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Reduction of Polychlorinated Dibenzo-*p*-Dioxins and Dibenzofurans Levels in Chloranil from China

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Chloranil is an important raw material in dye industry, but it is considered as a source for polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/F) (Alock and Jones, 1997; Christmann et al., 1989). We have presented the levels of PCDD/F in chloranil produced by old industrial processes in China. The highest one contained 13.6 μg/g of octachlorinated dibenzo-*p*-dioxin (OCDD) and 16.3 ng/g international toxic equivalency (I-TEQ) (Zhang et al., 2000).

Since most of the chloranil is exported to European countries for some manufactures, the processes have been improved to reduce PCDD/F to levels less than the legally binding limit values. Six chloranil samples produced by new process were collected from four different chemical or pharmaceutical factories. Three of them are in the south of China and one is in the north. *p*-chloranil is the dominant chloranil product in China so all of the samples we got were *p*-chloranils. The reforms include absorption of PCDD/F on active carbon and substituting hydroquinone for trichlorophenol or pentachlorophenol as raw material. Absorption on active carbon is not an economic process and only one factory tried to use it so we didn't investigate it. In the old process, high concentrations of PCDD/F will occur in the production because of the contaminated phenol. High temperature may be partly responsible for PCDD/F too. The new process can be completed under a lower temperature. The reform has dramatically reduced PCDD/F in chloranil.

MATERIALS AND METHODS

All of the solvents and materials for extraction and cleanup were purchased from Promochem GmbH or ICN Biomedical GmbH (both Germany). ^{13}C-labeled PCDD/F were obtained from Cambridge Isotope Laboratories, Inc. (Massachusetts, USA). About 0.5 g of chloranil, spiked with 17 ^{13}C-labeled 2,3,7,8-substituted PCDD/F standards, was firstly dissolved in 5 ml benzene. Then an ultrasonic bath was used for 15 min to dissolve completely. Afterwards the extract was chromatographed over 4 columns: alumina, silica mixture, florisil and

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Table 1. Levels and I-TEQ of PCDD/F in the chloranil samples (ng/g)

	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6
Total TCDD	nd*	nd	nd	nd	nd	nd
Total PeCDD	nd	nd	nd	nd	nd	nd
Total HxCDD	nd	nd	nd	0.01	nd	0.05
Total HpCDD	nd	nd	nd	0.47	nd	0.06
OCDD	0.33	4.49	0.53	14.51	nd	0.07
Total PCDDs	0.33	4.49	0.53	14.99	nd	0.18
2378 TCDD	nd	nd	nd	nd	nd	nd
12378 PeCDD	nd	nd	nd	nd	nd	nd
123478 HxCDD	nd	nd	nd	nd	nd	nd
123678 HxCDD	nd	nd	nd	0.01	nd	0.01
123789 HxCDD	nd	nd	nd	nd	nd	nd
1234678 HpCDD	nd	nd	nd	0.22	nd	0.04
Total TCDF	0.10	0.12	0.04	nd	nd	0.09
Total PeCDF	0.17	nd	0.05	nd	nd	0.36
Total HxCDF	nd	nd	1.30	0.54	1.50	2.15
Total HpCDF	0.47	0.46	1.54	12.29	4.95	4.60
OCDF	4.23	12.63	36.36	99.59	2.33	3.54
Total PCDFs	4.97	13.20	39.30	112.42	8.77	10.73
2378 TCDF	0.05	0.06	0.02	nd	nd	0.04
12378 PeCDF	0.12	nd	0.05	nd	nd	0.16
23478 PeCDF	0.03	nd	nd	nd	nd	0.03
123478 HxCDF	nd	nd	0.07	0.03	1.50	1.20
123678 HxCDF	nd	nd	nd	0.03	nd	0.16
123789 HxCDF	nd	nd	nd	0.16	nd	0.09
234678 HxCDF	nd	nd	nd	0.04	nd	nd
1234678 HpCDF	0.30	0.31	1.27	6.62	2.98	2.85
1234789 HpCDF	nd	nd	nd	1.23	0.32	0.48
Total PCDD/F	5.30	17.69	39.82	127.41	8.77	10.91
I-TEQ	0.02	0.03	0.06	0.22	0.19	0.20

* not detectable (<0.01 ng/g); I-TEQ contribution assumed to be 0 ng/g.

olson. ^{13}C-labeled 1,2,3,4-tetrachlorinated dibenzo-*p*-dioxin (TCDD) was added as an internal standard for recovery. Quantification of PCDD/F was performed on a high resolution gas chromatography (60-m Rtx 2330 polar capillary column, Restek Ltd., USA) coupled with a high resolution mass spectrometry (HRGC/HRMS) in EI mode by tracing the M^+, $(M+2)^+$ or the most intensive ions of the isotope cluster (Finnigan MAT95s, Resolution=10,000, Finnigan Ltd., USA). The detail has been described elsewhere (Schramm et al., 1995; Henkelmann et al., 1996; Wu et al., 1998).

RESULTS AND DISCUSSION

Table 1 presents the PCDD/F levels and total TEQ for all of the six samples in ng/g. The isomers with high chlorinated level especially octachlorinated dibenzo-*p*-dioxin and dibenzofuran (OCDD/F) were main contributors to TEQ. The levels of PCDD/F in chloranil have been dramatically reduced compared to previous results detected 2 to 3 years ago (Zhang et al., 2000).

The change in the industrial process, substituting hydroquinone for trichlorophenol or pentachlorophenol as raw material, is an effective method to reduce PCDD/F levels in chloranil. One of the major applications of chloranil in China is in the manufacture of C. I. Violet 23, which is used in a variety of consuming goods such as textiles, paints and plastics. We have concluded from our former results that chlorinated phenols were the real source of PCDD/F in the old process. Unfortunately it was difficult to know which dyes or pigments were made from chloranil produced by new process and there was no information on the contamination of PCDD/F in hydroquinone. Therefore further investigation is necessary. Different methods were compared for the extraction (Christmann et al., 1989; Remmers et al., 1992; Williams et al., 1989; Zhang et al., 2000) and benzene was found to be the most effective especially for the recoveries of hexachlorinated dibenzofurans (HxCDF) and heptachlorinated dibenzofurans (HpCDF). Despite the large reduction for TEQ, they are still at a considerable level of total PCDD/F. So chloranil is still a kind of sources for PCDD/F and further improvements should be performed.

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