MATRIX-EFFECT FREE ANALYTICAL METHODS FOR DETERMINATION OF PERFLUORINATED CARBOXYLIC ACIDS IN ENVIRONMENTAL AND BIOLOGICAL SAMPLES

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The sample matrix can often have significant effects upon the performance of analytical methods for the quantitative determination of perfluorinated carboxylic acids (PFCA) in environmental and biological samples. These effects can include reduction of the extraction recoveries due to binding of analytes and interferences, or enhancement of the signal observed at LC/MS/MS concentrations. We have developed methods for the determination of perfluorinated carboxylic acids in environmental matrices (soil, sediment and sludge) that address these issues, with limits of quantitation of 1 ppb. Extraction recoveries determined at spiked levels ranging in another soil degradation studies were used. Matrix enhancement and suppression are reduced to a negligible extent using novel solid-phase extraction (SPE) procedures. The same procedures are used to purify extracts from biological matrices with similar success, with limits of quantitation of 1-5 ppb. Quality control data have been developed that demonstrate (1) recovery of laboratory fortifications, (2) freedom from matrix enhancement or suppression and (3) absence of significant background interference.

INTRODUCTION

- Perfluorinated carboxylic acids (PFCAs) are persistent compounds that exist in the environment as a result of the manufacture, use and disposal of fluorochemical products. They have the general structure

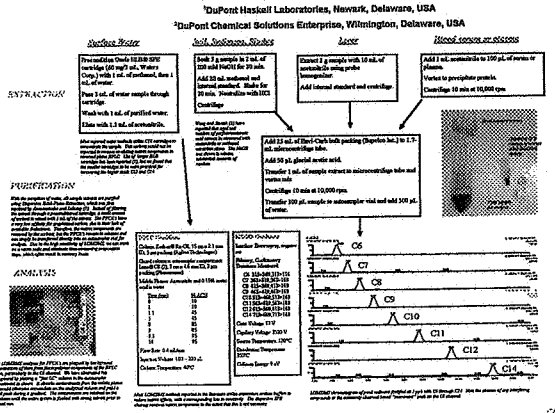
$$CF_3(CF_2)_nCOOH$$

- Analytical methods for determination of PFCAs are typically based on gas chromatography with tandem mass spectrometry (LC/MS/MS), using an electrospray interface operating in the negative ion mode.
- The most common problem observed in LC/MS/MS determination of PFCAs is suppression or enhancement of the desired signal due to the presence of matrix components.
- We have developed rapid, simple and sensitive methodologies to purify extracts of environmental and biological samples so that matrix effects are not observed. The methods use:
  - Polymer and reverse phase PFCA resins that are selective.
  - Active ion pair, ion-pair solid phase extraction chemistry.
  - Minimum background noise from interference components of the LC/MS system.
  - Partial addition of internal standards. (Clean)

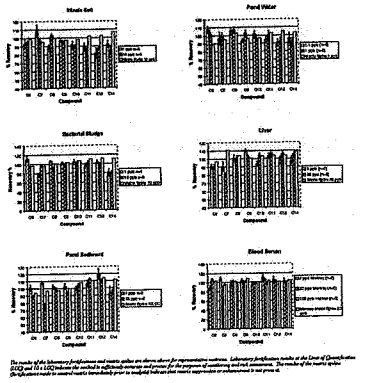
MATERIALS AND METHODS

- Standards of the linear isomers of PFCAs, a were purchased commercially (Aldrich and Fluorochem). The compounds evaluated were
  - Perfluorobutanoic acid (C4)
  - Perfluorohexanoic acid (C6)
  - Perfluoroheptanoic acid (C7), also commonly referred to as PFOA
  - Perfluorooctanoic acid (C8)
  - Perfluorodecanoic acid (C10)
  - Perfluoroundecanoic acid (C11)
  - Perfluorododecanoic acid (C12)
  - Perfluorotridecanoic acid (C13)
- The internal standard used was dual ^{13}C perfluorooctanoic acid. This was custom synthesized by DuPont, but is now commercially available from Wellington Lab Sciences.
- Analytical standards of 3 (ethoxycarbonyl) and 6-(ethoxycarbonyl) heptanoic acid were also custom synthesized by DuPont.

References: [1] W. R. Ai et al. Environ. Sci. Technol. 2002, 36(4), 2201. [2] M. Wang et al. Determination of C4-C8 Perfluorinated Substances by Ion Chromatography, DIONEX 2001 presentation. [3] M. Sakuratani et al. J. of AOAC International 84, 481, 2001.



RESULTS



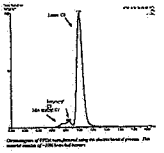
The results of the laboratory fortifications and matrix spikes are shown above for representative matrices. Laboratory fortification results at the Limit of Quantitation (LOQ) and 10 x LOQ indicate the method is sufficiently rugged and robust for the purposes of monitoring and risk assessment. The results of the matrix spike fortifications made to several matrix immediately prior to analysis indicate that matrix suppression or enhancement is not present.

Alternative HPLC Conditions for resolving branched and linear isomers

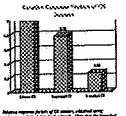
Mobile Phase: Acetonitrile and 0.1% acetic acid in water	
Time (min)	%ACN
0	10.0
1	10.0
2	22.0
3	22.0
11	22.0
18	22.0

The respective HPLC conditions are as stated above.

If PFCA's are manufactured using the electrochemical fluorination process, or if they originate from materials manufactured using this process, they can contain a mix of linear and branched isomers. If they or their precursors are manufactured using the telomerization process, they will be linear isomers. Unfortunately, the LC conditions are optimized at first for the linear and linear isomers are poorly resolved from each other and at only between and branched of the branched materials are not available. However, it may be useful to separate these isomers from each other, in order to obtain a diagnostic ratio of the linear to the sum of the branched. This is easily done simply by using a different gradient.



Chromatogram of PFOA isomers obtained using the electrochemical process. The material consists of 70% linear and branched.



Relative response factors of C8 isomers obtained using authentic analytical standards of each. Note that the linear has a slightly greater response than the branched isomers. This may affect the accuracy of quantitation of isomers in blend or electrochemical results in an unknown mix.

CONCLUSIONS

Any PFCA analytical method used to generate data for the purposes of monitoring or risk assessment should:

- Extract and recover all analytes from both weathered samples.
- Be fully documented and validated for all analytes and matrices covered, and demonstrate acceptable accuracy and precision including fortification and recovery within the actual sample matrix itself.
- Be specific enough to avoid false positive results, and include a confirmatory procedure (such as a second MS/MS transition) to eliminate doubt of false positives.
- Report data determined within the calibration range established for each analyte.

The methods described here fit these criteria, and in addition:

- *Matrix enhancement or suppression is negligible, even with non-buffered HPLC mobile phases.*
- *Sample preparation is simple and rapid.*
- *Extracted samples may be analyzed from dram vessels. If desired.*
- *Background due to HPLC instrument components is eliminated from the chromatogram.*