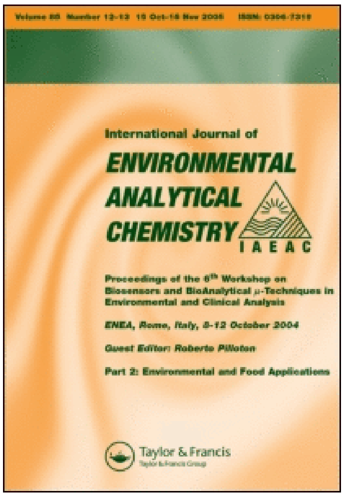

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INTERFERENCE OF TRANSFORMER OIL MATRICES TO THE INTERNAL STANDARDS ON PCB QUANTIFICATION

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Polychlorinated biphenyls (PCBs) are toxic, persistent, global environmental contaminants which were formulated as complex mixtures of congeners. Many methods have been developed in the past to analyze PCB in transformer oil samples for regulatory purposes. The most important consideration in the cleanup procedure is the ability to remove the oil from the sample matrix, since trace amount of oil will interfere with the subsequent GC-MS analysis. Electron capture detection (ECD) has been the most common method for gas chromatographic analysis of PCBs because of its high sensitivity toward halogenated compounds. ECD can also respond to some non-PCB compound resulting in biased concentrations of PCB. In this work, a two-stage cleanup method, using DMSO liquid/liquid extraction and HPLC column chromatography, has been applied to two types of transformer oil. Five internal standards have been selected to show their performance in the presence of different oil matrices. The comparison of the PCB quantification at different conditions for GC-MS and GC-ECD will be demonstrated.

KEY WORDS: PCB, transformer oil, high performance liquid chromatography.

INTRODUCTION

Electron capture detection (ECD) has been the most common method for gas chromatographic analysis of polychlorinated biphenyls (PCBs)[2] because of its high sensitivity toward halogenated compounds. ECD can also respond to non-PCB compounds such as halogenated naphthalenes, chloroaromatics, phthalate and adipate esters, and others which may be differentiated from PCBs only on the basis of retention time. In addition, there are other interferences which do not give discrete peaks. Elemental sulphur can interfere with PCB analysis in sediment and other samples which have been subjected to anaerobic conditions. Another non-specific interference is mineral oil[3], a complex mixture of hydrocarbons, which is used as a dielectric fluid. Mineral oil in old transformers often contains PCBs as a result of cross-contamination from original PCBs. A typical analysis of mineral oil for PCBs entails simple dilution with hexane to reduce the viscosity and also achieve a concentration in the linear range of ECD[4]. The mineral oil in the diluted sample affects the ECD response. The effect on the quantification of 11 individual PCBs by oil matrix in different oil concentrations has been reported by Turman[5]. In order to achieve more accurate analysis for PCBs, a variety of methods have been published in the literature[6]. Most of these methods put emphasis on the clean up procedure. Cleanup techniques have been developed involving a combination of liquid/liquid extraction[7], Florisil[8], silica gel[9], aluminium oxide[9] and benzenesulfonic acid[9] column adsorption chromatography.

Factors, such as the interactions of matrix-internal standards, background level, and a matrix quenching effect on the detector, may lead to biased PCB results. Therefore, the use of one or more internal standards that are similar in analytical behaviour to the compounds of interest is necessary. In this work, a comparison of analytical results using different internal standards in various oil matrices measured by a Gas Chromatograph-Mass Spectrometer (GC-MS) and three GC-ECDs is reported.

EXPERIMENTAL

Materials

Solvent and reagents: Aroclor 1242 and 1260 (Supelco); hexane (non UV, Caledon); dichloromethane (HPLC grade, Aldrich); Sulphuric acid (Caledon); NBS transformer oil (NBS); Voltesso oil (ESSO); hexachlorobenzene (HCB, Ultra Scientific); octachlorostyrene (OCS, Ultra Scientific); PCB-83 (Ultra Scientific); PCB-122 (Ultra Scientific); d_{10}-fluoranthene (d_{10}-FLT, MSD Laboratories).

High-performance liquid chromatography (HPLC) cleanup

The cleanup procedure was carried out on a Hewlett Packard Model 1090 Liquid Chromatography controlled by the HPLC ChemStation (Pascal series) equipped with Rheodyne 7125 syringe loading sample injector, Waters Energy Analysis (NH_2) column (300 × 7.8 mm, 5-mm) with a guard column cartridge (ASP-Hypersil-NH_2), and with Diode-Array Detector monitoring at wavelengths 245, 254, and 270 nm. The mobile phase was 10% dichloromathane-hexane at a flow rate of 1.00 or 2.00 mL/min as described. The chromatographic separations were run at room temperature.

GC-ECD conditions

GC-ECD-1: Consisted of a Hewlett Packard 5830 gas chromatograph equipped with a splitless injector and an electron capture detector with a ^{63}Ni source. The capillary column (30 m × 0.25 mm i.d.) was coated with a 0.25 um film of DB-5 (5%-phenyl/95%-methyl silicone). The injector temperature was 280°C. The GC oven temperature program was 50°C for 2 min, temperature-ramped to 290°C at 20°C/min, and held for 20 min. The detector temperature was kept at 330°C. The microprocessor-controlled unit was Hewlett Packard 18850A GC Terminal.

GC-ECD-2: Consisted of a Hewlett Packard 5890II gas chromatograph equipped with a splitless injector, FID, ECD and a 30 meter DB-5 column. The GC oven temperature program was 90°C for 0.5 min, temperature-ramped to 200°C at 15°C/min and held for 5 min, then to 285°C at 5°C/min and held for 10 min. Detector temperature was kept at 320°C. The instrument was equipped with Hewlett Packard 7673A autoinjector and data was processed and recorded on an HP Vetra ES micro-computer.

GC-ECD-3: The GC configuration was the same as GC-ECD-2. The GC oven temperature program was 90°C for 2 min, temperature-ramped to 180°C at 15°C/min, to

240°C at 3°C/min, to 285°C at 10°C/min, and then held for 9 min. Detector temperature was kept at 320°C. The instrument was equipped with Hewlett Packard 7673A autoinjector and data was processed and recorded on an HP Vetra QS/165 microcomputer.

GC-ECD analysis

One microlitre of the sample solutions was injected onto the gas chromatograph column. The presence of PCBs in the sample was determined from retention times that were within ± 0.1 min of the calibration standard or retention time corrected for the time shift of internal standards. Quantitation of the PCBs in the oil samples was accomplished by comparing the internal standard corrected total area of 22 major Aroclor peaks (1242/1254/1260) to the total area of the corresponding peaks in the standard solution.

GC-MS analysis

The Hewlett Packard 5890II GC was equipped with on column injector and DB-5 capillary column (30 m × 0.25 mm, 0.25 mm coating 5%-phenyl/95%-methyl silicone) and a 10 m × 0.5 mm deactivated fused silica precolumn. The analytical column was inserted directly into the mass spectrometer. The injector temperature was 280°C. The GC was set at a constant pressure of 10 psi. After an injector of 2 uL sample, the GC oven temperature program started at 90°C with a 2 min. hold, 90°C to 180°C at 15°C/min no hold, 180°C to 240°C at 3°C/min, no hold, 240 to 285°C at 10°C/min with 5 min hold. A Hewlett Packard 5970 MSD was operated at 70eV electron energy with a source temperature of 180°C. Data was collected using a HP G1034C ms ChemStation software. A window defining standard was used to determine the range of retention times for each homologue (congener group). A calibration standard was used to determine ion ratios and response factors. To be identified as a PCB, the extracted ion peak would have to fall within the predefined homologue time frame, have a parent as well as two daughter ion peaks, and have a proper ratio of parent to daughter ion.

Matrices preparation and cleanup procedures

1) Matrix N: The NBS transformer oil was diluted with isooctane at a ratio of 1:50.
2) Matrix E: The Voltesso transformer oil (non-PCB contaminated) was diluted with isooctane at a ratio of 1:50.
3) Matrices DN (or DE): NBS (or Voltesso) transformer oil (exactly, 4.0 g) was diluted with hexane (20.0 mL) and vigorously shaken for two minutes with concentrated sulphuric acid (20.0 mL) in a separatory funnel. The acid layer was drained into a waste container. Five mL of deionized water was added and drained to remove excess acid. Fifteen mL of dimethyl sulphoxide (DMSO) was added into the separatory funnel and shaken for two minutes. The phases were allowed to separate completely before draining the DMSO. This procedures was repeated twice with 10 mL of DMSO each time. Hexane (20.0 mL) was added to the combined DMSO solution and vigorously shaken for one minute. The hexane layer was passed through an acid/base/silver nitrate/silica column then concentrated to 4.0 mL. This cleanup procedure was found to remove most of the oil (> 98%) from the sample.

4) Matrices HN (or HE): Matrices DN (or DE) (100 uL) was injected into HPLC equipped with an amino-silane column operated at 1.00 mL/min with 10% dichloromethane-hexane as the eluent. The fraction was collected between 12.75 to 18.00 minute (window for Aroclor 1242, 1254, and 1260) and concentrated to 100 uL by ultra-pure nitrogen gas. The Oil matrix should be further reduced after this procedure.
5) Matrix GE: Sample was prepared in the same manner as HE except that the HPLC was operated at a flow rate of 2.00 mL/min and the fraction was collected between 6.30 and 9.00 minute.

Sample preparation

Concentrations of PCBs in various matrices are listed in Table 1.

RESULTS AND DISCUSSION

As reported by ASTM[10], the mineral oil content of the sample matrix can depress the ECD response and thus yield erroneously low readings. For sample N1, N2, E1, and E2, as shown in Tables 2 and 3, the amount of PCBs detected were lower than spiked values. The PCB recoveries for samples DN, DE, HN, HE, and GE were in agreement with the spiked values when using octachlorostyrene (OCS), PCB-83, and PCB-122 as standards. Ion chromatograms of these samples also indicated that the interferences from the oil matrix were reduced significantly. There are no manifest difference on PCB recoveries between the DMSO L/L cleaned matrices (DH and DE) and the HPLC cleaned matrices (HE and HE). Over 98% of oil was removed by DMSO L/L cleanup procedure[6]. A further removal of 80% of the remaining oil was achieved by subsequent HPLC cleanup, as estimated by HPLC and GC-FID chromatograms.

Figure 1 illustrates HPLC chromatogram of different matrices. The major oil component eluted at retention time 10.50–12.75 min (Figure 1a–1d) which has minimum overlap with Aroclor's elution window at 12.75–17.00 min (Figure 1e). Some ingredients eluted at 12.50–24.00 min of matrix E (diluted Voltesso transformer oil), probably bearing strong chromophores, were removed from DMSO L/L cleanup process (Figure 1b). The remaining component of NBS transformer oil (Figure 1c) from the L/L cleanup process was very easily separated from Aroclor mixture in the HPLC column (Figure 1d). These may explain the high recovery and small variation of sample DN1 listed in Table 2. Figure 2 illustrates the GC-FID chromatogram of four different matrices which might describe the matrix interference effect on PCB quantitation by using different internal standards.

The result of triplicate analysis by GC-ECD-1 is presented in Table 2. The recoveries for DN, HN, DE, and HE matrices-containing samples corrected for HCB were higher than those corrected for other standards. This might be due to the coelution of HCB with the major portion of oil matrix.

PCBs in samples N1, N2, E1, and E2 could not be identified and quantified by GC-MS owing to the significant oil content. Samples containing matrices DN, HN, DE, and HE were identified and quantified by GC-MS for individual PCB congeners (Table 4).

When the GC-MS method was used, the quantitation of mono-, di-, tri-, and tetrachloro biphenyls was affected by the oil matrix and caused uncertainties. Such

Table 1 Sample preparation.

Sample I. D.	*SD1*	*N1**	*E1**	*SD2*	*N2***	*E2***	*SD3*	*DN1*	*DE1*	*DN2*	*DE2*	*HN1*	*HE1*	*GE1*	*HN2*	*HE2*	*GE2*	*SD4*	*GE3*
Martix Congeners	–	N	E	–	N	E	–	DN	DE	DN	DE	HN	HE	GE	HN	HE	GE	–	GE
Concentration*** (μg/g)	1.0	1.0	1.0	0.4	0.4	0.4	2.0	2.0	2.0	0.4	0.4	2.0	2.0	2.0	0.4	0.4	0.4	10.0	10.0

* : equivalent to 50 times dilution of oil sample containing 50 μg/g of PCBs.

** : equivalent to 50 times dilution of oil sample containing 20 μg/g of PCBs.

*** : total concentration of Aroclor 1242, 1254 and 1260 (1:1:1 ratio).

All samples were spiked with standards HCB, OCS, PCB-83, PCB-122 and d_{10}-FLT 1 μg/g each.

Table 2 % Recoveries of triplicate analysis obtained from GC-ECD-1.

Recovery corrected for		*N1*	*N2*	*DN1*	*DN2*	*HN1*	*HN2*	*E1*	*E2*	*DE1*	*DE2*	*HE1*	*HE2*
Uncorrected value	mean	39	52	74	100	81	114	36	38	68	80	60	98
	s.d.	4	8	15	7	27	18	3	5	3	13	16	10
HCB	mean	72	75	123	125	117	111	65	76	138	127	142	138
	s.d.	12	6	6	11	5	5	3	4	12	2	0	8
OCS	mean	71	78	98	96	111	111	65	78	101	99	110	104
	s.d.	8	1	3	3	6	12	3	2	6	3	5	11
PCB-83	mean	88	94	101	103	112	104	82	93	107	106	113	116
	s.d.	12	2	4	9	6	6	7	2	3	1	1	6
PCB-122	mean	89	88	95	97	113	105	80	87	101	92	105	99
	S.D.	9	4	4	11	9	13	1	6	12	2	1	6

s.d.: standard deviation; HCB: hexachlorobenzene; OCS: octachlorostyrene.

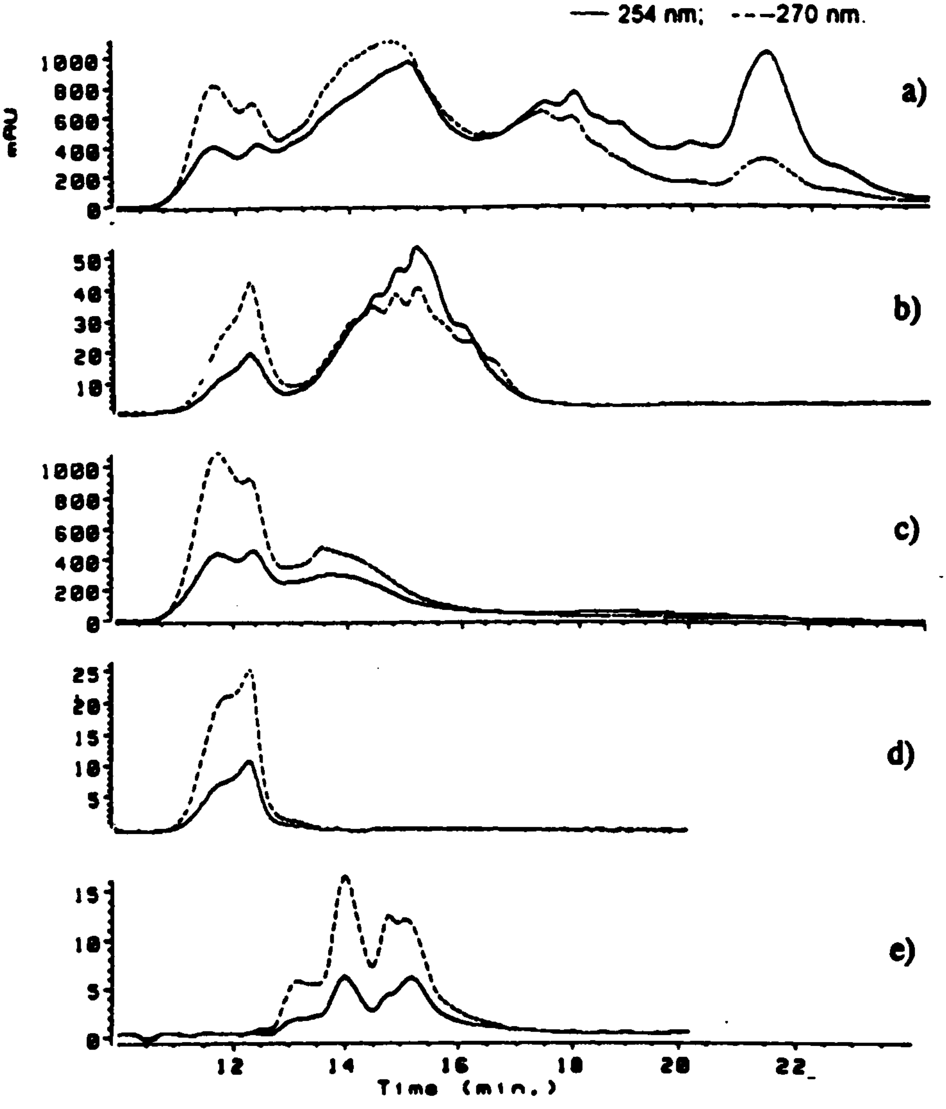
Recoveries calculated were on the basis of comparing with corresponding standard matrix blank solutions (SD1, SD2, SD3 and SD4).

Table 3 Comparison of the recoveries obtained from three different GC-ECDs and corrected for HCB, OCS, PCB-83 and PCB-122.

Recovery corrected for	*Instrument*	*N1*	*N2*	*DN1*	*DN2*	*HN1*	*HN2*	*E1*	*E2*	*DE1*	*DE2*	*HE1*	*HE2*	*GE1*	*GE2*	*GE3*
HCB	GC-ECD-1	69	68	119	135	113	114	65	80	125	129	142	143	116	136	115
	GC-ECD-2	67	71	109	104	105	93	65	64	125	120	110	102	–	–	–
	GC-ECD-3	72	88	115	130	106	107	58	51	129	138	134	131	–	–	–
OCS	GC-ECD-1	70	79	96	98	108	108	68	80	96	98	113	115	89	97	95
	GC-ECD-2	71	68	101	99	102	93	73	67	106	103	103	103	–	–	–
	GC-ECD-3	74	79	100	112	105	107	68	69	101	115	115	110	–	–	–
PCB-83	GC-ECD-1	83	95	97	111	107	108	90	95	103	107	114	105	–	–	–
	GC-ECD-2	84	80	98	99	107	94	86	77	100	100	105	97	–	–	–
	GC-ECD-3	78	77	99	103	103	101	83	78	93	105	110	101	–	–	–
PCB-122	GC-ECD-1	86	83	91	109	106	114	80	80	92	95	105	107	–	–	–
	GC-ECD-2	96	93	99	99	120	93	101	91	74	95	115	97	–	–	–
	GC-ECD-3	81	70	97	108	109	102	81	68	94	99	110	99	–	–	–

HCB: hexachlorobenzene; OCS: octachlorostyrene.

Recoveries calculated were on the basis of comparing with corresponding standard matrix blank solutions (SD1, SD2, SD3, and SD4).



HPLC Chromatogram Conditions:

Injection volume: 100 uL
Solvent: 10% dichloromethane/hexane
Column: Amino-silane preparative column

Flow rate: 1.00 mL/min
Detector: Diode Array Detector

a) Matrix E b) Matrix DE c) Matrix N d) Matrix DN
e) Mixture of Aroclor 1242, 1254, and 1260 in a total concentration of 15 μg/g at a ratio of 1:1:1.

Figure 1 HPLC chromatograms of matrices E, DE, N, DN and Aroclor mixture.

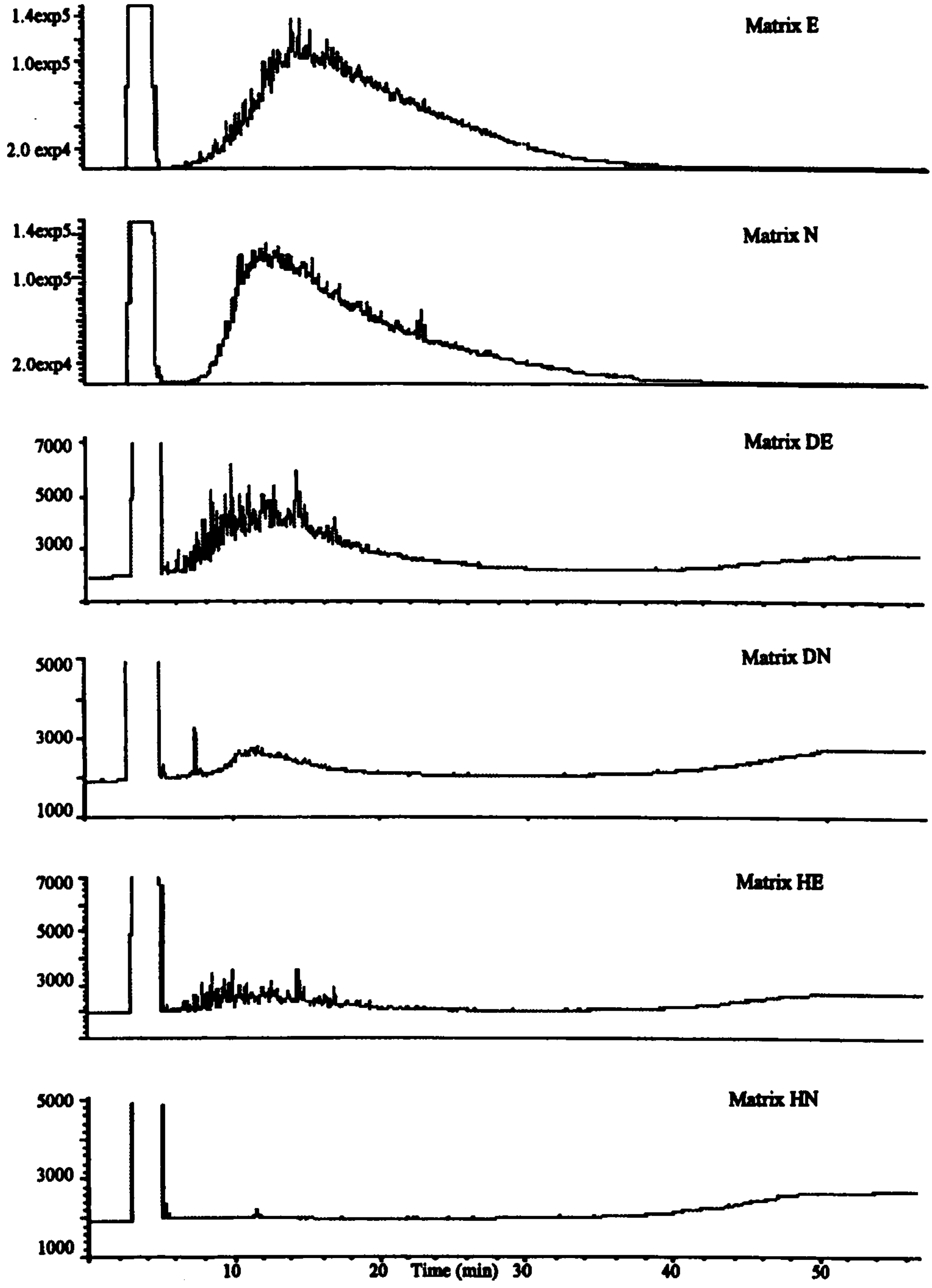


Figure 2 GC-FID chromatogram of matrices E, N, DE, DN, HE and HN.

Table 4 Recoveries obtained from GC-MSD quantitation corrected for d$_{10}$-FLT.

Homolog	*DN1*	*DN2*	*HN1*	*HN2*	*DE1*	*DE2*	*HE1*	*HE2*
Cl$_1$-PCB	69	–	154	–	–	–	–	–
Cl$_2$-PCB	99	115	100	111	99	103	92	96
Cl$_3$-PCB	93	85	96	107	105	14	90	91
Cl$_4$-PCB	95	119	88	102	106	48	92	101
Cl$_5$-PCB	96	106	94	105	105	102	84	99
Cl$_6$-PCB	91	95	88	88	99	74	82	79
Cl$_7$-PCB	94	92	92	89	101	101	83	85
Cl$_8$-PCB	91	–	98	–	101	–	90	–

–: unable to quantitate or detect; FLT: fluoranthene.

The calculation of % recoveries of each homolog were on the basis of standard solutions: SD3 for DN1, DE1, HN1 and HE1; SD2 for DN2, DE2, HN2 and HE2.

interference led to incorrect signal peak ratios or poor detection. The most serious interference occurred with mono-chlorinated biphenyls which was barely quantifiable for samples DN1 and HN1 with recoveries of 69% and 154% respectively.

Assuming that, when using OCS to quantify HCB by GC-ECD-1, OCS behave the same as in the blank (SD0) and matrix GE (GE0) solution, the recovery of HCB was approximately 35% less in the matrix than in the blank (Table 5-I). When the analysis was repeated by MS using d$_{10}$-FLT as the internal standard, it gave 6 and 27% less recovery for the GE matrix for OCS and HCB respectively as listed in Table 5-II. These results were consistent with GE1, GE2, and GE3 in Table 3.

Table 5 Comparison of HCB, OCS and d$_{10}$-FLT.

I. GC-ECD-1 results

Sample	*SD0*	*GE0*
Area ratios of HCB/OCS	0.511 ± 2.5%	0.408 ± 1.5%

* Triplicate analysis.

II. GC-MSD results

Sample		*SD0*	*GE0*
Area ratios of	OCS/d$_{10}$-FLT	0.099	0.093
	HCB/d$_{10}$-FLT	0.181	0.132

FLT: fluoranthene; HCB: hexachlorobenzene; OCS: octachlorostyrene.

Sample SD0: containing d$_{10}$-FLT (2.5 μg/g), OCS (1.25 μg/g) and HCB (1.25 μg/g) in iso-octane.

GE0: containing d$_{10}$-FLT (2.5 μg/g), OCS (1.25 μg/g), HCB (1.25 μg/g) and oil matrix in iso-octane.

CONCLUSION

The use of appropriate internal standards such as OCS, PCB-83, or PCB-122 for the GC-ECD method can enhance accuracy and precision for the quantitation of Aroclor-patterned PCB in oil. For dirty sample, it is advisable to include more than one internal standard to improve accuracy. When the oil matrix is removed or reduced through sample cleanup procedures, better accuracy can be achieved for both GC-ECD and GC-MS methods.

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