

Effective Approaches to Optimizing Recovery of PCDD/DF for Sediments

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1. Introduction

In the analysis of chlorinated dibenzo(p)dioxins and dibenzofurans, it is critical to provide accurate results in support of investigative and monitoring programs. Many aspects of the analysis contribute to the accuracy of the results being produced. One area that has received little attention is the initial removal of water from a solid matrix. This has recently been shown to be a critical aspect of the analysis and our experiences in this area are presented in this paper.

The analysis of solid matrices for chlorinated dibenzo(p)dioxins and dibenzofurans begins with a drying step prior to initiating the extraction step. Published methods such as SW846 - method describes the use of sodium sulphate to effect the drying of soil and sediment samples. The solvent required for the extraction of PCDD/DF in this method is toluene. This drying step is essential in order to remove the barrier that water can be in terms of contact between the solvent and the organics adsorbed on the surface of the matrix. In sediments it is particularly critical as a result of the complex network of pores present in the sediment matrix and the possibility of the entrapment of moisture within those pores. The use of chemical drying agents as opposed to using a physical drying step has traditionally been preferred because of the volatility of target organic contaminants and concern to prevent potential losses.

This paper will present the findings of a study comparing the use of sodium sulphate as a chemical drying agent with a physical, air drying step. The benefits and limitations of the two approaches will be discussed.

The extraction of sediments for PCDD/DF is required in support of many monitoring programs of the Great Lakes and also of rivers in reviewing the potential impact of industrial or other dischargers on the natural ecosystem. The results discussed within this paper were developed as a result of one such study carried out in support of investigations being carried out by Ministère des Pêches et des Océans (MPO).

2. Experimental

A group of ten samples required the analysis of PCDD/DF and the initial approach taken to the extraction was to dry the sample with sufficient sodium sulphate to produce a free-flowing mixture. This is the standard approach as described in published methods. The samples were spiked with a range of $^{13}\text{C}_{12}$ - labeled surrogate standards and extracted in a soxhlet extractor overnight using toluene as the solvent and under conditions producing at least 4 solvent cycles/hour. After the extraction was complete, the extracts were concentrated to a small volume and subjected to a multi-adsorbent column separation in order to remove potential interferences in the instrumental analysis. The cleaned up extracts were fortified with labeled internal standards and analyzed by HRGC/HRMS. The instrumental conditions used were similar to those described in USEPA Method 8290¹¹ and involved the use of 5 calibration standards ranging from (0.5 pg to 500 pg) and monitoring at least 2 ions for each congener group of interest. A certified reference solution (NIST #1614) was also analyzed in conjunction with these samples in order to assess the accuracy of the standards being used to calculate the concentrations of PCDD/PCDF.

Quality assurance steps carried out included the analyses of a method blank, a reference material, evaluation of surrogate recovery, duplicate sample results and sample matrix spike results. The reference material was one which was prepared within the MPO laboratory. The sample was prepared by combining a reference soil from CIL (Ref. # EDF 2513) (10% by weight) with a sediment sample from the analytical set (90% by weight) which had been previously air dried and analyzed at least 2 times to assess the concentration of PCDD and PCDF native to the material. The value of this particular in-house reference material is the inclusion of the sediment matrix within the sample. The contribution of the sediment matrix increases the complexity of the overall sample and provides better information regarding the performance of a method for the specific matrix. The target value was calculated from the combination of the values of contaminants in each of the contributing portions. Since this approach provides a greater uncertainty in the true value of the in-house reference material, the acceptance criteria for the results from this sample were broader than would be appropriate for a well characterized, reference material.

Selected samples were also analyzed by an independent laboratory, the laboratory of the Ministère de l'Environnement et de la Faune du Québec (MEF). This laboratory used an air drying technique to remove moisture from the sediments prior to subjecting the samples to soxhlet extraction.

The calculation of concentration of PCDD/DF was carried out for all samples by an internal standard technique.

3. Results and Discussion

The results obtained from this study indicate clearly the importance of implementing an effective drying step prior to analysis. This is especially so if a solvent such as toluene is used as the extractant. Solvents such as methylene chloride or combinations such as hexane/acetone have more water miscibility than toluene and hence have a greater probability of effecting a good extraction in the presence of small amounts of moisture.

The results from the sodium sulphate drying step showed good surrogate recoveries on all samples ranging from 71 - 127%. The method blank presented with acceptably low levels of contamination, duplicate results were within 25% and the matrix spike recovery on all of the soils showed accuracy of 86 - 128%. A solution of NIST 1614 certified reference solution was used to assess the accuracy

of the T₄CDD standards used to calibrate and quantify the results. The result of this analysis was a value of 67.1 pg/μL versus a target value of 67.8 ± 2.3 pg/μL - an accuracy of 99%. In addition, the results from the MPO reference material supplied with the samples was within acceptance limits.

Reference sediment samples, prepared as described above were also analyzed by both laboratories as part of this project. These samples had been previously air dried and homogenized and showed the capability of the method within each facility. The results of this analysis were found to be within acceptable limits, and both laboratories were using comparable methodology. The results of the analysis of one of these samples, together with the target values are provided in Table 1.

Table 1

	ZENON RESULT pg/g	MEF RESULT pg/g	TARGET VALUE pg/g
2,3,7,8-TCDD	59	57	46
1,2,3,7,8-PeCDD	120	105	96
1,2,3,4,7,8-HxCDD	110	98	90
1,2,3,6,7,8-HxCDD	110	87	89
1,2,3,7,8,9-HxCDD	130	94	90
1,2,3,4,6,7,8-HpCDD	230	168	171
OCDD	730	517	577
2,3,7,8-TCDF	61	47	47
1,2,3,7,8-PeCDF	120	93	87
2,3,4,7,8-PeCDF	120	87	86
1,2,3,4,7,8-HxCDF	120	92	90
1,2,3,6,7,8-HxCDF	110	90	96
2,3,4,6,7,8-HxCDF	140	83	93
1,2,3,7,8,9-HxCDF	140	73	82
1,2,3,4,6,7,8-HpCDF	220	148	171
1,2,3,4,7,8,9-HpCDF	160	98	112
OCDF	360	268	261

In reviewing these results in isolation, the quality of the original data would be unquestioned. However, if we also review the results of the target analytes analyzed by the air-drying technique, major incompatibilities of data come to light. Table 2 shows the results for the analysis of the toxic isomers of PCDD and PCDF for two samples analyzed using both drying techniques. The enrichment factor is calculated from the ratio of the result from air drying divided by the result from sodium sulphate drying. It can be seen from the data presented in Table 2 that the air drying process produced results higher than those developed by sodium sulphate drying. The range of difference for one of the samples was up to 7.3. In a second sample, the differences were found to be more substantial and variable with different congener groups showing a range to a factor of 14 between the two techniques. Since the only difference in the analytical protocol was the drying step and when dried reference samples were analyzed, results were comparable from the two laboratories, it is demonstrated that the effective removal of moisture is a critical step. This step can introduce discrepancies of an order of magnitude or more in the accuracy of the analysis.

Table 2

	Drying Technique		Enrichment Factor	Drying Technique		Enrichment Factor
	Sodium Sulphate	Air Dried		Sodium Sulphate	Air Dried	
Analytes						
2,3,7,8-TCDD	<0.5	<0.3	N/A	<0.8	<0.4	N/A
1,2,3,7,8-PeCDD	1.1	<0.2	<0.18	<1.2	<0.4	N/A
1,2,3,4,7,8-HxCDD	<1.0	<0.2	N/A	<2.2	<0.4	N/A
1,2,3,6,7,8-HxCDD	0.8	1.8	2.3	<1.3	<0.3	N/A
1,2,3,7,8,9-HxCDD	<0.8	<0.3	N/A	<1.2	<0.5	N/A
1,2,3,4,6,7,8-HpCDD	7.1	36	5.1	5.9	72	12
OCDD	67	251	3.7	38	527	14
2,3,7,8-TCDF	2.5	2.7	1.1	<0.8	6.6	>8.4
1,2,3,7,8-PeCDF	1.6	<0.2	<0.13	<1.6	<0.2	N/A
2,3,4,7,8-PeCDF	1.0	<0.2	<0.2	<1.5	2.1	>1.4
1,2,3,4,7,8-HxCDF	1.6	2.7	1.7	<1.4	3.5	>2.5
1,2,3,6,7,8-HxCDF	0.5	1.2	2.3	<1.3	1.5	>1.2
2,3,4,6,7,8-HxCDF	0.8	1.9	2.3	<1.1	<0.3	N/A
1,2,3,7,8,9-HxCDF	<0.9	<0.3	N/A	<1.3	<0.5	N/A
1,2,3,4,6,7,8-HpCDF	10	49	4.9	2.5	27	11
1,2,3,4,7,8,9-HpCDF	<0.9	<0.6	N/A	<1.3	<1	N/A
OCDF	5.5	40	7.3	3.8	44	12
Surrogate Standards:						
13C-2,3,7,8-TCDD	102	94		90	96	
13C-1,2,3,7,8-PeCDD	127	121		90	91	
13C-1,2,3,6,7,8-HxCDD	98	96		102	94	
13C-1,2,3,4,6,7,8-HpCDD	100	107		109	81	
13C-OCDD	102	106		109	69	
13C-2,3,7,8-TCDF	105	118		85	98	
13C-1,2,3,7,8-PeCDF	105	129		88	95	
13C-1,2,3,6,7,8-HxCDF	94	111		99	98	
13C-1,2,3,4,6,7,8-HpCDF	95	124		111	85	

4. Recommendation

Removal of moisture from soil, waste or sediment samples is critical to the effective extraction of contaminants using non-water miscible solvents. The effect of the presence of small quantities of water is not always obvious because the extraction of the labeled materials used in monitoring the effectiveness of the sample preparation steps may mask the reduction in recovery of more strongly absorbed contaminants. Reference soils are often similarly not of value in fully evaluating the quality of the results in a data set since they are usually prepared by drying a large sample aliquot, grinding, homogenizing well and sub-aliquoting the material for the analysis and development of reference values.

Although some losses have been shown to occur during the air drying step²¹, the advantages of this technique in optimizing the recovery of analytes would provide superior accuracy than the technique of drying very wet samples with sodium sulphate. We therefore recommend air drying overnight in a clean fume hood for samples with large amounts of moisture associated with them, such as sediments.

5. References

¹ U.S EPA Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition, Revision 2, January 1995. Method 8290.

² Foster Roberts, M.G., Nicol, K., Donison, H., Mills, W., Prucha, B., Proceedings of the 12th international Symposium on Dioxins and Related Compounds, Tampere, Finland, August, 1992; Volume 8, p 49.

