DEVELOPMENT OF AN OPTIMIZED METHOD FOR THE DETERMINATION OF PCDF/PCDD IN UTILITY FLUIDS

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ABSTRACT

Five analytical methods for determining concentrations of PCDFs and PCDDs in dielectric fluids were evaluated. The results of the evaluation were then used to develop an optimized method which was validated by analyzing triplicate aliquots of two electrical utility fluids. The final extracts were analyzed using both low and high resolution mass spectrometry.

INTRODUCTION

The Electric Power Research Institute (EPRI) recently funded a series of projects (EPRI Research Projects RP2028-5 to RP2028-10) to evaluate and improve analytical techniques for assaying PCDFs and PCDDs in dielectric fluids from electrical equipment. These projects included an interlaboratory study by five laboratories which used analytical methods of their choosing to analyze dielectric fluids. The dielectric fluid samples used for the study were either from equipment that had been in-service or were prepared by spiking fluids with known concentrations of PCDFs and PCDDs.

The objectives of the current project (RP2028-21) were to review the analytical methods used by the laboratories and to develop a combined, optimal method for this assay. This was accomplished by comparing the results obtained previously using each of the methods and then ranking them on the basis of accuracy and precision. Further information for contrasting the methods was obtained by carrying out additional experiments to measure the analyte enrichment efficiency of the individual component steps of each method. Based on the results of the ranking and the analyte enrichment efficiency experiments, a new method was developed and validated by analyzing spiked and unspiked (naturally contaminated and synthetically contaminated) dielectric fluids using both low-resolution and high-resolution mass spectrometry.

RESULTS AND DISCUSSION

COMPARISON OF THE FIVE ANALYTICAL METHODS

Each of the five laboratories employed a pre-separation step, prior to the analyte enrichment steps, to remove the bulk sample matrix. Two laboratories used activated alumina columns, two used carbon columns, and one used preparative scale gel permeation chromatography. Three also used washes with either acid/base modified silica gel or concentrated sulfuric acid to remove ionic and easily oxidizable materials from the sample.

Each laboratory then used one or more liquid chromatography columns to fractionate the sample. Three used activated alumina columns, one used a florisil column, and another used both alumina and florisil columns. The PCDFs and PCDDs were then detected and quantified by either low-resolution or

accurate method employed a four column analyte enrichment procedure consisting of an acid/base modified silica gel column, a carbon column, an acid modified silica gel column, and an acidic alumina column.

ANALYTE ENRICHMENT EFFICIENCIES OF THE COMPONENT STEPS

Efficient analyte enrichment for PCDFs and PCDDs requires that the target analytes are retained in the solution that passes through the enrichment steps, while other compounds are discarded. Since mass spectrometry with selected-ion-recording is highly selective, it will not respond to other compounds in the sample extract unless they have a molecular ion or fragment ion of the same mass as the target analytes. Thus an analyte enrichment procedure may be effective in removing compounds that produce direct chemical interference, while being ineffective in removing other non-target compounds. Unfortunately, these other compounds can affect the gas chromatography resolution, which is usually immediately evident, or cause sensitivity changes in the mass spectrometer's ion source. This latter effect, which may not be noticed unless it is anticipated, can dramatically reduce the quantitative accuracy of a method.

The following procedure was used to determine the effectiveness of the enrichment steps in removing non-target analytes from the extract. Solutions of each sample were initially analyzed multiple time by gas chromatography using flame ionization and electron capture detection to determine average detector responses. These values represented the responses from a non-enriched solution. Separate aliquots of the solutions were then passed through each of the enrichment steps and the resulting solutions analyzed to determine the reduction in detector response. The equation used to calculate the enrichment efficiency was $E_{en} = [1-(R_{es}/R_{os})] 100\%$, where E_{en} was the enrichment efficiency in percent and R_{es} and R_{os} were the responses of the enriched and unenriched solutions, respectively. It was not necessary to measure the percentage of PCDF and PCDD retained through the enrichment steps, since prior results from each of the methods indicated near quantitative recoveries of the isotopically labeled internal standards. The enrichment efficiencies for the component steps are summarized in Table I.

DEVELOPMENT AND VALIDATION OF AN OPTIMIZED METHOD

Based on the results of the data comparison and the results of the analyte enrichment study, an enrichment sequence of three columns was chosen for the optimized method (See Table 1). The enrichment steps consisted of the Silica-I column, the Alumina-IV column, and the Carbon-II column. This sequence was validated by analyzing two sets of triplicate aliquots of a mineral oil sample (6 aliquots) and an askarel sample (6 aliquots). One triplicate set of each matrix was spiked with known concentrations of "2,3,7,8" substituted PCDD and PCDF isomers, while remaining two sets were unspiked. The enriched extracts from each of the 12 experiments were then analyzed by both low-resolution and high-resolution mass spectrometry.

The analyses of the unspiked oils revealed that the mineral oil did not contain PCDF or PCDD isomers at concentrations above the detection limit. The askarel sample also did not contain PCDD isomers, however, it did contain all of the "2,3,7,8" substituted PCDF isomers at concentrations ranging from 110 parts-per-billion (ppb) for octachlorodibenzofuran to 4,200 ppb for 1,2,3,4,7,8-hexachlorodibenzofuran. The mean concentrations for the "2,3,7,8" substituted PCDF isomers found in the askarel are summarized in Table II.

The results from the analyses of the spiked samples are summarized in Table III. Each of the sample aliquots was spiked with 200 ppb of the "2,3,7,8" substituted tetrachloro and pentachloro isomers,

500 ppb of the hexachloro and heptachloro isomers, and 1,000 ppb of the octachloro isomers. Since the askarel sample

TABLE 1. ANALYTE ENRICHMENT EFFICIENCIES

Enrichment Step[1]	Askarel Fluid FID[2]	Askarel Fluid ECD[3]	Mineral Oil Fluid FID	Mineral Oil Fluid ECD
Silica-I	30%	100%	62%	56%
Silica-II	21	33	15	55
Silica-III	24	37	20	51
Alumina-I	100	90	99	67
Alumina-II	100	90	99	61
Alumina-III	100	91	97	67
Alumina-IV	100	100	99	63
Alumina-V	62	54	87	26
Alumina-VI	97	91	93	60
Carbon-I	100	100	100	65
Carbon-II	100	100	99	46
Acid Wash	26	33	21	49

1 Refer to EPRI Publication EL-6416
2 Flame Ionization Detection
3 Electron Capture Detection

TABLE II. MEAN CONCENTRATIONS OF "2,3,7,8" SUBSTITUTED ISOMERS FOUND IN THE ASKAREL SAMPLE

PCDF Isomer	LRMS Mean Concentration	HRMS Mean Concentration
2,3,7,8-TCDF	327 ppb	353 ppb
1,2,3,7,8-PeCDF	727	553
2,3,4,7,8-PeCDF	2,130	1,470
1,2,3,4,7,8-HxCDF	4,170	4,000
1,2,3,6,7,8-HxCDF	967	810
1,2,3,7,8,9-HxCDF	1,130	957
2,3,4,6,7,8-HxCDF	1,670	1,470
1,2,3,4,6,7,8-HpCDF	720	617
1,2,3,4,7,8,9-HpCDF	900	783
OCDF	110	167

TABLE III. Spike Recoveries Using Optimized Method

PCDD/PCDF Isomer	Percent Recovery LRMS		Percent Recovery HRMS	
	Mineral Oil	Askarel	Mineral Oil	Askarel
2,3,7,8-TCDF	86	--	95	--
2,3,7,8-TCDD	100	72	100	104
1,2,3,7,8-PeCDF	108	--	82	--
2,3,4,7,8-PeCDF	120	--	82	--
1,2,3,7,8-PeCDD	104	100	70	92
1,2,3,4,7,8-HxCDF	98	--	89	--
1,2,3,6,7,8-HxCDF	101	--	83	--
1,2,3,7,8,9-HxCDF	112	--	87	--
2,3,4,6,7,8-HxCDF	112	--	98	--
1,2,3,4,7,8-HxCDD	110	111	86	99
1,2,3,6,7,8-HxCDD	91	99	87	89
1,2,3,7,8,9-HxCDD	100	102	87	93
1,2,3,4,6,7,8-HpCDF	100	--	79	--
1,2,3,4,7,8,9-HpCDF	120	--	95	--
1,2,3,4,6,7,8-HpCDD	104	103	87	97
OCDF	113	--	100	--
OCDD	88	82	95	90

contained levels of PCDF isomers that were in many cases much higher than the spiking level, only the PCDD recoveries were used to evaluate accuracy. The results from the analyses of the spiked samples are summarized in Table III.

CONCLUSIONS

The new method provided efficient analyte enrichment of the PCDD/PCDF isomers from the two utility fluid matrices. The recoveries of the spiked analytes ranged from 70-120%, while the overall precisions were approximately 4% and 5% for the low and high resolution mass spectrometry analyses, respectively. Minimal interference from non-target analytes were observed, as indicated by freedom from chromatographic degradation or ion source sensitivity changes.

It is recommended that further evaluation of the method be carried out through an interlaboratory round-robin study. The study would include the analysis of at least three representative samples of in-service utility fluids. Two samples, a mineral oil and an askarel oil, would be spiked with known concentrations of selected PCDF/PCDD isomers in order to assess the accuracy of the method. The "ruggedness" of the method would be evaluated by involving laboratories with both extensive and limited dioxin experience.