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# Interfering contaminants in carbon dioxide solvent used in the supercritical fluid extraction of polychlorinated biphenyls

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## Abstract

In supercritical fluid extraction (SFE), contaminants in the CO<sub>2</sub> can also be concentrated, interfering with analyte quantitation and increasing analyte detection limits. As an example, we measured levels of electron capture-responding contaminants in three grades of CO<sub>2</sub>, using off-line GC-ECD. In all cases, the contaminant is chlorotrifluoroethylene (CTFE) grease, which significantly affects congener specific analysis of polychlorinated biphenyls (PCBs). For total PCB levels of 30–300 ng/ml, the PCB/CTFE grease ratio should be  $\geq 0.6$  to allow quantitation of the 21 largest PCB peaks to within 10–20% of the true value. Accurate quantitation of coplanar congeners or total PCB mass, both sums of many small peaks, requires PCB/CTFE  $\geq 6$ . © 1998 Elsevier Science B.V.

**Keywords:** Carbon dioxide; Polychlorinated biphenyls; Chlorotrifluoroethylene

## 1. Introduction

Supercritical fluid extraction (SFE) is useful for extracting trace pollutants like polychlorinated biphenyls (PCBs) [1,2]. Solvent purity is important; contaminants in the supercritical solvent can be concentrated along with analytes, interfering with analyte quantitation and increasing detection limits. This problem can be especially severe when analyte concentrations are parts per billion (ppb) or lower.

Therefore, we have determined levels of electron capture detector (ECD) responding contaminants in samples of three grades of CO<sub>2</sub>, using an SFE apparatus and off-line GC-ECD analysis. In each case, the contaminant is chlorofluorocarbon grease, a mixture of oligomers of chlorotrifluoroethylene

(CTFE) [3]. We also examine this contaminant's effect on trace level, congener specific, PCB analysis. Although contaminants in gas cylinders can vary between manufacturers and different lots from the same manufacturer, we present this study to convey what the analyst might encounter in using SFE for trace level analysis.

## 2. Experimental

### 2.1. Sampling

Three different grades of commercially available CO<sub>2</sub> were sampled. 'SFC grade' (manufacturer specification of 10<sup>5</sup> parts per trillion (ppt) non-volatile organic contaminants) and 'SFE grade' (10 ppt ECD responsive contaminants) were from the

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same supplier. The 'SFC/SFE grade' (<1000 ppt ECD responsive contaminants) was from a second supplier. Gas contaminants were collected using a Suprex Prepmaster<sup>TM</sup> SFE with heated restrictor and sorbent trap collection system (Accutrap<sup>TM</sup>). The SFE apparatus allowed precise monitoring of the CO<sub>2</sub> sample size and operating parameters. Three samples were analyzed for each grade. For the SFC/SFE and SFE grades, the first few samples were discarded because of possible carry over from previous runs.

Each sample contained ca. 90 g CO<sub>2</sub>. The CO<sub>2</sub> (450 atm., 50°C, density=0.947 g/ml) was routed through the instrument as usual, including the empty 5 ml sample cell. The restrictor was heated to 50°C and adjusted to 1.5 ml/min mean flow-rate (momentary fluctuations up to ±0.3 ml/min). The contaminants were collected in the sorbent trap (0°C, packed with Florisil<sup>TM</sup>, 60–100 mesh, US Silica). The Florisil<sup>TM</sup> had been previously heated 6.5 h at 450°C. The trap was repacked with clean Florisil<sup>TM</sup> for each sample. After 60 min, the CO<sub>2</sub> flow was stopped and the trap heated to 30°C and then flushed with 5 ml hexane (Omnisolve, EM Science), pumped at 1.0 ml/min. Prior to every 60 min run, an otherwise identical 15 min 'pre-run' was performed to pre-clean the instrument and the trap. The hexane from the pre-run was discarded, with the Florisil<sup>TM</sup> retained in the trap for the 60 min run. Extracts were concentrated into a final solvent of iso-octane (Omnisolve). PCB congeners 30 and 204 were added as internal standards.

A procedural blank was obtained by rinsing the trap – loaded with clean Florisil<sup>TM</sup> – with hexane as usual. The hexane was concentrated and run with internal standards as above. Although no 15 min pre-run was performed, the trap was pre-rinsed with 5 ml hexane, which was discarded.

## 2.2. Standards

A standard solution of CTFE grease was made by dissolving 115 mg into 100 ml hexane, followed by two successive 100-fold dilutions into iso-octane. After correcting for the undissolved high molecular weight components, the final standard concentration was 108 ng/ml. PCB standards were made by introducing either 0.5 ml or 0.05 ml of a mixture of

Aroclors [4] (250 ng/ml Aroclor 1232+180 ng/ml Aroclor 1248+180 ng/ml Aroclor 1262=610 ng/ml total PCBs) into 1 ml volumetric flasks and diluting to volume with iso-octane, producing total PCB concentrations of 305 ng/ml or 30.5 ng/ml, respectively. An additional PCB standard with CTFE grease present (54 ng/ml) was made at both PCB levels. Internal standards were added to all standards.

## 2.3. Gas chromatography and gas chromatography-mass spectrometry (GC-MS)

Extracts and standards were analyzed using a Hewlett-Packard 5890A gas chromatograph with ECD. The instrument and temperature program were optimized for congener-specific PCB analysis [5]. Detector temperature was 330°C and make-up gas (Ar/CH<sub>4</sub>) flow-rate was 25–30 ml/min. Carrier gas (H<sub>2</sub>) velocity was 50 cm/s. The injection port temperature was 300°C and injections (2 µl) were performed in the splitless mode (0.7 min purge delay). The column was a J&W DB-5 capillary column (30 m×0.25 mm I.D., 0.25 µm film thickness). The oven temperature program was 90°C initial temperature, 1°C/min to 240°C, 15°C/min to 300°C, hold 30 min at 300°C.

Mass spectrometric analyses were conducted on a Finnigan MAT ion trap mass spectrometer (Magnum) with electron impact ionization, coupled to a Varian GC. The column was a Finnigan MSSEL fused-silica capillary column (30 m×0.25 mm I.D., 0.25 µm film thickness), interfaced directly into the ion trap. Ultra-pure helium (10 psi head pressure) was the carrier gas. The interface temperature was 300°C. The GC temperature program was: 90°C, increase 1°C/min to 240°C, then increase 10°C/min to 300°C, hold 4 min.

## 3. Results and discussion

### 3.1. Identification of contaminant

ECD chromatograms were acquired for each grade of CO<sub>2</sub> (Fig. 1). They closely resemble the CTFE grease chromatogram (Fig. 2), strongly suggesting that CTFE grease is the contaminant in every case. For 17 major peaks in the CTFE standard, 12–13

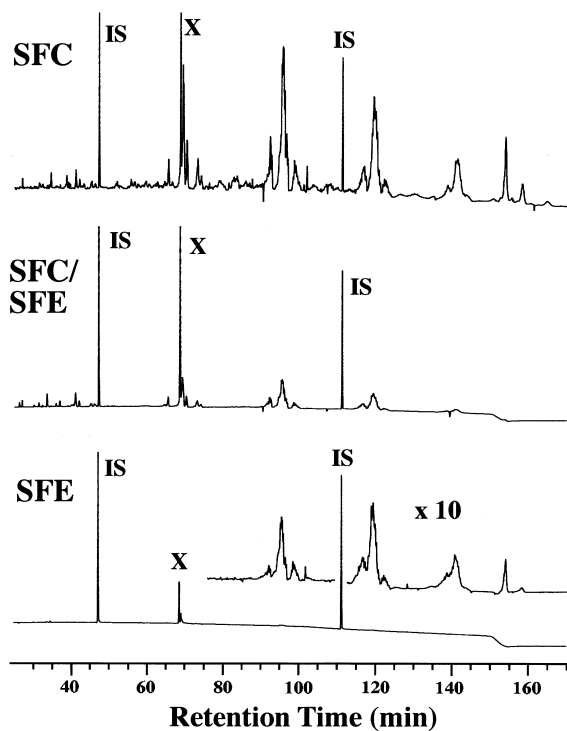


Fig. 1. All traces have same vertical scale. Top trace: ECD chromatogram of sample extract from SFC grade CO<sub>2</sub>. Middle trace: SFC/SFE grade. Bottom trace: SFE grade; trace labelled '×10' is chromatogram of SFE grade sample extract that has been concentrated an additional factor of 10. All traces: peak clusters due to the grease are evident at 65–75 min, 88–103 min, 112–125 min, 133–145 min and 153–160 min. Compare with Fig. 2. 'IS' = internal standard: PCB congener 30 at 47.3 min and PCB congener 204 at 111.3 min. 'X' = extraneous contaminant: the two peaks at ca. 68 min (co-eluting with a CTFE grease peak cluster) are not included in the analyses.

could be found in each grade within  $\pm 0.05$  min of the retention time (total run time 180 min) and the remainder within  $\pm 0.2$  min. Relative peak intensities within and between peak clusters are similar for all gas samples and the CTFE standard. This is excellent agreement in all cases and strongly identifies the contaminant as CTFE grease. CTFE-based lubricants are commonly used in the specialty gas industry and their contamination of chromatographic gases is known [6]. To our knowledge, however, the presence of CTFE in CO<sub>2</sub> has not been conclusively demonstrated nor its interference with congener-specific PCB analysis quantitatively assessed before.

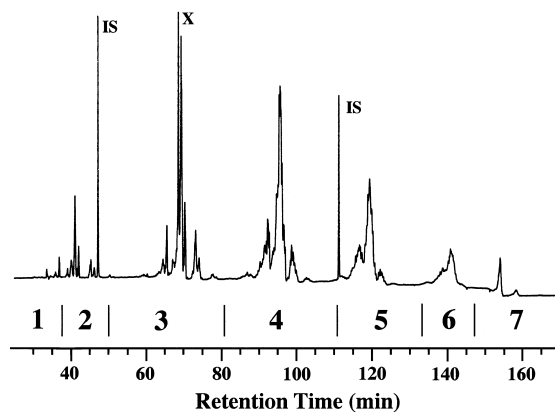


Fig. 2. ECD chromatogram of chlorotrifluoroethylene (CTFE) grease (108 ng/ml). 'IS' = internal standard: PCB congener 30 at 47.3 min and PCB congener 204 at 111.3 min. 'X' = extraneous contaminant: the two peaks at ca. 68 min (co-eluting with a CTFE grease peak cluster) are not included in the analyses. The numerals between the trace and the time scale denote the chromatographic regions, with the boundaries marked by short vertical lines. The time intervals are listed in Table 1.

The SFC grade CO<sub>2</sub> was also sampled by directly connecting the cylinder to the SFE apparatus' restrictor; CO<sub>2</sub> was allowed to flow through the restrictor and sorbent trap for 5 h (unknown flow-rate). The trap was rinsed with 4 ml hexane; the GC–ECD chromatogram was identical to Figs. 1 and 2. Chromatograms of the procedural blank and additional organic solvent and GC carrier gas blanks were featureless, implying that the SFC grade CO<sub>2</sub> was the source of contamination. Since contaminant levels vary reproducibly and sensibly when analysing the different CO<sub>2</sub> grades, we conclude that each grade of CO<sub>2</sub> is individually a source of the contamination.

Regions 1–4 (indicated in Fig. 2 and Table 1) of the SFC grade and the CTFE grease standard were analyzed by GC–MS. For both, fragment masses and isotope patterns were clearly consistent with chlorofluorocarbons and matched the electron impact mass spectra of various CTFE oligomers in the literature [7,8]. Our results do not match published mass spectra of perfluoropolyethers (PFPEs) [9,10], which are used in similar applications as CTFE oligomers [11,12]. The other grades contained insufficient contaminant material for GC–MS detection.

Table 1  
Concentration of chlorotrifluoroethylene (CTFE) grease in carbon dioxide (pg/g CO<sub>2</sub>)

Sample	Chromatographic region <sup>a</sup>							Total <sup>c</sup>
	1	2	3	4	5	6	7	
	5'–38' <sup>b</sup>	38'–50'	50'–81'	81'–111'	111'–133'	133'–147'	147'–170'	
SFC	166 <sup>d</sup> ±64 <sup>e</sup>	49±17	267±61	534±101	345±67	161±36	85±27	1442±208
SFC/SFE	76±155	10±10	38±9	71±24	49±14	11±12	1±3	180±49
SFE	10±8	0.4±0.2	0.6±0.8	2.9±0.4	0.1±0.1	0.0±0.1	0.0±0.1 <sup>f</sup>	4.0±1.2
Blank <sup>g,h</sup>	74	2.1	1.2	0.5	2.6	0.1	0.0	6.5

<sup>a</sup> See Fig. 1 for corresponding chromatograms; regions indicated in Fig. 2.

<sup>b</sup> Elution times, in min.

<sup>c</sup> Total of regions 2–7.

<sup>d</sup> Contaminant levels not blank corrected.

<sup>e</sup> Uncertainties correspond to 95% confidence level.

<sup>f</sup> Zero standard deviation; uncertainty assigned on basis of region 6 uncertainty.

<sup>g</sup> Converted to pg CTFE grease/g CO<sub>2</sub> by dividing by mean CO<sub>2</sub> sample mass.

<sup>h</sup> *n*=1, no uncertainties assigned.

### 3.2. Contaminant levels

Peak areas were converted into pg CTFE grease/g CO<sub>2</sub> (ppt) using relative response factors obtained from the grease chromatograms. For all grades, contamination was within the manufacturers' specifications. Average contaminant levels are in Table 1. Region 1 is not included in determining total contaminant concentration. Relative uncertainties are highest there and the procedural blank is ~7 times greater than the SFE grade, suggesting that region 1 peaks are not contaminants from the CO<sub>2</sub>. Instead, we suspect that the Florisil<sup>TM</sup> used in the sorbent trap absorbed volatiles from laboratory air. No CO<sub>2</sub> flowed through the trap for the procedural blank, suggesting that the flow of CO<sub>2</sub> actually cleaned the Florisil<sup>TM</sup> of region 1 compounds.

### 3.3. Effect of CTFE grease upon congener specific PCB analysis

We also examined the effect of CTFE grease contamination upon the computer-automated quantitation (Chemstation,<sup>TM</sup> Hewlett-Packard) of standards with high (305 ng/ml) and low (30.5 ng/ml) levels of total PCB. The integrator recognizes 103 peak retention times representing 129 PCB congeners [5]. Chromatograms for the standards containing PCBs and CTFE grease (54 ng/ml) were compared to those of standards containing solely

PCBs. All standards were directly injected into the GC-ECD. Fig. 3 shows chromatograms of the low level standards. The upper trace, without the grease, has a baseline that allows for accurate integration. In the lower trace, the grease's broad peaks create a baseline that hinders accurate quantitation. We are interested in the grease's effect on quantitation of total PCBs ( $\Sigma$ PCB), coplanar congeners (congeners exhibiting dioxin-like toxicity [13]) and the most abundant congeners. These results are summarized in Table 2.

With grease present,  $\Sigma$ PCB is overestimated by 12–43%, indicating that grease components are misinterpreted as PCBs by the integrator. The grease co-elutes with 36 PCB peaks, representing 48 PCB congeners and 40% of  $\Sigma$ PCB. As an additional comparison, a CTFE grease standard (108 ng/ml) with no PCBs present was integrated as if PCBs were being analyzed and 112 ng/ml  $\Sigma$ PCB was 'found'.

The concentration of the coplanar congeners is overestimated by 17–48% with grease present. We analyze for nine of twelve coplanar congeners with the highest toxic equivalency factors [13]. Two (81 and 167) elute independently under our GC conditions and seven more (77, 105, 114, 118, 156, 157 and 189) co-elute with one or two non-coplanar congeners. These nine peaks account for 6.4% of  $\Sigma$ PCB.  $\Sigma$ PCB and coplanar congener quantitation depend on many small peaks whose true intensities

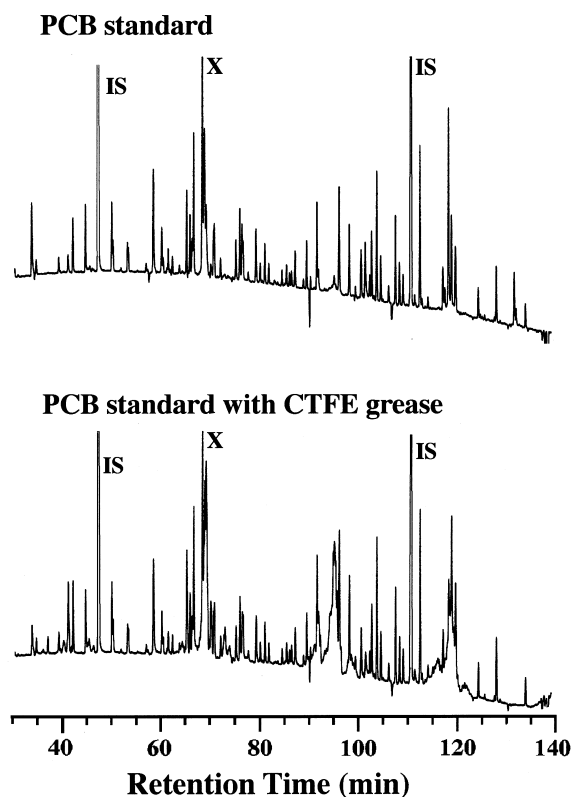


Fig. 3. Top trace: ECD chromatogram of PCB standard (30.5 ng total PCB/ml). Bottom trace: ECD chromatogram of same PCB standard with 54 ng/ml of chlorotrifluoroethylene (CTFE) grease added. Broad peak clusters due to the grease are evident between 60–70 min, 70–75 min, 88–103 min and 112–122 min. 'IS' = internal standard: PCB congener 30 at 47.3 min and PCB congener 204 at 111.3 min. They are vertically off-scale. 'X' = extraneous contaminant: the two peaks at ca. 68 min (co-eluting with a CTFE grease peak cluster) are not included in the analyses.

are highly susceptible to interference from co-eluting grease components. Only at the high PCB level do errors decrease to reasonable levels (12–17%), implying  $[305 \text{ ng/ml } \Sigma\text{PCB}]/[54 \text{ ng/ml CTFE}] = \text{PCB}/\text{CTFE} \geq 6$  for accurate quantitation.

In contrast, CTFE grease less strongly affects the quantitation of the 21 largest peaks, which represent 31 congeners and 66% of  $\Sigma\text{PCB}$ . With grease present, these peaks were overestimated by 7–17%. This analysis is less vulnerable to CTFE grease contamination because only 8 of the 21 predominant peaks co-elute with the grease. The 21 peaks can be integrated with reasonable accuracy (within ~20%)

at the low PCB level (30 ng/ml  $\Sigma\text{PCB}$ ) in the presence of 54 ng/ml CTFE grease, implying  $\text{PCB}/\text{CTFE} \geq 0.6$ .

### 3.4. Strategies for minimizing CTFE grease interference

Higher purity  $\text{CO}_2$ , shorter dynamic extractions or static extractions using small amounts of lower purity  $\text{CO}_2$  will all decrease CTFE interference. For example, 140 ng/ml CTFE grease is accumulated in the final extract using  $\text{CO}_2$  contaminated at 1500 pg CTFE/g  $\text{CO}_2$  (our SFE conditions, 60 min dynamic extraction). The lowest quantifiable PCB level is 80 ng/ml if quantitating the 21 predominant congeners. Switching to 4 pg CTFE grease/g  $\text{CO}_2$  decreases the lowest quantifiable PCB level to 0.22 ng/ml.

Alternatively, since kinetics more often limit extraction efficiency than analyte solubility in supercritical  $\text{CO}_2$  [1], long static extractions, using less volume of lower purity  $\text{CO}_2$ , could still efficiently extract analytes while accumulating less grease. A static extraction (our SFE conditions, 15 ml  $\text{CO}_2$ ) using  $\text{CO}_2$  contaminated at 1500 pg CTFE/g  $\text{CO}_2$  would improve the lowest quantifiable PCB level to 14 ng/ml.

Finally, on-line SFE/GC could improve detection limits and sensitivity 1000-fold, because the entire amount of extracted analyte is used. However, contaminants are also strongly concentrated, hampering full exploitation of SFE/GC [14–16]. For instance, accurate quantitation of 0.1 ng  $\Sigma\text{PCB}$  delivered on-line (corresponding to a 2  $\mu\text{l}$  off-line injection of 50 ng/ml  $\Sigma\text{PCB}$ ) requires a contaminant level less than 2 pg CTFE grease/g  $\text{CO}_2$  (our SFE conditions, 60 min dynamic extraction). Decreasing dynamic extraction time to 10 min—or using 15 ml  $\text{CO}_2$  in a static extraction—would allow 10 pg CTFE grease/g  $\text{CO}_2$ , the manufacturer's specification for the SFE grade and the highest purity grade currently commercially available.

## 4. Conclusion

CTFE grease is the major PCB interfering contaminant in samples of three grades of  $\text{CO}_2$  used for SFE. At  $\Sigma\text{PCB}$  levels of 30–300 ng/ml, moderate

Table 2  
Results of automatic integration for PCB analysis-effects of CTFE grease

Standard	Total PCB			Predominant congeners <sup>a</sup>			Coplanar congeners <sup>b</sup>		
	cal. <sup>c</sup> (ng/ml)	obs. <sup>d</sup> (ng/ml)	% diff.	cal. <sup>c</sup> (ng/ml)	obs. (ng/ml)	% diff.	cal. <sup>c</sup> (ng/ml)	obs. (ng/ml)	% diff.
Low PCB	30.5	32.4	6	20.1	20.0	-1	1.94	1.89	-2
Low PCB+CTFE <sup>f</sup>	30.5	43.5	43	20.1	23.6	17	1.94	2.86	48
High PCB	305.0	307.9	1	201.3	198.7	-1	19.41	19.23	-1
High PCB+CTFE <sup>f</sup>	305.0	340.5	12	201.3	216.0	7	19.41	22.75	17

<sup>a</sup> 21 largest peaks in PCB standard [4], containing 31 congeners and 66% of the total PCB mass.

<sup>b</sup> 9 peaks that include 9 coplanar congeners and co-eluting non-coplanar congeners.

<sup>c</sup> cal.=calculated (stock standard concentration, 610 ng/ml total PCB, divided by the dilution factor).

<sup>d</sup> obs.=observed.

<sup>e</sup> Obtained by dividing the amount experimentally obtained for the 610 ng/ml PCB standard (CTFE-free) by the appropriate dilution factor.

<sup>f</sup> CTFE=CTFE grease, present at 54 ng/ml.

amounts of CTFE grease (54 ng/ml) can cause an overestimation of  $\Sigma$ PCB levels by 10–40%. Reasonably accurate quantitation of the most abundant PCB congeners is possible provided PCB/CTFE $\geq$ 0.6. For off-line GC–ECD analysis, shorter dynamic extractions, static extractions using minimal amounts of lower purity CO<sub>2</sub>, or switching to higher purity CO<sub>2</sub> can all minimize CTFE grease interference. However, even the highest purity commercially available CO<sub>2</sub> appears only marginally suitable for trace PCB analysis with on-line SFE/GC. Our on-going research is addressing methods of removing CTFE grease from CO<sub>2</sub>.

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