

Quantitative Determination of Fluoroalkyl Sulfonamides in Aqueous Systems

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Overview

Goal: To develop a quantitative GC/MS/MS method for the analysis of fluoroalkyl sulfonamides in aqueous matrices.

Methods:

1. Extraction & preconcentration of analytes using solid phase extraction.
2. Analysis by GC/MS/MS.
3. Quantitation based on calibration curves constructed from standards.

Observations:

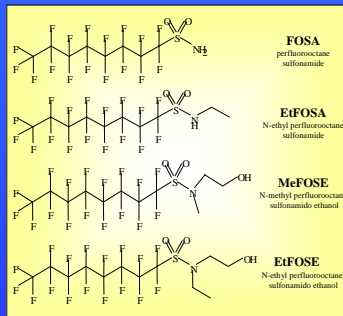
1. A solid phase extraction procedure can be used for quantitative determination of fluoroalkyl sulfonamides.
2. GC/MS/MS can be used for differentiation and quantitation of fluoroalkyl sulfonamides.

Introduction

Fluoroalkyl compounds are:

- globally distributed; polar, urban & rural regions
- found in a wide range of biota (human blood, birds, marine mammals, mollusks)
- bioaccumulative (levels increase with trophic level)
- persistent
- POSF (perfluorooctanesulfonyl fluoride) is a building block for a family of chemistries with applications in:
 - protection of paper & packaging
 - fabric, upholstery & carpet protection
 - shampoos & cosmetics
 - herbicide & insecticide formulations
 - cleaning products (windows, cars, carpets etc)
- POSF chemistry based on electrochemical fluorination (ECF)
 - Structural isomers --> branching
 - Homologues of C₂-C₁₃; odd and even numbers of fluorinated carbon
 - Perfluorinated carbon chain
- C₂-based ECF chemistry phased out amidst concerns about bioaccumulation and environmental persistence

Structures of Analytes



Presence of Fluoroalkyl Sulfonamides in the Environment

- Urban & rural air samples of outdoor^{2,3,4} and indoor⁴
 - EtFOFA, MeFOSE, EtFOSE detected^{2,3,4}
 - 17-2000 pg/m³
- FOSA detected in biota:
 - human serum⁹
 - fish & marine mammals⁶
 - mink & river otters⁷
- Fast food - Canadian Total Diet Study⁸
 - EtFOFA: 10-23500 pg/g
- In vitro biodegradation of EtFOFA⁹
 - forming FOSA & perfluorooctanesulfonate (PFOS)

Research Goals

Long Term Goals:

- Understand the fate and transport of fluoroalkyl substances in a municipal wastewater treatment plant

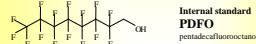
Short Term Experimental Goals:

- Develop analytical methods
 - quantitative determination of fluoroalkyl substances in aqueous and solid matrices
- Determine the balance of mass-flow in a municipal wastewater treatment plant

Sampling and Analysis

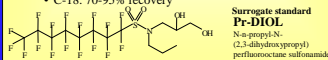
Instrumental Details

- GC/MS/MS
 - HP 5890 GC coupled to Finnigan TSQ 700
 - Alltech EC-Wax column
 - 30M column
 - 0.25 mm ID
 - 0.25 um film thickness
 - Positive Chemical Ionization (CI) with CH₄



Sample Preparation

- Centrifugation of wastewater
- Solid Phase Extraction
 - 25 mm Empore Disks
 - In-Vial Elution using EtOAc
- Evaluated SDB & C-18
 - SDB: 50-60% recovery
 - C-18: 70-95% recovery

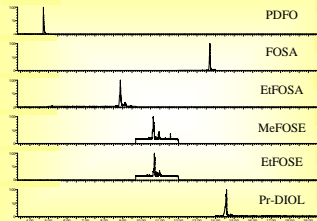


Sampling and Analysis

Selected Reaction Monitoring

Compound (mw)	Precursor Ion (m/z)	Product Ion (m/z)	Product Ion Structure
PDFO (400)	401	381	[M-HF] ⁺
FOSA (499)	500	64	[SO ₂] ⁺
EtFOFA (527)	528	92	[SONHC ₂ H ₅] ⁺
MeFOSE (557)	558	57 540	[N(CH ₃)CH ₂ CH ₂] ⁺ [M-H ₂ O] ⁺
EtFOSE (571)	572	71 554	[N(CH ₂ CH ₃)CH ₂ CH ₂] ⁺ [M-H ₂ O] ⁺
Pr-DIOL (615)	616	115 598	[N(CH ₂ CH ₂ CH ₃)CH ₂ CH(OH)CH ₂] ⁺ [M-H ₂ O] ⁺

Standard Chromatogram



Conclusions

- First application of GC/MS/MS for quantitation of fluoroalkyl sulfonamides
 - quantitation on structurally specific transitions
 - unambiguous identification of analytes
- SPE applied to extraction of fluoroalkyl sulfonamides from aqueous samples
 - SPE: sample clean-up, extraction and preconcentration step
 - Recovery evaluated using structurally related fluoroalkyl sulfonamide surrogate standard
 - new SPE media needed to accommodate larger volume of wastewater?

Remaining Research

Application to Mass Balance:

- Determination of fluoroalkyl sulfonamides in
 - wastewater
 - sludge
- Combine with results of LC/MS/MS analyses:
 - sulfonates ~200 ng/L decrease
 - carboxylates ~100 ng/L decrease
 - sulfonamides ~50 ng/L increase

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