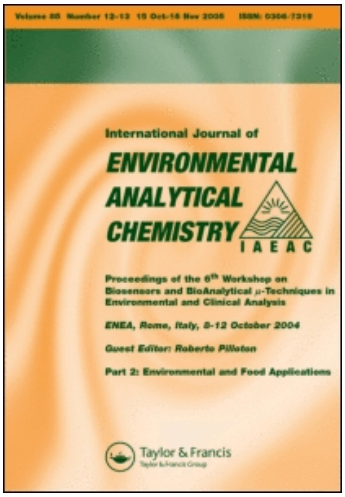

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The Effect of Temperature on GPC for the Separation of PCBs from Transformer Oil and Subsequent Analysis by GC-MSD

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THE EFFECT OF TEMPERATURE ON GPC FOR THE SEPARATION OF PCBs FROM TRANSFORMER OIL AND SUBSEQUENT ANALYSIS BY GC-MSD

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The analysis of PCBs often involves lengthy and expensive cleanup procedures to remove interferences associated with environmental sample matrices. Gel permeation chromatography (GPC) has proven to be a useful tool in removing many of these interferences from environmental samples, especially from difficult matrices such as oils, lipids and sediments. This paper describes the effect of temperature upon the GPC column in separating PCBs from transformer oil and its implication on GC-MS analysis.

KEY WORDS: PCBs, GPC, temperature, transformer oil, GC-MS.

INTRODUCTION

Gel permeation chromatography (GPC) has proven to be a useful analytical tool for separating compounds of interest from interfering compounds associated with a variety of matrices. GPC has been applied to the isolation of pesticide residues from oils and fats[1], composite fish samples[2], human adipose tissue[3] as well as liver and kidney samples from animal tissues[4]. GPC has also been applied to the isolation of polychlorinated biphenyls (PCBs) from environmental matrices including sediment extracts, marine biota, oily waste extracts[5,6] and mineral oils[7].

Automated GPC has been used in the determination of dioxins and furans from fat, motor oil and sediment extracts[8] as well as the clean up of environmental extracts for the analysis of semivolatiles, pesticides, polycyclic aromatic hydrocarbons and PCBs in waste oils[9].

The separation of compounds is based mainly upon molecular size, however, mechanisms including adsorption and partition as well as other effects may be involved[10,11]. The authors found no references on the study of temperature effects on the separation of PCB from transformer oil using GPC. Increasing the temperature of the column has reportedly had an effect on analytes in high speed and high performance GPC[12–14]. It has also been reported that column temperature affects the viscosity and density of the mobile phase[15]. This same study reported that column efficiency generally increased with increasing temperature due to a decrease in the viscosity of the mobile phase.

PCB analysis utilizing gas chromatography coupled to an electron capture detector has been the method of choice for the past two decades. The method boasts sensitivity and selectivity for patterned PCB mixtures such as Aroclors. The detector itself is not severely affected by the presence of diluted oil. This detection system however is not capable of discriminating PCBs from other halogenated compounds and may produce unsatisfactory results for non-patterned PCBs and complex aroclor mixtures.

The mass spectrometer (MS) has the ability to provide confirmation about the presence of a compound, by virtue of its spectral uniqueness. This method of analysis is also able to monitor the progress of sample cleanup by the addition of labelled surrogates. Our experience has shown however, that the detector is severely affected by the presence of as little as 0.2% oil (w/v). The interferences occur mainly in the mono through tetra-chlorinated biphenyl regions. Aroclor 1242 was used in this experiment since this PCB mixture contains many of these components.

The purpose of this study was to assess the affect of column temperature on the ability of GPC to separate PCBs from transformer oil for PCB analysis by GC-MS.

EXPERIMENTAL PROCEDURES

Gel permeation chromatography

Chromatographic Column: 600 mm × 25 mm I.D glass column with associated end caps and fittings. Stationary Phase: 70 g of Envirobeads S-X3 Select. Pump: FMI lab pump, model QSY, FMI pulse dampener, model PD-60-LF. Injector: 6 ml sample loop with associated plumbing and four way valve. Syringe: 10 ml with luerlok fitting. Circulating Water Bath (variable temperature: Lauda RM6 (–20°C to 120°C).

Gas chromatography

Gas Chromatography (GC) analysis was accomplished using a HP 5890 with a electron capture detector (ECD) and a flame ionization detector (FID). Two GC columns, DB-5, 30 m, 0.25 mm I.D., 0.25 microns film thickness, were connected in parallel from the injector to each detector. Splitless injection of 2 ul.

Mass spectroscopy

An HP5890 GC was interfaced to a mass selective detector (MSD) HP5970A. The column was a DB-5, 30 m, 0.25 mm I.D., 0.25 microns film thickness. 2 ul of sample was injected directly onto the column. The MSD was operated in the electron impact and selective ion monitoring (SIM) mode.

Reagents and standards

Solvents were distilled in glass grade and included; dichloromethane (DCM), hexane and isooctane. Voltesso transformer oil was obtained from Esso. PCB standards included Aroclor 1242, an isotopically labelled surrogate solution consisting of one congener from

each homologue from Cl–3 to Cl–10 (except for Cl–9) each at a concentration of 0.4 ng/ul and a surrogate recovery standard, PCB #101. Gases included ultra high purity He and N2.

Method

The GPC column was packed with 70 g of Envirobeads S-X3 Select to a height of 460 mm in a 600 mm glass column. The column was eluted with DCM at a flow of 7 cc/min.. The pressure on the pulse dampner (located between the pump and the column) was between 41 and 43 psi.. The GPC column temperature was maintained by wrapping the column with 0.5 in. I.D. tygon tubing and circulating water inside the tygon tubing via a variable-temperature circulating water bath. The solvent and GPC column sample lines (tygon tubing, 1.5 mm I.D., 0.3 mm O.D.) were placed into the reservoir of the water bath. Once the water bath had reached the desired temperature, the column was allowed to equilibriate for a minimum of two hours at a low flow of 1 to 2 ml/min.. The flow through the column was gradually increased to 7 ml/min..

The retention time of the transformer oil was determined by injecting 0.5 g onto the column and collecting at 1.5 min. intervals into preweighed aluminum weighing boats. This was repeated at the three different temperatures, 35°C, 20°C and –10°C. The oil profiles were determined gravimetrically after allowing the solvent to evaporate. The weight % of oil recovered for each weighing boat was plotted against intervals as shown in Figure 1.

The retention time window for PCBs determined by injecting 1 ug of Aroclor 1242 and collecting the eluent into round bottom flasks at 1.5 minute intervals between 9 and 30 minutes. The 1.5 minute interval fractions were then analysed by GC/ECD/FID. The PCB retention time window was determined to be between 25.5 and 29 minutes. Following the definition of the retention time window, triplicate analyses were performed at the three temperatures.

A stock solution of oil was prepared by diluting one gram of transformer oil with isooctane to a final volume of 25 ml. Two and one half millilitres of this solution were transferred to a 7 ml amber vial. One microgram of Aroclor 1242 was added before the solution was made up to a final volume of 5.0 ml. Approximately, 2 ml of concentrated H_2SO_4 was added to the vial and the vial was shaken for 2 minutes.

After shaking, the stock solution stood for 15 minutes allowing the separation of the two phases. Each sample was prepared by pipeting 500 ul of the stock solution into a 15 ml centrifuge tube. The surrogate solution was added just prior to loading the sample into the GPC sample loop. The sample and three rinses of the centrifuge tube were drawn into the loop and injected onto the column. Four fractions, 0–24 min., 24–26 min., 26–29 and 29–31 min., were collected for each sample. At 20°C and –10°C, PCBs were collected from 26–29 minutes, 0.5 minutes after the predetermined elution window to minimize the amount of oil collected in this fraction. At 35°C the PCB collection window was collected from 26–29, 26.15–29 and 26.5–29 minutes for the lst, 2nd and 3rd replicate respectively.

Following collection, the 24–26 and 26–29 min. fractions were rotovaped down, exchanged to hexane and rotovaped down to approximately 2 to 3 mls. The concentrated fractions were transferred along with 3 small hexane rinses of the flask to a 15 ml centrifuge tube calibrated at 0.5 ml. The concentrate plus hexane rinses were blown down below 450 ul using nitrogen. Fifty microlitres of carbon-13 labelled PCB recovery standard #101 was spiked into each fraction and the final volume of 500 ul was made up

with isooctane. The 500 ul was mixed thoroughly using a 9" glass pasteur pipette. The same pasteur pipette was then used to transfer the sample to a clean labelled 1.5 ml amber vial. Prior to GC-MS analysis an aliquot from the 24–26 and 26–29 min. fractions was screened by GC-ECD/FID to ensure the sample had a minimum amount of oil.

RESULTS AND DISCUSSION

Figure 1 displays the elution profile of 0.5 g of transformer oil at −10°C, 20°C and 35°C. The elution profiles at −10°C, and 20°C appear to be very similar having significant amounts of oil in the collection window 26–29 minutes. The profile at 35°C, however, appears to have shifted to the left indicating the oil at 35°C has eluted earlier. This earlier elution time resulted in a lower concentration of oil being present in the PCB collection window of 26–29 minutes. GPC column temperature does not appear to influence the retention times of PCBs eluting from the column. The column temperature, however, does influence the retention time of transformer oil. The separation of PCBs from the transformer oil increases with increased GPC column temperature. This is evident when comparing results between 35°C and −10°C for Figures 1 and 2.

There is some flexibility in the PCB collection window. The optimal collection window will depend upon the concentration of PCB being analysed and the degree of separation of PCBs from the transformer oil. Delaying the start of the PCB collection window to minimize the amount of oil present could result in lower PCB recoveries. This is demonstrated in the results from Table 1 where the later collection time of 26.5–29 minutes resulted in lower surrogate recoveries. It was also observed that surrogate recoveries tend to decrease with decreasing column temperature. This may be due to quantitation errors as result of the high background.

The GC-FID chromatograms presented in Figure 2 demonstrate the effect of different GPC column temperatures upon the elution of transformer oil in the PCB collection window. At 35°C, there has been a significant separation of transformer oil from the

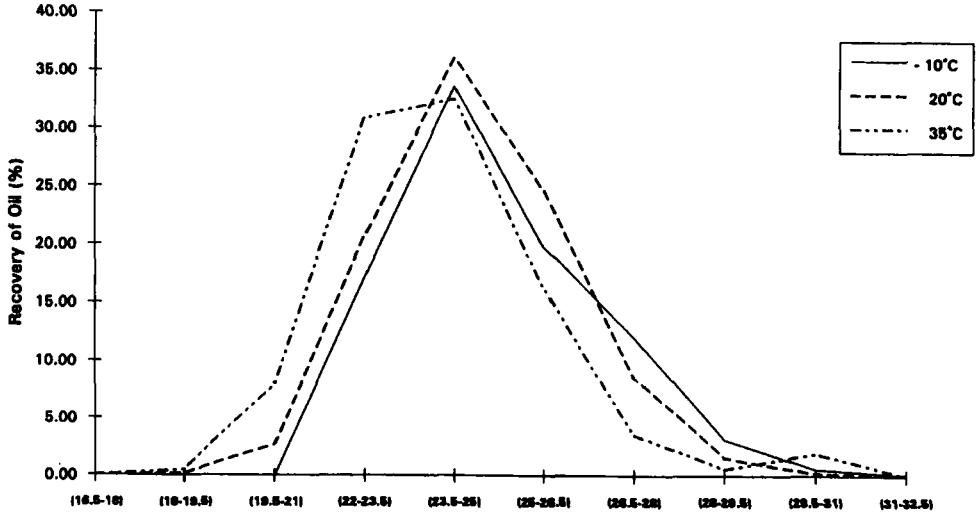

Figure 1 Gravimetric elution profile of oil at different temperatures.

Table 1 Carbon-13 labelled surrogate recoveries.

Project: gpc *Sample type: pcb*											
Sample ID *Collection time (min.)*	*std*	*35°C* *26–29*	*35°C* *26.15–29*	*35°C* *26.5–29*	*std*	*20°C* *26–29*	*20°C* *26–29*	*20°C* *26–29*	*–10°C* *26–29*	*–10°C* *26–29*	*–10°C* *26–29*
Recovery %											
*CL3-PCB	87	68	60	55	107	72	67	73	59	47	45
*CL4-PCB	89	73	71	68	109	77	76	76	63	75	72
*CL5-PCB	90	92	91	85	96	93	91	81	54	45	36
*CL6-PCB	109	103	104	89	103	102	106	100	67	47	49
*CL7-PCB	107	94	109	97	98	91	99	87	51	34	33
*CL8-PCB	86	71	77	67	79	89	83	88	78	76	72
*CL10-PCB	87	77	73	76	97	113	121	130	102	75	79

* represents carbon-13 labelled recovery standards

** std represents the standard run with samples during GC-MS analysis.

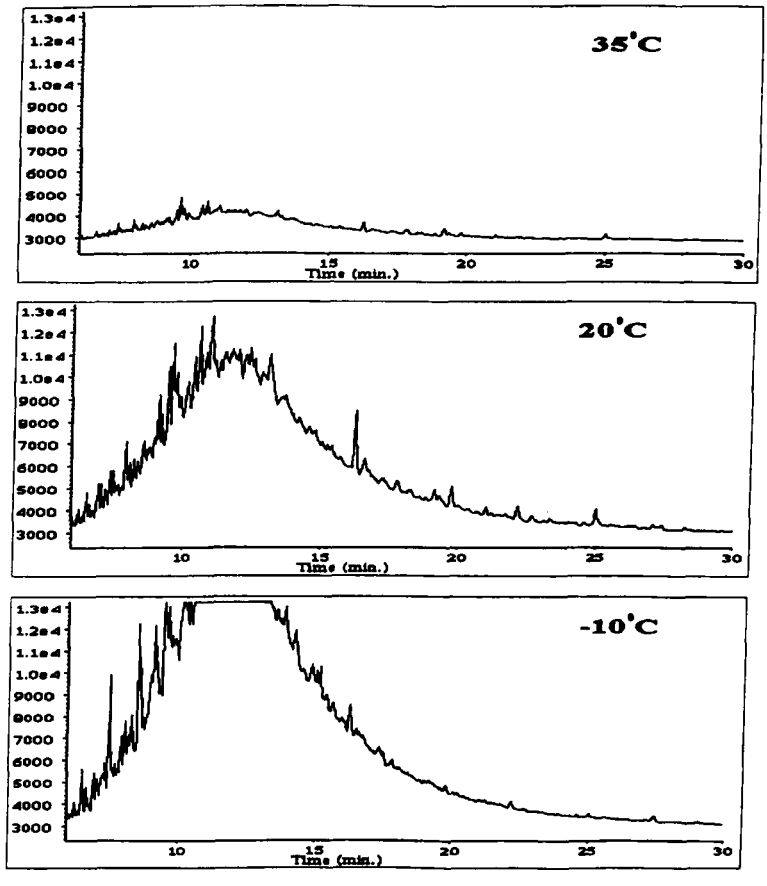

Figure 2 GC-FID chromatograms of oil in the PCB collection window, with GPC column temperature at 35°C, 25°C and –10°C.

PCB collection window. However, as the column temperature decreases to 20°C and −10°C, the degree of separation decreases. This supports the previously cited literature (15) that mobility within the column tends to increase with increasing temperature. It is anticipated that even greater column temperatures would further increase the mobility within the column thereby minimizing the elution of transformer oil within the PCB retention time window. The increased separation of oil from the PCB fraction results in significantly less interference in the GC-MS analysis.

The separation of PCBs from transformer oil at 35°C, 20°C and −10°C can be observed in the total ion chromatograms (TICs) in Figure 3. The TICs demonstrate that the separation of PCB from the transformer oil was not very effective as the temperature was lowered to −10°C compared with the degree of separation achieved at ambient

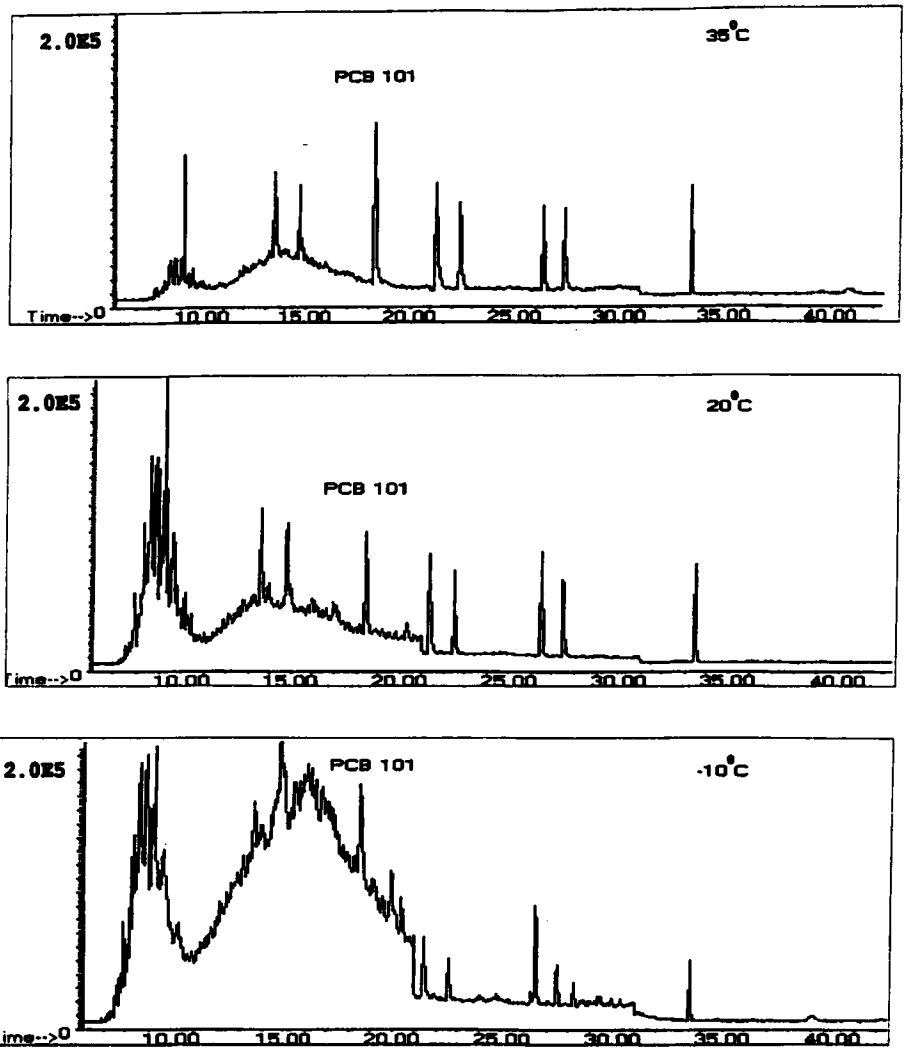

Figure 3 GC-MSD total ion chromatograms for surrogates collected at 35°C, 25°C and −10°C.

(20°C) and 35°C. At 35°C a significant decrease in the level of interferences associated with the transformer oil matrix is apparent. This was a result of increased separation of transformer oil from the PCB retention time window. The TICs demonstrate the region of interference associated with the transformer oil with respect to GC-MS quantitiation. The most affected retention times are between 11 and 21 minutes, which mainly includes the mono to tetra chlorobiphenyls.

Figure 4 includes the extracted ion chromatograms (EIC) for the tri and tetra chlorinated PCB surrogates from the respective TICs described above. These EICs further demonstrate the difficulty involved in GC-MS quantitation with the presence of oil in the extract. The increased column temperature has reduced the level of interference for the tri and tetra homologues allowing for more accurate GC-MS quantitation.

It is estimated that the method detection limit for Cl–3 and Cl–4 are approximately 5 ug/g, 2.5 ug/g and 1 ug/g per congenor at –10°C, 20°C and 35°C respectively. This difference in detection limit at the three different temperatures reflects the influence of the oil matrix upon the quantitation of PCBs by GC-MS.

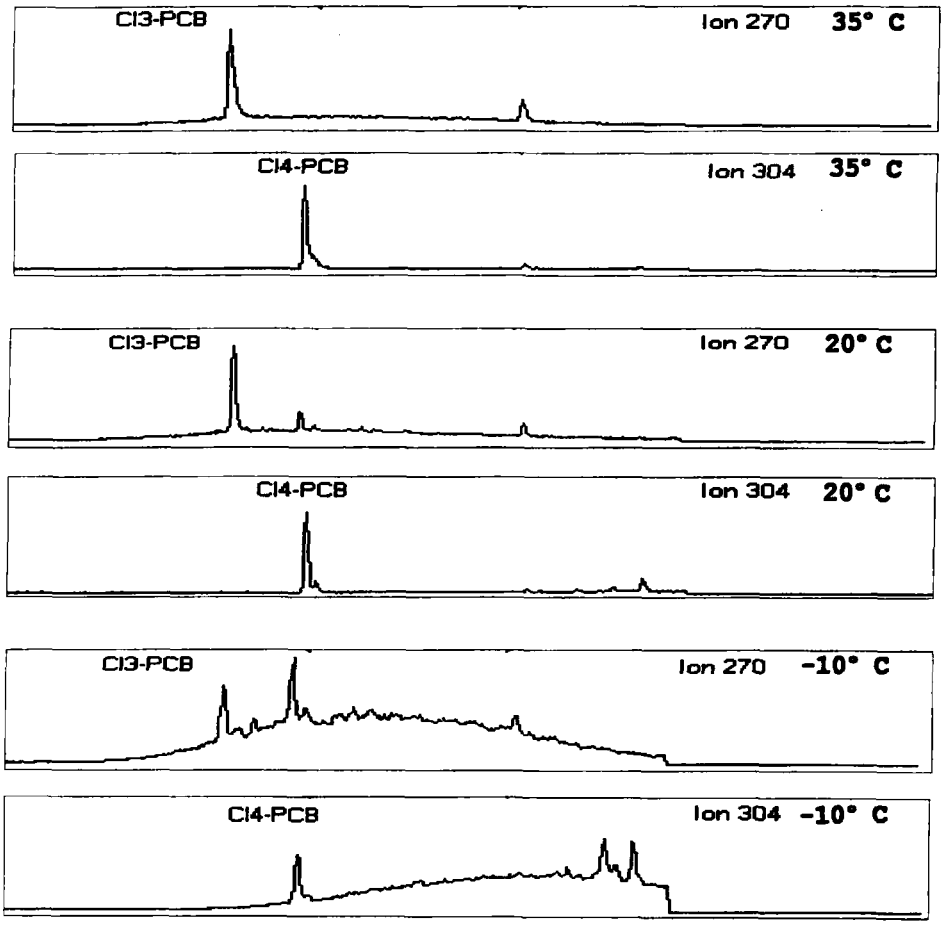

Figure 4 GC-MSD extracted ion chromatograms for Cl3 labelled PCB surrogates.

CONCLUSIONS

Results indicate differences in GPC column temperature can influence the ability to isolate PCBs from transformer oil for GC-MS quantitation. With increased column temperature, oil tends to elute from the column earlier resulting in better separation between the oil and PCBs. This in turn reduces the degree of interference associated with the transformer oil matrix allowing for more reliable quantitation of the mono to tetra homologue regions.

Further studies are necessary to determine the effects of even greater temperatures being applied to the GPC column with respect to the separation of PCBs from transformer oil for GC-MS quantitation.

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