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Gas chromatography mass spectrometry determination of polychlorinated biphenyls in waste oils

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ABSTRACT

A capillary gas chromatographic-mass spectrometry with quadruple ion trap was applied to nine polychlorinated biphenyl (PCB) congeners in waste oil. The optimized procedure involves solvent extraction using dimethyl sulfoxide (DMSO) in first step and mixture of ethyl acetate and hexane in second step. Extraction efficiency was monitored by using pyrene-d10 as surrogate standard. The separation of PCB congeners was done in VF-5MS (30 m x 0.25 mm x 0.25 μ m) column and analysed on GC-MS using selective ion monitoring mode (SIM). The method was calibrated using two internal standards; phenanthrene-d10 and chrysene-d12. Correlation coefficients of all studied congeners ranged from 0.9993 to 0.9999 for 7 point calibration. Recoveries of PCB congeners from waste oil are over 94 % with RSD below 5 % (n = 6). The method is suitable for the analysis of PCB congeners in waste oils with high sensitivity and accuracy.

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KEYWORDS

Polychlorinated biphenyls;
Solvent extraction;
Waste oils;
Gas chromatography mass spectrometry.

INTRODUCTION

Organic pollutants in traces levels threaten our environment as they cause potentially dangerous public health risks. Their use regulated through legislation, requires continuous and regular monitoring of factories effluents and import hazardous goods. Industrial waste oils are classified as toxic residues owing to the presence of toxic chemicals such as heavy metals, polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs), among others. The interest of the PCBs as an environmental pollutant began in 1966 when they were catalogued as hazardous waste^[1]. PCBs were used in the manufacture of transformers and ca-

pacitors, as dielectric and heat transferring fluids, fluids in hydraulic and vacuum systems, plasticizers and as flame retardants (fire preventives) because of their ability to withstand at very high temperatures. PCBs are compounds artificially synthesized from the substitution of hydrogen atoms by chlorine atoms in the biphenyl molecule. This substitution is possible in any position and in combinations of 1 to 10 chlorine atoms in each molecule^[2]. The 209 possible PCB congeners have only been synthesized under laboratory conditions by cadogan coupling^[3]. This mishmash of congeners, as well as their similar physical and chemical properties makes PCBs difficult compounds to analyse^[4]. Aliphatic hydrocarbons are main components of the sample ma-

trices, effective methods for PCBs separation from aliphatic hydrocarbons have been investigated keenly^[5-8]. To separate PCBs from aliphatic hydrocarbons, researchers have used partition between non-polar solvent and non-proton polar solvent, such as dimethyl sulfoxide^[9,10], acetonitrile^[11] and dimethylformamide^[12]. Solid phase extraction (SPE) system is also reported for pre-concentration of sample^[13-15]. Recently a new technique solid-phase microextraction (SPME) is developed for the extraction and concentration for PCBs^[16]. The analytical methods for PCBs are currently based on their separation by gas chromatography (GC) using capillary columns with specific detectors such as electron capture detector (ECD)^[17] and mass spectrometry (MS)^[18-20]. Waste mineral oil (fuel oil, used lubricating oils etc.) is a hazardous waste and transboundary movement of waste oil is not permitted, nevertheless the import of waste oils has been taking place in India. It has been found that waste oils containing hazardous contaminants (like PCBs, PAHs, heavy metals etc.) are often dumped in the countries which do not have sufficient monitoring mechanisms. PCBs are added to waste oils by intentional or accidental mixing. Because of their oily appearance and mineral oil miscibility, they are mixed with other waste oils. In many cases, PCBs owners deliberately mix PCBs with other waste oils in order to hide PCBs, thus saving expenses for the disposal of PCBs^[21]. This investigation was undertaken in order to establish a suitable solvent extraction method for low concentration of PCB congeners and their analysis by GC-MS with ion trap analyser in waste oil samples.

EXPERIMENTAL

Reagents

The solvents ethyl acetate, hexane and dimethyl sulfoxide (DMSO) were HPLC grade and sulphuric acid (98 %) was A. R. grade used in the present work. Silica gel (100–200 mesh, Sigma–Aldrich) activated at 200 °C for 6 hours and anhydrous sodium sulphate (A. R. grade) were used in the clean-up stage. Water was purified with a Milli-Q plus system (Millipore).

Standard solutions

The mixture of PCBs was purchased from

AccuStandard (M-680A). Phenanthrene-d10 and chrysene-d12 from AccuStandard (M-680-IS-10X) and pyrene-d10 from Sigma Aldrich were used as an internal standards and surrogate standard respectively. All the solutions were prepared in 1:1 ethyl acetate and hexane mixture. Solutions of 0.0156–12.50 mg kg⁻¹ were prepared from the stock solution for calibration of different congeners and 0.3 mg kg⁻¹ of internal standards were added to each.

Extraction procedure

Sulphuric acid treatment

Portion of about 5.0 g of waste oil sample was accurately weighed and transferred in to separating funnel. Then 10 ml mixture of sulphuric acid and water (1:1) was added cautiously. The solution was shaken thoroughly and discarded the aqueous layer. The same procedure was repeated two times. It may be necessary to wash the oily layer of sample (approximately 2–4 times) with 10 ml of water until the wash water is neutral to pH paper.

Solvent Extraction

The sample from sulphuric acid treatment was transferred in to a glass centrifuge tube and 1 ml of 2.5 mg kg⁻¹ of pyrene-d10 was added. The first extraction was carried out by 10 ml DMSO and water (95:5) then repeated the same with 8 ml and finally 5 ml after keeping the tubes into centrifuge machine (3500 rpm) for 10 minutes. Then 10 ml water was added in extraction portion. This was further extracted with 10 ml ethyl acetate and hexane (1:1) mixture, repeated the same with 8 ml and finally with 5 ml after keeping in centrifuge machine for 10 minutes. The extracted portion was reduced in rotary evaporator and made up in 5 ml after adding 1.5 µg of internal standards and finally injected 1 µL into GC.

Sample cleanup

A variety of substances in waste oil can be simultaneously extracted and cause interference in the determination of PCBs by GC-MS. Therefore the extraction was purified using silica gel column. The clean-up procedure was as follows: The concentrated extracts were applied to open glass column (0.45 m, 1 cm i.d.) filled with (from bottom to top) glass wool, silica gel (100–200 mesh) and anhydrous sodium sul-

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phate (2 cm). The extracts were eluted with a less polar solvent (hexane 30 ml) which is a good solvent to elute the non polar PCBs^[22] from silica column, reduced the volume in rotary evaporator and made up in 5 ml after adding 1.5 µg internal standards and finally injected 1 µL into GC.

Instrumental analysis of PCBs

The analysis of PCBs was carried out by an integrated system of gas chromatography, equipped with automatic injection system and coupled to a mass spectrometric system with quadruple ion trap analyser. Varian CP-3800 GC, Saturn-2200 mass spectrometer with auto injector CP-8410 was used for analysis. The separation of congeners was done in a 30 meter length, 0.25 mm internal diameter and 0.25 µm film thickness coated with 5% phenyl-95% methylpolysiloxane Varian VF-5MS column. Helium was used as the carrier gas at 9.6 psi pressure and 1 ml min⁻¹ flow. The injector was used at constant temperature and 280 °C. The initial oven temperature was 80 °C (4 min isothermal) to 180 °C (at 20 °C min⁻¹) to 250 °C (at 2 °C min⁻¹) to 280 °C (at 10 °C min⁻¹) isothermal for 4 minutes. The injection volume was 1 µL in split less mode. The temperature of ion trap, manifold and transference line was 220 °C, 50 °C and 280 °C respectively. The mass spectrometer was used in SIM mode under electron impact at 70 eV and scan time 1 second.

RESULT AND DISCUSSION

PCB congeners identified in GC-MS-SIM

In order to determine the PCB congeners present in the mixture of AccuStandard (M-680A) a chromatogram with the 2.50-12.50 mg kg⁻¹ concentration of PCBs and 0.3 mg kg⁻¹ internal standards spiked in PCBs free waste oil followed by optimized procedure was obtained (Figure 2). Using the NIST-2.0 library search and Varian Workstation-MS data review version 6.6 software, 11 compounds were identified in the mixture, 9 of them are PCBs another two are phenanthrene-d10 and chrysene-d12. Generally PCBs elute in GC in an increasing order of the number of chlorine atoms in the biphenyl molecule^[23]. This condition is fulfilled by the majority of the identified congeners. All calculations were done using quantitation ion abun-

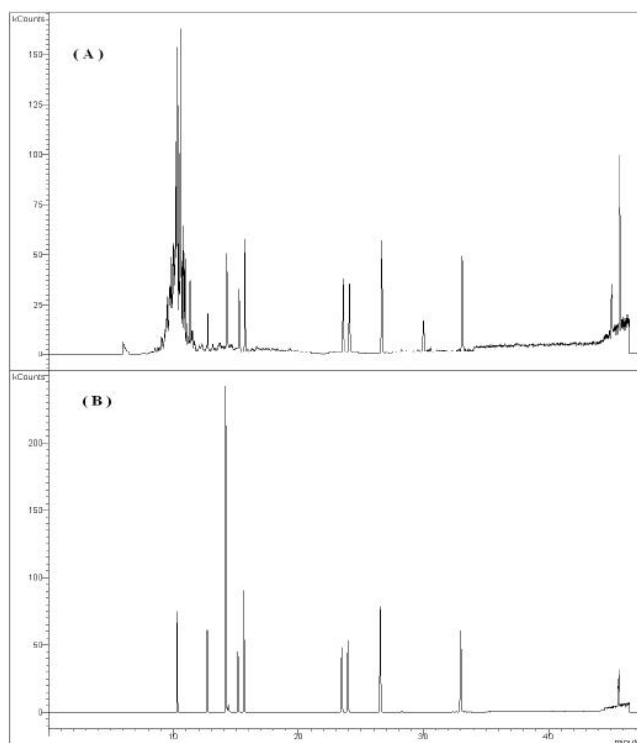


Figure 1 : TIC of spiked PCBs (1.0-5.0 mg kg⁻¹) waste oil sample without sulphuric acid treatment (A) and TIC of spiked PCBs (1.0-5.0 mg kg⁻¹) waste oil sample with sulphuric acid treatment (B).

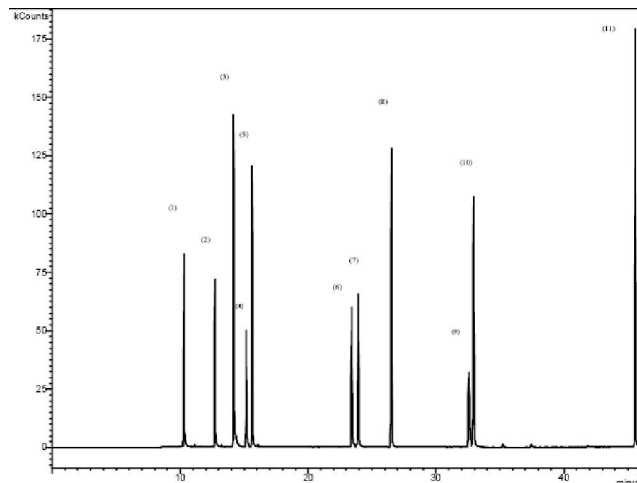


Figure 2 : TIC chromatogram of PCB congeners, M-680A from AccuStandard, 2.50-12.50 mg kg⁻¹ in ethyl acetate hexane mixture

Peaks: (1) PCB 1, (2) PCB 5, (3) phenanthrene-d10, (4) PCB 29, (5) PCB 50, (6) PCB 87, (7) PCB 154, (8) PCB 188 (9) chrysene-d12, (10) PCB 201 and (11) PCB 209.

dance. The confirmation ions were used to confirm the peak being integrated. TABLE 1 shows the structure of PCBs, IUPC identification number of PCBs, quantitation ion, confirmation ions, retention time (R.T.)

TABLE 1 : Retention time of PCBs, internal standards and surrogate standard

Structure	IUPAC no.	Quantitation ion	Confirmation ion	RT (min.)	Internal standard
2	1	188	152	10.28	Phenanthrene-d10
2,3	5	222	152	12.70	Phenanthrene-d10
2,4,5	29	256	186	15.16	Phenanthrene-d10
2,2',4,6	50	292	220	15.62	Phenanthrene-d10
2,2',3,4,5'	87	326	254	23.44	Phenanthrene-d10
2,2',4,4',5,6'	154	360	288	23.96	Phenanthrene-d10
2,2',3,4',5,6,6'	188	394	322	26.55	Chrysene-d12
2,2',3,3',4,5',6,6'	201	430	356	32.98	Chrysene-d12
2,2',3,3',4,4',5,5',6,6'	209	498	428	45.60	Chrysene-d12
Phenanthrene-d10	---	188	187	14.16	--
Chrysene-d12	---	240	236	32.58	--
Pyrene-d10	---	212	208	21.92	Phenanthrene-d10

at which the congeners eluted and internal standards used for different PCBs .

Sulphuric acid treatment

Comparing the chromatograms obtained without sulphuric acid treatment and with sulphuric acid treatment, a better baseline was observed from the sulphuric acid treatment (Figure 1). It was also found that sulphuric acid treatment gives better recovery of PCB congeners.

Quality control

The quality control of the method was evaluated with the following parameters; linearity, accuracy, limits of detection (LoDs), limits of quantification (LoQs), repeatability, recovery and reproducibility. The LoDs and LoQs were calculated from the following equation^[24].

$$\text{LoDs} = 3s / m \quad (1)$$

$$\text{LoQs} = 10s / m \quad (2)$$

Where s is the sample standard deviation for the 6 replicates analyses and m is the slope of calibration curve.

Linearity

In the present work, the linearity of the method was determined by injecting 1 μL of spiked blank matrix extracts. Linear calibration graphs were constructed by least squares regression of concentration versus peak area and height ratio (analyte / I.S.) of the calibration standards. The calibration graphs obtained for 0.0156-2.50 mg kg^{-1} for PCBs 1, 5 and 29, 0.0313-5.00 mg kg^{-1} for PCBs 50, 87 and 184, 0.0468-7.50 mg kg^{-1} for PCBs 188 and 201 and 0.0781-12.50 mg kg^{-1} for PCB 209 were linear over the concentration range examined. Correlation coefficients of all studied PCB congeners ranged from 0.9993 to 0.9999 for 7 point calibration (TABLE2).

Accuracy

Analysis of mixture of M-680A at different concentrations spiked in PCBs free waste oil followed by optimized procedure was performed to evaluate the accuracy of the GC-MS-SIM method. The concentration of PCBs was calculated from calibration curves and the accuracy of the results is expressed in terms of relative error (TABLE 2).

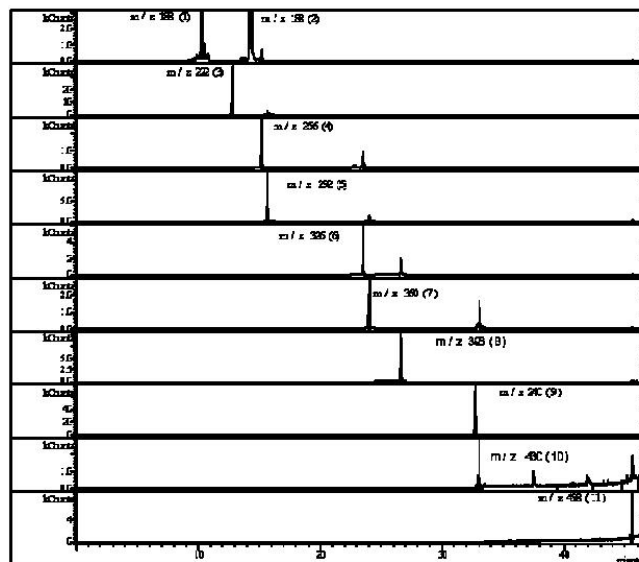


Figure 3 : SIM chromatograph of PCB congeners spiked in PCBs free waste oil sample

Peaks: (1) PCB 1, (2) phenanthrene-d10, (3) PCB 5 (4) PCB 29, (5) PCB 50, (6) PCB 87, (7) PCB 154, (8) PCB 188, (9) chrysene-d12, (10) PCB 201 and (11) PCB 209.

Limits of detection and limits of quantification

LoDs and LoQs values are specified in TABLE 2 were calculated through the definition based on the standard deviation of the signal of the blank injections following IUPAC recommendations^[25]. The limits calcu-

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lated from the equations 1 and 2 for PCBs which is spiked in PCBs free waste oil sample and followed by optimized procedure are LoDs 0.10-0.13 $\mu\text{g kg}^{-1}$ and LoQs 0.30-0.42 $\mu\text{g kg}^{-1}$.

Recovery study

Waste oil (PCBs free) was spiked with a known amount of congeners (1.0-5.0 mg kg^{-1}) along with 2.5 mg kg^{-1} of surrogate standard. The extraction procedure was followed, the extracts were subjected to GC-MS and the recoveries of each congeners and surrogate standard were calculated by reference to the calibration graphs. The TABLE 3 illustrates that recovery results which shows within the commonly accepted range 94.8-98.0 % recovery and 2.1-4.1 % RSD. Figure 3 shows example of SIM chromatogram for PCB con-

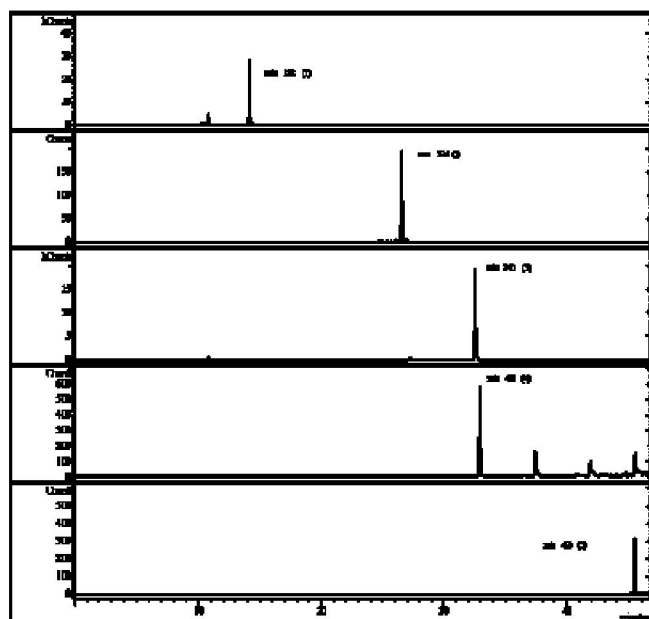


Figure 4 : SIM chromatogram of waste oil sample
Peaks: (1) phenanthrene-d10, (2) PCB 188 (3) chrysene-d12, (4) PCB 201 and (5) PCB 209.

TABLE 2 : Validation parameters of the PCB congeners

PCBs	Correlation coefficients	AccuStandard	Relative error (%)	LoDs ($\mu\text{g kg}^{-1}$)	LoQs ($\mu\text{g kg}^{-1}$)
		M-680A ($\mu\text{g kg}^{-1}$)			
1	0.9995	15.6	+0.961	0.13	0.42
5	0.9997	15.6	-0.641	0.13	0.42
29	0.9996	15.6	+0.320	0.13	0.42
50	0.9999	31.3	-0.638	0.10	0.32
87	0.9993	31.3	-0.319	0.10	0.32
154	0.9994	31.3	0.000	0.10	0.32
188	0.9997	46.8	-0.384	0.12	0.40
201	0.9996	46.8	+0.277	0.12	0.40
209	0.9994	78.1	-0.128	0.10	0.30

TABLE 3 : Recovery of spiked PCBs from waste oil

PCBs and surrogate	Amount of PCBs (mg kg^{-1})	% Recovery (silica gel)		% Recovery (sulphuric acid)	
		Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
1	1.0	89.5	8.2	94.8	4.1
5	1.0	90.1	5.6	95.0	3.9
29	1.0	91.4	5.2	96.8	3.5
50	2.0	87.9	6.8	96.0	3.0
87	2.0	90.2	3.2	95.0	4.0
154	2.0	90.2	5.9	97.0	3.4
188	3.0	89.9	8.0	96.5	3.2
201	3.0	84.0	9.0	95.0	3.8
209	5.0	85.0	2.2	98.0	2.1
Pyrene-d10	2.5	96.0	2.5	98.0	1.8

TABLE 4 : Reproducibility of PCBs

PCBs	PCBs spiked ($\mu\text{g kg}^{-1}$)	% RSD	R.T. (min.)	% RSD	Area counts	% RSD
			mean		mean	
1	15.6	5.8	10.28	0.047	17529	1.82
5	15.6	8.2	12.70	0.047	5092	1.65
29	15.6	5.9	15.16	0.017	4121	1.65
50	31.3	9.8	15.62	0.025	8005	1.75
87	31.3	5.8	23.44	0.025	6794	1.95
154	31.3	7.8	23.96	0.048	6772	1.95
188	46.8	2.5	26.55	0.048	7381	2.07
201	46.8	9.2	32.98	0.016	7421	2.05
209	78.1	4.5	45.60	0.016	15660	1.97

geners spiked waste oil sample.

Reproducibility

The reproducibility of the extraction procedure and Varian CP-3800 GC, Saturn-2200 mass spectrometer CP-8410 with VF-5MS column was studied for six replicate spiked samples containing 0.5-2.5 mg kg^{-1} of PCBs (TABLE 4). The RSD in area counts for total PCB was less than 3 % (two sets of six replicate injections). The RSD of extraction procedure and retention times were 2.5 to 10.5 % which is below the CLP maximum allowable RSD of 15 %.^[26]

APPLICATION OF THE METHOD TO REAL SAMPLES

The developed method was applied to the waste oil samples. According to the Indian EPA, Hazardous Wastes (Management, Handling and Transboundary Movement) rule 2008, the limit of PCBs in waste oil is less than 2 mg kg^{-1} . The average and standard deviation of individual PCB concentrations measured in waste

TABLE 5 : Mean concentration with SD of PCB congeners in waste oils samples (mg kg⁻¹)

PCBs	Sample 1 Mean±SD	Sample 2 Mean±SD	Sample 3 Mean±SD	Sample 4 Mean±SD	*Sample 5 Mean±SD	Sample 6 Mean±SD	*Sample 7 Mean±SD
1	ND	ND	ND	ND	ND	ND	3.20 ± 1.10
5	1.10 ± 0.77	1.20 ± 1.41	ND	0.30 ± 0.42	ND	ND	ND
29	ND	ND	ND	ND	ND	ND	ND
50	ND	0.30	ND	ND	ND	ND	ND
87	ND	ND	ND	ND	ND	ND	ND
154	ND	ND	ND	ND	ND	ND	ND
188	ND	ND	ND	ND	0.40	ND	ND
201	ND	ND	0.50 ± 0.39	ND	1.40 ± 0.80	0.60 ± 0.21	ND
209	ND	ND	ND	ND	4.40 ± 1.10	ND	ND

ND: not detected *Sample shows PCB congeners greater than the limit given in Indian EPA, Hazardous Wastes (Management, Handling and Transboundary Movement) rule 2008.

oil samples are presented in TABLE 5. Two samples were found PCBs greater than the limit given in EPA. Figure 4 shows SIM chromatogram of sample.

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