ANALYSIS OF MINED CLAY PRODUCTS FOR PCDDs/PCDFs BY HIGH-RESOLUTION MASS SPECTROMETRY (HRGC/HRMS) AND QUADRUPOLE ION STORAGE MASS SPECTROMETRY/MASS SPECTROMETRY (QISMS/MS)

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Introduction

A recent preliminary survey by the US Food and Drug Administration's Center for Veterinary Medicine was conducted to determine the PCDDs/PCDFs concentrations in mined clay products used in manufacturing of animal feed ingredients. As a result of the discovery of dioxin contaminated feed in 1997, ball clay from select sites in an area called the Mississippi embayment were sampled and all of the samples revealed elevated dioxin levels. This clay proved to be the source of the contamination in the feed [(1)]. The main purpose of this survey is to determine if elevated dioxin or furan levels can be found in other mined clay products used in feed/feed ingredients [(2)]. This limited survey includes collecting samples of clays, as well as, any other mined product that may be used in the processing of plant protein meal and finished feed. Sixteen one pound duplicate samples of various mined clay products were collected from dealers or manufacturers located in Alabama, Arkansas, Louisiana, Mississippi, Kentucky, Tennessee and Texas. One set was sent to the EPA laboratory located at Stennis Space Center, Mississippi, and the other set was sent to the FDA laboratory located at Jefferson, Arkansas for analysis. EPA extracted and analyzed their set by HRGC/HRMS. The remainder of the extracts were then shipped to the FDA laboratory for analysis by QISMS/MS. The FDA set of samples were analyzed by HRGC/HRMS and QISMS/MS after the submission of this abstract. The purpose of this study is to demonstrate that the quadrupole ion storage mass spectrometer can be used as a possible alternative determination or, supplemental technique in the analysis of PCDDs/PCDFs.

Materials and Methods

Sample Preparation

Samples were prepared using a modified version of EPA Metho1613 [(3)]. A mixture of 5 g of product and 5 g of anhydrous sodium sulfate was transferred into a pre-baked 43 mm x 150 mm glass fiber thimble, topped with pre-cleaned glass wool, and placed in a 50 mm Soxhlet extractor. The mixture was spiked with 20 ul of ^{13}C-labeled sample fortification solution (5 pg/ul of 2,3,7,8 Cl substituted dioxins and furans) and extracted with 350 ml of benzene at an extraction rate of 2 drops per second and allowed to extract for a minimum of 16 hours. The extract was concentrated using a 3-bulb Snyder column and solvent exchanged to a final volume of 50 ml hexane. The extract underwent sequential acid/base silica gel, carbon, and alumina column chromatographic

cleanup [4]. Ten microliters of the internal standard solution containing two internal standards (20 pg/ul of ^{13}C 1,2,3,4-TCDD and ^{13}C 1,2,3,7,8,9 HxCDD) was added to each of the sample extracts and the sample volume adjusted to a final volume of 20 ul with nonane before analysis.

High Resolution Analysis

Prior to analysis, mass spectral resolution and mass calibration were checked and all QA/QC control parameters were verified to be within specified control limits [3]. The Kratos Concept mass spectrometer was operated in a mass drift correction mode using perfluorokerosene to provide lock masses. Chromatographic separations were achieved using a J&W 60 m x 0.32 mm DB-5MS (0.25 mm film thickness). All calibration standards (Cambridge Isotopes), QA/QC check samples, blanks, and authentic samples were processed and analyzed under identical conditions.

The selected ion current profile (SICP) areas for the characteristic ions for each native and labeled analyte were measured. Each homologous group was monitored in succession as a function of GC retention times to ensure that all compounds are detected. In addition, the ion current generated by each lock mass ion was also monitored throughout its respective RT window. Replicate method blanks contained measurable quantities of only 1,2,3,4,6,7,8-Cl substituted heptadioxin and octadioxin. The average background quantities of these two congeners plus an additional 1 s amount (i.e. hepta 2.2 pg and octa 22 pg) was subtracted from each sample. Authentic samples spiked with native 2,3,7,8-Cl substituted tetras at 0.2 pg/g, pentas-heptas at 1 pg/g, and octas at 2 pg/g demonstrated average precisions and accuracies of within 20%. Replicates of authentic samples showed reproducibility of within 20% for tetra-hepta congeners and 50% for the octas.

Ion Trap Analysis

All EPA extracts were analyzed on a Varian Saturn 2000 ion trap gas chromatograph/mass spectrometer equipped with a Model 3800 gas chromatograph, Model 1079 universal capillary injector with electronic flow control and high performance insert, Model 8200 autosampler and MS/MS capability. The mass spectrometer settings are as follows: trap temperature at 220 ^{o}C, manifold temperature at 40 ^{o}C, transferline temperature at 270 ^{o}C, scanning rate at 0.5 sec/scan and electron multiplier at 200 V above 10^5 gain. Gas chromatograph conditions are as follows: electronic flow control set to 1.0 ml/min. Injector conditions are as follows: 140 ^{o}C for 0.01 minutes, 200 ^{o}C/min to 280 ^{o}C and hold for 41 minutes, splitter initially off and on at 2.0 min. with split flow set to 50 ml/min. Autosampler conditions are as follows: no solvent plug, uptake speed at 1 ul/sec, injection speed at 0.5 ul/sec, upper and lower air gap set to on, and amount injected is 2 ul. All other gas chromatograph and mass spectrometer parameters are described elsewhere [5,6]. Data were recorded and stored for 2 to 4 selected ions in the MS/MS product ion spectrum for each congener.

Prior to analysis, the extracts were transferred to an autosampler vial and sufficient nonane was added to allow for the autosampler injection, where applicable.

Results and Discussion

Table 1 provides a comparison of HRGC/HRMS and QISMS results for 17 PCDDs/PCDFs in 7 of the 16 collected mined clay products. Five samples contained no detectable PCDDs/PCDFs by either analytical method. For the samples that contained

detectable amounts, the results were comparable between the two measuring techniques. Primarily, the samples contained elevated levels of OCDD and HpCDD with lower levels of PeCDD, HxCDDs and OCDF. Five samples (Bentonite, Ground Clay and Montmorillonite) contained OCDD in the ppb levels, while the others were in the ppt levels. All labeled congener recoveries were within the recovery range requirements of Table 7 as stated in EPA Method 1613. EPA/ECL reported detection limits (LODs) of 0.2 ppt for the tetras, 0.6 ppt for the pentas through heptas and 4.0 ppt for the octas by HRGC/HRMS. The QISMS was able to achieve similar detection levels based on 3:1 signal to noise, except for the HxCDDs which were about four times higher. ARL/FDA reported detection limits (LODs) of 0.3 ppt for the tetras-pentas, 0.7 ppt for HxCDF, 2.5 ppt for HxCDD and 3.0 ppt for octas by QISMS. These two determinative techniques experience different matrix and/or instrument system derived interference [7]. However, since EPA Method
1613 applies to many different types of matrices, each matrix should be evaluated separately to determine if all method performance criteria are met. The QISMS has demonstrated that it could be a viable alternative measuring technique for determining PCDFs/PCDDs in mined clay products at slightly higher limits of detection. The use of QISMS could allow an increase in sample throughput with a subset of samples being confirmed by HRGC/HRMS.

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Table 1 Results from the Preliminary Survey of Mined Products in Manufacturing Feed/Feed Ingredients (pg/g dry weight).

Sample Matrix	Ground Clay		Bentonite		AlCaSi		Lime		Bulk Clay		Attapulgite Clay		Montmorillonite	
Sample Number	36324		33872		30115		37950		36311		17106		31946	
Analytical Method	HRMS	QISMS	HRMS	QISMS	HRMS	QISMS	HRMS	QISMS	HRMS	QISMS	HRMS	QISMS	HRMS	QISMS
2,3,7,8-TCDD	0.72	0.6	1.55	NC	ND	ND	ND	ND	ND	NC	ND	ND	ND	NC
1,2,3,7,8-PeCDD	3.51	3.6	8.67	9.0	0.41	0.4	ND	0.4	0.53	0.5	ND	ND	2.14	1.8
1,2,3,4,7,8-HxCDD	5.75	NC	12.16	9.0	0.64	ND	ND	ND	0.64	ND	ND	ND	2.47	NC
1,2,3,6,7,8-HxCDD	6.23	5.7	15.64	10.4	ND	ND	0.74	ND	0.66	ND	ND	NC	2.58	4.8
1,2,3,7,8,9-HxCDD	7.87	8.9	20.38	14.7	0.30	ND	2.41	2.7	1.7	ND	ND	NC	3.09	4.1
1,2,3,4,6,7,8-HpCDD	179.92	181.0	361.47	376.5	0.62	2.8	9.77	9.0	12.97	12.3	ND	NC	84.9	96.2
OCDD	17920(1)	NR	37520(1)	NR	3.98	7.5	145.34	137.1	82.18	74.6	6.84	14.6	10052(1)	NR
2,3,7,8-TCDF	ND	ND	0.23	NC	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,2,3,7,8-PeCDF	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
2,3,4,7,8-PeCDF	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,2,3,4,7,8-HxCDF	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,2,3,6,7,8-HxCDF	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
2,3,4,6,7,8-HxCDF	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,2,3,7,8,9-HxCDF	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,2,3,4,6,7,8-HpCDF	0.36	ND	0.58	NC	ND	ND	0.19	ND	ND	ND	ND	ND	ND	ND
1,2,3,4,7,8,9-HpCDF	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
OCDF	ND	ND	21.87	NA	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

(1) Quantitated by external standardization (LRMS).
ND = Not Detected
NC = Not Confirmed
NA = Not Analyzed due high OCDD.
NR = Not reported for this study (exceeded calibration range).