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Analysis #0615.01
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FC-143 in Water/Wastewater by SPME/GCMS

Reference:

1. *Low-Level Determination of FC-143 in Water*, CH2M Hill, Inc., October 1991.
2. Method 8260B, Revision 2, SW-846, USEPA, December 1996. (BFB Tuning) Sarrion, M.N.; Santos, F.J.; Galceran, M.T.
3. *In Situ Derivatization/Solid-Phase Microextraction for the Determination of Haloacetic Acids in Water.* Analytical Chemistry, Vol. 72, No. 201, October 15, 2000, pp. 4865-4873.
4. SPME Applications Guide Bulletin 925A – Supelco.
5. Agilent Technologies Operations Manual.

Cross Reference:

The following procedure is cross-referenced in this document:

MC-EX-001, "GC/MS Preventative and Corrective Maintenance."

Scope:

This method is applicable to the measurement of the ammonium perfluorooctanoate in water and wastewater. The limit of quantitation is 1.0 µg/L.

Basic Principle:

Ethyl esters of the target and surrogate are converted from their respective acidic compounds using techniques for esterification. The sample is acidified to <3 using 1:1 HCL. Ion paring agent, diethyl sulfate, ethanol and sulfuric acid are used to convert the acid into the ethyl esters. The sample is mixed on a stir plate at a specified setting for a specific time. The sample is then absorbed onto a 100 µm PDMS fiber for 10.0 minutes and injected into a GC/MS system equipped with a capillary column. The analysis is performed using internal standard calibration by GC/MS.

Apparatus:

1. Hewlett-Packard Model 5890 (Series I and II) or 6890 Gas Chromatograph or equivalent
2. Hewlett-Packard Model 5971, 5972, and 5973 Mass Selective Detector or equivalent
3. Hewlett-Packard Chemstation Software, Thru-Put Systems Target data system or equivalent
4. Solid Phase Microextraction (SPME) – Supelco - 100 µm Polydimethylsiloxane (PDMS) fiber, fiber pen for manual injection, and injector guide, or equivalent
5. 15 mL – Clear vial with Teflon/silicon septum or equivalent
6. Stir Plate – VWR – mini stirrer, Model 200 or equivalent
7. Stir Bars – VWR Teflon stir bars ½" X 5/16" or equivalent
8. Disposable Glass pipettes
9. 10 mL Class A graduated cylinder

10. Syringes – 1 mL, 10 mL, 10 µL, 25 µL, 50 µL

11. Timers – Capable of measuring time to 30 minutes.

12. Class A volumetric flasks, assorted sizes

13. Analytical balance – Capable of weighing to 0.0001 g

Reagents:

1. 1:1 HCL reagent grade or equivalent

2. Ethanol – AAPER Chemical – Absolute 200 Proof or equivalent

3. Chromatography column – J&W DB-5MS, 30M x 0.25 mm ID, 1.0 µm df or equivalent

4. UPC helium for carrier gas

5. Pentadecafluorooctanoic acid Ammonium salt — Fluka, 98% pure or equivalent

6. 4-Bromofluorobenzene – 2000 ppm BFB Chem Service ampulated solution in methylene chloride or equivalent, for tuning agent and internal standard

7. Heptadecafluorononanoic acid – Fluka, 97 % pure or equivalent for surrogate standard

8. Tetrabutylammonium hydrogen sulfate (TBA-HS) – Fluka, 99% pure or equivalent. Ion pairing reagent

9. Diethyl Sulfate –Aldrich, 98% or equivalent Ethylation reagent

10. Sulfuric Acid – ACS grade or equivalent

11. Deionized water

Standards:

Note: Working stocks are prepared by diluting stock solutions to the appropriate concentration with a syringe and volumetric flask.

1. Stock Pentadecafluorooctanoic acid Ammonium salt (FC-143) – Weigh approximately 0.02 g pentadecafluorooctanoic acid ammonium salt into a 10 mL volumetric flask and dilute to volume with ethanol. Record in database or Dept 26 spikes and special mixes notebook. This is a stock solution.

2. Working Stock FC-143 -pentadecafluorooctanoic acid ammonium salt – Dilute the stock pentadecafluorooctanoic acid ammonium salt solution to 500 ppm using ethanol in a volumetric flask.

3. Internal standard/Tuning Solution BFB – 4-Bromofluorobenzene – Dilute 2000 ppm ampulated stock solution to 50 ppm in MeOH. This is the internal standard spike. Spike all standards and samples with 20 µL per 1 mL of final volume.

4. Stock Heptadecafluorononanoic acid surrogate – Weigh approximately 0.02 g Heptadecafluorononanoic acid into a 10-mL volumetric flask and dilute to volume with ethanol. Record in database or Dept 26 spikes and special mixes notebook. This is a stock solution.

5. Working Stock Heptadecafluorononanoic acid – Dilute the stock Heptadecafluorononanoic acid solution to 500 ppm using ethanol.

6. Ion Paring Agent – Tetrabutylammonium hydrogen sulfate (TBA-HS) weigh approximately (0.016 g to 100 mL deionized water)

7. Diethyl Sulfate solution 0.15 Molar in ethanol – 2mL of diethyl sulfate in 100 mL of ethanol.

8. Calibration Levels

Level 1: F1432.5:	25 µL of calibration and surrogate intermediate + 10 µL of internal standard	to 5.0 mLs deionized water, 0.5 mL 1:1 HCL,
Level 2: F1435.0	50 µL of calibration and surrogate intermediate + 10 µL of internal standard	to 5.0 mLs deionized water, 0.5 mL 1:1 HCL,
Level 3: F14310.0:	100 µL of calibration and surrogate intermediate + 10 µL of internal standard	to 5.0 mLs deionized water, 0.5 mL 1:1 HCL,
Level 4: F14315.00:	150 µL of calibration and surrogate intermediate + 10 µL of internal standard	to 5.0 mLs deionized water, 0.5 mL 1:1 HCL,
Level 5: F14320.00:	200 µL of calibration and surrogate intermediate + 10 µL of internal standard	to 5.0 mLs deionized water, 0.5 mL 1:1 HCL,
Level 6: F14325.0	250 µL of calibration and surrogate intermediate + 10 µL of internal standard	to 5.0 mLs deionized water, 0.5 mL 1:1 HCL,
MDL/LOQ standard:	10 µL of calibration and surrogate intermediate + 10 µL of internal standard	to 5.0 mLs deionized water 0.5 mL 1:1 HCL,

Safety Precautions:

FC-143 is extremely dangerous in the neat room form. The time weighted average exposure limits is 0.1 mg/m^3. Therefore, extreme care must be used when working with this compound. Also, heating of the neat standard or any concentrated solution must be avoided. Any handling of the neat product must be done in a hood with a second analyst observing the process and acting as a safety spotter.

The compounds used as surrogate standards are also dangerous. These compounds form hydrofluoric acid upon heating or breakdown. Therefore, the exposure of the neat material to any concentrated solution must be avoided.

Sample Preservation and Holding Time:

Samples must be prepared within 7 days of date collected. Extracts should be analyzed at time of ethylation.

Extracts and standards must be kept at –20 to -10°C prior to analysis.

Personnel Training and Qualifications:

Each analyst performing the instrumental analysis will work with an experienced analyst for a period of time until they can independently calibrate the instrument, use the chromatographic data system to set up sequences, perform the calculations, interpret the chromatograms, and enter the data into the LIMS. They will also follow the department training manual for analysts. Proficiency is measured through documentation audits of the tasks listed and overchecking of data.

Extraction/Ethylation Procedure:

NOTE: Prepare Standards/ Samples only when ready for analysis as variations in ethylation time and absorption time will affect results. A timer is used which can measure two separate times, one for ethylation and one for absorption onto the fiber.

1. Measure 5.0 mL of deionized water (standards) or sample into 15 mL clear vial and add 0.5 mL of 1:1 HCL to pH the solution below 3.

2. Spike Standards with appropriate amount of target and surrogate working stock solution and samples with 50 µL of 500 ppm Heptadecafluorononanoic acid surrogate solution. Add 10 µL of 50 ppm BFB internal standard to each vial prior to ethylation.

3. Add a rinsed stir bar and 250 µL of TBA-HS ion paring agent.

4. Add 1.0 mL of 0.15 molar Diethyl Sulfate and 1.0 mL 200 proof ethanol.

5. Cautiously add 10 drops of concentrated Sulfuric Acid.

6. Recap vial tightly and place on the VWR mini stirrer, Model 200, stir plate at speed 4 for 30.0 minutes (see NOTE below).

7. Following the 30.0 minute ethylation process; insert the 100 µm PDMS fiber in its withdrawn position at a setting of 1.0 on the fiber pen through the Teflon/silicon septum, lower the fiber into the headspace for 10.0 minutes to allow absorption.

8. After 10.0 minutes, raise the fiber into the up position and remove it from the vial. Change the pen height from 1.0 to 3.6 on the fiber pen. Insert the pen into the injection port and lower the fiber into the port. Press the START button to initiate the injection.

NOTE: Consistent speed rate and timing for the ethylation, absorption and insertion steps greatly increases the reproducibility and precision of the method. Conditions above may change to increase sensitivity, reproducibility and overall chromatography.

GC/MS Analysis:

Instrument Setup

Detector –	Mass selective detector (MSD)
Detector temperature –	300°C
Oven Temperature Program –	45°C for 3 minutes, 5°C/minute to 85°C, then 70°C/minute to final temperature of 300°C, hold for 10 minutes
Carrier –	Helium, Constant flow mode – 1.5 mL/minute
Injection –	Fiber insertion 4 +minutes
Injector Temperature–	275°C
Injection Mode –	Splitless Purge flow to split vent 40 mL/minute at 2 minutes

The conditions listed above may be changed to improve the linearity, sensitivity, or overall chromatography on each GC/MS system.

Calibration:

A. Calibration consists of analyzing standards at 6 concentration levels and producing response factors. The relative standard deviation of the response factor determines the suitability of the average relative response factor for calculation of concentration.

1. An aliquot of 0.5 ng/µL BFB must analyzed and meet the criteria described in **Table I.** If the criteria are not met, the mass spectrometer must be retuned and BFB reanalyzed until all criteria are met. For BFB fiber analysis, Spike 50 µL of 50 ppm BFB working standard into 5.0 mL deionized water with 0.5 mL 1:1 HCL and place on the stir plate, insert the fiber pen, set to 1.0 through the septum and lower the fiber for 10.0 minutes. Raise the fiber, remove the pen and insert into the injection port. Start the injection.

2. If the performance criteria are met for the BFB solution, perform an initial calibration by injecting the six calibration standard solutions referenced previously.

3. At the end of the calibration standard injections, inject the MDL/LOQ solution. The system must be able to detect FC-143 in the MDL/LOQ solution. If the system does not detect FC-143, then the tuning and calibration procedure must be repeated under conditions that will yield a detection for FC-143 in the MDL/LOQ solution. Instrument maintenance as outlined in MC-EX-001, may be required.

4. Due to the nature of the technique, initial calibrations may require multiple days for analysis. In the event a calibration carries into a second day, prior to resuming calibration standard injection, first inject and pass BFB as stated previously, then inject a comparison standard from the already injected standards and confirm system stability by response factor comparison. Response factors must be within 20% drift in order to continue with calibration. If the % drift exceeds 20%, then corrective action and a new initial calibration may need to be performed.

B. Calculate the response factor for FC-143 and the PFNA surrogate for each calibration solution.

Calculation of the response factor (RF):

$$RF = \frac{[A(x) \times C(is)]}{[A(is) \times C(x)]}$$

Where:

A(x) = Area of the quantitation ion for the compound being measured

C(is) = Concentration of the specific internal standard

A(is) = Area of the quantitation ion for the specific internal standard

C(x) = Concentration of the compound being measured

C. For FC-143 and the surrogate PFNA, calculate the mean RF from the RFs of the six calibration standards. Calculate the relative standard deviation:

$$\%\ RSD = \frac{SD}{Avg\ RF} \times 100$$

Where:

$$SD = \frac{\sum RF - avg\ RF}{n-1} \quad and \quad Avg\ RF = \frac{\sum RF}{n}$$

If the RSD of the response factors is less than or equal to 15%, then the average relative response factor is used for quantitation. If the %RSD exceeds 15% then a linear curve may be used for quantitation.

D. Continuing calibrations

Verify the MS tune and initial calibration at the beginning of every 12-hour work shift during which analyses are performed.

1. An aliquot of 0.5 ng/µL BFB must be analyzed and meet the criteria described in Table 1. If the criteria are not met, the mass spectrometer must be retuned until all criteria are met. See A 1. above for injection procedure.

2. Perform a continuing calibration check by injecting an aliquot of the mid-point calibration standard. Calculate the percent drift:

$$\%\ Drift = \frac{C(i) - C(c.)}{C(i)} \times 100$$

Where:

C(i) = Calibration check compound standard concentration

C(c) = Measured concentration using selected quantitation method

The percent drift for FC-143 should not be greater than ± 20%. If the %drift exceeds 20%, then corrective action must be taken and a new initial calibration may need to be performed.

3. The absolute areas of the quantitation ions of the internal standard must fall within –50% to +100% of the average area from the last initial calibration. If the area for the internal standard is not within this window then corrective action must be taken and documented.

4. The MDL/LOQ standard must be injected after a compliant BFB and a compliant continuing calibration check standard. You must be able to detect FC-143 in the MDL/LOQ solution. If the system does not detect FC-143, then the tuning and calibration procedure must be repeated under conditions that will yield a detection for FC-143 in the MDL/LOQ solution. Instrument maintenance as outlined in MC-EX-001 may be required.

Analysis of Samples:

1. Analyze a 5.0 mL aliquot of each sample extract under the same conditions used for the initial and continuing calibrations.

2. At the conclusion of data acquisition, use the same software to tentatively identify peaks within the retention time window of interest. Examine the ion abundances of components of the chromatogram. If the ion abundance of the FC-143 ion used for quantitation (69 amu) exceeds the calibration range, dilute the aliquot and reanalyze. When preparing dilutions, add sufficient internal standard to maintain the same concentration as that of the ICAL.

Qualitative Analysis:

A compound is identified by comparison of the sample mass spectrum (after background subtraction) with the mass spectrum of a standard of the target compound (standard reference spectra). In order to verify identification, the following criteria should be met:

1. The sample component retention time should be within 10 seconds of the time observed for the component when a calibration solution was analyzed.

2. All ions in the reference spectra at >10% of the most abundant ion should be present in the sample mass spectra and should agree within absolute 20%. An example spectrum for the ethylated form of FC-143 is presented in **Figure 1.**

Quantitative Analysis:

Once a compound has been identified, quantitation will be based on the internal standard technique and the integrated abundance from the extracted ion current profile (EICP) of the primary characteristic ion.

$$Concentration\ (\mu g/L) = \frac{A(x) \times I(is)}{A(is) \times RF\ V(o)}$$

Where:

A(x) = Area of the quantitation ion for the compound to be measured

I(is) = Amount of internal standard added to the water sample (in micrograms)

A(is) = Area of the quantitation ion for the appropriate internal standard

RF = Average response factor from the current initial calibration

V(o) = Original water sample volume (in liters)

Quality Assurance:

At least one deionized water blank, laboratory control spike, and spike duplicate is analyzed with every group. A matrix spike and matrix spike duplicate are analyzed per analytical batch, unless insufficient client sample volume is supplied. In such cases, a LCSD must be substituted for the MS/MSD extraction. The spiking solution contains all analytes of interest. A surrogate standard spiking solution containing perfluorononanoic acid is also added.

The advisory QC windows are 70 – 130 for the mean recovery of the LCS/LCSD, MS/MSD, and surrogate. If the recovery falls outside these windows, corrective action may be taken based on the nature of the non-conformance. The corrective action must be documented and may include reinjection, re-extraction, instrument maintenance, and preparation of new calibration standards. Statistical QC windows will be generated and acted upon once sufficient data points have been collected.

Revision Log:

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Ver. #	Effective Date	Change
01	APR 0 9 2001	New

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Prepared by: 383 Date: 04-09-01

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Quality Assurance

Table I

BFB Key Ion Abundance Criteria

Mass	Ion Abundance Criteria
50	15% to 40% of mass 95
75	30% to 60% of mass 95
95	base peak, 100% relative abundance
96	5% to 9% of mass 95
173	less than 2% of mass 174
174	greater than 50% of mass 95
175	5% to 9% of mass 174
176	greater than 95% but less than 101% of mass 174
177	5% to 9% of mass 176

Figure 1