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AR226-0078
EM-16

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Laboratory Report

LCMSMS Analysis of Extracts reported in: "Preliminary Report Analysis of Perfluorinated Compounds in Environmental Samples" by P. Jones and K. Kannan

Report number: FACT-GEN-008

Testing Laboratory

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1 Introduction

Sample extracts, prepared by P. Jones and K. Kannan according to FACT-M-4.0, were screened using a Micromass Platform II, a single quadrapole LCMS. These same extracts were re-screened by FACT using a Micromass Quattro II, a triple quadrapole instrument (LCMSMS), which provides a more selective analysis than a single quad instrument. Interferences that may provide a false positive response in LCMS analysis can be eliminated with the LCMSMS.

Extracts from samples of sea eagle plasma, bald eagle plasma, and fish were analyzed quantitatively for PFOS using the LCMSMS. In general, PFOS levels determined by LCMSMS were approximately half of those determined using LCMS. It is likely that matrix interference at or around mass 499 complicated the original LCMS analysis. This type of matrix interference near mass 499 has been observed in other biological samples.For the LCMSMS analysis, quantitation was based on the 499 → 99, 130 daughter ions response.

In the LCMSMS analysis, low levels of PFOS (< 5 ppb) were detected in several of the fish samples; these values are significantly lower than those reported by Jones and Kannan. It is likely that a matrix interferent caused an anomolously high response in the LCMS analysis.

No PFOS above the limit of detection was detected in the remaining fish samples analyzed by LCMSMS. Again, this is in contrast to the LCMS analysis.

Additionally, all samples of eagle plasma were screened for the following fluorochemicals: PFOSA, PFOSAA, M570, M556, POAA, PFHS, and PFDS (see Appendix B for definitions of FACT acronyms). Very low levels (< 5 ppb) of PFOSA were observed in the North American bald eagle plasma samples. No PFOSAA, M556, POAA, or M570 was detected in any samples.

PFHS was detected in every Baltic sea eagle plasma sample, while PFDS was preliminarily (no standard material available for confirmation) detected in every North American bald eagle plasma sample.

This data is screening quality only. Only 2 high level (250-ppb) PFOS matrix spike samples (eagle plasma) were extracted and analyzed.

2 Sample Receipt

P. Jones and K. Kannan delivered samples to the Environmental Lab. The samples were extracted and analyzed by them using an Environmental Lab LCMS on March 15-19, 1999. After LCMS analysis, the extracts were submitted to FACT for LCMSMS analysis. There was no extraction paperwork submitted with the samples. It is assumed that sample volume and final extract volume were the same.

3 Holding Times

There is no holding time criteria associated with these samples for LC/ESMSMS analysis.

4 Methods - Analytical and Preparatory

Analytical methods

FACT-M-3.1, Extraction of Potassium Perfluorooctanesulfonate or Other Fluorochemical Compounds from Serum or Other Fluid for Analysis Using HPLC-Electrospray/Mass Spectrometry: modified by NOT extracting a matrix curve for use in quantitation. A pre-existing curve, extracted from rabbit sera, was used for quantitation. This modification will have the greatest effect on the fish samples. Extraction efficiencies of most of the target fluorochemicals from the fish tissues are likely to be significantly lower than those from the plasma. For this reason, LCMSMS reported values for the fish tissue samples should be considered to be minimum.

FACT-M-4.1, Analysis if Potassium Perfluorooctanesulfonate or Other Fluorochemical in Serum or Other Fluid Using HPLC-Electrospray/Mass Spectrometry: modified by quantitating samples versus a standard curve extracted from rabbit sera, not from the sample matrix.

HPLC/ESMS and HPLC/ESMSMS

In HPLC, an aliquot of extract is injected and passed through a reverse phase liquid chromatographic column. Based on the affinity of the analyte for the stationary phase in the column relative to the liquid mobile phase, the analyte is retained for a characteristic amount of time. For example, in a standard solution PFOS may elute at 8.0 minutes. Retention times between a standard PFOS solution and the analyte extracted from groundwater in this analysis were matched on the HPLC system to within 1%.

Following HPLC separation, ESMSMS provides a rapid and accurate means for analyzing a wide range of organic compounds, including fluorochemicals. Electrospray, an ionization technique used primarily for detection of molecular ions, is generally operated at relatively mild temperatures. Molecules are ionized, and a primary ion, characteristic of the analyte, is selected. This ion is bombarded with high-energy gas; subsequent collisions create smaller secondary ionic fragments unique to the primary ion, which are detected.

For example, for PFOS ($C_8F_{17}SO_3^-$) analysis, ion 499 is selected as the characteristic primary ion. This ion is fragmented into other ions such as 80 amu (corresponding to SO_3^-), and 130 amu ($CF_2SO_3^-$). Each of these secondary fragments is detected and can be used to differentiate PFOS from other compounds that might have the same characteristic 499 amu primary ion, but different chemical compositions and secondary ion fragmentation patterns.

5 Analysis

5.1 Quantitative Analysis

For both the LCMS and LCMSMS analysis, quantitative results are based upon comparison of analyte peak area in the sample with analyte peak areas generated using a standards extracted from rabbit sera. The extraction efficiency of PFOS from sera of other animals has been determined to be between 75-95% at all levels within the range of quantitation. It is likely that the extraction efficiency of PFOS from eagle plasma is approximately the same.

5.2 Qualitative Analysis

Eagle plasma sample extracts were qualitatively screened for PFOSA, PFOSAA, M556, M570, POAA, PFHS, and PFDS. During the analysis, the extracts were bracketed by a minimum number of standards to monitor analyte retention time. Other than relative comparisons, no quantitative results are available.

No PFDS standard material is available. Preliminary identification of PFDS in the extracts is based upon response of 3 reasonable daughter ions (599→80, 99, 130) at a reasonable retention time.

5.3 Blanks

Two container blanks were provided and extracted by Jones and Kannan. Extraction blanks were also prepared. No analytes were detected in the extracts of either the container blanks or the extraction blanks.

5.4 Matrix Spikes

One PFOS matrix spike at 250 ppb was prepared for each of two eagle plasma samples. Both matrix spikes showed greater than 80% recovery.

5.5 Laboratory Control Samples

Laboratory Control Samples are not a component of this study.

5.6 Sample Related Comments

All data is screening quality only. All analytical results of fish tissue extracts should be considered to be very preliminary, as the extraction efficiency of the target fluorochemicals from these matrices is not characterized.

6 Data Summary

Extracts from samples of sea eagle plasma, bald eagle plasma, and fish were analyzed quantitatively for PFOS using The LCMSMS. In general, PFOS levels determined by LCMSMS were approximately half of those determined using LCMS. It is likely that matrix interference at or around mass 499 complicated the LCMS analysis. For the LCMSMS analysis, quantitation was based on the 499 → 99, 130 daughter ions response. Matrix interference at 499 has been observed in other biological samples.

Low levels of PFOS (< 5 ppb) were detected in several of the fish samples; these values are significantly lower than those reported by Jones and Kannan. It is likely that a matrix interferent caused an anomolously high response in the LCMS analysis. This type of anomaly has been observed by FACT on other samples analyzed by LCMS and LCMSMS.

No PFOS above the limit of detection was detected in the remaining fish samples analyzed by LCMSMS. Again, this is in contrast to the LCMS analysis.

Additionally, all samples of eagle plasma were screened for the following fluorochemicals: PFOSA, PFOSAA, M570, M556, POAA, PFHS, and PFDS (see Appendix B for definitions of FACT acronyms). Very low levels (< 5 ppb) of PFOSA were observed in the North American bald eagle plasma samples. No PFOSAA, M556, POAA, or M570 was detected in any samples.

PFHS was detected in every Baltic sea eagle plasma sample, while PFDS was preliminarily (no standard material available for confirmation) detected in every North American bald eagle plasma sample.

This data is screening quality only. Only 2 high level (250-ppb) PFOS matrix spike samples (eagle plasma) were extracted and analyzed.

7 Data / Sample Retention

Samples and extracts will be retained for future evaluation, if necessary.

8 Attachments

8.1 **Attachment A:** Table of LCMSMS Results for the Analysis of Eagle Plasma and Fish Tissue Samples
8.2 **Attachment B:** Table of FACT acronyms and formulas
8.3 **Attachment C:** Data associated with LCMSMS analysis
8.4 **Attachment D:** LCMS report by P. Jones and K. Kannan

9 Signatures

Harold Johnson, Advanced Chemist — Date 4/7/99

Kris Hansen, Ph.D., FACT Group Leader — Date 4/7/99

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Sample number	Tissue:	Location:	ng PFOS / mL	PFHS?	PFDS?
WTEA-SWE-93-020	Sea Eagle Plasma	Baltic	125	detected	
WTEA-SWE-93-017	Sea Eagle Plasma	Baltic	93	detected	
WTEA-SWE-93-012	Sea Eagle Plasma	Baltic	215	detected	
629-38263	Bald Eagle Plasma	N. America	165		detected
629-38264	Bald Eagle Plasma	N. America	198		detected
629-07411	Bald Eagle Plasma	N. America	494		detected
629-35547	Bald Eagle Plasma	N. America	1047		detected
629-36389	Bald Eagle Plasma	N. America	226		detected
629-37030	Bald Eagle Plasma	N. America	371		detected
629-37021	Bald Eagle Plasma	N. America	374		detected
F980086	Carp, whole body	Pine River, MI	BLD		
F970312	Lake Trout whole body	Siskiwit, MI	BLD		
F970310	Lake Trout whole body	Siskiwit, MI	BLD		
1998095	Brown Trout muscle	Detroit River, MI	BLD		
F97187	Ciscowet muscle	Lake Superior	BLD		
1998095	Brown Trout Liver	Detroit River, MI	BLQ		
1998064	Channel Catfish egg	Lake St. Claire, MI	BLQ		
1998064	Channel Catfish egg	Lake St. Claire, MI	BLQ		
F980081	Lake Trout, whole body	Pine River, MI	BLQ		
F970181	Lake Trout, whole body	Lake Superior	BLD		
F97002	Walleye, whole body	Detroit River, MI	BLD		
1998064	Channel Catfish muscle	Lake St. Claire, MI	BLD		

BLQ = below limit of quantitation (10 ppb)
BLD = limit of detection (approximately 1 ppb)