DETERMINATION OF PCDD/PCDF IN POLYVINYL CHLORIDE (PVC) AND IN RELATED MANUFACTURING PROCESS SAMPLES

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1. Introduction

Recent reports of the finding of dioxins in raw samples of pure PVC polymer from various manufacturers by the Swedish environmental agency have resulted in increasing scrutiny of this material and of the manufacturing process whereby PVC is produced.[1)] The possible formation of dioxins in the production of ethylene dichloride (EDC) and vinyl chloride monomer (VCM), which are used in the production of PVC, is also of concern.[2)] The analysis of PVC resin for PCDD/PCDF is complicated because of the properties of the polymer. Since the material is not highly porous, conventional Soxhlet extraction using toluene or methylene chloride, as specified in U.S. EPA Methods 8290 and 1613, may not fully extract the PVC matrix, and this results in swelling and only partial dissolution of the material. Therefore, an extraction procedure which results in complete dissolution of the PVC resin, followed by liquid-liquid extraction of the dissolved material is preferable to the standard Soxhlet method. Properly implemented, a full dissolution procedure obviates the possibility that PCDD/PCDF imbedded in the PVC matrix will not be completely extracted. The present paper describes such a method which we have developed and applied to determine PCDD/PCDF in production samples of powdered PVC resin. Results of these analyses of PVC are reported herein. In addition, preliminary data obtained in the analyses of EDC and VCM samples, using other modified EPA Method 1613 procedures, will be presented.

2. Analytical Methods

The analytical methods applied for the determination of PCDD/PCDF in PVC resin are as follows. Dissolve about 6 grams of PVC resin in 75 mL of tetra hydrofuran, using a high speed Tissumizer to blend the mixture until a clear solution is formed. Add ^{13}C-labelled tetra- through octa-CDD/CDF internal standards and mix thoroughly. If a Matrix Spike is being prepared, also add the native PCDD/PCDF at this point. Slowly add about 50 mL of water to the THF/PVC solution, adding this in 10 mL portions, swirling the mixture after each addition. As water is added, the PVC reprecipitates as a floating gel and the THF/water solution becomes slightly cloudy. Remove and transfer the THF/water solution to a separate container, expressing the gel to remove as much of the liquid as possible. Add about 50 mL of hexane to the residual PVC gel and blend the mixture with the Tissumizer for about five minutes, until the gel is completely fragmented into very small aggregates. Allow the hexane and solids to separate, and then transfer the hexane to the bottle containing the THF/water solution. Repeat the extraction of the residual solids two additional times, using two 25 mL portions of hexane, mixing the hexane and solids with the Tissumizer as before, and transferring the hexane each time to the bottle containing the THF/water solution. Agitate the bottle containing the THF/water and hexane for about 15 minutes, and then allow the aqueous and organic layers to separate. Transfer the organic layer to a separate container, and extract the residual aqueous layer two additional times with 25 mL portions of hexane, combining the hexane fraction each time in the same bottle. Concentrate the pooled organic extract to a volume of about 5 mL, then dilute the concentrated solution with 30 mL of hexane and continue with the sample cleanup procedures specified in U.S. EPA Method 1613. Dilute the processed extract to a final volume of 10 μL with a standard solution containing $^{13}C_{12}$-1,2,3,4-TCDD and $^{13}C_{12}$-1,2,3,7,8,9-HxCDD and analyze the sample by GC-MS as specified in Method 1613.

3. Results and Conclusions

The results of analyses of two samples from each of the two different batches of powdered PVC resin using the methodology described above are shown in Table 1. Only OCDD was detected in these analyses, at levels ranging from 6.0 to 7.4 ppt. For these analyses, the OCDD level in the laboratory blank was of the same magnitude. It appears, therefore, that the OCDD observed in these analyses is actually attributable entirely to background. Good recoveries of the ^{13}C-labelled internal standards were achieved in these analyses.

In order to further demonstrate the efficacy of the methodology applied here, samples of the PVC resin were spiked with known quantities of the 17-2,3,7,8-substituted native PCDD/PCDF isomers, and the spiked samples were analyzed using the procedures described above. The results of some of these analyses are shown in Table 2. Two of these samples for which results are given in Table 2 (4P and 4Q) were spiked with 2.5 ppt of 2,3,7,8-TCDD; 5.0 ppt of 2,3,7,8-TCDF; 25 ppt of the penta- through heptachlorinated isomers; and 50 ppt of the octachlorinated isomers. The third sample for which results are given in Table 2 (4R) was spiked with 1.0 ppt of 2,3,7,8-TCDD; 2.0 ppt of 2,3,7,8-TCDF; 10 ppt of the penta- through heptachlorinated isomers; and 20 ppt of the octachlorinated isomers. Of course, all of these samples were also spiked with the ^{13}C-labelled PCDD/PCDF internal standards. As indicated by the results shown in Table 2, excellent recoveries of all of the 17 native PCDD/PCDF isomers were achieved in the analyses of these spiked samples, including the ultra-low level spike. Clearly, the methodology developed and applied here is highly effective for the determination of PCDD/PCDF in PVC resin.

4. References

1) B. Hileman, J. R. Long and E. M. Kirschner (1944): Chlorine Industry Running Flat Out Despite Persistent Health Fears. Chemical and Engineering News, November 21, 12-26.
2) A. Miller (1993): Dioxin Emissions from EDC/VCM Plants. Environ. Sci. Technol. 27, 1014-1015.

TABLE 1. ANALYSIS OF PVC RESIN SAMPLES FOR PCDD/PCDF

Sample Number	Concentrations Found (picograms per gram of sample oe parts-per-trillion[a]									
	Tetra CDFs	Tetra CDDs	Penta CDFs	Penta CDDs	Hexa CDFs	Hexa CDDs	Hepta CDF	Hepta CDD	Octa CDF	Octa CDD
Batch A Resin	ND 0.406	ND 0.820	ND 0.370	ND 0.577	ND 1.08	ND 0.914	ND 0.957	ND 0.854	ND 4.59	7.41
Batch A Resin	ND 0.508	ND 0.843	ND 0.623	ND 0.710	ND 1.06	ND 1.47	ND 1.56	ND 1.15	ND 2.96	6.30
Batch B Resin	ND 0.479	ND 0.794	ND 0.468	ND 0.743	ND 1.53	ND 1.04	ND 2.01	ND 1.07	ND 2.45	6.59
Batch B Resin	ND 0.265	ND 0.508	ND 0.315	ND 0.437	ND 0.416	ND 0.618	ND 0.596	ND 0.677	ND 2.38	5.95
Lab Blank	ND 0.539	ND 0.872	ND 0.491	ND 1.14	ND 1.40	ND 1.24	ND 1.48	ND 1.78	ND 5.08	7.66
Lab Blank	ND 0.380	ND 0.689	ND 0.357	ND 0.767	ND 0.920	ND 1.43	ND 1.92	ND 1.08	ND 2.21	6.57

a. The designation ND indicates "None Detected" in excess of the minimum detectable concentration which is listed directly below the ND designation.

TABLE 2. ANALYSIS OF PVC RESIN SAMPLES SPIKED WITH NATIVE PCDD/PCDF

Sample No.	4P. Batch B PVC Resin			4Q. Batch B Resin			4R. Batch B Resin		
Native Isomer Added	Quantity Found (ng/total sample	Quantity Added (ng/total sample)	% Recovery of Spike	Quantity Found (ng/total sample)	Quantity Added (ng/total sample)	% Recovery of Spike	Quantity Found (ng/total sample)	Quantity Added (ng/total sample)	% Recovery of Spike
2378-TCDF	0.0258	0.0250	103	0.0249	0.0250	100	0.0115	0.0100	115
2378-TCDD	0.0138	0.0125	110	0.0125	0.0125	100	0.0063	0.0050	126
12378-PeCDF	0.136	0.125	109	0.135	0.125	108	0.0616	0.0500	123
23478-PeCDF	0.136	0.125	107	0.137	0.125	110	0.0606	0.0500	121
12378-PeCDD	0.122	0.125	98	0.120	0.125	96	0.0543	0.0500	109
123478-HxCDF	0.127	0.125	102	0.126	0.125	101	0.0557	0.0500	111
123678-HxCDF	0.145	0.125	116	0.144	0.125	115	0.0619	0.0500	124
234678-HxCDF	0.139	0.125	111	0.149	0.125	119	0.0591	0.0500	118
123789-HxCDF	0.120	0.125	96	0.118	0.125	94	0.0539	0.0500	108
123478-HxCDD	0.126	0.125	101	0.140	0.125	112	0.0542	0.0500	108
123678-HxCDD	0.128	0.125	102	0.124	0.125	99	0.0553	0.0500	111
123789-HxCDD	0.0867	0.125	69	0.0862	0.125	69	0.0341	0.0500	68
1234678-HpCDF	0.134	0.125	107	0.132	0.125	106	0.0618	0.0500	124
1234789-HpCDF	0.105	0.125	84	0.106	0.125	84	0.0437	0.0500	87
1234678-HpCDD	0.140	0.125	112	0.140	0.125	112	0.0614	0.0500	123
OCDF	0.236	0.250	94	0.239	0.250	96	0.105	0.100	105
OCDD	0.236	0.250	94	0.235	0.250	94	0.112	0.100	112