Analysis of PCDDs and PCDFs in vinyl chloride monomer

Morten Isaksen
Norsk Hydro Research Centre, P.O. Box 2560, N-3901 Porsgrunn, Norway
Tore-Erling Jørgensen
Norsk Hydro Research Centre, P.O. Box 2560, N-3901 Porsgrunn, Norway
Kjersti Langeland
Norsk Hydro Research Centre, P.O. Box 2560, N-3901 Porsgrunn, Norway

1. Introduction

There has been several claims the last years that the chemical industry is a major source of PCDDs and PCDFs to the environment. The US Environmental Protection Agency (EPA) Draft Dioxin Reassessment report released in 1994[1)] referred particularly to the VCM (vinyl chloride monomer)/PVC (poly vinyl chloride) industry as a possible source which led the VCM/PVC industry to initiate characterisation programs in their plants. One difficulty has been that standard methods like EPA 1613 have not been suitable for several industrial matrices. No suitable method for the extraction and clean-up of VCM (liquid under high pressure) has previously been described in the literature. In 1992 Norsk Hydro a.s. published data[2)] on dioxin emissions from the production of vinyl chloride monomer. The data showed that VCM contained dioxins. This result was however based on a single spot sample which was extracted under less controlled conditions. Work has now been carried out to improve the sampling and the extraction/clean-up technique to give more statistical significant values for PCDDs and PCDFs in VCM. At the same time it was investigated whether the addition of hydroquinone to VCM would lead to generation of any PCDDs and PCDFs. Hydroquinone is added (5 ppm) when VCM is transported through warmer climates to prevent polymerisation.

2. Experimental

Three parallell samples were taken of VCM with added hydroquinone (A, B, C) from a ship tank after loading of the ship. Three parallell samples of the pure VCM product without the hydroquinone (D, E, F) were taken from the production process itself. The plant was under normal operation. Measures were taken to assure that the samples were representative. The VCM samples were taken out in steel containers prepared in advance by thorough washing with water, methanol, dichloromethane and toluene.

The containers were cooled down to -35 °C. The resulting liquid VCM was then easily tapped into the evaporation flask where it was slowly evaporated under controlled conditions. Internal standards according to US EPA 1613 had been added to the evaporation flask in advance. After the evaporation of VCM, the flask was repeatedly extracted with toluene. The extract was evaporated until dryness before sealed and sent for analysis.

All the extracts were analysed with regard to PCDDs and PCDFs by ALTA Analytical Laboratories, California, USA, according to method US EPA 1613.

3. Results

Table 1 shows the isotopic recovery results for internal standards in the samples. In addition the clean-up recoveries were all between 81 and 97 %. These recoveries show that the extraction and clean-up is satisfactory.

Table 2 shows the results of the analyses. In all samples of VCM without hydroquinone and in two samples with hydroquinone, the results vary from non-detected to sub-ppq levels, but no consistent congener pattern is found. At such extremely low levels, arbitrarily variations due to sampling, clean-up and analysis may give the rise to relatively large differences. In the last sample (with hydroquinone) several congeners of PCDDs and PCDFs were detected at levels less than 1 ppt. No rational explanation can be given, but also these levels are so low that arbitrarily variations may be the cause. By statistical analysis (t-distribution) it was found that all the detected values (for all samples) are within the same interval of confidence (95 %).

6. Conclusions

A satisfactory method for extraction and clean-up regarding dioxins in VCM has been developed.

The results demonstrates that there are no process-generated PCDDS and PCDFs in vinyl chloride monomer. Published data[2)] in the past were probably due to contamination.

Addition of hydroquinone to VCM for transport does not lead to generation of PCDDs and PCDFs.

7. References

1)US EPA (1994): "Estimating Exposure to Dioxin-Like Compounds", EPA/600/6-88/005Ca.
2) Norsk Hydro a.s (1992): "PVC and the Environment", Oslo.

8. Acknowledgement

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Table 1: Isotopic recovery results of internal standards

Congeners	Isotopic recoveries in %					
	A	B	C	D	E	F
^{13}C-2378-TCDD	80	77	93	83	86	80
^{13}C-12378-PeCDD	93	73	86	82	86	84
^{13}C-123478-HxCDD	104	81	107	95	92	96
^{13}C-123678-HxCDD	101	87	104	92	101	93
^{13}C-1234678-HpCDD	93	82	94	91	89	89
^{13}C-OCDD	71	52	69	57	62	65
^{13}C-2378-TCDF	108	93	103	96	99	93
^{13}C-12378-PeCDF	90	74	75	80	78	85
^{13}C-23478-PeCDF	93	73	86	84	92	85
^{13}C-123478-HxCDF	95	82	90	90	88	84
^{13}C-123678-HxCDF	80	65	80	79	70	74
^{13}C-234678-HxCDF	79	68	82	74	69	72
^{13}C-123789-HxCDF	91	74	89	77	79	84
^{13}C-1234678-HpCDF	70	59	73	61	70	70
^{13}C-1234789-HpCDF	74	56	70	64	65	67

SOUR (po)

Table 2: Concentrations of PCDDs and PCDFs in all VCM samples, given in pg/kg.

Congeners	VCM with hydroquinone			VCM without hydroquinone		
	A	B	C	D	E	F
2378-T4CDD	nd (4)	nd (4)	nd (2)	nd (3)	nd (3)	nd (3)
12378-P5CDD	nd (6)	nd (6)	nd (3)	nd (3)	nd (3)	nd (3)
123478-H6CDD	nd (4)	nd (12)	nd (4)	nd (3)	nd (4)	nd (3)
123678-H6CDD	nd (3)	nd (11)	nd (4)	nd (3)	nd (3)	nd (2)
123789-H6CDD	nd (3)	nd (11)	nd (4)	nd (3)	nd (3)	nd (2)
1234678-H7CDD	nd (3)	nd (5)	4	nd (1)	nd (2)	nd (4)
OCDD	nd (6)	26	8	nd (5)	nd (6)	33
2378-T4CDF	nd (3)	nd (4)	nd (4)	nd (2)	nd (2)	nd (2)
12378-P5CDF	nd (6)	nd (5)	10	nd (4)	nd (4)	nd (4)
23478-P5CDF	nd (5)	nd (4)	5	nd (3)	nd (3)	nd (3)
123478-H6CDF	nd (2)	nd (1)	23	nd (1)	nd (1)	nd (1)
123678-H6CDF	nd (2)	nd (1)	15	nd (1)	nd (1)	nd (1)
123789-H6CDF	nd (2)	nd (2)	5	nd (1)	nd (2)	nd (2)
234678-H6CDF	nd (2)	nd (1)	9	nd (1)	nd (1)	nd (2)
1234678-H7CDF	nd (4)	nd (2)	61	nd (1)	nd (1)	nd (2)
1234789-H7CDF	nd (2)	nd (2)	9	nd (2)	nd (1)	nd (3)
OCDF	24	nd (9)	31	nd (5)	nd (6)	20

nd: not detected. Limits of detection are given in brackets.