Analyte:	Fluoroacetate Ion	Method No.:	S301
Matrix:	Air	Range:	0.020-0.137 mg/cu m
OSHA Standard:	0.05 mg/cu m - skin	Precision ($\overline{CV}_T$):	0.060
Procedure:	Filter collection, deionized water extraction, ion chromatography/electrolytic conductivity detection	Validation Date:	12/23/77

1. Synopsis

A known volume of air is drawn through a cellulose ester membrane filter to collect sodium fluoroacetate.

Sodium fluoroacetate is extracted from the filter with 5 mL of deionized water, and the resulting sample is analyzed by ion chromatography using electrolytic conductivity detection.

2. Working Range, Sensitivity, and Detection Limit

2.1 This method was validated over the range of 0.020-0.137 mg/cu m at an atmospheric temperature of 25°C and pressure of 758 mm Hg, using 480-liter samples. For this sample size, the working range is estimated to be 0.01-0.16 mg/cu m. The upper limit of the range of the method is dependent on the capacity of the cellulose ester membrane filter.

The sensitivity of the method for the instrumental conditions used during the validation study was 6 μmho/cm/microgram fluoroacetate ion. In other words, a 100-microliter injection of a 20 microgram/mL solution of sodium fluoroacetate gave a peak whose height was 92% of full scale on a 1-volt recorder. The ion chromatograph was set on range 10 μmho/cm.

The detection limit of the analytical method is estimated to be 20 ng of sodium fluoroacetate per injection, corresponding to a 100-microliter aliquot of a 0.2 microgram/mL standard. This corresponds to a 1 microgram per sample filter.

3. Interferences

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

Any anion that has the same retention time as fluoroacetate at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered proof of chemical identity.

Commercial pesticide grade sodium fluoroacetate is approximately 90% pure. Anions other than fluoroacetate that are likely to be present are fluoride and chloroacetate. They are used in the production of sodium fluoroacetate. Under the conditions in this method, fluoride elutes after 4.5 minutes, fluoroacetate after 6.4 minutes, and chloroacetate after 10.7 minutes. Nigrosine black dye is added to sodium fluoroacetate to prevent consumption by man. It does not interfere in the analysis.

4. Precision and Accuracy

The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 0.020-0.137 mg/cu m was 0.060. This value corresponds to a standard deviation of 0.003 mg/cu m at the OSHA standard level. Statistical information can be found in Reference 11.1. Details of the test procedures can be found in Reference 11.2.

A collection efficiency of 1.00 was determined for the collecting medium, thus no bias was introduced in the sample collection step, and no correction for collection efficiency is necessary. The Coefficient of Variation is a good measure of the accuracy of the method. The analytical method recovery was determined to be 0.969 for a collector loading of 11.82 micrograms. In storage stability studies, the mean of samples analyzed after 7 days were within 2.2% of the mean of samples analyzed immediately after collection. Experiments performed in the validation study are described in Reference 11.2.

5. Advantages and Disadvantages

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

The collection device is small, portable and involves no liquids.

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

6. Apparatus

Filter Unit. The filter unit consists of a 37-mm diameter Toyo-cel cellulosic ester membrane filter (0.8 micrometer pore size) from Nuclepore* and a 37-mm polystyrene two-piece cassette filter holder. The filter is held in the two-piece holder, supported by a backup pad. Secure the cassette holder together with tape or shrinkable band.

Personal Sampling Pump. A calibrated personal sampling pump whose flow rate can be determined to an accuracy of 5%. Each personal sampling pump must be calibrated with a representative filter cassette in the line to minimize errors associated with uncertainties in the volume sampled.

Manometer.

Thermometer.

Dionex ion chromatograph Model 10 or 14** equipped with a 100-microliter sample loop and an electrolytic conductivity detector.

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

Filtration unit for protection of the anion analytical column from particulate contamination: Swinnex (13-mm) fitted with 13-mm diameter/0.8 micrometer pore size cellulose ester membrane filters. The filter unit can be obtained from Millipore.

6.8 Tweezers.

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

6.10 Scintillation Vials: 20 mL, with Polyseal caps and shrinkbands.

Volumetric Flasks: 100 mL.

Volumetric Pipets: 1, 5, 10, and 15 mL.

6.13 Ruler with mm graduations.

7. Reagents

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

7.1 Sodium fluoroacetate.

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* This was the only suitable filter found. Other filters produced interferences or were not wettable by water.

** Dionex Corporation, Sunnyvale, CA.

7.2 Deionized water.

7.3 Ion chromatograph eluant, 0.005 M $Na_2B_4O_7 \cdot 10\ H_2O$. Add 7.63 g $Na_2B_4O_7 \cdot 10\ H_2O$ to 4 liters of deionized water. Dissolve the salt, then filter to remove particles which are greater than 1 micrometer.

7.4 0.1 M $Na_2B_4O_7 \cdot 10\ H_2O$. Add 153 g of $Na_2B_4O_7 \cdot 10\ H_2O$ to 4 liters of deionized water. Filter the solution to remove particles greater than 1 micrometer. This is used to periodically clean the analytical column.

7.5 Standard Sodium Fluoroacetate Solution (100 micrograms/mL). Dissolve 10 mg of sodium fluoroacetate in 50 mL of deionized water in a 100-mL volumetric flask. Make to volume.

8. Procedure

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

Collection and Shipping of Samples

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

8.2.2 Remove the cassette plugs and attach the outlet of the filter cassette to the personal sampling pump inlet with flexible tubing.

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

8.2.4 A sample size of 480 liters is recommended. Sample at a flow rate of 1.5-2.0 liters/minute. The flow rate should be known with an accuracy of 5%.

8.2.5 Set the flow rate as accurately as possible using the manufacturer's directions. Since it is possible for a filter to become plugged by heavy particulate loading or by the presence of oil mists or other liquids in the air, the pump rotameter should be observed frequently, and the sampling should be terminated at any evidence of a problem.

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

Remove the filter from the cassette filter holder with clean tweezers and place it into a 20-mL scintillation vial containing 5 mL of deionized water.

8.2.8 With each batch or partial batch of ten samples, submit a blank filter from the same lot of filters used for sample collection. This filter must be subjected to exactly the same handling as the samples except that no air is drawn through it. Label this filter as the blank.

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

10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. Never transport, mail, or ship the bulk sample in the same container as the sample or blank filter.

8.3 Analysis of Samples (Reference 11.3)

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

Column Temperature: Ambient
Pump: 25% of total capacity (115 mL/hr)
Column Pressure: 400 psig
Flow Rate: 115 mL/hour
Mobile Phase: 0.005 M $Na_2B_4O_7 \cdot 10\ H_2O$

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

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

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

8.3.5 Filter blanks must be analyzed following the same procedure as that used for the samples.

9. Calibration and Standardization

A series of standards, varying in concentration over the range corresponding to approximately 0.1 to 3 times the OSHA standard for the substance under study, is prepared and analyzed under the same ion chromatograph conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg/5 mL versus peak height. Standard solutions must be analyzed at the same time that the sample analysis is done.

From the stock standard solution (Section 7.5) appropriate aliquots are withdrawn and dilutions are made in deionized water. Prepare at least 5 working standards to cover the range of 1-15 micrograms/mL. This range is based on a 480-liter sample.

Analyze samples as described in Section 8.3.

Prepare a standard calibration curve by plotting concentration of sodium fluoroacetate versus peak height.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak height from the standard curve. No volume correction is needed, because the standard curve is based on mg/5 mL deionized water and the volume of sample injected is identical to the volume of the standards injected.

10.2 For concentrated samples which require dilution after initial analysis to bring them within the linear range of the standard curve (as in Section 8.3.4), apply the appropriate dilution factor to obtain the correct weight of sodium fluoroacetate in the sample.

10.3 A correction for the blank must be made for each sample.

$$\text{mg} = \text{mg sample} - \text{mg blank}$$

where

mg sample = mg found in sample filter

mg blank = mg found in blank filter

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

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

where:

f = flow rate sampled (liters/min)

t = sampling time (min)

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

P_2 = pressure of air sampled (mm Hg)

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

T_2 = temperature of air sampled (°K)

10.5 The concentration of sodium fluoroacetate in the air sample can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{mg} \times 1000 \text{ (liters/cu m)}}{\text{Corr. Air Volume Sampled (liters) (Section 10.4)}}$$

11. References

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

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

11.3 Dionex Ion Chromatograph Instruction Manual, Dionex Corp., Sunnyvale, CA (Jan. 1978).