MASS SPECTRAL CONFIRMATION OF CHLORINATED AND BROMINATED DIPHENYL ETHERS IN HUMAN ADIPOSE TISSUES

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ABSTRACT

Evidence of the occurrence of polychlorinated and polybrominated diphenyl ethers (PCDPEs and PBDPEs) in human adipose tissue specimens from the United States was found during the analysis of these tissues for dioxins and furans. Additional studies were conducted to confirm the presence of the PCDPEs and the PBDPEs in the tissue specimens. Selected sample extracts were analyzed by mass spectrometry using both full scan and selective ion monitoring modes. The analysis of a PCDPE standard solution and two commercial fire retardant samples were used in the confirmation. The occurrence of hexa- through decachlorinatd diphenyl ethers and hexa- through decabromodiphenyl ethers were confirmed in the tissue specimens.

KEY WORDS

Polychlorinated diphenyl ethers,PCDPE, polybrominated diphenyl ethers, PBDPE, dioxins, furans, gas chromatography, mass spectrometry, human adipose tissue.

INTRODUCTION

Polychlorinated diphenyl ethers (PCDPEs) and polybrominated diphenyl ethers (PBDPEs) have been recognized as potential interferences to the determination of polychlorinated dibenzofurans (PCDFs) and polybrominated dibenzofurans (PBDFs). The unique structures of the halogenated diphenyl ethers are such that the loss of two halogen atoms from the molecular ions in the mass spectrometer ion source can yield radical cations that are indistinguishable in mass from those produced by PCDF and PBDF compounds.

As a result, high resolution mass spectrometric protocols for the determination of PCDFs and PBDFs have been developed so that information is generated to indicate the presence of PCDPEs and PBDPEs. Such a method was used for the determination of PCDFs and PBDFs in human adipose tissue composites from the fiscal year 1987 National Human Adipose Tissue Suvey specimen repository. Nearly all of the adipose extracts analyzed indicated the presence of hexa- through decachlorinated diphenyl ethers and hexa- through octabrominated diphenyl ethers.

The levels of the PCDPE and PBDPE concentrations in the tissue extracts were initially estimated by extrapolating calibration data generated for the PCDFs and PBDFs. In order to substantiate these preliminary findings, additional analyses were conducted to confirm the identification and quantitation of these compounds.

EXPERIMENTAL

Selected NHATS sample extracts from the analysis for halogenated dioxins and furans were used for the confirmation analysis effort. No additional sample preparation was necessary. The additional analyses were conducted by both full scan HRGC/MS and selected ion monitoring HRGC/HRMS using a VG70 250S high resolution mass spectrometer.

Analytical standards for the confirmation of the PCDPEs were provided by Dr. D.T. Williams of Health and Welfare Canada and included 8 specific congeners representing tetrachloro through decachloro diphenyl ethers. Individual standards for the brominated diphenyl ethers were not available for this

effort. However mixed isomer standards of brominated fire retardants (Bromkal 70-5-DE and 79-8-DE) were available to establish retention windows and full scan spectra of the PBDPEs.

The HRGC/MS (full scan) analysis was achieved using a 30 m DB-5 column. Data was acquired across a mass range of 100 - 1000 amu over a 1.5 s cycle time, such that both PCDPEs and PBDPEs could be detected within a single analysis.

In order to confirm the presence of the PCDPEs and PBDPEs at lower concentration levels (pg/g), selected extracts were analyzed by HRGC/HRMS (selected ion monitoring) with mass resolution of greater than 10,000. The analyses for both the PCDPEs and PBDPEs were conducted under the same conditions that were used for the analysis for the halogenated furans. However, the ions previously monitored for the halogenated dioxins were eliminated from the acquisition parameters and additional ions were added to monitor responses indicative of the molecular ion cluster, the loss of two halogens from the molecular ion cluster, and the loss of a fragment representing either COCl or COBr.

The identification of the PCDPEs and PBDPEs were based on qualitative criteria, which included either full scan spectra which matched reference compounds (full scan) or the simultaneous response of up to seven characteristic ions (selected ion monitoring) with ion ratios that were within 20% of theoretical values.

RESULTS

The results of the full scan HRGC/MS analysis demonstrated the presence of a single HxBDPE and a single NCDPE. These congeners were estimated to be present at the highest concentrations (approximately 1 ng/g levels) in each of the adipose tissue extracts. Figure 1 provides the full scan spectra for these two compounds from a human adipose tissue sample.

The HRGC/HRMS (selected ion monitoring) experiments provided detailed qualitative information regarding the presence of the halogenated diphenyl ethers in human adipose tissues. Both the PCDPEs and PBDPEs were determined to be prevalent in tissues from all age groups and census divisions. The congeners detected ranged from hexa- to deca- substituted PCDPEs and PBDPEs.

The PCDPEs were quantitated versus authentic standards and the results were compared to original estimates based on the PCDF relative response factors. These results are in good agreement as presented in Table 1 below. However, it must be noted that the sample preparation was not optimized for PCDPE recovery and hence the values most likely are low estimates of the true concentrations. Table 2 provides a synopsis of the PBDPEs that were confirmed in the selected samples that were analyzed for this effort.

This paper will present additional information on the specific experimental conditions, details on the qualitative identifications based on HRGC/HRMS chromatograms and ion ratio criteria and estimates of the PCDPE and PBDPE concentrations for the 48 composite NHATS samples that represent three age groups and nine census divisions.

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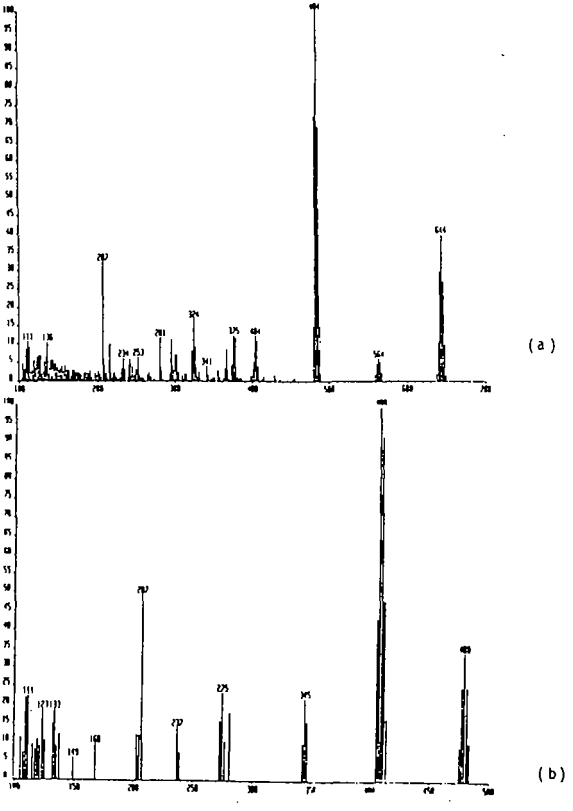

Figure 1. Full scan (100 - 1000 amu) mass spectra of a) a HxBDPE and b) a NCDPE in a human adipose tissue sample from the Middle Atlantic Census Divison, 15 -44 age group.

Table 1. PCDPEs detected in adipose tissues from the East North Central (EN) census division.

Table 1. Comparison of PCDPE concentations using RRFs from authentic standards versus PCDF RRFs.

Census Division (a)	Age Group	Approximate Concentration (pg/g) (b)				
		HxCDPE	HpCDPE	OCDPE	NCDPE	DCDPE
MA	15-44	5.7 (4)	6.6 (7)	110 (100)	800 (1000)	73 (ND) (c)
MA	45+	7.5 (5)	6.1 (5)	150 (200)	560 (1000)	75 (10)
PA	45+	13 (10)	10 (5)	230 (200)	780 (1000)	90 (ND)
SA	45+	5.6 (4)	5.0 (3)	160 (100)	760 (1000)	92 (ND)
WN	45+	12 (10)	7.8 (10)	250 (200)	1380 (2000)	140 (ND)

(a) - MA = Middle Atlantic, PA = Pacific, SA = South Atlantic, WN = West North Central
(b) - PCDPE concentrations determined versus authentic PCDPE standards (lipid basis). Parenthetical values are estimated PCDPE concentrations using corresponding PCDF RRFs.
(c) - ND = Not detected.

Table 2 PBDPEs confirmed in selected human adipose tissue extracts

Table 2. PBDPEs confirmed in selected human adipose tissue extracts.

Census Division (a)	Age Group	Number of Isomers Detected				
		HxBDPE	HpBDPE	OBDPE	NBDPE	DBDPE
SA	15-44	1	3	5	2	1
SA	45+	2	3	5	2	1
SA	0-14	2	3	5	2	0
EN	0-14	2	3	5	2	1
EN	45+	2	5	NA (b)	NA	0

(a) - SA = South Atlantic, EN = East North Central.
(b) - Not analyzed.