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## ANALYSES OF PCDDs AND PCDFs IN VIRGIN SUSPENSION PVC RESIN

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### ABSTRACT

A dissolution method has been used for analyses of PCDDs and PCDFs in PVC. The method has been validated through repeat analyses in two laboratories. The results show that there are no PCDDs and PCDFs in virgin suspension PVC resin.

Keywords: PCDDs, PCDFs, PVC, dissolution method, sub-ppt analyses, HRMS

### 1. INTRODUCTION

In 1994 the Swedish EPA published data<sup>1</sup> which contained the results of the analyses of two samples of suspension PVC (polyvinyl chloride) resin. Both of the analyses indicated the presence of PCDDs and PCDFs in the PVC. Subsequently, the UK Ministry of Agriculture, Fisheries and Food<sup>2</sup> (MAFF) decided to investigate these findings and to assess their relevance to the contamination of food. The MAFF work analysed PVC articles which had been manufactured for use as either food packaging or food processing equipment. These analyses also showed the presence of PCDDs and PCDFs in the matrix. Due to the low levels which were found and the variability of the results, it was not clear whether the PCDDs and PCDFs were present within the matrix and originated from the virgin suspension PVC production or whether they were present as a result of external contamination or in case of the MAFF work as a result of manufacturing PVC articles. Moreover, there was also no consistent 2,3,7,8-congener pattern within the several analyses, which is not supportive for PVC process generated PCDDs and PCDFs contamination. The work reported here was commissioned by the European Council of Vinyl Manufacturers (ECVM) to determine the PCDDs and PCDFs contents, at sub-ppt levels, of virgin suspension PVC resin samples from its member companies.

## 2. SAMPLES

All of the samples were taken in triplicate according to a strict protocol which ensured that they were taken from the same stage of the process (immediately after the final drier) and that the possibility for external contamination was minimised. All members of ECVI sent samples of virgin suspension PVC resin for analyses.

## 3. EXTRACTION AND CLEAN-UP

The Swedish EPA results were obtained by a method<sup>3</sup> which uses toluene\* extraction in a Soxhlet apparatus; the MAFF work employed a dissolution method using acetone. As PVC powder sinters into a rigid mass when it is subjected to Soxhlet extraction using toluene, any process generated PCDDs and PCDFs could be locked within the PVC particles and may be rendered unavailable for extraction under these conditions. Consequently, a dissolution method was considered essential to the complete extraction of PCDDs and PCDFs. Such a method has been reported<sup>4</sup> recently and validated for use with PVC. The method uses tetrahydrofuran (THF) to completely dissolve the PVC sample (10% w/w). Internal standards, at least one isomer per group, were added to the solution and the PVC was precipitated using water. Repeated extractions with hexane were used to recover the PCDDs and PCDFs from the PVC gel and from the THF/water phase. This method was used in this work.

The bulk of the analytical work was carried out at the Analytical Services Group, AEA Technology, Harwell, Didcot, UK. Here, the hexane extract was concentrated and cleaned up using multiple column chromatography: silica gel, acid and base modified silica gel and Florisil<sup>5</sup>. Some samples which were analysed by the Department of Chemistry, Wright State University, Dayton, USA, were cleaned up according to EPA method 1613.

## 4. INSTRUMENTAL ANALYSIS

AEA analysed the final extracts using HRGC/HRMS - an HP5890 series II on line with a VG Autospec - equipped with a 60m DB5 MS column and operating at a resolution of 9500-10000.

Wright State University used HRGC/HRMS - a Kratos MS890 - equipped with 60 m DB5 column and operating at a resolution of 11000.

## 5. QUALITY ASSURANCE AND QUALITY CONTROL (QA/QC)

The quality of the analytical work performed at AEA was ensured by:

- giving special attention to limits of quantifications (LOQs)
- HRGC/HRMS instrument performance checks
- validating the method by spiking dissolved PVC samples with native congeners at concentrations of 5 ppt for tetra congeners, 25 ppt for penta to hepta congeners and 50 ppt for octa congeners
- carrying out the analyses in accordance with a protocol, plus one amendment, which were both approved by the authors and AEA
- analyses of some samples at Wright State University<sup>4</sup>, USA, where the dissolution method was developed

## 6. RESULTS

The validation carried out by AEA with spiked samples demonstrated the repeatability of the results. Table 1 displays the recoveries obtained for both the internal standards and the native spikes from a composite PVC matrix. The composite matrix is a mixture of all individual PVC samples on an equal weight basis. Only 1 ppt of OCDD was found in the unspiked matrix, and this was lower than the 3 ppt which was found in the method blank - see Table 1.

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\* toluene was chosen because the Swedish EPA provided a very wide variety of industrial samples of unknown origin

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Table 2 shows the analyses completed by AEA. The limits of quantification are all at less than 1 ppt for tetra to hepta congeners and less than 2 ppt for the octa congeners. Similar results are presented in Table 3 which shows the LOQs obtained by the Wright State University.

Comparison of Tables 2 and 3 reveals a good consistency between results from the two laboratories. There is of course some variation regarding the reporting of the quantified values and the levels of quantification but this is to be expected when analyzing for sub-ppt levels of concentrations.

## 7. CONCLUSIONS

The results demonstrate that virgin suspension PVC resin from 11 major production sites in Europe does not contain any process generated PCDDs and PCDFs at concentrations above the limit of quantification, which are less than 2 ppt. Quantified values reported in the past for virgin suspension PVC resins were probably due to contamination occurring during sampling and storage.

We have found that it takes some time before a laboratory can reduce its background levels in blanks to the sub ppt levels.

The PCDDs and PCDFs found in the MAFF investigation (also analysed at AEA) were not related directly to the PVC but could either be present as a result of sample contamination or as a result of the manufacturing process of PVC articles.

The validated dissolution method has proven to be reproducible for analyses of PCDDs and PCDFs in PVC and is therefore recommended for future analyses. In any analyses at sub ppt levels special attention should be given to cleanliness.

## 8. REFERENCES

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Table 1: Recoveries of  $^{13}\text{C}_{12}$ -Internal Standards and concentrations of native congeners in procedure blank and unspiked sample. Recoveries of  $^{12}\text{C}_{12}$  2378 congeners that were spiked on PVC

Congener	$^{13}\text{C}_{12}$ Int.Stds. spiked conc ng kg <sup>-1</sup>	Procedure Blank		Unspiked PVC		$^{12}\text{C}_{12}$ Spiked PVC duplicate samples		
		$^{13}\text{C}_{12}$ Rec %	$^{12}\text{C}_{12}$ conc. ng kg <sup>-1</sup>	$^{13}\text{C}_{12}$ Rec %	$^{12}\text{C}_{12}$ conc. ng kg <sup>-1</sup>	added ng kg <sup>-1</sup>	$^{12}\text{C}_{12}$ Rec 1 %	$^{12}\text{C}_{12}$ Rec 2 %
2378-T4CDD	40	103	nd (0.7)	104	nd (0.5)	5	91	102
12378-P5CDD	40	63	nd (0.6)	70	nd (0.7)	25	80	73
123478-H6CDD	60	92	nd (1.1)	100	nd (0.8)	25	73	73
123678-H6CDD			nd (0.9)		nd (0.7)	25	72	76
123789-H6CDD	60	93	nd (1.0)	131	nd (0.8)	25	78	78
1234678-H7CDD	60	112	0.9	90	nd (1.1)	25	96	88
OCDD	120	86	3.6	89	1.09	50	112	80
2378-T4CDF	40	97	nd (0.5)	91	nd (0.6)	5	90	87
12378-P5CDF			nd (0.5)		nd (0.3)	25	88	92
23478-P5CDF	40	89	nd (0.5)	73	nd (0.3)	25	84	88
123478-H6CDF			nd (0.3)		nd (0.4)	25	78	80
123678-H6CDF	60	83	nd (0.3)	83	nd (0.3)	25	75	75
123789-H6CDF			nd (0.4)		nd (0.5)	25	75	78
234678-H6CDF	60	113	nd (0.3)	119	nd (0.4)	25	76	78
1234678-H7CDF	60	93	0.4	80	nd (1.2)	25	84	84
1234789-H7CDF			nd (0.6)		nd (0.5)	25	84	79
OCDF	40	98	nd (1.7)	93	nd (1.6)	50	82	104

nd indicates not detected above the LOQ which is listed below the nd designation

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Table 2: AEA analyses of PVC from different manufacturing sites (concentrations in ng kg<sup>-1</sup>)

Manufacturing Site codes	Blank	A	B	C	D	E	F	G	H	I	J	K
Congeners												
2378-T4CDD	nd (0.1)	nd (0.4)	nd (0.3)	nd (0.4)	nd (0.2)	nd (0.3)	nd (0.2)	nd (0.2)	nd (0.2)	nd (0.3)	nd (0.2)	nd (0.4)
12378-P5CDD	nd (0.3)	nd (0.3)	nd (0.3)	nd (0.4)	nd (0.4)	nd (0.4)	nd (0.3)	nd (0.4)	nd (0.2)	nd (0.4)	nd (0.3)	nd (0.4)
123478-H6CDD	nd (0.3)	nd (0.6)	nd (0.4)	nd (0.8)	nd (0.6)	nd (0.5)	nd (0.4)	nd (0.5)	nd (0.4)	nd (0.4)	nd (0.4)	nd (0.6)
123678-H6CDD	nd (0.2)	nd (0.5)	nd (0.3)	nd (0.7)	nd (0.5)	nd (0.5)	nd (0.4)	nd (0.4)	nd (0.3)	nd (0.4)	nd (0.4)	nd (0.5)
123789-H6CDD	nd (0.3)	nd (0.6)	nd (0.4)	nd (0.7)	nd (0.5)	nd (0.5)	nd (0.4)	nd (0.5)	nd (0.3)	nd (0.4)	nd (0.4)	nd (0.6)
1234678-H7CDD	nd (0.1)	nd (0.6)	0.4	0.2	0.1	nd (0.4)	nd (0.5)	nd (0.7)	0.3	nd (1.0)	nd (0.8)	0.8
OCDD	nd (0.3)	0.6	0.9	1.1	0.5	0.8	0.9	0.5	1.9	0.8	0.7	1.3
2378-T4CDF	nd (0.2)	nd (0.3)	nd (0.2)	nd (0.3)	nd (0.2)	nd (0.3)	nd (0.3)	nd (0.2)	nd (0.3)	nd (0.3)	nd (0.2)	nd (0.3)
12378-P5CDF	nd (0.1)	nd (0.2)	nd (0.1)	nd (0.2)	nd (0.2)	nd (0.1)	nd (0.3)	nd (0.2)	nd (0.1)	nd (0.2)	nd (0.1)	nd (0.2)
23478-P5CDF	nd (0.1)	nd (0.2)	nd (0.1)	nd (0.2)	nd (0.2)	nd (0.1)	nd (0.2)	nd (0.2)	nd (0.1)	nd (0.2)	nd (0.1)	nd (0.2)
123478-H6CDF	nd (0.2)	nd (0.2)	nd (0.2)	nd (0.3)	nd (0.2)	nd (0.1)	nd (0.1)	nd (0.2)	nd (0.2)	nd (0.2)	nd (0.2)	nd (0.2)
123678-H6CDF	nd (0.1)	nd (0.1)	nd (0.1)	nd (0.2)	nd (0.2)	nd (0.2)	nd (0.2)	nd (0.1)	nd (0.1)	nd (0.2)	nd (0.2)	nd (0.2)
123789-H6CDF	nd (0.2)	nd (0.2)	nd (0.2)	nd (0.4)	nd (0.3)	nd (0.3)	nd (0.4)	nd (0.2)	nd (0.2)	nd (0.2)	nd (0.3)	nd (0.3)
234678-H6CDF	nd (0.2)	nd (0.2)	nd (0.2)	nd (0.3)	nd (0.2)	nd (0.1)	nd (0.1)	nd (0.2)	nd (0.2)	nd (0.2)	nd (0.2)	nd (0.2)
1234678-H7CDF	nd (0.1)	nd (0.3)	0.2	nd (0.2)	nd (0.3)	0.2	0.2	nd (0.2)	0.1	nd (0.4)	nd (0.3)	nd (0.3)
1234789-H7CDF	nd (0.2)	nd (0.4)	nd (0.2)	nd (0.4)	nd (0.5)	nd (0.3)	nd (0.3)	nd (0.2)	nd (0.2)	nd (0.2)	nd (0.2)	nd (0.2)
OCDF	nd (0.4)	nd (1.0)	1.0	nd (1.2)	nd (0.5)	nd (1.0)	nd (1.0)	0.4	0.3	nd (1.4)	nd (1.1)	nd (1.0)

nd indicates not detected above the LOQ which is listed below the nd designation

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Table 3: Wright State University analyses of PVC samples (concentrations in ng kg<sup>-1</sup>)

Manufacturing side codes Congener	Blank 1	Composite PVC	C	G	Blank 2	A	I
2378-T4CDD	nd (0.2)	nd (0.2)	nd (0.2)	nd (0.2)	nd (0.3)	nd (0.2)	nd (0.4)
12378-P5CDD	nd (0.4)	nd (0.3)	nd (0.3)	nd (0.2)	nd (0.3)	nd (0.2)	nd (0.5)
123478-H6CDD	nd (0.3)	nd (0.3)	nd (0.3)	nd (0.3)	nd (0.2)	nd (0.2)	nd (0.5)
123678-H6CDD	nd (0.3)	nd (0.3)	nd (0.3)	nd (0.3)	nd (0.2)	nd (0.2)	nd (0.4)
123789-H6CDD	nd (0.3)	nd (0.3)	nd (0.3)	nd (0.3)	nd (0.2)	nd (0.2)	nd (0.4)
1234678-H7CDD	nd (0.5)	nd (0.3)	nd (0.3)	nd (0.3)	nd (0.2)	nd (0.2)	nd (0.4)
OCDD	0.8	0.9	0.6	0.6	nd (0.7)	nd (0.6)	nd (1.6)
2378-T4CDF	nd (0.1)	nd (0.1)	nd (0.1)	nd (0.1)	nd (0.1)	nd (0.1)	nd (0.2)
12378-P5CDF	nd (0.1)	nd (0.1)	nd (0.1)	nd (0.1)	nd (0.1)	nd (0.1)	nd (0.2)
23478-P5CDF	nd (0.2)	nd (0.2)	nd (0.2)	nd (0.1)	nd (0.1)	nd (0.1)	nd (0.2)
123478-H6CDF	nd (0.2)	nd (0.2)	nd (0.2)	nd (0.2)	nd (0.2)	nd (0.2)	nd (0.3)
123678-H6CDF	nd (0.2)	nd (0.2)	nd (0.2)	nd (0.2)	nd (0.2)	nd (0.2)	nd (0.3)
123789-H6CDF	nd (0.5)	nd (0.4)	nd (0.3)	nd (0.4)	nd (0.3)	nd (0.2)	nd (0.3)
234678-H6CDF	nd (0.3)	nd (0.3)	nd (0.2)	nd (0.2)	nd (0.2)	nd (0.2)	nd (0.3)
1234678-H7CDF	nd (0.8)	nd (0.5)	nd (0.4)	nd (0.4)	nd (0.3)	nd (0.2)	nd (0.4)
1234789-H7CDF	nd (0.6)	nd (0.4)	nd (0.3)	nd (0.4)	nd (0.3)	nd (0.2)	nd (0.6)
OCDF	1.0	nd (0.6)	1.0	0.7	nd (0.3)	nd (0.4)	nd (0.6)

nd indicates not detected above the LOQ which is listed below the nd designation

In this Table we give the results for two blanks, because the composite PVC and samples A and G were analysed at a different time than the samples A and I.