

American Society of Mass Spectrometry (ASMS) Summary of DuPont Presentations

ASMS Annual Meeting, 2004

Quantitative Determination of Extractable PFOA in Textiles and Carpets by LC/MS/MS

Michael P. Mawn, Richard G. McKay, Timothy W. Ryan, Bogdan Szostek, Robert C. Buck

Introduction :

Analytical methods were developed to quantify the amount of perfluorooctanoic acid (PFOA) extracted from textile and carpet samples through contact with water, sweat, and saliva simulants. The analysis is challenging because of the diverse nature of the samples and solvent extracts. The carpet and textile samples are composed of nylon, cotton, polyester, or cotton-polyester blends. Other compositional differences may include dyes, mesh backing, adhesives, fillers, and surface treatments. Finally, textiles and carpets have diverse physical properties such as woven and nonwoven fabrics as well as cut-pile and Berber style carpeting.

Methods :

The carpet and textile samples are extracted in water, sweat, or saliva simulants using a wrist action shaker. The saliva simulant requires protein precipitation with acetonitrile followed by centrifugation before LC/MS/MS analysis. The PFOA is focused on an RX-C8 column using 0.15% acetic acid in water. The peak focusing enables the use of large sample injection volumes with good peak shape. An added benefit is that it also enables inorganic salts that are present in the sweat and saliva simulants to be diverted to waste before subsequent elution of the PFOA with 80% acetonitrile. The PFOA is analyzed using negative ion ESI under MS/MS conditions. Matrix effects are minimized with use of a dual labeled ^{13}C -PFOA internal standard.

Preliminary Results :

Initial work consisted of determining optimum extraction conditions and times with serial extractions to generate extraction profiles. The water, sweat, and saliva simulants result in a linear calibration curve using the ^{13}C -PFOA internal standard over the concentration range of 0.08 ng/mL to 10 ng/mL. The limit of quantitation (LOQ) of 80 pg/mL corresponds to 1 ng/g PFOA in the textile and carpet samples. Despite the diverse nature of the textile and carpet samples the resulting post extraction fortified samples have routine recoveries within 15% deviation due to the use of the ^{13}C -PFOA internal standard.

Determination of Telomer B Alcohols by Liquid Chromatography-Tandem Mass Spectrometry in Environmental Matrices.

¹DuPont Haskell Laboratory, Newark, DE; ²DuPont Chemical Solutions Enterprise, Wilmington, DE; Bogdan Szostek¹; Keith B. Prickett¹; Robert C. Buck²;

Introduction

Fluorinated telomer alcohols (FTOHs), named after a production process called telomerization, are used as intermediates for production of various fluorosurfactants and polymers. The FTOHs are long-chain, linear, partially fluorinated alkyl alcohols. The environmental and biological fate of these alcohols have recently been a subject of many studies. These studies require sensitive and selective analytical methods to monitor the FTOHs in various environmental matrices. The FTOHs have been traditionally analyzed by GC/MS with either with CI or EI ionization. However, the GC/MS methods often are of insufficient sensitivity and require cumbersome sample preparation and clean up. These drawbacks can be alleviated by use of LC-MS/MS, that results in more selective and sensitive, simpler sample preparation methods

Keywords: Chromatography, Liquid -, High Pressure (HPLC); Ionization, Electrospray; MS/MS; Quantitative Analysis;

Methods

The major steps in method development will include the optimization of chromatographic conditions for efficient separation of FTOHs and optimization of MS ionization conditions. FTOHs can be ionized in the negative ion electrospray mode, but an efficient formation of deprotonated molecular ions of these compounds is much dependent on the chemical composition of chromatographic mobile phase. Formation of negative deprotonated molecular ions is inhibited by presence of ammonium acetate in mobile phase and considerable differences in that respect are seen between acetonitrile and methanol. Therefore, careful optimization of mobile phase composition is needed.

American Society of Mass Spectrometry (ASMS) Summary of DuPont Presentations

Novel Aspect: LC/MS/MS methodology developed for analysis of fluorinated telomer alcohols in environmental matrices

Preliminary results

Initial data obtained for 8-2 FTOH using a single-quadrupole LC/MS indicates that the FTOH can be ionized by negative ion electrospray if a mobile phase of appropriate composition is used. The FTOHs can be successfully separated using reverse-phase chromatographic columns and are relatively easily separable from potential interferences such as perfluorinated carboxylic acids. Additionally, preliminary data indicates that 8-2 FTOH can be efficiently extracted from aqueous matrix either by acetonitrile or methyl-tert butyl ether (MTBE). MTBE being a water immiscible solvent extracts fewer potential interferences or matrix that would cause matrix effects. Additional consideration for these analytes is relatively high volatility and low water solubility of these analytes, resulting in high losses of these analytes from aqueous matrix. Appropriate extraction and sample preservation procedures will be developed for other FTOHs to allow their analysis in aqueous matrices. Presentation will describe our efforts in developing and validating LC/MS/MS method for analysis of three major fluorinated telomer alcohols in various environmental matrices. More complex matrices as soils will also be investigated. Efficient sample clean up procedure based on reverse-phase solid phase extraction (SPE) has not been demonstrated for FTOHs. This will be evaluated for FTOHs and if successful, will be applied to soil samples.

ASMS Annual Meeting, 2003

Investigation of anionic and nonionic fluorosurfactants by liquid chromatography-mass spectrometry.

Bogdan Szostek, Janet C. Maslanka, Vladimir Capka

DuPont Haskell Laboratory for Health and Environmental Sciences, Newark, DE, USA

Fluorosurfactants comprise a class of surfactants that can be distinguished by their superior stability in harsh thermal and chemical environments and effectiveness in wetting, leveling of surfaces, and lowering surface tension at very low application concentrations. These properties of fluorosurfactants constitute their use as additives in floor waxes, paint, finishes, adhesives, and find use in polymer, electronic, cleaning, metal technology. The class of fluorosurfactants that was investigated in this work is derived from Telomer B Alcohols (TBA). The Telomer-based fluorosurfactants are obtained by modification of the polar end group of TBAs. The Telomer-based fluorosurfactants are usually complex mixtures of chemical species that often have not been comprehensively speciated. Components of the mixtures possess no chromophores making traditional spectroscopic detection for LC separations not feasible. Determination of individual components of fluorosurfactants poses challenging analytical problem in respect to separation, detection, and quantitation. Two classes of fluorosurfactants: anionic fluoroalkylphosphate surfactant and non-ionic ethoxylate fluorosurfactant were investigated by liquid chromatography-mass spectrometry. This work emphasized the chromatographic separation of the components of these complex mixtures, their identification, establishment of figures of merit for mass spectrometric detection, and development of analytical methodology for analysis in aqueous matrices.

Mass spectrometry with negative electrospray ionization was used for detection of anionic fluoroalkylphosphates. The separation of components of fluoroalkylphosphate surfactant mixture can be achieved on reverse-phase LC columns. Mono fluoroalkylphosphate esters, subgroup of species in the fluoroalkyl phosphate surfactant, exhibit strong tendency to severe peak tailing on reverse-phase columns. Acceptable peak shapes can be achieved either by addition of triethyl amine (TEA) to the mobile phase or careful selection of the brand of the column. Luna C18 column and 50 mM ammonium acetate were found to give acceptable separation and peak shapes for mono fluoroalkylphosphate esters without TEA addition. It had been observed that fluoroalkylphosphates would accumulate in the LC/MS system, creating serious background and carry over issues. This was somewhat alleviated by use of mobile phase of high ionic strength and injector wash solvent of 50 mM ammonium acetate in 50/50% water/methanol.

The nonionic ethoxylate fluorosurfactant was studied by GC-FID and positive ion electrospray mass spectrometry. The nonionic ethoxylate fluorosurfactant components are efficiently separated and detected by GC/FID. However, this approach has a limited sensitivity (mg/mL) and selectivity with respect to speciation. Similarly, the GC/MS with EI ionization, even though provides more structural information about individual components, is not sufficient to

American Society of Mass Spectrometry (ASMS) Summary of DuPont Presentations

uniquely identify the number of ethoxylate groups in the chemical component. The nonionic ethoxylate surfactants are easily ionized with electrospray by formation of adducts with metallic cations or ammonium ions present in the mobile phase. Use of ammonium acetate in mobile phase shifts the adduct formation to predominantly ammonium adducts. The separation that is obtained on a reverse-phase column is based mainly on the length of the fluorinated chain, grouping in a single peak species of different length of ethoxylate chain (Figure 1). The peak areas for individual peaks are linear with the concentration of ethoxylate fluorosurfactant for data obtained in scan mode (600-2000 m/z) allowing quantitation down to 0.5 mg/L of ethoxylate fluorosurfactant. Collision induced fragmentation (CID) was studied for Telomer- derived ethoxylate species. The TBA ethoxylates share the same fragmentation pattern despite the length of the ethoxylate chain or the TBA present. The fragmentation is focused on multiple losses of ethoxylate unit (mass 44).

Determination of Biotransformation Products of Fluorotelomer 8-2 Telomer B Alcohol in Environmental Matrices by Liquid Chromatography – Tandem Mass Spectrometry (LC/MS/MS).

Vladimir Capka¹, Richard F. Rossi¹, Ning Wang², Patrick W. Folsom²

¹DuPont Haskell Laboratory for Health and Environmental Sciences, PO Box 50, Newark, DE, 19714

²DuPont Central Research and Development, Glasgow Business Community 301, PO Box 6101, Newark, DE 19714

Fluorinated surfactants are used in many consumer products due to their exceptional stability under a wide variety of environmental and thermal conditions and their superior wetting and surface tension lowering properties. The 8-2 telomer B alcohol is the primary intermediate used in the synthesis of a variety of telomer-based fluorinated surfactants. The presentation focuses on development and validation of analytical methods for acidic biodegradation products of 8-2 telomer B alcohol. Validation of analytical method for simultaneous determination of 2-perfluorooctylethanoic acid (2-PFOEA), 2H-hexadecafluoro-2-decanoic acid (2H-HDF-2-DA), perfluorooctanoic acid (PFOA), and perfluorohexanoic acid (PFHA) for use in various studies for evaluation of environmental persistence and metabolic pathways of 8-2 telomer B alcohol in environmental bacterial sludge matrix was performed.

Due to stringent sensitivity and selectivity requirements, lack of UV-absorbing chromophores, and the specific design of the studies these methods were intended for, an approach utilizing liquid chromatography with mass spectrometric detection was used. The analytes are separated using reverse-phase liquid chromatography and detected using negative ion electrospray ionization in multiple reaction monitoring (MRM) mode for sensitivity reasons.

Investigation of MS/MS fragmentation patterns of 8-2 telomer B alcohol metabolites revealed, as expected, that the most stable fragment for PFHA and PFOA resulted from the loss of CO₂. Under increased collision energy, this fragment then undergoes further fragmentation in easily interpretable manner. The stability of this ion comes from the high electron deficit at the carboxylic carbon due to highly electronegative fluorine atoms that are weakening the bond with the carboxylic group.

On the other hand, for 2-PFOEA and 2H-HDF-2-DA, the fragmentation pattern was very different than would be expected for the non-fluorinated acidic analogs of these analytes. Due to the acidic nature of the hydrogen atoms adjacent to the fluorocarbon chain, the most intense fragment came from simultaneous elimination of CO₂ and one (for 2H-HDF-2-DA) or two (for 2-PFOEA) molecules of HF yielding an extremely stable acetylene fluorocarbon analog ion, which does not undergo any further fragmentation upon increasing collision energy.

The chromatographic peaks were well focused and well separated from early eluting matrix. Optimization of sample preparation from bacterial sludge matrices was performed. Methods of liquid-liquid extraction, ion-pair liquid-liquid extraction, and protein precipitation were used.

Simple liquid-liquid extraction (extraction to MTBE after acidification with H₂SO₄) resulted only in moderate recoveries (~65 %) at initial sludge cell density ($A_{600nm} = 0.05$). Furthermore, at full cell density (cells allowed to reproduce for 3 days) severe loss of 2-PFOEA and 2H-HDF-2-DA occurred, indicating the interference of increased cell count with the extraction procedure.

American Society of Mass Spectrometry (ASMS) Summary of DuPont Presentations

Ion-pair liquid-liquid extraction (triple-extraction to MTBE after alkalization with Na_2CO_3 and addition of tetrabutylammonium hydrogensulfate) produced quantitative recoveries for PFHA and PFOA but insufficient recoveries for 2-PFOEA and 2H-HDF-2-DA.

Methods of protein precipitation with acetonitrile resulted in complete recovery of all four analytes at high (200 ppb) and low (60 ppb) concentrations and at both, initial and full cell density extraction conditions.

Extensive quality control measures were incorporated into LC/MS/MS method, providing proof of method validity for each extraction procedure. The method was found to provide reliable data for all three extraction procedures without any matrix effects, as evidenced by quantitative recoveries of matrix, solvent, and instrument quality control samples.

It has been shown that, under gradient conditions, the analytes under investigation produce background signals in blank samples, causing difficulties with quantitation. Experiments were performed that indicated that this may be due to their presence at trace levels in common chromatographic solvents. Other factors, such as their accumulation in the LC/MS system may also be causing increased background and carryover.

The method developed is suitable for environmental fate and biopersistence studies with 8-2 telomer B alcohol and its acidic metabolites in bacterial sludge matrix. The direction of future research will focus on control of system background issues and method development in alternative environmental biological matrices.

ASMS Annual Meeting, 2002

Analysis of Complex Mixtures of Fluoroalkylphosphate Surfactants by Liquid Chromatography-Negative Ion Electrospray Ionization Mass Spectrometry.

Bogdan Szostek, Vladimír Čápka, Janet C. Maslanka

DuPont Haskell Laboratory for Health and Environmental Sciences, Newark, DE, USA

Anionic fluorosurfactants find widespread applications as very effective surface wetting agents, powerful surface tension depressants, and possess diverse foaming abilities. These specific properties of fluorosurfactants constitute their broad applications as additives in hair and personal care products, floor waxes, paints, finishes, adhesives, and find use in polymer, electronic, cleaning, metal technology. Analysis of anionic fluoroalkylphosphate surfactants poses analytical challenges. These analytes are complex mixtures of a variety of anionic fluorinated species and quantitative instrumental methods for their component analysis have never been previously developed. Components of the mixtures contain no chromophores and exhibit problematic behavior on common (reverse-phase, silica-based) chromatographic columns. The purpose of this research was to develop an LC separation method for the major components of complex mixtures of fluoroalkyl phosphates with mass spectrometric detection. The investigated mixtures contained three different classes of fluoroalkyl phosphates: mono-esters (single fluorinated chain), mixed esters (diester with fluorinated and isopropanol chains), and bis esters (diester with two fluorinated chains).

All investigated classes of fluoroalkyl phosphates are easily ionized in negative ion electrospray. Molecular ions of mono, bis, and mixed esters are observed. Bis-esters undergo in-source fragmentation to mono-esters. The extent of fragmentation is dependent on the cone voltage. Mono-esters and to a lesser degree bis esters undergo two consecutive losses of m/z 20 (HF) in-source. The CID fragmentation patterns for fluoroalkyl phosphates are simple and easily interpretable. The base peak for mono and bis esters is the phosphate ion (m/z 97). Bis-esters fragment to the respective mono-esters. Mixed esters lose predominately the fluoroalkyl chain, followed by loss of isopropanol. Isobaric bis-esters can be distinguished by the presence of ions representing the mono esters in the daughter ion spectrum.

The chromatographic separation of individual fluoroalkyl phosphates can be obtained with a relatively simple gradient of water/methanol mobile phase. However, fluoroalkyl phosphates exhibit peak shape problems on silica-based chromatographic columns. Good peak shapes and separation can be obtained for mixed and bis-esters with

American Society of Mass Spectrometry (ASMS) Summary of DuPont Presentations

aqueous mobile phase, but mono-esters exhibit extreme tailing. Mono-ester peaks can be focused by addition of TEA to mobile phase, but bis ester peaks start fronting. Mixed ester peaks are least influenced by the chemistry of mobile phase/column and generally are well shaped. Therefore, mobile phase containing TEA was used for analysis of mono and mixed esters and 10 mM ammonium acetate was used for analysis of bis esters.

Fluoroalkyl phosphates exhibit a strong tendency to adsorb onto surfaces. Initial results indicate that the adsorption processes require a long time to reach equilibrium. The degree of adsorption and the kinetics of the adsorption depend on the sample solvent. The best results (least adsorption) were observed for samples prepared in 50/50 % water/methanol. Slow kinetics of the adsorption is manifested by gradual decrease of signal and mandates frequent reruns of calibration standards in order to compensate for the response drift. Appropriate sample solvents need to be used to alleviate adsorption and minimize carry over.

Further research is necessary to fully explain the adsorption behavior of fluoroalkyl phosphates and define appropriate sample preparation and analysis conditions. Further optimization of chromatographic conditions is required to define systems where separation with good peak shapes for all classes of fluoroalkyl phosphates is achieved.