Ammonium Sulfamate

Analyte:	Sulfamate Ion	Method No:	S348
Matrix:	Air	Range:	6.4-27.3 mg/cu m
OSHA Standard:	15 mg/cu m	Precision ($\overline{CV}_T$):	0.056
Procedure:	Filter collection, extraction with water, ion chromatography	Validation Date:	6/9/78

1. Synopsis

A known volume of air is drawn through a mixed cellulose ester membrane filter to trap the particulate present.

The filter is transferred to an ointment jar and extracted with distilled water.

An aliquot of the sample is injected into an ion chromatograph equipped with an anion exchange resin and a conductivity detector.

The peak height of the resulting sample peak is used as a measure of analyte concentration by comparison with corresponding peak heights obtained from the injection of standards.

2. Working Range, Sensitivity, Detection Limit

2.1 The method was validated over the range of 6.35-27.34 mg/cu m at an atmospheric temperature and pressure of 21-23°C and 758-765 mm Hg, using a 90-liter sample.

The method may be extended to higher values by further dilution of the sample solution.

The detection limit of the analytical method is estimated to be at least 0.90 mg/cum for a 90-liter sample.

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.

It must be emphasized that any other compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data based on a single set of conditions cannot be considered proof of chemical identity.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 6.35-27.34 mg/cu m was 0.0556. This value corresponds to a 0.849 mg/cu m standard deviation at the OSHA standard level. Statistical information can be found in Reference 11.1. Details of the test procedure are found in Reference 11.2.

4.2 In validation experiments, this method was found to be capable of coming within ±25 % of the "true value" on the average of 95% of the time over the validation range. The concentrations measured at 0.5, 1, and 2 times the OSHA standard were identical to the dynamically generated concentrations (n=18). The collection efficiency was determined to be 100% and the analytical recovery was determined to be 93.9% for a collector loading of 676 µg. In storage stability studies, the mean of samples analyzed after seven days was within 1.0% of the mean of samples analyzed the day after collection. Experiments performed in the validation study are described in Reference 11.2.

5. Advantages and Disadvantages

5.1 The sampling device is small, portable and involves no liquids Interferences are minimal and most of those which do occur may be eliminated by altering chromatographic conditions.

5.2 The samples are analyzed by means of a quick, instrumental method.

6. Apparatus

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

6.1.1 Filter. The filter unit consists of a mixed cellulose ester membrane filter, 0.8 micrometer pore size and 37-mm diameter, supported by a cellulose backup pad, and a 37-mm, three-piece filter holder held together by tape or a shrinkable band.

6.1.2 Personal Sampling Pump. A calibrated personal sampling pump is needed whose flow can be determined to an accuracy of ±5% at the recommended flow rate. 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.

Ion Chromatograph equipped with a conductivity detector and a 100-µL sample loop.

Anion precolumn, 3-mm I.D. x 150-mm glass, packed with weak anion exchange resin (Dionex).

Anion separator column, 3-mm I.D. x 500-mm glass, packed with weak anion exchange resin (Dionex).

Anion suppressor column, 6-mm I.D. x 250-mm glass, packed with cation exchange resin (Dionex).

Syringe, 10-mL for injection.

Microliter syringes. One hundred-microliter and other convenient sizes for making standard solutions.

Ointment jars, 2 oz., with Teflon-lined cap.

Volumetric flasks, 25-mL and other convenient sizes for making standard solutions.

Reagents

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

Ammonium sulfamate, reagent grade.

Distilled water.

Carbonate/Bicarbonate Eluent. Prepare by dissolving 1.008 grams $NaHCO_3$ and 1.018 grams Na_2CO_3 in 4 L of distilled water (0.003 M $NaHCO_3$/0.0024 M Na_2CO_3).

Ammonium Sulfamate Stock Solution, 27 mg/mL. Prepare by dissolving 0.65 grams of ammonium sulfamate in 25 mL of distilled water.

8. Procedure

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

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

Collection and Shipping of Samples

8.3.1 Assemble the filter in the three-piece filter holder and close firmly to insure that the center ring seals the edge of the filter. The cellulose membrane filter is held in place by a cellulose backup pad and the filter holder is held together by plastic tape or a shrinkable cellulose band. If 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 Remove the filter holder plugs and attach to the personal sampling pump tubing. Clip the filter holder to the worker's lapel.

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

8.3.4 A sample size of 90 liters is recommended. Sample at a known flow rate of between 1.5 and 2.0 liters per minute. The flow rate should be known with an accuracy of at least $\pm 5\%$.

8.3.5 Turn the pump on and begin collection. Set the flow rate as accurately as possible using the manufacturer's directions. Since it is possible for filters to become plugged by heavy particulate loading or by the presence of oil mists or other liquids in the air, the pump rotameter should be checked frequently and readjusted as needed. If the rotameter cannot be readjusted, terminate sampling.

8.3.6 Terminate sampling at the predetermined time and note sample flow rate, collection time and ambient temperature and pressure. If pressure reading is not available, record the elevation.

8.3.7 After sampling, holders should be firmly sealed with filter holder plugs in both the inlet and outlet.

8.3.8 Carefully record sample identity and all relevant sample data.

8.3.9 With each batch of samples, submit one filter which is subjected to exactly the same handling as the sample. Label this as a blank. Submit one blank for every ten samples.

8.3.10 The filter holders should be shipped in a suitable container designed to prevent damage in transit.

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

8.4 Analysis of Samples

8.4.1 Preparation of Samples

1. Open the filter holder. Carefully remove the cellulose membrane filter from the holder with the aid of appropriate tweezers and transfer the filter to the 2-oz. ointment jar.

2. Add 25 mL of distilled water to the jar and properly cap the unit. Gently swirl the jar to ensure that the filter is thoroughly wetted.

Analysis by Ion Chromatography. The eluting solvent is an aqueous solution consisting of 0.003M HCO_3^- and 0.0024 M $CO_3^=$. The typical operating conditions for the ion chromatograph are:

1. 2.3 mL/min solvent flow rate.

2. Ambient column temperature.

3. 550 psi system pressure.

4. 100 µL sample loop.

5. Sensitivity 100 µMhos full scale.

Injection. The first step in the analysis is the injection of the sample into the ion chromatograph via a sample loop injection valve. A 100-µL sample size is recommended for this analysis. Duplicate injections of each sample and standard should be made. No more than a 3% difference in peak height is to be expected.

8.4.4 The peak height is measured and compared to those prepared using standards as described in Section 9.

Determination of Analytical Method Recovery

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

8.5.2 Procedure for Determining Recovery. A known amount of the analyte, preferably equivalent to the sample concentration expected, is deposited on a representative cellulose membrane filter and air-dried. The analyte is then extracted from the filter with 25 mL of distilled water and analyzed as described in Section 8.4.

For the validation studies conducted to determine the precision and accuracy of this method, an amount of the analyte equivalent to that present in a 90-liter sample at the selected level was used to determine the analytical method recovery. A stock solution containing 27.05 milligrams of ammonium sulfamate per milliliter of distilled water was prepared. Twenty-five, 50 and 100 µL aliquots of the solution were added to the cellulose membrane filters and air-dried to produce samples equivalent to 90-liter collections at 0.5, 1 and 2X the OSHA standard level. The analytical samples were allowed to stand overnight. A parallel blank filter was also prepared except that no sample was added to it. All filters were then extracted and analyzed as described in Section 8.4.

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

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

9. Calibration and Standardization

From the stock standard solution, prepare at least six working standards to cover the concentration range of 675-2700 µg/25 mL. Transfer 25 to 100 µL-aliquots of the stock standard into 25-mL volumetric flasks and dilute to volume with distilled water.

This series of standards is analyzed under the same ion chromatographic conditions and during the same time period as the unknown samples. It is convenient to express concentration of

standards in µg/25 mL, because samples are extracted in this amount of distilled water. Curves are established by plotting concentrations in micrograms per 25.0 mL versus peak height.

9.3 To minimize effect of variations in the ion chromatograph conditions and detector response due to sample cell conditions (especially temperature) frequent standardization should be practiced.

10. Calculations

10.1 Read the concentration, in µg/25 mL, corresponding to the peak height from the standard curve. No volume corrections for sample aliquots analyzed are needed, because the standard curve is based on µg per 25.0 mL and the volume of sample injection is identical to the volume of the standards injected.

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

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

where:

µg sample = µg found in sample filter
µg blank = µg found in blank filter

10.3 Divide the total weight by the recovery (Section 8.5.2) to obtain the corrected µg/sample.

$$\text{Corrected } \mu g/\text{sample} = \frac{\text{Total Weight}}{\text{Recovery}}$$

10.4 For personal sampling pumps with rotameters only, the following corrections 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)

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

$$\text{mg/cu m} = \frac{\text{Corrected μg (Section 10.3)}}{\text{Volume of Air Sampled in Liters}}$$

11. References

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

11.2 Backup Data Report for Ammonium Sulfamate, No. S348, prepared under NIOSH Contract No. 210-76-0123, June 9, 1978.