Bull. Environ. Contam. Toxicol. (1995) 54:640–646
© 1995 Springer-Verlag New York Inc.

Environmental
Contamination
and Toxicology

Measurement of Total Polychlorinated Biphenyls (PCBs) in Catalytic Combustion Effluents Using a Simple HPLC Procedure

S. P. Perera,[1] T. M. Jefferies[2]

[1]School of Chemical Engineering, University of Bath,
Bath BA2 7AY, United Kingdom
[2]School of Pharmacy and Pharmacology, University of Bath,
Bath BA2 7AY, United Kingdom

Received: 27 April 1994/Accepted: 1 September 1994

Polychlorinated biphenyls (PCBs) are a class of 209 synthetic organic chemical compounds which possess excellent dielectric and fire resistant properties (Erickson 1986; Kolaczkowski *et al* 1990; Crittenden *et al* 1990). The production, use and toxicity of PCBs has been discussed in detail by various authors (Crittenden *et al* 1990; Kolaczkowski *et al* 1987; Hetzinger 1974). In recent years, increasing concern has been shown by the scientific community and by the public about the effectiveness of thermal incineration as an environmentally satisfactory means of destroying polychlorinated biphenyls. Therefore, a greater need for alternative, more efficient, low energy processes such as catalytic combustion, has been discussed (Kolaczkowski *et al* 1987). The principles, general developments and rationale behind the selection of catalytic combustion as a suitable process for commercial incinerators has been discussed elsewhere (Kolaczkowski *et al* 1992; Perera *et al* 1991). This paper forms part of the research programme (Kolaczkowski *et al* 1990; Crittenden *et al* 1987; Perera *et al* 1992) carried out to investigate the catalytic combustion of Aroclor 1242 in a packed bed reactor using chromia on an alumina support and other oxidation catalysts. It was essential for these studies to be able to determine the PCB destruction efficiencies of the catalytic processes examined.

The high efficiency of capillary GC columns permits the resolution of an Aroclor into a chromatogram consisting mainly of individual PCB congeners. Depending upon the sample, its concentration and the chromatographic conditions used, the chromatogram may typically contain 50-150 peaks. Quantification requires each peak to be identified and individual response factors assigned before the amount of each congener present may be calculated. Response factors vary between instruments, and the high cost of purchasing all the individual PCB standards required is prohibitive. A commonly adopted alternative method is to measure only the 6 or 7 individual PCB congeners that are available as a commercial mixture and attempt to convert the answer into a value for an Aroclor. This would not accurately measure the destruction efficiency of PCBs since it was not known whether the catalytic process would show any discrimination in efficiency according to the level of chlorination. In other studies, gas chromatography-mass spectrometry has been used to measure PCBs grouped into the sub-groups according to their level of chlorination. This method is based upon

---

Correspondence to: S. P. Perera

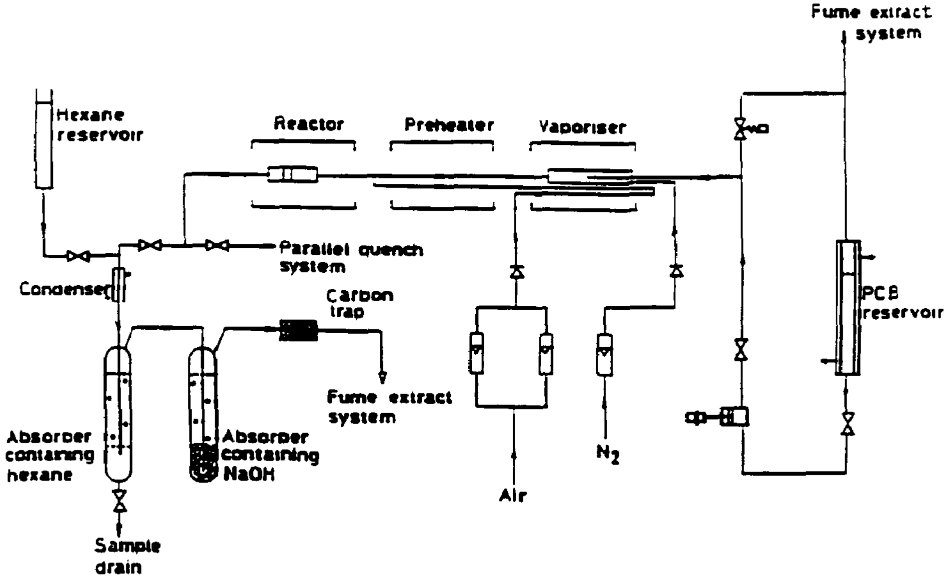

Figure 1. Schematic diagram of the experimental catalytic combustion apparatus

the procedure described by Erickson in 1988 and has been successfully used by us to measure PCB residues in milk (Seymour 1986). However, all the capillary GC methods are complex procedures that provide far more information than that required for the measurement of PCB destruction efficiency. Two approaches have been attempted to produce a simple, single-peak GC assay for total PCBs, and both have been examined by us experimentally. Perchlorination of all PCB congeners into decachlorobiphenyl has been studied because it greatly simplifies the analysis and produces a compound that is well removed from most interfering peaks. However, this technique has been found to be qualitatively and quantitavely unreliable (Duniner *et al* 1980). Dechlorination of all PCB congeners into biphenyl using nickel boride was proposed as an alternative (Dennis *et al* 1979) but we have found this method to be unsatisfactory and do not recommend its use (Seymour *et al* 1986). The procedure is not sufficiently robust or reliable and the reaction requires the use of expensive reagents in considerable quantities. When dealing with high concentrations of PCBs, the studies required a simple method to measure the total amount of Aroclor contained in the effluent collected after combustion. HPLC is routinely used as a simple clean-up step to separate PCBs and pesticides from milk fat (Seymour 1986), and it was considered that, with modification, this procedure could be developed into a quantitative analytical method. This paper describes this simple, quantitative HPLC method that measures all PCBs as a single peak.

MATERIALS AND METHODS

HPLC grade heptane, propan-2-ol and analytical grade hexane were obtained from Merck Ltd (Bristol, UK). Standard Aroclor 1242 samples were from

Alltech Associates Ltd (Carnforth, UK). PCB waste was supplied by Rechem International Ltd (Pontypool, UK).

The column used was a 150 x 7.5mm i.d. PLRP-S (10μm, 100nm pore diameter) column (Polymer Laboratories, Shropshire, UK). This was used with a LDC Analytical Constametric III pump and a Rheodyne injection valve fitted with a 20μl injection loop. Detection was achieved using a Pye Unicam LC-UV detector set at a wavelength of 254nm and AUFS of 1. Mobile phase flowrate was 1 ml/min. A Spectra-Physics, SP 4270 integrator was used for peak area determination.

A mobile phase composed of 35% v/v heptane in propan-2-ol was prepared and filtered. Then it was degassed for 15 minutes using helium gas. Individual samples of unreacted PCBs and products (reactor effluent) which were collected in hexane were filtered and diluted in mobile phase. The sample was diluted on a volume/volume basis so that the concentration of PCBs was within the linear calibration range of the HPLC. All glassware was thoroughly cleaned by distilled water, acetone and hexane. All glassware coming into contact with samples was rinsed with hexane prior to use.

The schematic diagram of the experimental apparatus is shown in Figure 1. Detailed description of the apparatus and the methods have already been presented (Kolaczkowski *et al* 1990; Perera *et al* 1992). In summary, the PCB fluid (Aroclor 1242) was stored in a 100ml graduated glass reservoir maintained at 30°C. The PCB was pumped through a vaporiser maintained at 400°C. The preheater was at 450°C. Then they were mixed with a preheated air stream and fed into the reactor. The products from the reactor were directed into one of two quench systems, where the unreacted PCBs and other liquid products were collected. An activated carbon trap (6cm x 2cm O.D.) was also incorporated into the apparatus in order to minimise escape of any uncondensed PCBs with trapping solvent.

RESULTS AND DISCUSSION

The large numbers of individual PCB congeners present in commercial PCB products such as the Aroclors makes the quantitative analysis of all these products a complex and challenging analytical problem. For the purpose of measuring the PCB destruction efficiency of various catalytic incineration processes, a complex analytical GC procedure was not required or justified. HPLC using silica-ODS materials is capable of resolving Aroclors into numerous peaks, for example Aroclor 1254 was resolved into about fifteen peaks using a μBondapak C_{18} column (Issaq *et al* 1984) with acetonitrile-water (60:40 v/v). Using 2μl volumes to inject 10μg Aroclor 1254, detection sensitivity was enhanced by monitoring at 205-210 nm compared with 254 nm. For the measurement of a single value for "Total PCBs" this approach also provided more information than was required and so an HPLC procedure using a polymeric column previously employed as a clean-up step (Seymour *et al* 1986) has been developed into a quantitative analytical procedure.

The polymeric poly(styrene-divinylbenzene) materials available as HPLC columns are hydrophobic, and are intended to be used with reversed phase conditions, *ie* water plus miscible organic solvents. They may also be used with non-aqueous solvent mixtures such as heptane and isopropanol to resolve fats from PCBs and pesticides (Seymour *et al* 1986). It is considered that the fats are excluded from the polymeric material and the PCBs and pesticides to have retention which is dependent upon the amount of heptane present in the mobile phase. PCBs and organochlorine pesticides are not soluble in isopropanol, and so their retention on the column may be increased by raising the percentage of isopropanol in the mobile phase. In this study the percentage of isopropanol was increased to 65% in order to increase PCB retention without unduly increasing peak width or beginning to separate the PCBs into groups, as occurs with C_{18} columns (Issaq *et al* 1984). Column temperature was maintained at 35°C to increase column efficiency and yield reproducible retention times.

Various polyaromatic hydrocarbons were then examined for their suitability as internal standards. Compounds were selected on the basis of the number of aromatic rings present, and included acridine (3), triphenylene (4), perylene (5) and coronene (6). Compared to Aroclor 1242 which had a retention time of 3.2 mins, retention times were 2.7, 7.0, 10.5 and 9.7 mins, respectively. All the compounds except triphenylene showed severe tailing under these conditions. Triphenylene gave symmetrical, although slightly broad, peaks with a suitable retention time, and so was tested as an internal standard (Figure 2). Figures 2(a), 2(b) and 2(c) show typical chromatograms of Aroclor 1242 (20mg/l), catalytic combustion effluent and waste samples of Aroclor 1242 (supplied by Rechem International Ltd), with triphenylene, respectively.

Although this LC method was developed to meet the needs of a research project incinerating only Aroclors, it was considered appropriate to examine the selectivity of the method towards some other organochlorinated compounds that commonly occur in industrial wastes. Compared to Aroclor 1242 with a retention time of 3.2 mins, the retention times of chlorobenzene, trichlorobenzene and trichloroethylene were found to be 2.1, 1.8 and 2.3 mins respectively (Figs 3a, 3b and 3c). Retention times for Aroclor 1254 and 1262 were 3.5 and 3.8 mins respectively. The conditions therefore do have some useful selectivity for PCB measurement as a single peak. Sensitivity of detection was also more than adequate for the calibration range selected, and was intentionally reduced by employing 254 nm (at 1.0 AUFS), rather than lower wavelengths. For Aroclor 1242, sensitivity could be increased by factors of 2.1, 4.0 and 5.7 using detection wavelengths of 230 nm, 220 nm or 210 nm respectively. This was not required since it would mean additional dilutions of the collected hexane samples. Additionally, the measurement of a single peak for all the PCB congeners increased the absorbence of the response. In this method, the calibration range was from 0.02 to 4μg on-column, whereas the study using C_{18} columns and detecting at 205-210 nm used 10μg on-column. The method described here is capable of being used at a x50 increase in sensitivity by changing the detection conditions to 210 nm at 0.1 AUFS, if required.

A 6-point calibration plot of PCBs was carried out using standard solutions of Aroclor 1242 in mobile phase (35% v/v heptane in iso-propanol) made up in the concentration range 1mg/l to 200mg/l. The standard peaks were accomplished by the injection of 20μl solutions into the column. The ratios of PCBs peak area(s)/internal standard area(s), were plotted against the

Aroclor 1242 concentrations (μg/ml) in order to construct a working standard curve. The equation for the regression line was found to be $y = 0.04x - 0.008$, with a correlation coefficient (r) of 0.999.

The precision was determined by replicate injections ($n = 6$) of four calibration solutions and the single peak of Aroclor 1242 measured. The precision (RSD, $n = 6$) for the measurement of Aroclor 1242 as a single peak at 15, 50, 100 and 150mg/l in mobile phase was found to be ± 3.7, ± 4.3, ± 3.0 and ± 2.8%, respectively. Omission of the internal standard also produced a linear calibration plot with a correlation coefficient of 0.998, but this assumes that the volume injected is highly reproducible, which is not always the case. For this reason the presence of an internal standard is preferred.

The PCB destruction efficiency was then determined for various flowrates of Aroclor 1242. The results (Table 1) show that as the flowrate of PCB increased the conversion and catalyst bed temperature also increased. Therefore the controlled experiments were performed using PCB flowrates below 0.35ml/min in order to maintain the catalyst bed temperature below 750°C. Further increases in PCB flowrates could result in temperature increases in the bed, which may be detrimental to the catalyst.

Table 1. 20% Cr_2O_3/Al_2O_3 2.2cm long, 5.0169g weight catalyst bed, air flow 6 l/min

PCB flowrate (ml/min)	catalyst bed temperature (°C)	% conversion of PCBs	RSD (n = 5)%
0.22	610	48.6	± 2.7
0.25	620	55.7	± 3.1
0.31	700	62.6	± 3.5
0.32	700	63.5	± 3.8
0.35	720	74.0	±2.1
0.4	900	99.2	±3.0

Overall, a simple and precise HPLC method has been developed which is suitable for the determination of total PCBs when present as an Aroclor mixture. Furthermore, this method may be applicable to other samples that require a single measurement of total PCBs. The method could also be used as a rapid screening procedure for routine samples of waste gases or other environmental samples. Those that produce positive results could then be examined by GC-MS for confirmation that the HPLC peak consisted of PCB congeners. A further use for the method could be as a clean-up step for GC-MS by collection of the PCB peak following a large volume injection. This would simplify the GC-MS analysis and protect the GC column from potential contamination by the injection of highly complex samples, which

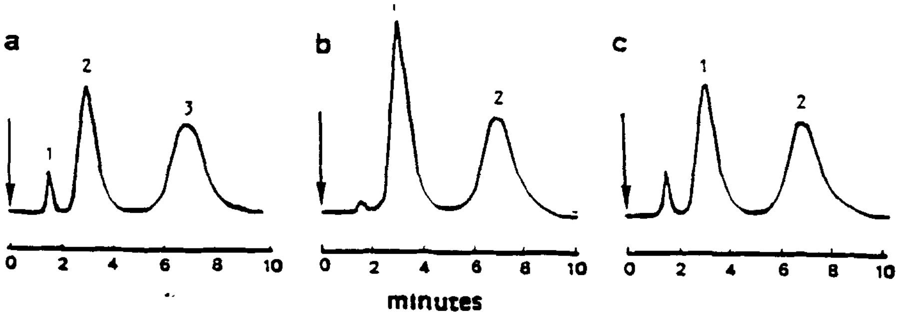

Figure 2. (a) Typical chromatogram of an Aroclor standard solution (20 μl of Aroclor 1242, mg/1) plus internal standard (Is), triphenylene Peaks 1 - hexane; 2 = Aroclor; 3 = Is; (b) Sample collected from catalytic combustion of Aroclor 1242 plus internal standard (Is) Peaks: 1 = catalytic combusiton products; 2 = Is; (c) Waste sample of PCBs (mainly Aroclor 1242) supplied by Rechem International Ltd) Peaks: 1 = waste sample of PCBs; 2 = Is

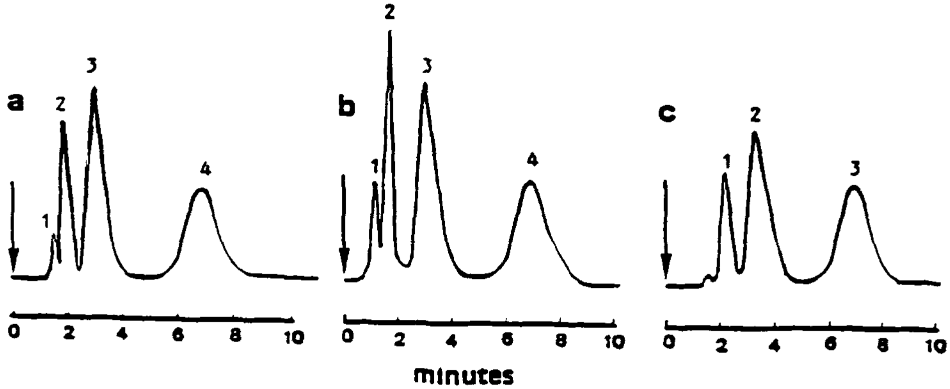

Figure 3. Typical chromatograms of Aroclor 1242 (20mg/l) plus some organochlorinated compounds that commonly occur in industrial wastes. For chromatographic conditions see Experimental section. (a) Peaks: 1 = hexane; 2 = chlorobenzene; 3 = Aroclor 1242; 4 = Is; (b) Peaks: 1 = hexane; 2 = trichloroethylene; 3 = Aroclor 1242; 4 = Is; (c) Peaks: 1 = trichlorobenzene; 2 = Aroclor 1242; 3 = Is

tends to reduce sensitivity.

Acknowledgments. The analytical studies in this paper were carried out to support the work of Professor B D Crittenden and Dr S T Kolaczkowski in the development of a catalytic combustor for destruction of PCBs, which was funded by the Science and Engineering Research Council. The assistance of Kevin Smith (School of Pharmacy and Pharmacology) in the development of the HPLC assay is gratefully acknowledged.

REFERENCES

Crittenden BD, Perera SP, Kolaczkowski ST (1990) Polychlorinated biphenyls, Environmental Protection Bulletin No 004:25-32

Dennis WH, Chang YH and Cooper WJ (1979) Catalytic dechlorination of organochlorine compounds v PCBs - Aroclor 1254, Bull Environ Contam Toxicol, 22:750-753

Duinker JC, Hillebrand MTJ, Palmork KH and Wilhelmson S (1980) An evaluation of existing methods for quantitation of PCBs in environmental samples and suggestions for an improved method based on individual components, Bull Environ Contam Toxicol, 25:956-964

Erickson MD (1986) Analytical Chemistry of PCBs, Butterworth, New York

Erickson MD, Stanley JS, Turman KJ, Going JE (1988) Environ Sci Technol 22:71-76

Hutzinger O, Safe S, Zitko V (1974) The Chemistry of PCBs. CRC Press, Cleveland

Issaq HJ, Klose J, Muschik, GM (1984) Separation of PCBs (Aroclor 1254) by high performance liquid chromatography. J Chromatogr 302:159-166

Kolaczkowski ST, Crittenden BD, Ullah U and Sanders N (1987) In: Kolaczkowski ST, Crittenden BD (eds), Management of hazardous and toxic wastes in the process industries. Elsevier Applied Science, London:489-502

Kolaczkowski ST, Beltran F, Crittenden BD and Jefferies TM (1990) Trans IChemE 68B:49-56

Kolaczkowski ST, Crittenden BD and Perera SP (1991) Catalytic combustion of PCBs, paper presented at IChemE, Applied Catalysis meeting, Bath, UK, 25 September:353-358

Kolaczkowski ST, Crittenden BD and Perera SP (1992) Catalytic combustion of PCBs - catalyst screening trials, Trans IChemE 70(B):27-38

Perera SP, Kolaczkowski ST and Crittenden BD (1992) Catalytic combustion of PCBs - catalyst screening trials, Trans IChemE 70(B):27-38

Seymour MP, Jefferies TM and Notarianni LJ (1986) Large-scale separation of lipids from organochlorine pesticides and polychlorinated biphenyls using a polymeric HPLC column, Analyst 111:1203-1205

Seymour MP, Jefferies TM and Notarianni LJ (1986) Limitations in the use of nickel bromide dechlorination for the analysis of PCBs, Bull Environmen Contam Toxicol, 37:199-206