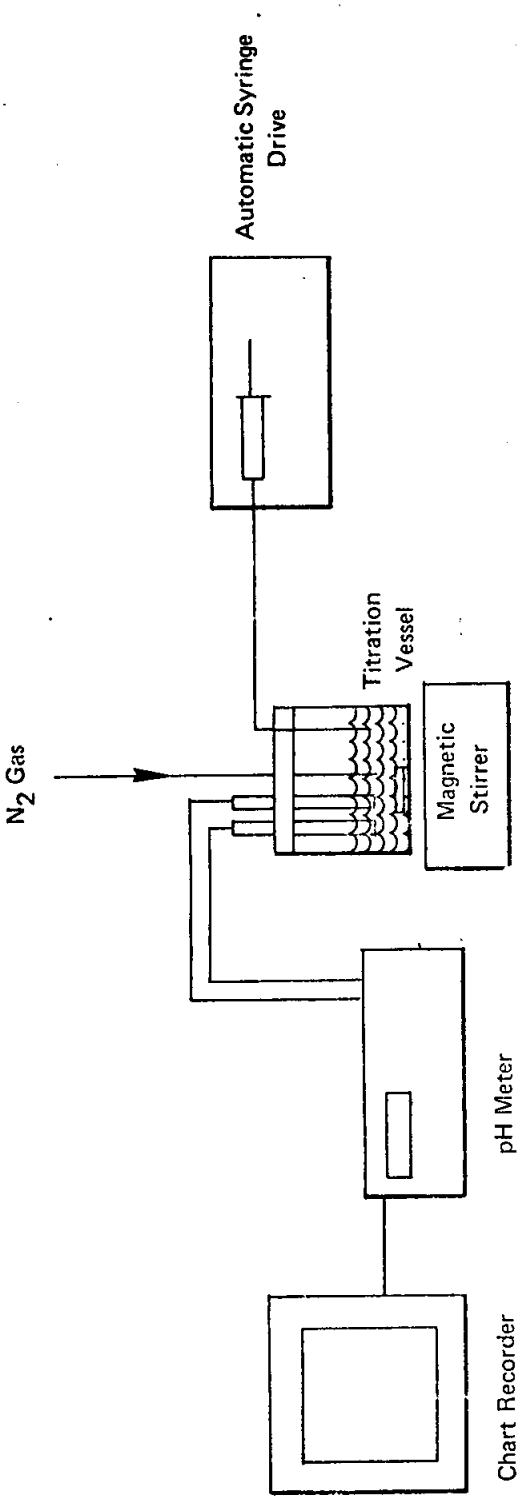

Figure S381-1 APPARATUS USED FOR THE BACK-TITRATION OF SODIUM HYDROXIDE

data obtained for the full set of 18 analytical samples are shown in Table S381-1. The average analytical method recovery found was 99.7%.

Assessment of Sodium Carbonate Interference and Reactivity of the Fluoropore Filters to Sodium Hydroxide

Before collection of generated samples was attempted, two sources of other possible difficulties were investigated. The first was the effect of the presence of sodium carbonate due to reaction of sodium hydroxide with atmospheric CO_2 (Eq. 1) on the analytical method

$$2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O \qquad (1)$$

and the second was long term reaction of NaOH with the filter, i.e., storage stability of samples on the filters.

Interference by sodium carbonate in the analytical method for total alkalinity was checked by titration of a known amount of sodium carbonate (1450 µg). This amount would correspond to the amount expected if 1094 µg of NaOH collected on a filter fully reacted with atmospheric CO_2. The method was found to give accurate alkalinity data independent of whether the sodium was added as NaOH or Na_2CO_3 as shown below:

Comparison of Alkalinity Data Obtained for Titration of NaOH and Na_2CO_3

µg Added	mmoles of Alkalinity Added	mmoles of Alkalinity Found
1466[a]	0.0366	0.0363
1466[a]	0.0366	0.0370
1450[b]	0.0274	0.0276
1450[b]	0.0274	0.0280

[a]Added as NaOH

[b]Added as Na_2CO_3

Since one mole of $CO_3^=$ consumes 2 moles of H^+ and one mole of Na_2CO_3 is formed from 2 moles of NaOH the analytical method directly gives the amount of NaOH which was initially present on the filter before reaction with atmospheric CO_2.

The Fluoropore filters were found to be inert to NaOH for at least a one week period as shown by recoveries given below from spiked samples which were allowed to sit for 7 days.

Table S381-1

Data Sheet: Sodium Hydroxide, No. S381

Analysis*

Level	0.5S			1S			2S	
µg added	µg found	Recovery	µg added	µg found	Recovery	µg added	µg found	Recovery
379	380	1.003	757	747	0.987	1466	1456	0.993
379	385	1.016	757	696	0.919	1466	1448	0.988
379	393	1.037	757	739	0.976	1466	1480	1.010
379	410	1.082	757	730	0.964	1466	1364	0.930
379	424	1.119	757	730	0.964	1466	1468	1.001
379	391	1.032	757	730	0.964	1466	1397	0.953
n =		6						6
mean =		1.048			0.962			0.979
std. dev. =		0.0439			0.0232			0.0310
CV_1 =		0.0419			0.0241			0.0317

$$\overline{CV_1} = 0.0334$$

$$\overline{CV_A} + \overline{AMR} = 0.0360$$

*These samples were analyzed for total alkalinity present and the resulting data expressed as NaOH.

Analytical Data for "Spiked" NaOH Samples
Stored for Seven Days

µg added	µg found	Recovery
757	734	0.970
757	742	0.980
757	725	0.958
757	734	0.970
757	704	0.930
757	742	0.980
	n = 6	
	mean	0.965
	CV	0.0195

This data also indicated storage stability of the analytical samples; the average recovery value obtained for "spiked" samples analyzed after 1 day was 0.963 vs. 0.964 for seven day old "spiked" samples.

Assessment of the Accuracy of the Titration Method

An independent check of the titration method for total alkalinity was obtained by analyzing samples of NaOH collected on filters for total sodium by atomic absorption (see Attachment A). A blank Fluoropore filter had a sodium content which was equivalent to that of the solvent blank and was within the error of the measurement. Good agreement was observed between the results obtained using these two methods, as shown in Table S381-2, the average recovery (Na ÷ Alkalinity) being 1.047.

Table S381-2

Comparison of Results Obtained Using Titration and Sodium Analyses of Collected Samples*

Volume Collected (liters)	µg NaOH found	Concentration mg/cu m
a. Samples analyzed by titration		
391	2680	6.85
391	2656	6.79
389	2605	6.70
		Ave: 6.78
b. Samples analyzed for sodium		
391	2783	7.12
390	2696	6.91
394	2869	7.28
		Ave: 7.10

*Six samples were collected simultaneously.

Detection Limit

The detection limit for the determination of alkalinity using the titration method was taken to be twice the standard deviation obtained from titration data of 6 determinations of blank filter samples. The data are shown below:

Sample	Volume of NaOH Added (ml)
1	4.469
2	4.425
3	4.424
4	4.500
5	4.410
6	4.425
n = 6	
mean	4.442
std dev	0.0347

The detection limit thus corresponds to 0.069 ml of titrant. Using 0.0102 N NaOH as titrant this translates to 28.2 μg of NaOH.

Sampling and Analysis

Sodium hydroxide particulate was generated using the basic Aerosol Generation and the Dilution/Sampling System described in Attachments B and C. The Environmental Research Corporation Fluid Atomization Aerosol Generator was used for these studies. The generator was modified so that nitrogen gas was passed through the atomization chamber to prevent formation of sodium carbonate in the atomized solution. Test atmospheres at a concentration 2X the OSHA standard level were generated by atomization of an aqueous solution of sodium hydroxide containing 12 grams of NaOH per liter into a dry, solvent-free air stream flow. The atomizer nitrogen flow was 9 liters per minute; aerosol from the Collison type atomizer was diluted with 108 liters per minute of air. The generation/dilution system was operated so that a concentration of 2X the OSHA standard level was produced in the mainline, then twofold and fourfold dilutions made to obtain concentrations at 1X and 0.5X the OSHA standard levels. The exact dilution ratios were obtained by introducing propane gas into the air stream and measuring the relative concentrations obtained at each of the dilution arms using a hydrocarbon analyzer. The dilution ratios were determined to be 1.00; 0.580; 0.200, respectively, for the 2S, 1S and 0.5S dilution arms. Twelve samples, six each at 0.5S and 2S dilution arms were collected simultaneously with six samples from the 1S dilution arm;

the latter six samples were analyzed by atomic absorption and were used together with the dilution ratios as the independent method for verifying the generator concentration. In a separate experiment, fourteen samples at 1X the OSHA standard level were collected from a similarly generated test atmosphere. These samples were split such that two samples were analyzed by AA (see the section on Independent Verification of Generator Concentration) and the other twelve samples were analyzed as described in the storage stability section. All the samples were collected at 1.5 liters per minute for 4 hours (360 liters). The data for the 18 samples in Table S381-3 were obtained based on analysis using NIOSH Method No. S381 and were composited from these generated samples.

Particle Size Distribution

Studies were also conducted to determine the particle size distribution of the sodium hydroxide aerosol produced in the test chamber. The method used was sampling with an Andersen Cascade Impactor (Particle Fractionation Personnel Sampler) and determining the amount of sodium hydroxide deposited at each stage or collected on the final 25-mm Fluoropore filter stage by the titration method with the addition of the appropriate amount of excess of hydrochloric acid.

The data obtained by the back titration analysis of sodium hydroxide collected at each stage of the cascade impactor are tabulated below. The effective cutoff aerodynamic diameter in micrometers for each stage are based on manufacturer's quotation which has been determined at a flow rate of 1.4 liters per minute. Under the experimental conditions of this test, the flow rate was 1.51 liters per minute. The cumulative percent is based on cumulating from the last stage of the impactor.

Stage	Particle Size Range Cut-Off Diameter (μm)	μg NaOH Found	% Total Particulate	Cumulative Percent
1	4.7 and up	B.D.L.*	< 1	100.0
2	< 4.7 - 3.3	1259	46.6	100.0
3	< 3.3 - 2.1	B.D.L.	< 1	> 53.4
4	< 2.1 - 0.65	B.D.L.	< 1	> 53.4
Backup Filter	< 0.65	1441	53.4	53.4
	TOTAL	2700		

*B.D.L. = Below Detection Limit (28.2 μg NaOH)

Table S381-3

Data Sheet: Sodium Hydroxide
Sampling and Analysis

Test Level	---------found----------			Taken*	
	μg	Liters	mg/cu m	mg/cu m	Recovery
0.5S	280	369	0.759	0.724[a]	
	287	367	0.782	0.724	
	262	369	0.710	0.724	
	280	370	0.757	0.724	
	268	370	0.724	0.724	
	294	361	0.814	0.724	
		n = 6			
		mean	0.758		1.047
		std.dev	0.0379		
		CV_2	0.0500		
1S	930	392	2.372	2.258[b]	
	912	387	2.357	2.258	
	936	389	2.406	2.258	
	860	391	2.199	2.258	
	924	391	2.363	2.258	
	932	391	2.384	2.258	
		n = 6			
		mean	2.347		1.039
		std.dev	0.0744		
		CV_2	0.0317		
2S	1436	372	3.86	3.62[a]	
	1429	372	3.84	3.62	
	1449	372	3.90	3.62	
	1442	373	3.87	3.62	
	1455	372	3.91	3.62	
	1442	371	3.89	3.62	
		n = 6			
		mean	3.88		1.072
		std.dev	0.0264		
		CV_2	0.0068		
		$\overline{CV}_2$	0.0344		

* Based on sodium analysis of simultaneously collected samples.
[a] Based on the mean of 5 measurements at the 1S dilution arm and the determined dilution ratios.
[b] Based on two samples taken simultaneously at the 1S level.

Storage Stability

Studies were done to assess the stability of sodium hydroxide samples collected on Fluoropore filters and stored for 7 days under ambient conditions in the filter cassettes. For these studies, a set of 14 samples was collected at 1X the OSHA standard level from a dynamically generated test atmosphere. Six of these samples were analyzed as described in Section 8.4 of NIOSH Method S381 after overnight storage. Another six samples were stored for 7 days and analyzed similarly. The remaining two samples were analyzed for sodium to independently determine the generator concentration. The data for these samples were shown in Table S381-4 and indicate that sodium hydroxide samples are stable for a 7-day period. The average recovery for the 1 day old samples was 103.9% vs. 104.0% for the seven day old samples.

Collection Efficiency

The collection efficiency of 37-mm Fluoropore filters for sodium hydroxide was determined by collecting 6 filter samples at a test concentration of 7.50 mg/cu m for a 360-liter sample. The physical layout of the filter series (front and backup) used for all samples was such that the two filters were physically separated from each other and only the backup filter was supported by a cellulose backup pad. Three of the backup filters were analyzed by titration and three were analyzed for sodium by atomic absorption. The collection efficiency was also determined at 4.40 mg/cu m for a 615-liter sample using backup impingers filled with 20 ml of H_2O and analyzed for alkalinity by titration. The overall average collection efficiency found was at least 99% at these test levels studies as indicated by the data summarized in Table S381-5.

Independent Method of Verifying Generator Concentration

The concentration of NaOH produced by the aerosol generation/dilution system was verified by analyzing acid extracts of samples collected on the filters for sodium using atomic absorption. The "taken" concentration given for the 1S test level in Table S381-3 was determined from two other simultaneously collected samples at the 1S level. The "taken" concentrations given for the 0.5S and 2S levels in Table S381-3 were calculated from data obtained for five simultaneously collected samples at the 1S level and the dilution ratios.

The data for the seven samples used to determine the "taken" concentrations are shown in Table S381-6. Good agreement was observed between the "taken" and found concentrations as shown below; the average recovery (Found ÷ Taken) being 1.052.

Table S381-4

Data Sheet: Sodium Hydroxide

Studies in Stability of Collected Samples

Expt. A: Samples Stored 1 Day

Test Level	Found			Taken*	
	µg	Liters	mg/cu m	mg/cu m	Recovery
1S	930	392	2.372	2.258	
	912	387	2.357	2.258	
	936	389	2.406	2.258	
	860	391	2.199	2.258	
	924	391	2.363	2.258	
	932	391	2.384	2.258	
		mean	2.347		1.039
		CV_2	0.0317		

Expt. B: Samples Stored 7 Days

1S	912	391	2.332	2.258	
	869	369	2.355	2.258	
	903	378	2.389	2.258	
	891	389	2.290	2.258	
	930	391	2.379	2.258	
	917	392	2.339	2.258	
		mean	2.347		1.040
		CV_2	0.0152		

* Calculated from sodium analyses of 2 samples collected simultaneously.

Table S381-5

Collection Efficiency of Sodium Hydroxide on Fluoropore Filters

Test Level mg/cu m	Volume (liters)	μg Found			% Collected in Front
		Front	Backup	Total	
7.50*	360	2680	B.D.L.[a]	2680	100.0
	359	2656	B.D.L.[a]	2656	100.0
	359	2605	B.D.L.[a]	2605	100.0
	361	2703	1.0[b]	2704	100.0
	360	2696	1.0[b]	2697	100.0
	362	2869	1.0[b]	2870	100.0
4.40*	615	2699	B.D.L.[c]	2699	100.0
	615	2715	B.D.L.[c]	2715	100.0
			Average Collection Efficiency		100.0**

* The test concentration noted is based on the average found for the simultaneously generated samples.

** The average collection efficiency can also be expressed as at least 99.0% on the basis of the detection limit and the average μg found on the front filters.

B.D.L. = Below Detection Limit; the detection limit was 28.2 μg NaOH.

[a] Backup filter samples analyzed by titration for alkalinity.

[b] Backup filter samples analyzed by atomic absorption for sodium and corrected for background concentration.

[c] Backup impinger filled with H_2O and analyzed by titration for alkalinity.

Table S381-6

"Taken" Sodium Hydroxide Concentrations Obtained
by Analysis of Sodium Using Atomic Absorption

	Volume (liters)	µg NaOH (by Na)	Level (mg/cu m)
Experiment 1	385	870	2.260
	393	887	2.257
		Average:	2.258[a]
Experiment 2	362	737	2.036
	361	761	2.108
	359	761	2.120
	362	775	2.141
	362	760	2.099
		n = 5	
		mean	2.101[b]
		CV	0.0188

[a] This data was used as the "taken" concentration for the 1S level shown in Table S381-3 and the storage stability data given in Table S381-4.

[b] This data and the dilution ratios of 1.00:0.580:0.200 for the 2S:1S:0.5S dilution arms was used in calculating the "taken" concentrations of 0.724 and 3.62 mg/cu m given for the 0.5S and 2S levels shown in Table S381-3.

Comparison of Taken vs. Found Concentrations

Level	Taken Levels Obtained Using Sodium Data (mg/cu m)	Level Found Using Titration Data (mg/cu m)	Recovery Found/Taken
0.5S	0.724[a]	0.758	1.046
1.0S	2.258	2.347	1.039
2.0S	3.62[b]	3.88	1.072
		Average:	1.052

[a]Derived from the dilution ratio of 0.345 for the 0.5S and 1.0S ports.

[b]Derived from the dilution ratio of 1.724 for the 1.0S and 2.0S ports.

Precision and Accuracy

The precision of the method was determined by using the statistical procedures described in Reference 2 and summarized in Attachment D. The precision of the analytical method was assessed using the data in Table S381-1. The pooled Coefficient of Variation ($\overline{CV}_1$) for the three sets of analytical samples was found to be 0.0332.

Precision and accuracy of the total sampling and analytical method was evaluated using the data in Table 381-3 and the results obtained from collection efficiency and storage stability tests. The pooled Coefficient of Variation ($\overline{CV}_2$) for the three sets of samples collected from dynamically generated test atmospheres is 0.0344. 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 latter was determined as described in the section on independent method of verifying generator concentration.

The average recovery (concentration found ÷ concentration taken) for all three levels was 1.052. The difference between taken and found concentrations is considered to result from experimental uncertainties in the value for the taken concentration and does not represent a bias in the method. Further confidence in the accuracy of the tested method is established by the results of the collection efficiency test and the storage stability tests described above. Bartlett's test for homogeneity of variances of the respective coefficients of variation at 0.5, 1 and 2X the OSHA standard for sampling and analysis was applied to the data for sodium hydroxide. The data (Table S381-3) gave a chi squared value of 5.83, indicating that the hypothesis of equal variance is satisfied at p (probability) less than 0.01. Thus $\overline{CV}_T$ is calculated based on the pooled data. The total Coefficient of Variation ($\overline{CV}_T$) is 0.0622.

References

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

2. Memoranda, Kenneth A. Busch (Chief, Statistical Services BLCD) to Deputy Director, DLCD, dated 1/6/75, 11/8/74, Subject: "Statistical Protocol for Analysis of Data from Contract CDC-99-74-45".

3. Sodium Hydroxide, NIOSH Method No. S381, prepared under NIOSH Contract No. 210-76-0123, with validation data 7/8/77.

ATTACHMENT A

ANALYSIS OF SODIUM USING ATOMIC ABSORPTION

To check on the accuracy of the titration method for determination of sodium hydroxide, experiments were performed to determine sodium concentrations in selected samples using atomic absorption. This work was carried out on a Perkin-Elmer atomic absorption spectrophotometer, Model 303, with a recorder readout accessory. A hollow cathode Perkin-Elmer sodium lamp was used as the light source. An air-acetylene flame was used with flows of 25 and 5 liters per minute for the air and the acetylene, respectively. A wavelength of 330.3 nm and slit setting of 4 were used with a noise suppression of 3.

Standard sodium solutions were prepared by volumetric dilution of "Fisher Certified" 1000 ppm sodium standard in distilled water. Standards were prepared to cover the range of 10-100 ppm.

Collected sodium hydroxide samples were prepared for analysis by extraction with 0.1 N HCl (10 mℓ) and analyzed by aspiration either directly into the flame or after dilution. No significant change in signal was observed due to the presence of 0.1 N HCl. The order of analysis was two samples, one standard, etc., with a full set of standards analyzed at the beginning and end of the set. A comparison of the results obtained for collected samples analyzed by titration and sodium analysis is given below:

Comparison of Results Obtained Using Titration and Sodium Analyses of Collected Samples*

Volume Collected (l)	µg NaOH found	Concentration mg/cu m
a. Samples analyzed by titration		
391	2680	6.86
391	2656	6.79
391	2605	6.70
	Avg:	6.78
b. Samples analyzed for sodium		
391	2783	7.12
390	2696	6.91
394	2869	7.28
	Avg:	7.10

* Six samples were collected simultaneously.

ATTACHMENT B

DILUTION AND SAMPLING SYSTEM FOR AEROSOL TEST ATMOSPHERES

The dilution and sampling system used to produce the appropriate aerosol test atmospheres is shown schematically in Figure S381-B-1. Basically, the system consists of a main horizontal line into which aerosol and dilution air are introduced and three vertical dilution and sampling sections which branch off the main line. These branches are designated as A, B, and C in Figure S381-B-1. The dilution and sampling branches A and C are identical and each is equipped with a sampling manifold with six sample ports. The dilution and sampling branch B, on the other hand, is equipped with a sampling manifold with 14 sample ports. Figures S381-B-2 and S381-B-3 show these dilution and sampling branches in more detail.

Aerosol dilution ratios in the system are fixed by the action of critical flow orifices. Usually an aerosol with a concentration twice the OSHA standard is prepared in the main line, and this aerosol sampled without dilution in one dilution/sampling section and diluted twofold and fourfold in the other two sections. Other dilution modes may be accommodated simply by changing the critical orifices.

Aerosol dilution occurs in the Teflon venturi-shaped inserts shown in Figures S381-B-2 and S381-B-3. Dilution air is injected radially into the venturi throat. The quantity of dilution air introduced is fixed by a critical orifice which is connected to one of the constant pressure air manifolds as described in the section on air supply below.

Isokinetic sampling probes, six for branches A and C, and 14 for branch B, are located approximately thirty centimeters downstream of each diluter. The probes convey aerosol to sample collectors (filter cassettes) mounted radially around the outside of the sampling section. There is a luer fitting on each sample port to mate with the filter cassette. Sample flow rate is fixed at 1.5 liters per minute by critical orifices (sapphire orifices supplied by Richard H. Bird and Co., Waltham, Mass.) mounted on the sample manifold (Figure S381-B-1).

As is indicated in Figure S381-B-1, a critical orifice is located downstream from the sample probes in each dilution/sampling branch. This orifice is protected from contamination by a Filterite high efficiency filter. For the dilution/sampling branches A and C, there are seven outwardly flowing streams in each branch -- one stream is that which flows through the orifice mentioned above (flow rate Q_T) and the other six are the sample streams (total flow rate Q_S). For the dilution/sampling branch B, the flowing streams consist of one which flows through a critical orifice downstream from the sample probes (flow rate Q_T) and fourteen from the sample streams (total flow rate Q_S). There are two inflowing streams -- the dilution air stream (flow rate Q_D) and the aerosol stream entering from the main line (flow rate Q_A). The dilution ratio, R, in

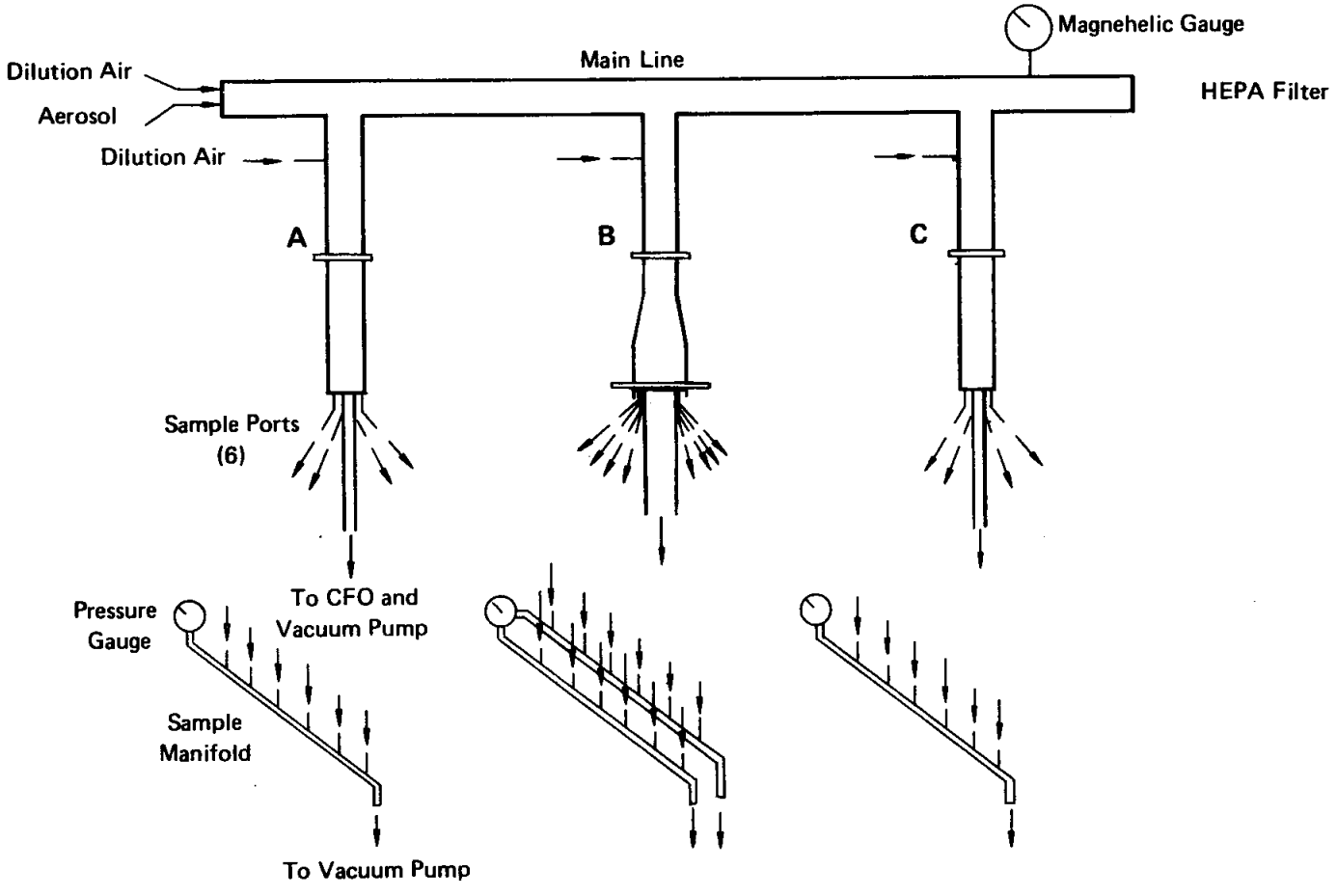

FIGURE S381–B–1 AEROSOL DILUTION AND SAMPLING SYSTEM

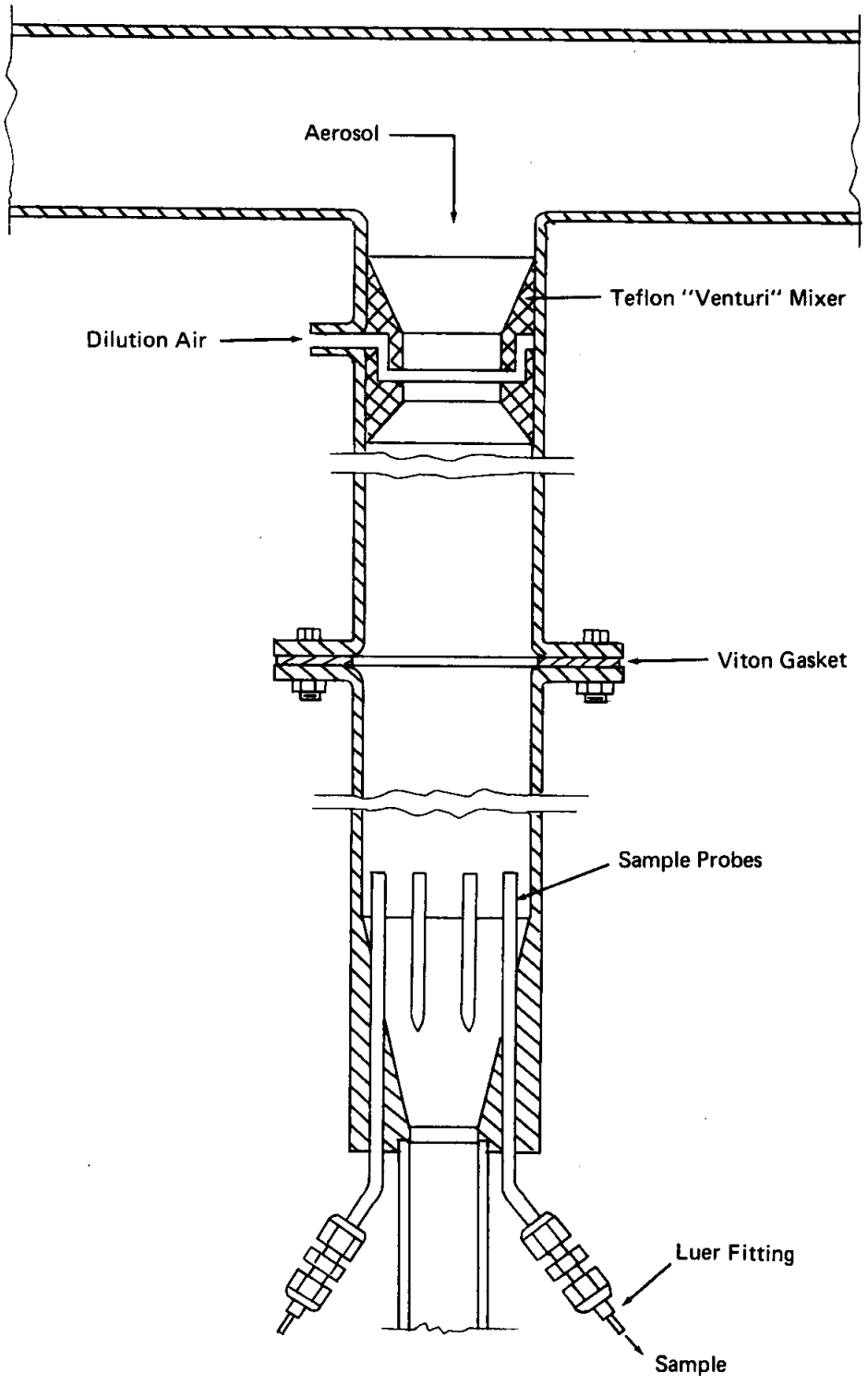

FIGURE S381–B–2 CROSS–SECTIONAL VIEW OF DILUTION AND SAMPLING SECTION (BRANCHES A AND C)

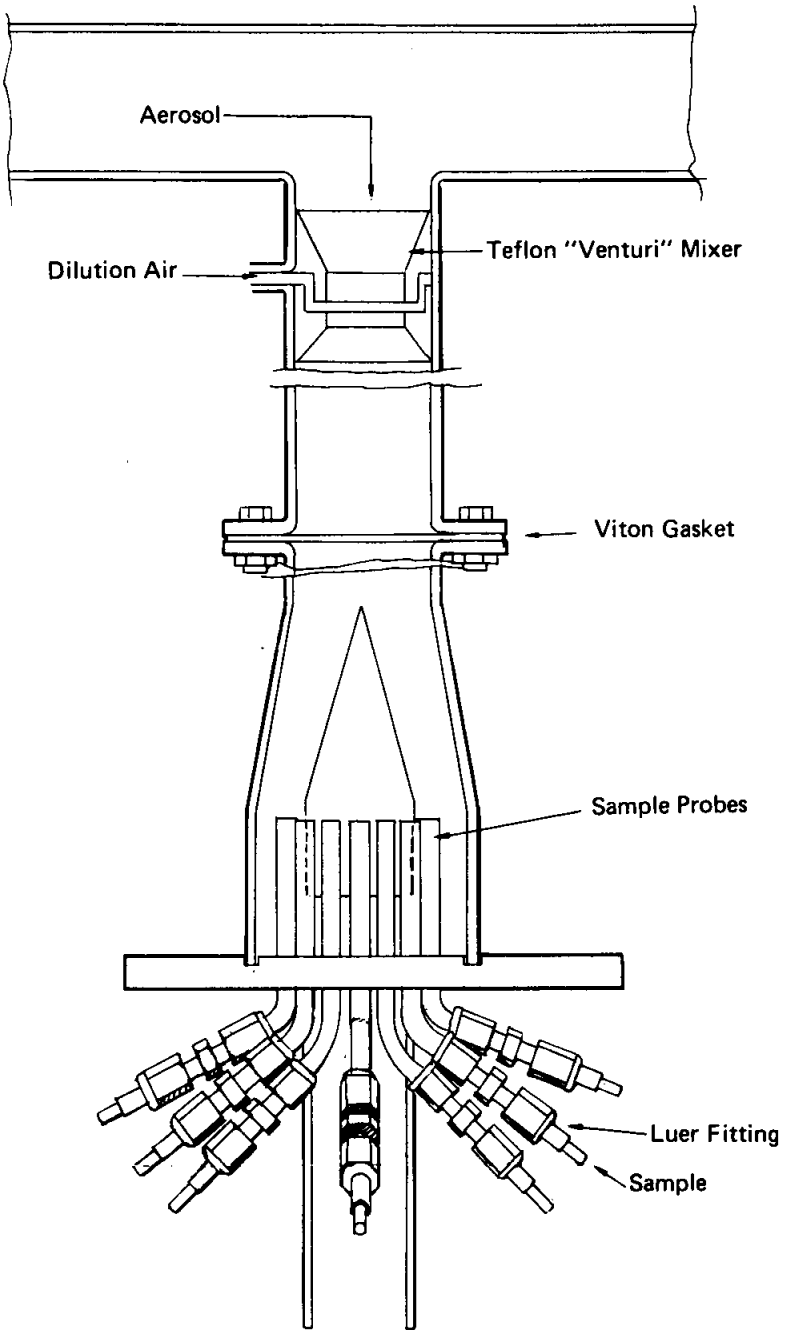

FIGURE S381–B–3 CROSS-SECTIONAL VIEW OF DILUTION AND SAMPLING SECTION (BRANCH B)

each branch is given by the correlation:

$$R = \frac{Q_A}{Q_A + Q_D}$$

or, since $Q_T + Q_S = Q_D + Q_A$ (with the assumption of uniform pressure and temperature in the system),

$$R = \frac{Q_T + Q_S - Q_D}{Q_T + Q_S}$$

The flow rates, Q_T, Q_S and Q_D are controlled by the action of critical orifices; consequently the dilution ratios are fixed solely to flow through the critical orifices.

Dilution ratios are measured by adding a small quantity of hydrocarbon gas to the main line and measuring the relative concentrations in each of the three sampling sections using a Beckman 402 hydrocarbon analyzer. No measurable differences (within 1%) in the hydrocarbon concentration were found among the six or fourteen sample ports at any of the three sampling branches. The dilution ratios are rechecked periodically and the typical values are shown in the following section.

The main line flow rate is about 130 liters per minute when a 2X OSHA standard concentration is being generated in the main line. Flow through the dilution/sampling branches is approximately 70 liters per minute.

Excess aerosol from the main line is passed through a HEPA filter and then vented to a hood.

Air Supply

Air from the house compressed air system is treated by successive passage through a cotton filter, a silica gel bed, a high efficiency glass fiber filter, and a membrane filter. These collections remove respectively, oil and water droplets, water vapor, and fine particles.

The treated air then passes to two parallel air supply manifolds, each of which is equipped with valves for controlling air flow to various parts of the generation/dilution system. One of the manifolds supplies air to the dilution system. The second supplies air to the aerosol generator, either directly or through calibrated rotameters as may be required by the particular generator being used. Pressure in each manifold is maintained at a fixed level by Moore Nullmatic pressure regulators and is measured with bourdon gauges (6" Ashcroft test gauges).

Experimental Procedure

1) The aerosol generator parameters necessary to produce the desired aerosol concentration are found by making several trial runs. If

ATTACHMENT C

APPARATUS FOR THE GENERATION OF AEROSOLS

A number of different aerosol generators are available for the production of aerosols. Each of the following generators can readily be used in conjunction with the dilution and sampling system to produce the appropriate aerosol test atmosphere:

- Environmental Research Corporation Fluid Atomization Aerosol Generator Model 7330
- DeVilbiss Model 35A Ultrasonic Nebulizer
- Royco Model WA Aerosol Generator

The ERC and DeVilbiss generators are used to produce aerosols by spray drying or by atomization of suspended solid particles. For spray drying, the material to be dispersed is dissolved in an appropriate solvent, the solution atomized, and the resulting mist mixed with solvent-free air. The solvent evaporates and leaves the nonvolatile solute behind as a residue. Either solid or liquid solutes may be used. Aerosols with median diameters in the 0.03 to 0.5 micron particle size range may be prepared by spray drying with the ERC atomizer. Slightly larger particles may be prepared by spray drying from the DeVilbiss unit. Both aerosol concentration and particle size are functions of the concentration of solute in the atomized solution.

Aerosols of solid particles may also be prepared by suspending the particles in a solvent, atomizing the solution and vaporizing the solvent. Solid suspensions with particles up to several microns in diameter may be dispersed with the ERC and DeVilbiss atomizers.

The Royco generator is used primarily to atomize pure liquids. It was designed specifically for atomizing organic liquids such as dioctyl phthalate, and produces DOP aerosol with a median diameter of between 0.5 and 1.0 micron.

the spray drying procedure is being used, the concentration of the atomizer solution would be carried out in the trial runs.

2) Six samples, each consisting of two filters sampling in series, are taken from the 2X OSHA standard sampling ports to verify that the collection efficiency of the filters is adequate.

3) A full set of twenty-four samples are collected simultaneously.

Typical System Parameters

When the dilution/sampling system is set up to produce aerosols with a 2X OSHA standard concentration in the main line, typical values of the system parameters are:

Main line pressure:	+3 cm H_2O with respect to atmospheric pressure
Main line flow rate:	130 liters per minute
Sampling rate:	1.5 liters per minute
Flow rate through dilution/ sampling branch (approximate):	70 liters per minute

Dilution air flow rate (approximate):

2X OSHA standard, Branch C	0
1X OSHA standard, Branch B	36
0.5X OSHA standard, Branch A	53

Dilution ratios measured with hydrocarbon analyzer (Branch C: Branch B: Branch A)	1.00: 0.54: 0.22*

* The dilution ratio is influenced by system pressure and is experimentally determined periodically.

ATTACHMENT D

SUMMARY OF STATISTICAL TERMS AND FORMULAE

The statistical analysis employed in this program has been provided by NIOSH. The evaluation of the limits and guidelines are discussed in a series of memoranda from Busch (Reference A). Some key terms, statistical formula, acceptable limits and statistical tests which have been used in these reports are noted and summarized herein.

Mean - Arithmetic mean or average, defined as the sum of all the observations divided by the number of observations (n).

Standard deviation - defined as the positive square root of the variance which is defined as the sum of squares of the deviations of the observations from the mean ($\bar{x}$) divided by one less than the total number of observations (n-1).

$$\text{std dev} = \sqrt{\frac{\sum_{i=1}^{n} (x_i - \bar{x})^2}{n - 1}}$$

CV - Coefficient of Variation or Relative Standard Deviation, defined as the standard deviation divided by the mean.

$$CV = \frac{\text{std dev}}{\text{mean}}$$

CV_1 - Coefficient of Variation for the six analytical samples at each of the 0.5, 1, and 2X OSHA standard level.

CV_2 - Coefficient of Variation for the six generated samples at each of the 0.5, 1 and 2X OSHA standard level.

$\overline{CV}$ - Pooled Coefficient of Variation; in this program, the value is derived from the coefficients of variation obtained from the analysis of 6 samples at each of the three test levels - 0.5, 1 and 2X OSHA standard level. The mathematical equation is expressed as:

$$\overline{CV} = \sqrt{\frac{\sum_{i=1}^{n} f_i \, (CV_i)^2}{f}}$$

where:

f_i = degrees of freedom, equal to number of observations minus one, at the i^{th} level.

CV_i = Coefficient of Variation of the observations at the i^{th} level

$$f = \sum_{i=1}^{n} f_i$$

$\overline{CV}_1$ - Pooled Coefficient of Variation calculated as above based on data for the 18 analytical samples

$\overline{CV}_{A+\overline{DE}}$ - This is a derived correction to include error due to the use of the desorption efficiency factor which is an average of 6 values.

$$\overline{CV}_{A+\overline{DE}} = \overline{CV}_1 \sqrt{7/6} = 1.0801 \ \overline{CV}_1$$

$\overline{CV}_{A+\overline{AMR}}$ - This is a correction factor analogous to the desorption efficiency factor noted above except that this notation is used where the factor is associated with analytical method recovery (AMR).

$$\overline{CV}_{A+\overline{AMR}} = 1.0801 \ \overline{CV}_1$$

$\overline{CV}_2$ - Pooled Coefficient of Variation based on the data for the 18 generated samples.

$\overline{CV}_S$ - Coefficient of Variation of the sample collection, the value is dependent on the data from the 18 analytical and 18 generated samples.

$$\overline{CV}_S = \sqrt{\left(\overline{CV}_2\right)^2 - \left(\overline{CV}_1\right)^2}$$

$\overline{CV}_P$ - Coefficient of Variation due to the pump error, assumed to be equal to 0.05.

$\overline{CV}_T$ - Coefficient of Variation of total procedure which consists of the composite variations in sampling and analysis, desorption efficiency, and the pump error.

$$\overline{CV}_T = \sqrt{\left(\overline{CV}_S\right)^2 + \left(\overline{CV}_{A+\overline{DE}}\right)^2 + \left(\overline{CV}_P\right)^2}$$

or:

$$\overline{CV}_T = \sqrt{\left(\overline{CV}_2\right)^2 - \left(\overline{CV}_1\right)^2 + 1.1667 \left(\overline{CV}_1\right)^2 + \left(0.05\right)^2}$$

In cases where $\overline{CV_2} < \overline{CV_1}$, take $\overline{CV_s} = 0$, and replace $\overline{CV_1}$ by a pooled estimate ($\overline{CV_1}^*$) based on CV_1 and CV_2:

$$\overline{CV_T} = \sqrt{(\overline{CV_2})^2 + 0.1667\ (\overline{CV_1}^*)^2 + (0.05)^2}$$

where:

$$\overline{CV_1}^* = \sqrt{\frac{f_1\ (\overline{CV_1})^2 + f_2\ (\overline{CV_2})^2}{f_1 + f_2}}$$

and f_1 and f_2 are the respective values used in the calculation of CV_1 and CV_2.

Grubb's Test for Rejection of an Observation

This test is applied in order to determine if one of the observations should be rejected as being an outlier. The following equation was used for the test:

$$B_1' = \frac{x - \bar{x}}{s} \quad \text{or} \quad \frac{\bar{x} - x}{s}$$

where:

x = observation being tested

$\bar{x}$ = mean of all observations

s = standard deviation based on n degrees of freedom.

For any 6 observations, a value can be rejected if $B_1' \geq 2.130$. The B_1' limit is based on a 1% significance level (i.e., a B_1' value calculated from the data can be expected to exceed 2.13 only 1% of the time if the observation is a legitimate one conforming to the underlying theory).

Bartlett's Test for Homogeneity of Coefficients of Variation

This test is applied in order to test the feasibility of "pooling the Coefficients of Variation" for any set of 18 generated samples (i.e., 6 at each of the 0.5, 1 and 2X OSHA standard level). The following equation for chi squared, with n-1 degrees of freedom, was used:

$$\text{Chi Squared} = \frac{f \ln \left(\overline{CV}_2\right)^2 - \sum_{i=1}^{n} f_i \ln \left(CV_{2i}\right)^2}{1 + \frac{1}{3(k-1)}\left[\left(\sum_{i=1}^{n} \frac{1}{f_i}\right) - \frac{1}{f}\right]}$$

where:

$\overline{CV}_2$ = Pooled Coefficient of Variation of 18 generated samples.

CV_{2i} = Coefficient of Variation of 6 generated samples at the i^{th} level.

f_i = Degrees of freedom associated with $(CV_{2i})^2$ and equal to number of observations at the i^{th} level minus one.

i = 1, 2, 3..... n

$f = \sum_{i=1}^{n} f_i$

k = number of variances being tested; in this program $k = 3$.

In order to pass Bartlett's test at the 1% significance level, chi squared must be less than or equal to 9.21 when $k = 3$.

Reference

A. Kenneth A. Busch Memoranda to Deputy Director, DLCD, on the subject "Statistical Protocol for Analysis of Data from Contract No. CDC-99-74-45", dated 1/16/75, 11/8/74.

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Ten NIOSH Analytical Methods. Set-3

Stanford Research Inst, Menlo Park, Calif

Prepared for

National Inst for Occupational Safety and Health, Cincinnati, Ohio

1977