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Recovery of PCBs by Liquid-Liquid Extraction Using Different Solvents and its Identification by GC-MS

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Abstract

The paper highlights the extraction technique for PCBs from environmental water samples, which is based on the choice of suitable solvent and methodology for better recovery. The method adopted for extraction of PCBs is liquid-Liquid extraction. In this technique water samples containing hydrophobic analyte like PCBs are subjected to organic solvents like dichloromethane (DCM), hexane, cyclohexane and the combination of DCM : hexane (1 : 1), DCM : diethyl ether (1 : 1). The efficiency of extraction process was monitored for these solvents and percentage recovery of PCBs was studied. It was confirmed that dichloromethane, hexane, DCM : hexane (1 : 1), cyclohexane, DCM : diethyl ether (85 : 15) showed the extraction efficiency of 69.8, 34.6, 24.8, 15.7 and 21.0% respectively of the PCB analytes from water samples. The extract was subjected to instrumental analysis by gas chromatograph mass spectrometer for its identification. Quantification was done after plotting the calibration curve.

Key words : PCB recovery, Liquid-liquid extraction, Different solvents, Identification.

Polychlorinated biphenyls (PCBs) possess a potential to bioaccumulate in living systems and are persistent in environment. Because of their impact on human health, particularly with regard to growth and development, PCBs become matter of concern (1). The major sources of PCBs in environment are due to the usage of dielectric fluids in capacitors, transformers, hydraulic fluids, fire retardant and plasticisers. The chemical and biological stability of PCBs are primarily responsible for PCB accumulation in environment (2). Tuning of analytical technique to detect each individual PCB congener to ppt level is important factor of analysis. Besides the identification upto trace levels in environment, measures are also taken to minimize the generation and distribution of PCBs in secondary sources (3). They are sparingly soluble in water and can be transported by rivers over land and into the sea. PCBs are highly lipophilic with a consequence 99%of its mass is found in soil. They are also found in many environmental metrices predominantly in water, mammals, and fishes. It is observed that the concentration level of PCBs in soil, sediment and food is in ppb and sub-parts per trillion in water (2). The concentration in all matrices generally span large range since everything from highly polluted to pristine environment has been monitored. The present paper highlights the extraction technique for PCBs from water samples, which is based on the choice of suitable solvent and methodology for better recovery. The method adopted in this paper is liquid-liquid extraction. In this technique, water samples containing hydrophobic analyte like PCBs are subjected to organic solvents like dichloromethane (DCM), hexane, cyclohexane, combination of DCM : hexane (1 : 1) , and DCM : diethyl ether (85 : 15).

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Methods

PCBs are non-polar compounds and show their affinity towards non-polar solvents like hexane, dichloromethane, cyclohexane that act on the principle of like dissolves like (4). The combination of solvents also plays an important role in extraction efficiency (5, 6). As analyte recovery is directly related to contact between extraction solvent and analyte (7, 8), the choice of extraction solvent and it composition was studied. In this experiment, 3, 3′, 4, 4′-tetrachloro biphenyl (3, 3′, 4, 4′-TCB) congener was used, as it is carcinogenic in nature and also environ-

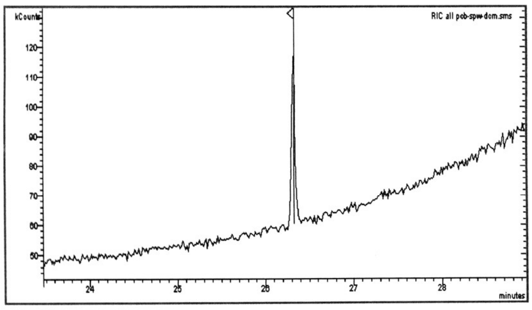

Figure 1. Reconstructed total ion chromatogram (RTIC) of spiked water sample extracted with dichlormethane showing 3, 3′, 4, 4′–TCB peak.

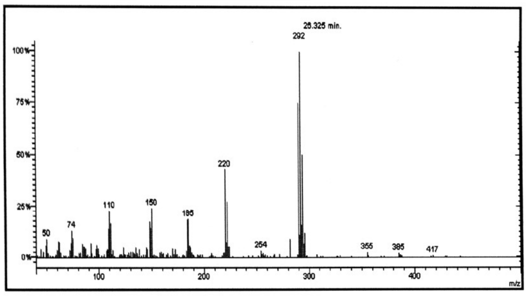

Figure 2. Fragmentogram of the peak 3, 3′, 4, 4′–TCB.

mental pollutant, hence the same PCB was used throughout the experiment. Working standard of 3, 3′, 4, 4′-TCB was prepared by diluting stock solution in cyclohexane, from this stock solution standards of different concentrations was prepared (0.09–0.9 ng/µl) for plotting the calibration curve. All solvents used for sample processing and analyses (dichloromethane, hexane, cyclohexane, diethyl ether) were Emerk, Suprasolv grade. The deionized water was used from MilliQ system (Millipore USA).

Sample Treatment

One hundred ml of deionized water was taken in 250 ml beaker and pH was adjusted >11 by adding NaOH ; 100µl of standard (90 µg/100 µl) was spiked, sonicated for 5 minutes and subjected to liquid-liquid extraction for recovery studies. The sample was taken in 500 ml separating funnel and 20 ml of methylene chloride was added. The mixture was shaken for 3–4 min with periodic venting to release excess pressure. Organic layer was separated from water phase and extract was collected in a 250 ml Erlenmeyer flask. Procedure was repeated thrice and total extract, 60 ml, thus collected was passed through a clean-up column having diameter 12 mm containing at least 10 cm anhydrous Na_2SO_4 at flow rate of 1 ml/min to remove the moisture content. The sample volume was reduced to 0.5 ml by flash evaporator.

Instrumentation

Analysis was carried out by Varian make GC-MS (Saturn 2200 MS with GC 3800CP) using DB-5 MS capillary column (length 30 m, 0.25 mm ID and 0.25-micron film). Injector temperature was set at 280 C and oven temperature was programmed from 60 C , hold for 2 minutes, heated to 300 C at 5 C/min. lon trap was heated to 240 C and acquisition mass range was from 40–450 Dalton (9). Other parameters of MS were set based on EPA method ; 525. 0.5 µl sample was injected into the GC and chromatogram was observed.

Results and Discussion

The calibration curve was plotted after injecting all the standards in triplicate having concentrations of 0.09, 0.225, 0.450, 0.720 and 0.900 ppm. With the help of software available with MS data station calibration curve plotted gave relative standard deviation (RSD) of 0.1921% and coefficient of detection 1. Figure 1 shows reconstructed total lon chromatogram (RTIC) of spiked water sample extracted with dichloromethane, having 3, 3′, 4, 4′–TCB Peak at retention time 26.3 minutes and peak area 13188.9. Figure 2 shows fragmentogram of the said peak, which was identified, by NIST 98 library as 3, 3′, 4, 4′–TCB. The sample injection was in triplicate to overcome the manual error of injection and the mean value was taken as concentration of the analyte. The injection volume was kept constant throughout the analysis. All samples were analyzed and after calculating the mean peak area the concentration of 3, 3′, 4, 4′–TCB in the sample was computed from the calibration curve. As the known concentration of 3, 3′, 4, 4′–TCB was added in the water sample the concentration after analysis gives directly percent recovery. This is also called the extraction efficiency of analyte with re-

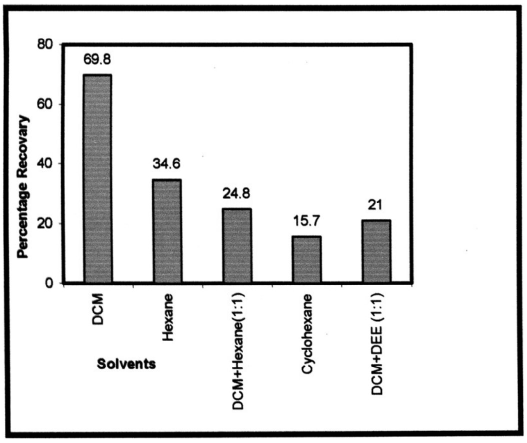

Figure 3. Percentage recoveries of PCBs in different solvents.

spect to that solvent. Figure 3 shows that dichloromethane has maximum extraction efficiency of 69.8% while cyclohexane has minimum extraction efficiency of 15.7%. The other solvents used are also having the less extraction efficiency. These data are useful while extracting the lower PCBs in water samples.

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