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Determination of 2,3,7,8-tetrachlorodibenzo-p-dioxin in commercial chlorophenols and related products

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Bestimmung von 2,3,7,8-Tetrachlordibenzo-p-dioxin in handelsüblichen Chlorphenolen und verwandten Produkten

Zusammenfassung. Ein von uns beschriebenes Verfahren [1] erlaubt die selektive Abtrennung von 2,3,7,8-TCDD von den übrigen PCDD und PCDF durch Fraktionierung an Alumina Woelm B Super I. Diese Methode wurde nun zur Bestimmung von 2,3,7,8-TCDD in verschiedenen Proben von Chlorphenolen und verwandten Produkten angewandt.

Analysenergebnisse für Pentachlorphenol, Pentachlorphenol-Natrium, 2,3,4,5-Tetrachlorphenol, 2,4-Dichlorphenoxyessigsäure, Hexachlorophenol und Chloranil werden berichtet. Während in Pentachlorphenol und Chloranil 2,3,7,8-TCDD bei einer Nachweisgrenze von ca. 0,03 ng/g (ppb) nicht nachgewiesen werden konnte, wurde 2,3,7,8-TCDD in allen übrigen Proben nachgewiesen. Mit Ausnahme von 2,4-Dichlorphenoxyessigsäure lagen die Konzentrationen an 2,3,7,8-TCDD unter 1 ng/g (ppb).

Summary. We have recently published a procedure [1] which allows the selective determination of 2,3,7,8-TCDD in the presence of a large excess of other polychlorinated dibenzodioxins (PCDD) and polychlorinated dibenzofurans (PCDF). This method was applied for the determination of 2,3,7,8-TCDD in several samples of chlorophenols and related products.

Analytical results are reported for pentachlorophenol, sodium pentachlorophenolate, 2,3,4,5-tetrachlorophenol, 2,4-dichlorphenoxyacetic acid, hexachlorophene, and chloranil. While 2,3,7,8-TCDD could not be detected at a limit of detection of about 0.03 ng/g (ppb) in pentachlorophenol and chloranil, 2,3,7,8-TCDD could be shown to be present in all samples of sodium pentachlorophenolate and also in the samples of 2,3,4,5-tetrachlorophenol, 2,4-D, and hexachlorophene. With the exception of 2,4-D, the concentration of 2,3,7,8-TCDD in these samples was below 1 ng/g (ppb).

Introduction

Analytical data on the PCDD/PCDF content of pentachlorophenol and sodium pentachlorophenolate have been published by several laboratories [2-7]. In these publications 2,3,7,8-TCDD has not been reported as being present in technical pentachlorophenol or pentachlorophenolate. However, in an interlaboratory study, conducted in 1983/84 by the Landesanstalt für Umweltschutz Baden-

Württemberg, FRG, pentachlorophenol (Witophen P) and sodium pentachlorophenolate (Witophen N) were analyzed by several laboratories for 2,3,7,8-substituted PCDD and PCDF, and one laboratory determined 2,3,7,8-TCDD in both samples at concentrations of 0.9 ppb and 0.25 ppb, respectively [8]. These results have, to my knowledge, not been confirmed by other laboratories at detection limits of 0.5 ppb [8]. A major problem in analyzing chlorophenols and especially pentachlorophenol for 2,3,7,8-TCDD is the fact, that they contain relatively large amounts of higher chlorinated PCDD and PCDF. Pentachlorophenol, e.g., contains up to 1 g of octachlorodibenzodioxin (OCDD) per kg of pentachlorophenol. The OCDD content of the chloranil sample analyzed here was in the same range. We have recently developed a method for selectively separating 2,3,7,8-TCDD from all other PCDD and PCDF, even if they are present at an extreme excess, by chromatography on basic alumina. We have now applied this procedure to the analysis of a number of chlorophenols and related products for 2,3,7,8-TCDD. Despite the fact that a product cannot be judged toxicologically solely on its content of 2,3,7,8-TCDD, due to the large scale production and widespread open use of chlorophenols it is, however, of interest to know whether and at what levels these products might contain 2,3,7,8-TCDD.

Materials and methods

Samples analyzed

Pentachlorophenol (PCP): Witophen P was obtained from Dynamit Nobel (lot no. 7777) and a second sample from a company which is using PCP for the production of PCP esters. From the same company a sample of PCP produced by Rhone Poulenc was received.

Sodium pentachlorophenolate (PCP-Na): Witophen N was obtained from Dynamit Nobel, Preventol PN (trade mark of Bayer AG) was a gift from SÜDÖL (Eislingen, FRG), and Dowicide G was purchased from Fluka.

Hexachlorophene (Pestanal grade, min. 99%) was purchased from Riedel-deHaen, 2,3,4,5-tetrachlorophenol (98%) from Aldrich, 2,4-dichlorphenoxyacetic acid (2,4-D, 98%) from EGA-Chemie (Steinheim, FRG), and chloranil is a product of Hoechst AG.

Analytical procedures

Sodium-pentachlorophenolate. 20 g of PCP-Na are dissolved in 250 ml water. After addition of 10 ng $^{13}\text{C}_{12}$ -2,3,7,8-

TCDD the solution is extracted twice with 150 ml of benzene. The benzene extract is washed with 200 ml 1 N NaOH and 200 ml H₂O, dried over Na₂SO₄, and concentrated to about 50 ml on a rotary evaporator equipped with a vacuum controller (Büchi, Switzerland). The solution is then applied to a column of 25 g Woelm Alumina B Super I and 20 g of Na₂SO₄. After sample application the column is rinsed with another 100 ml of benzene and 200 ml of hexane/dichloromethane (98:2). PCDDs and PCDFs are eluted with 150 ml hexane/dichloromethane (1:1). This fraction is concentrated to about 2 ml. For complete removal of dichloromethane, 50 ml hexane are added, the solution again concentrated to about 2 ml (OCDD precipitates) and taken up in up to 15 ml benzene. The separation of 2,3,7,8-TCDD from this mixture is accomplished by the procedure previously described [1]. The benzene solution is applied to a column filled with 2.5 g of Alumina Woelm B Super I and 2 g of Na₂SO₄, prewashed with 40 ml of hexane. The column is first eluted with 30 ml of hexane/dichloromethane (8:2). This fraction contains all PCDD and PCDF except 2,3,7,8-TCDD, which is subsequently eluted with 25 ml of hexane/dichloromethane (1:1). This TCDD containing fraction is concentrated to a few microliters and subjected to GC/MS analysis.

Pentachlorophenol. 20 g PCP are dissolved in 1.5 l of 2 N NaOH. 10 ng of ¹³C₁₂-2,3,7,8-TCDD are added and the solution extracted twice with 300 ml of benzene. The benzene extract is further treated as described above for PCP-Na.

Hexachlorophene and 2,3,4,5-tetrachlorophenol. To 1 g of sample (total amount available) 200 ml 1 N NaOH, 5 ng ¹³C-2,3,7,8-TCDD and 150 ml of benzene are added. The mixture is shaken in a separatory funnel for 10 min. The benzene extract obtained is further treated as described for PCP-Na.

2,4-Dichlorophenoxyacetic acid and chloranil. 20 g of sample are dissolved in the minimum amount of hot benzene (about 250 ml for 2,4-D and 400 ml for chloranil). 10 ng ¹³C₁₂-2,3,7,8-TCDD are added to the solution, which is subsequently allowed to stand overnight at room temperature. The solid material is filtered off. The benzene solution is washed with 2 N NaOH and water, and dried over Na₂SO₄. The benzene extract obtained is further treated as described for PCP-Na.

GC/MS analysis

The analyses for 2,3,7,8-TCDD were carried out with a HP 5890 gas chromatograph and a HP 5790B mass-selective detector, coupled with a direct interface. A 40 m Silar 10C fused silica capillary column (0.25 mm i. d.; Quadrex Corp., New Haven, Conn.) was used. Sample aliquots of 1–2 µl in benzene solution were injected splitless (injector temperature 300°C) and the column temperature was programmed as follows: 130°C, 1 min isothermal, 30°C/min to 195°C, 4°C/min to 230°C, 20°C/min to 255°C. Carrier gas was Helium at a head pressure of 150 kPa. Multiple ion monitoring was used. Quantitative determination of 2,3,7,8-TCDD is based on direct comparison of peak height and peak area of mass fragmentograms for m/z 321.95 and m/z 333.95 of 2,3,7,8-TCDD and ¹³C₁₂-2,3,7,8-TCDD respectively.

Table 1. Levels of 2,3,7,8-tetrachlorodibenzo-p-dioxin in commercial chlorophenols and related products

Product	2,3,7,8-TCDD ng/g (ppb)
Witophen N	0.42
Preventol PN	0.56
Dowicide G	0.21
Witophen P sample 1	n. d. ^a
Witophen P sample 2	n. d.
PCP sample Rhone Poulenc	n. d.
2,4-Dichlorophenoxyacetic acid	6.8
Hexachlorophene	0.3
2,3,4,5-Tetrachlorophenol	0.3

^a The limit of detection was in all three analyses about 0.03 ng/g

Results and discussion

The results of all 2,3,7,8-TCDD determinations are summarized in Table 1¹. In Fig. 1a–c mass fragmentograms and “reduced” mass spectra, obtained from multiple ion monitoring, for the 2,3,7,8-TCDD fraction of the 3 sodiumpentachlorophenate samples are shown. They proof the occurrence of 2,3,7,8-TCDD in these samples unambiguously since correct isotope ratios for M⁺, (M+2)⁺, (M+4)⁺, (M+6)⁺ and the corresponding fragment ions (M-COCl)⁺ are obtained. Further confirmation, e.g. by HRMS, is not indicated.

In Fig. 2 the mass fragmentograms of m/z 320, 322 (TCDD) and m/z 332, 334 (¹³C₁₂-2,3,7,8-TCDD) for the 2,3,7,8-TCDD fraction of one of the pentachlorophenol samples (Witophen P) are shown. They proof that 2,3,7,8-TCDD cannot be detected in this sample at a detection limit of about 0.03 ppb. The same result was obtained for all three PCP-samples analyzed. PCP and PCP-Na are usually prepared by different synthetic routes [8], which might explain this result. There has been speculation that 2,3,7,8-TCDD in Witophen N might result from 2,3,7,8-TCDD already present in the starting material trichlorobenzene, produced from hexachlorocyclohexane waste of lindan production. We have analyzed a sample of trichlorobenzene, used by Dynamit Nobel up to 1984 for the synthesis of PCP-Na, and determined a 2,3,7,8-TCDD concentration of 95 ppb. This could explain why we find 2,3,7,8-TCDD in Witophen N and not in Witophan P which is usually synthesized starting from phenol. This does not explain, however, the fact that we find 2,3,7,8-TCDD in all three PCP-Na samples. We can assume, that Preventol PN also was produced by Dynamit Nobel, since Bayer AG does not produce PCP-Na. This is indicated also by the isomer distribution pattern for the other PCDD/PCDF present in these two samples. The isomer distribution pattern for PCDD/PCDF in the Dowicide G sample is distinctly different from that of the other two samples (complete PCDD/PCDF analyses for these samples will be published elsewhere). Since 2,3,7,8-TCDD is found in Dowicide G as well we might assume that the source for 2,3,7,8-TCDD must not necessarily be the starting material but the synthetic process, except the

¹ It should be emphasized that, with the exception of one sample of Witophen P and for the sample of Witophen N, the time of production is not known for the various samples analyzed and current products may contain 2,3,7,8-TCDD at other concentration levels

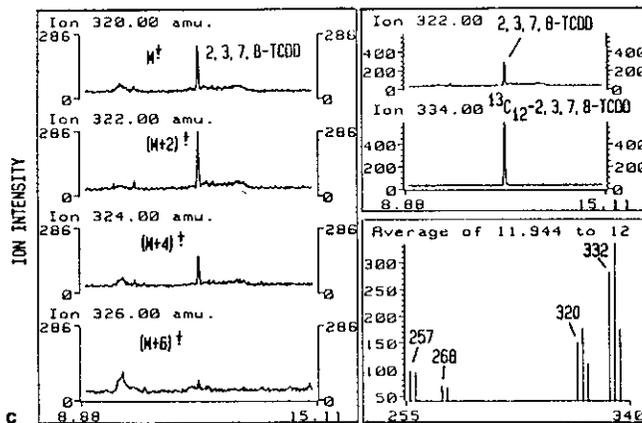
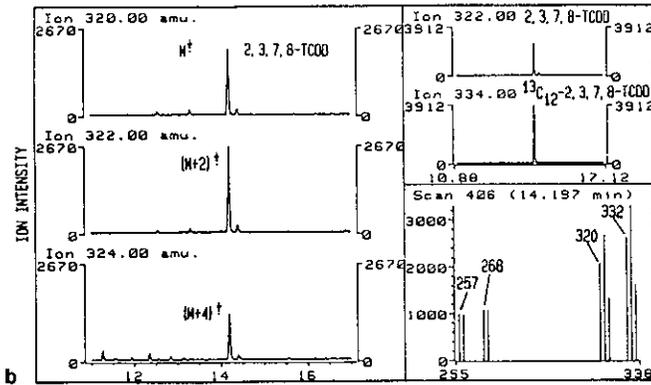
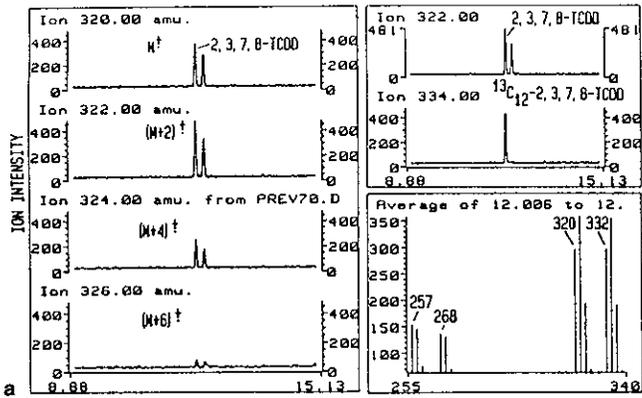


Fig. 1 a - c. Mass fragmentograms of the 2,3,7,8-TCDD fractions of the 3 sodium pentachlorophenate samples. a Preventol PN. b Witphen N. c Dowicide G. GC/MS conditions are described in the experimental section. In the left half of each figure ion intensities for M^+ , $(M+2)^+$, $(M+4)^+$, and $(M+6)^+$ of TCDD, corresponding to m/z 320, 322, 324, and 326 are shown, indicating the correct isotope ratios for a compound containing 4 chlorine atoms (76:100:49:11). In the upper right half of each figure ion intensity traces for m/z 322 [$(M+2)^+$ of TCDD] and m/z 334 [$(M+2)^+$ of $^{13}C_{12}$ -2,3,7,8-TCDD] are shown, proving identical retention times for the native and the ^{13}C -labelled 2,3,7,8-TCDD. In the lower right half "reduced" mass spectra for the peak eluting at the retention time of 2,3,7,8-TCDD are shown, proving correct isotope ratios for the molecular ions and fragment ions ($M-COCl$) $^+$ of 2,3,7,8-TCDD and $^{13}C_{12}$ -2,3,7,8-TCDD. The peak area of ^{13}C -2,3,7,8-TCDD corresponds to 0.5 ng/g for all 3 samples. (10 ng of standard were added to 20 g of sample.) Retention time differences in the three figures for 2,3,7,8-TCDD are due to the fact that the analyses were carried out on different columns varying somewhat in length

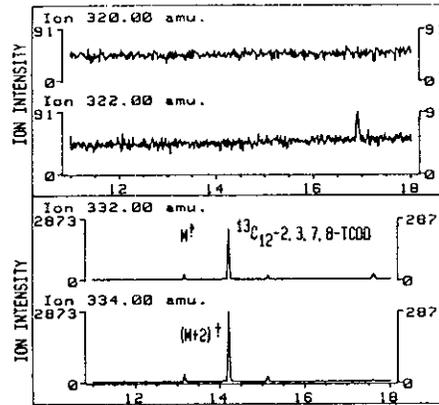


Fig. 2. Mass fragmentograms of the 2,3,7,8-TCDD fraction of Witphen P. Ion intensities for M^+ and $(M+2)^+$ of TCDD and $^{13}C_{12}$ -2,3,7,8-TCDD. The peak area of ^{13}C -2,3,7,8-TCDD corresponds to 0.5 ng/g (10 ng of standard were added to 20 g of sample)

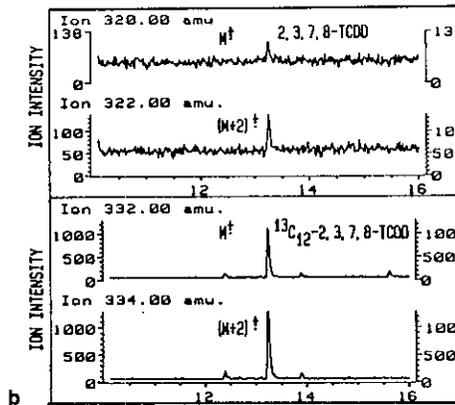
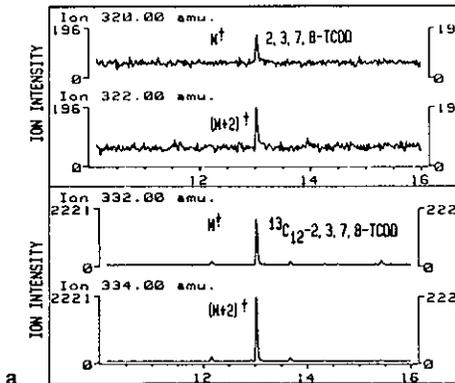


Fig. 3 a, b. Mass fragmentograms of the 2,3,7,8-TCDD fractions of hexachlorophene a and 2,3,4,5-tetrachlorophenol b. Ion intensities for M^+ and $(M+2)^+$ of TCDD and $^{13}C_{12}$ -2,3,7,8-TCDD. The peak area of ^{13}C -2,3,7,8-TCDD in corresponds in both figures to 5 ng/g (5 ng of standard were added to 1 g of sample)

starting material for Dowicide G also contains 2,3,7,8-TCDD. It might be of interest to further clarify this question by analyzing PCP-Na samples and corresponding starting material from other producers.

Although the bactericide hexachlorophene is synthesized from 2,4,5-trichlorophenol which of course is known to contain 2,3,7,8-TCDD, there are few definite data available in the literature on the levels of 2,3,7,8-TCDD in this product. Three samples analyzed by Baughman in 1974 [9]

showed 0.2–0.5 ng/g of 2,3,7,8-TCDD. The analysis of the hexachlorophen sample (Fig. 3a) gives a 2,3,7,8-TCDD concentration of 0.3 ppb which is in the same range as described by Baughman.

A sample of 2,3,4,5-tetrachlorophenol was also analyzed for 2,3,7,8-TCDD. The mass fragmentograms obtained for the TCDD-fraction are shown in Fig. 3b. A 2,3,7,8-TCDD concentration of 0.3 ng/g was calculated.

The analytical procedure applied for the analysis of 2,4-dichlorophenoxyacetic acid and chloranil was somewhat different from the previous samples, since here relatively large amounts of sample were analyzed without the possibility of extractive removal of the major component as this is possible with chlorophenols by alkaline extraction. We therefore tested the possibility to recrystallize the samples and analyze the mother liquor for 2,3,7,8-TCDD. When ^{13}C -labelled 2,3,7,8-TCDD is added to the completely dissolved sample no discrimination for the native and the labelled compound is expected to occur if some inclusion of 2,3,7,8-TCDD takes place during the crystallization process. Since recoveries of ^{13}C -2,3,7,8-TCDD were above 90% for both samples coprecipitation is obviously not significant. In case of the 2,4-D sample a 2,3,7,8-TCDD concentration of 6.8 ppb was found (Fig. 4a), in case of chloranil no 2,3,7,8-TCDD could be detected at a detection level of less than 0.05 ppb (Fig. 4b). This appears to be an elegant procedure for analyzing also other industrial products for 2,3,7,8-TCDD (and for other PCDD/PCDF isomers for which ^{13}C -labelled surrogates are available) at low levels of detection.

Conclusion

We have demonstrated that chlorophenols and related products can be analyzed for 2,3,7,8-TCDD very effectively (reliable and fast) at low levels of detection (below 0.05 ng/g). The basis of this successful analysis is threefold: 1) chromatography on a macro column of basic alumina as a first step in the clean-up procedure; 2) the separation of 2,3,7,8-TCDD from other PCDDs/PCDFs; 3) HRGC/LRMS which is isomer-selective for 2,3,7,8-TCDD. According to our experience the described procedures can readily be applied also to a number of other industrial products and corresponding waste samples [1, 10].

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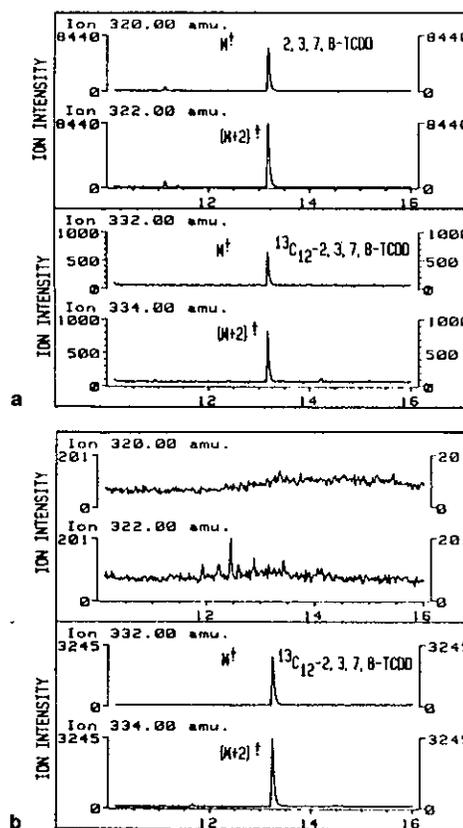


Fig. 4a, b. Mass fragmentograms of the 2,3,7,8-TCDD fractions of 2,4-dichlorophenoxyacetic acid a and chloranil b. Ion intensities for M^+ and $(M+2)^+$ of TCDD and $^{13}\text{C}_{12}$ -2,3,7,8-TCDD. The peak area of ^{13}C -2,3,7,8-TCDD corresponds in both figures to 0.5 ng/g (10 ng of standard were added to 20 g of sample)

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