

CHLORINATED DIPHENOQUINONES AS INDICATOR COMPOUNDS FOR THE OCCURRENCE OF CHLORINATED DIOXINES

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Introduction

While the formation of chlorinated dioxines from chlorinated phenols at elevated temperatures is well investigated, it has never been considered that the same conditions can also generate chlorinated 4,4'-diphenoquinones. Now that these substances have been discovered in a variety of samples, such as oil products from a waste pyrolysis plant, a flyash from a municipal waste incinerator and a sample of Kieselrot-slag, the question occurs how far the formation of the dioxines under specific conditions is correlated to that of the diphenochinones.

4,4'-diphenoquinones form a redox-pair with the corresponding 4,4'-dihydroxybiphenyls with variable equilibrium positions depending on the prevailing conditions. Basically, conditions that enable the coupling of phenols also have enough oxidative power to form diphenoquinones from structurally suitable dihydroxybiphenyls. After their formation, the quinones themselves can act as oxidants. Without stabilisation, a slow reduction to the dihydroxybiphenyls already takes place in aqueous solutions. However, as a result of the comparatively low redox-potential the reformation of the quinoid form is now far much easier than its first generation from the phenolic educts. Regarding the sample preparation procedure, the equilibrium is shifted completely to the dihydroxybiphenyls side, during the clean-up. Similar observations were made during the instrumental analysis of the substances. Therefore, the position of the redox equilibrium in the samples is no longer ascertainable after the analytical clean-up.

But independent of this, these substances, which result from the same precursors as the dioxines and are formed under the same conditions, but are much easier to analyze, can possibly serve as indicators for environmental contamination with chlorinated dioxines.

Materials and Methods

All solvents and chemicals for the clean-up were of analytical grade and from Merck KGaA, Darmstadt, Germany. RP-phenyl cartridges (500mg) for the solid-phase-extraction were obtained from Varian GmbH, Darmstadt, Germany. TFAA for the derivatisation of the analytes was purchased from CS-Chromatographie Service, Langerwehe, Germany. All analytical standards, both diphenoquinone and dihydroxybiphenyl derivatives, were supplied by Euronorm Standard Institute, Technical University of Munich, Freising/Weihenstephan, Germany. Two flyash samples collected from the electrical precipitator of two different German incineration plants in 1993, one sample of Kieselrot from the copper smelting-works in Marsberg, Germany, and light and heavy oils as well as decanter sludge from a waste pyrolysis plant were analysed.

The clean-up and measurement conditions were developed using dihydroxybiphenyl (DHB) and three different tetra-substituted compounds with chlorine (TCDHB), methyl (TMDHB) and methoxy (TMxDHB) groups. *Clean-up for non polar dihydroxybiphenyls (standard compounds TMDHB and TCDHB)*: 1g of the sample was dissolved in 30 ml acetone and filtered through a

folded filter. After washing the filter with additional 20 ml of acetone, 50ml of 0.1M NaOH were added and the organic solvent was removed by a rotary evaporator. The remaining solution was cleaned by shaking out with 50ml hexane and acidified to pH 3 with 1M HCl. Subsequently, the solution was shaken out two times with 50 ml hexane, the combined hexane phases were shaken out two times with 0.1M NaOH, and the combined aqueous phases were prepared for the solid phase extraction by acidifying it to pH 3 with 1 M HCl. *Clean-up for polar dihydroxybiphenyl (standard compounds: DHB, TMxDHB):* 1g of the sample was dissolved in 30 ml toluene and filtered through a folded filter. The filter was washed with additional 20 ml of toluene and the dihydroxybiphenyls were extracted from the organic phase by partitioning two times with 50 ml NaOH. The collected aqueous phase was acidified to pH 3 with 1M HCl and, prior to the application of the solid phase extraction, cleaned by partitioning with 50 ml hexane. After elution from the cartridges, the solvent was evaporated to dryness using a rotary evaporator. HPLC samples had simply to be taken-up in the desired amount of the eluting agent to be ready for injection. GC samples were derivatised with TFAA prior to injection.

All HPLC-analyses were performed with a Gynkotek model 480 pump equipped with an Antec Decade electrochemical detector. Gynkosoft software was used for recording and data analysis. The injection volume was 20µl for every analysis, the detector oven – containing injection port, pulse dampener, column and measuring cell – was thermostated to 35°C. The measuring cell was equipped with a glassy carbon working electrode and an Ag/AgCl reference electrode filled with a saturated LiCl solution in MeOH/H₂O (50:50). The optimum working electrode potential for the measurement of the dihydroxybiphenyls was +0,7V. A Kromasil 100 C18, 5µm, 250×4,6mm i. D. column was used for the chromatographic separation of the substances. The composition of the eluting agent depended on the polarity of the analytes. The more polar substances DHB and TMxDHB were eluted with MeOH/H₂O/THF (55:40:5) adjusted to pH 4 with citrate buffer. TCDHB and TMDHB were eluted with MeOH/H₂O (80:20) adjusted to pH 4 with citrate buffer. Quantitative analysis with HPLC was done by an external calibration method. Under the chosen conditions, the detector showed a reproducible linear response in a concentration range between 2 and 500ppb. The daily validity check of calibration was done by injecting standard solutions of 10, 100, and 200ppb prior to analysis. All native samples were analysed twice together with a blank.

HRGC-ECD was used to evaluate the TFAA derivatisation reaction. All analyses were carried out on a Chrompack CP 9002 gaschromatograph equipped with a Chrompack autosampler and controlled by a Chrompack Maestro data system (injection volume: 1µl, splitless; injection port temperature: 230°C; detector temperature: 280°C; column: DB5, 30m × 0.25mm layer thickness: 0.25µm; temperature program: initial 100°C; hold for one minute; ramped to 160°C at 20°C per minute; ramped to 250°C at 4°C per minute; hold for 5 minutes; carrier gas: hydrogen; pre-pressure: 0.8bar).

HRGC-MS measurement was performed on a Hewlett Packard 5890 Series II gas chromatograph, (injection volume: 1µl, splitless; injection port temperature: 260°C; carrier gas: helium; flow rate: 1.5 ml/min at 60°C; split: 1:10; column: fused silica SE54 30m × 0.25mm ID, layer thickness 0.25µm; column temperature program: initial 50°C; hold for one minute; ramped to 150°C at 70°C per minute; hold for 5 minutes; ramped to 260°C at 2°C per minute; hold for 30 minutes)) connected to a Finnigan 8200 high resolution mass spectrometer (transfer line: 280°C; ion source temperature: 250°C, electron beam current: 1mA; ion acceleration voltage: 3kV; electron beam energy: 70 eV; EI scan: m/z 520-33; rate: 1 s/decade with an inter-scan delay of 0,2s), controlled by a MASPEC Data System (Vers. 2.11) for Windows 95 (MSS, Manchester). All samples were injected manually. In the SIM mode, FC43 was used as lockmass.

Results and Discussion

None of the fly-ash samples contained TMDHB, but sample 1 was contaminated with 0.8 ppb 3,3',5,5'-TCDHB. The Kieselrot slag contained 23 ppb of the same substance. In this sample, also other chlorinated dihydroxybiphenyls have been found, but their structure could not be ascertained because of the lack of standards. The results of the analysis of light and heavy oils and decanter sludge are presented in Table 1. Comparative data on simultaneous analysis of diphenochinones and PCDD/Fs in environmental samples are still not available. During previous analysis of samples of Kieselrot in the region of Braunschweig (Table 2)¹, the slag was found to be contaminated with 21.6 ppm Σ PCDF and 3.4 ppm Σ PCDD. The PCDD/F with higher level of chlorination were dominating. The highest concentrations were found for HpCDF (9.5 ppm) and OcCDF (8.5 ppm). These concentrations resulted in a calculated amount of 290 $\mu\text{g}/\text{kg}$ TE.

Tab. 1. Occurrence of different substituted dihydroxybiphenyls in products of the waste pyrolysis plant (n.d. = not detected)

[ppb]	TMDHB	TCDHB	DHB
light oil 1	40	n.d.	243
light oil 2	25	8	n.d.
light oil 3	230	13	7
heavy oil 1	71	n.d.	n.d.
heavy oil 2	39	60	193
decanter sludge	1021	352	not treated

Tab. 2. Quantitative results of PCDD/Fs found in Kieselrot samples¹

Substance	ppb
<i>Furans:</i>	
TeCDF	1015
PeCDF	635
HxCDF	1890
HpCDF	9520
OcCDF	8560
<i>Dioxines:</i>	
TeCDD	58
PeCDD	1075
HxCDD	387
HpCDD	525
OcCDD	1350

The generally high contamination of Kieselrot with chloroorganics is a consequence of the presence of chlorides during the copper smelting process which is performed in a temperature range between 550 and 600°C². Notably, the average contamination with the extremely toxic 2,3,7,8-tetrachlorodibenzodioxine was found to be in the lower ppb range. It can be assumed that

the structural isomeric compounds 2,3,7,8-TCDD and 3,3',5,5'-TCDQ were both formed during this process and both in the same order of magnitude. Generally, Diphenoquinones/dihydroxybiphenyls seem to appear whenever thermal oxidative processes occur. The analyses show that dihydroxybiphenyls or diphenoquinones in thermal oxidizing treated matrices appear side by side with dioxines and further corresponding compounds, which may be caused by competing formation reactions.

The formation of dioxines from chlorinated phenols at elevated temperatures is well investigated. Mechanistically, one assumes a condensation of phenolic molecules by stepwise elimination of two molecules of HCl³. However, under the same conditions, in the temperature range of 250-700°C, phenols can also react by coupling in the para positions, which leads to double quinoid systems. Therefore, PCDD/Fs and chlorinated diphenoquinones/dihydroxybiphenyls can be expected always to be generated together. But, contrary to dioxines and furans, chlorinated dihydroxybiphenyls seem to be less stable under environmental conditions, possibly because of the reactivity of the hydroxy groups.

Till now, no investigation of the ratio of dioxins/furans to diphenoquinones/dihydroxybiphenyls during these processes has been made. Although the synthesis of diphenoquinones and dihydroxybiphenyls from differently substituted precursors has been thoroughly examined⁴⁻¹⁰, no kinetic data on this reaction has been published. Nevertheless, further comparative studies should reveal how far the production of both substance groups can be correlated. In the case, a correlation can be found, the monitoring of PCDD/Fs contaminations will be simplified.

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