

Utilization of Quartz Superfine Fibred Material for Concentrating Polychlorinated Dibenzo-p-dioxins, Dibenzofurans and Biphenils from the Atmosphere.

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Quantitative estimation of extremely toxic polychlorinated dibenzo-p-dioxines and associated compounds in the air at average concentration levels of 0.1-10  $\mu\text{g}/\text{m}^3$  requires a significant sample concentrating.

Considered was the problem of utilizing the superfine fibred bonded material in the concentration process of PCDD and PCB from the air based on quartz fiber of the SQF type. This material having the properties of an effective aerosol filter and low gas-dynamic resistance allows quick sampling. Modification of the quartz fiber surface gives an opportunity to create a complex adsorbent for vapor and aerosol sorbate components.

To test sorbents there was used a mixture of individual PCDD isomers with different level of chlorination from di to hepta and also a mixture of PCB such as Arochlor 1254.

To trap substances in a vapor phase the SQF fiber was coated with the modifier - m-bis[m-phenoxyphenoxy]benzen (5P4E) film or polydiethylene glycol sebacinat (DEGS) in a number of 3% of weight. Foamed polyurethane (PUF) with aerosol filter was used for comparison.<sup>1</sup> The fibred sorbent layer thickness was 0.5-30 mm, PUF - 50 mm.

To estimate the sorbent efficiency, the sorbates vaporized at 200°C were transported by a dedusted air current into the glass cooling chamber of 100 cm in height. The gas flow drawn through fibred filter-adsorbent cartridge and then consequently through three liquid traps filled with ethylene glycol. To determine the vapor/aerosol ratio we carried out experiments where aerosol component was trapped by high-effective glass-fiber filter AEC (USA), the vapor component - by liquid traps.

Sorbates were Soxhlet extracted with filtering materials by azeotrope benzen-ethanol during 8 h. Liquid trap content was extracted by three portions of hexan. All extracts were cleaned out by column chromatographic procedure, concentrated and analyzed with chromatomass-spectrometr NERMAG R10-10C in the electron impact ionization process with selective detection of characteristic ions.<sup>2</sup> The components were separated on the quartz capillary column 30m\*0.32 with the phase DB-5 at temperature programming.

The vapor/aerosol ratio data for different sorbates obtained in the experiment are given in Table 1. The exact of individual PCB isomers were not accurately identified on account of the standard lack, the results are given for chromatographically separated components, thier level of chlorination was determined from mass-spectrum.

Table 1. Vapor/aerosol ratio ( $C_V/C_A$ ) for used compounds in the experiment depending on the time of substanse output from the chromatographic column(RT)

Compound	RT	$C_V/C_A$	Compound	RT	$C_V/C_A$
TetCB	21.08	15.0	HxCB	25.22	0.5
TetCB	21.34	12.6	HxCB	25.40	0.3
TetCB	21.53	12.3	1. 2. 3. 4-TetCDD	25.56	0.7
2. 3-DiCDD	22.13	11.8	2. 3. 7. 8-TetCDD	26.06	0.4
PnCB	23.16	7.5	HPCB	26.42	0.25
1. 3. 6-TrCDD	23.17	8.0	HPCB	28.04	0.2
1. 2. 3-TrCDD	23.53	4.7	1. 2. 3. 7. 8-PnCDD	30.08	0.2
1. 3. 6. 8-TetCDD	24.01	1.1	1. 2. 3. 4. 7. 8-HxCDD	35.18	0.1
HxCB	24.45	0.7	1. 2. 3. 4. 6. 7. 8-HpCDD	39.10	0.04

It should be noted also that under filed conditions the greater shift is possible towards the aerosol component due to substanse sorption by dust particles in the air.<sup>3</sup>

The way of inert carrier surface modification by a liquid film dissolving sorbate was used to fix the vapor phase on SQF material. Because of scarce data on sorbate solubility when choosing the modifying agent we assumed that sorbates dissolve in substances of close polarity and with similar structural fragments. Apparently that apart from ability to dissolve the sorbate, the modifier should meet some requirements. First of all it is easy separation from the analyzed substances in the process of sample cleaning, low vapor pressure preventing modifier entrainment by air flow and rather low freezing temperature.

Among available substances such properties are peculiar to a number of unmovable chromatographic phases, two of which were taken for experiments: 5P4E and DEGS. It was found that the fiber surface could be coated up to 4% of modifier without structure change, the calculated film thickness being 0.05-0.15 $\mu$ m. For quantitative sorbate extraction the filtering material was Soxhlet extracted with azeotrope benzen-ethanol during 8 h, there was the complete washing of coated phase-modifier.

Extract cleanout by the column chromatography procedure allowed to separate DEGS from fractions containing PCDD and PCB, however the phase 5P4E hindered PCB estimation, therefore it was not used in our subsequent work.

The filtr-sorbent operation efficiency (K) was estimated from the formula:

$$K = 100m/m_1+m_2+m_3$$

where m - is the substance mass on a filtr, m<sub>1</sub>, m<sub>2</sub>, m<sub>3</sub> - is the substance mass in the corresponding liquid trap.

The obtained efficiency coefficient values are given in Table 2 (for Arochlor 1254 the data on the total component number).

Table 2. The efficiency coefficient values (K) for studied materials at filtration rate of 20cm/s. The layer thickness fibred sorbent is 20mm, foamed polyurethane is 50mm.

Compound	SQF + 5P4E	SQF + DEGS	PUF	PUF+SQF
1. 2-D1CDD	82	80	65	70
1. 3. 6-TrCDD	81	80	58	96
1. 2. 3-TrCDD	97	80	51	> 99
1. 3. 6. 8-TetCDD	95	97	56	97
1. 2. 3. 4-TetCDD	95	92	45	90
2. 3. 7. 8-TetCDD	98	97	44	90
1. 2. 3. 7. 8-PnCDD	98	98	35	> 99
1. 2. 3. 4. 7. 8-HxCDD	> 99	> 99	40	> 99
1. 2. 3. 4. 6. 7. 8-HpCDD	> 99	> 99	58	> 99
$\Sigma$ Arochlor 1254	85	85	40	92

The problem of modifier "entrainment" by the air flow and associated possible sorbate losses was verified from sorbent conservation after drawing through the clean air filter with the amount corresponding to 2000 m when recalculating relative to the real sampling device. The analysis of sorbents subjected to blowing showed some decrease (5-15%) in tetrachlorobiphenyls, di and trichlorodibenzo-p-dioxins, however, there were no variations in PCB content with the level of chlorination 5-7 and PCDD with the level of chlorination from tetra to hepta within the limits of measurement error.

Of special interest is the problem of minimal layer thickness of the filter-sorbent sufficient for complete sorbate absorption under real sampling conditions. The estimating measurements were carried out from absorption of the present sorbate amounts with material layer thickness variations from 0.5- to 3cm. The obtained results point to unexpedience of sorbent layer thickness increase above 2 cm because the layer resistance grows and does not result in essential trapping efficiency increase.

The SQF material, modified by 3 % DEGS was used under the field conditions for air sampling near pull and paper mills, the technological cycle for paper whitening of which is based chlor. The sample volume was 1000-1200 with the sampling rate 55-60m<sup>3</sup>/h, the absorbent layer thickness was 20 mm.

Before extraction treatment the exposed filteres were coated with 5 $\mu$ l of internal standard solution containing 5 ng 2. 3. 7. 8-TetCDD, generally labeled on C13 isotope (Cambridge Isotope Lab. Inc.) to control the extraction completeness. The filter treatment and extract cleanout were carried out described above. The sample was separated in components on quartz capillary column 50m\*0.32mm with the Phase DB-DIOXIN. The analysis results

are given in Table 3.

Table 3. The content of polychlorinated dibenzo-p-dioxins and dibenzofurans in the air of pulp paper mill territories,  $\mu\text{g}/\text{m}^3$ . N1, 2, 3-Neman, N4, 5, 6-Sovetsk, N7, 8, 9-Kaliningrad.

Compound	N1	N2	N3	N4	N5	N6	N7	N8	N9
2378-TetCDD	-	3.2	-	4.5	0.5	2.0	-	1.2	-
12378-PnCDD	1.2	1.0	-	3.1	-	1.3	-	1.8	-
123789-HxCDD	-	-	-	0.5	-	-	-	-	-
123678-HxCDD	-	0.5	0.8	-	0.5	-	0.5	-	-
123478 HxCDD	-	1.2	0.5	0.5	1.5	1.0	-	0.5	0.5
$\Sigma$ TrCDD	35.0	8.0	12.0	240.0	420.0	470.0	11.0	130.0	9.0
$\Sigma$ TetCDD	3.9	18.6	6.8	9.5	10.1	5.5	1.2	3.4	1.5
$\Sigma$ PnCDD	1.5	1.0	-	4.2	-	-	1.0	2.0	1.0
$\Sigma$ HxCDD	0.8	1.8	0.	1.5	2.0	2.0	0.5	1.0	1.5
$\Sigma$ HpCDD	0.5	-	-	1.3	0.5	0.5	-	-	0.5
OCDD	0.8	1.8	0.5	2.2	1.2	1.0	0.8	0.5	0.5
2378-TetCDF	0.5	1.0	-	3.5	0.8	0.5	-	-	-
12378-PnCDF	-	-	-	0.5	-	-	-	-	-
23478-PnCDF	-	0.5	-	1.0	1.0	-	0.5	0.5	0.5
123478-HxCDF	0.5	0.8	-	1.3	-	-	-	1.0	-
123678-HxCDF	-	-	-	-	-	-	-	0.5	-
234678 HxCDF	-	-	-	0.8	-	-	0.5	0.5	-
$\Sigma$ TetCDF	82.0	12.0	4.5	56.0	100.0	85.0	80.0	16.5	3.5
$\Sigma$ PnCDF	1.5	1.0	-	2.5	-	1.5	1.0	0.5	-
$\Sigma$ HxCDF	1.5	1.5	1.0	3.5	0.8	0.5	2.5	2.5	1.0
$\Sigma$ HpCDF	-	2.5	2.0	4.0	0.5	0.5	1.5	1.0	1.0
OCDF	-	1.5	1.0	1.5	0.5	-	1.0	-	-

- not found.

#### References.

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