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Method standardization of selected PAHs, PCBs and surfactants in sewage water

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Abstract

Water is the vital component of any living entity. Due to increasing urbanisation and industrialisation its quality is deteriorating. Sewage water includes waste generated from toilet, baths, showers, sinks, dishwashers, toilets and washing machines etc. untreated sewage water contains different organic as well as inorganic impurities. Among organic impurities PAH, PCB and surfactant are major concerns due to growing industrialisation. There is a need for simple and reliable methods for monitoring of these contaminants. Compounds selected for study were PAH-Naphthalene, Phenanthrene and Benzo(a)anthracene; PCBs-PCB 52 and PCB 44; surfactants - SDS and SDBS. Method was standardised for analysis of these selected compounds using GC-MS (PAH and PCB) and LC-MS-MS (surfactants). Retention time of PAHs Naphthalene, Phenanthrene, Pyrene and Benzo(a)anthracene was 7.72, 15.34, 18.54 and 21.54 min and PCBs code 52 and 44 was 16.87 and 17.24 min. The retention time of SDS and SDBS was 4.51 and 4.96 min. Limit of instrument detection for surfactants were 0.1 µg/mL while for limit of instrument detection for PAH and PCB were 0.001 µg/mL. Estimated value of LOQ for PAH and PCB were 0.0025 µg/mL while for surfactant it was 0.01 µg/mL. Recovery experiments were conducted using 2 different solvents ethyl acetate and Hexane: DCM (85:15) Highest recovery was observed in Hexane: DCM (85:15) for PAH and PCB. Average recovery for PAH and PCB were 72.8 and 75%. For surfactants, ethyl acetate gave the highest recovery (average 86.2%). Among PAHs, highest recovery was recorded for benzo(a)anthracene (73.6-84.8%) and among PCBs, PCB 52 recorded the highest recovery (68.8-73.6). Among the two surfactants, highest recovery was recorded for SDBS. Method was found to be selective and accurate and can be used for sewage water.

Keywords: Standardization, PAHs, PCBs, surfactants, sewage

Introduction

"Domestic wastewater" is water that comes primarily from houses and does not generally include industrial or agricultural wastewater. Sewage includes domestic, municipal, or industrial liquid waste products disposed of, usually via a pipe or sewer or both. Municipal wastewater effluent is a concern because of its composition and the total volume discharged. It is estimated that about 38,000 million litres per day (MLD) of wastewater is generated in India in the urban centres having population more than 50,000 (housing more than 70% of urban population). It is estimated that the projected wastewater from urban centres may cross 1,00,000 MLD by 2050 and the rural India will also generate not less than 50,000 MLD in view of water supply designs for community supplies in rural areas.

Polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) are two typical persistent organic pollutants (POPs) known for their toxicity, bioaccumulation, persistence, and impact on both ecosystems. PAHs result from the incomplete combustion of fossil fuels, from both natural and anthropogenic sources, and exist in the environment as complex mixtures. PAHs containing up to four benzene rings are considered 'light', while those containing more than 4 benzene rings are considered 'heavy'. Substantial volumes of PAH are emitted to the atmosphere and inputs of PAHs to wastewater are mainly from atmospheric deposition on to paved surfaces and runoff (Blanchard *et al.*, 2004) [1]. PCB commercial mixtures are widely used for different industrial applications such as dielectric fluids in capacitors and transformers, plasticizers in paints, adhesives, etc. (Breivik *et al*, 2002) [2]. PAHs and PCBs have been reported in river water in India (Chakraborty *et al.*, 2014) [3], other countries (Guzzella *et al.* 2008) [4].

Durell and Lizotte (1998) [5] studied that the PCB congener concentrations in the waste water effluents were mostly below 1 ng/L with the highest being 10 ng/L in some samples.

Surfactants (surface-active agents) are a diverse group of chemicals consisting of a polar, water-soluble head group and a nonpolar hydrocarbon tail group, which is not as soluble in water. These are the major components of laundry detergents, household, and personal care products and account for over half of all use of surfactants (Schramm *et al.*, 2003) [6]. Surfactant contamination has also been reported in surface water bodies receiving the treated/untreated sewage water (Schramm *et al*., 2003) [6].

For monitoring these contaminants, there is a need for simple and reliable methods. Even though, methods are available in literature (Manoli *et al.,* 2000; Ravindra *et al.,* 2008) [7, 9], these need to be standardised to suit to our conditions. Therefore, the study was under taken to standardise GC-MS method for PAH and PCB analysis and LC-MS-MS method for surfactant analysis.

Material and Method

Analytical standards of PAHs, PCBs and Surfactants

Analytical grade PAHs *viz.* Naphthalene (purity ≥98.5%) Phenanthrene (purity ≥97.5%), Pyrene (purity98%), and Benzo (a) anthracene (purity 99.9%), PCBs *viz* PCB 52 (purity 99.5%) and PCB 44(purity 99.8%) and surfactants SDS (purity ≥98.5%) and SDBS (purity ≥95%) were purchased from Sigma-Aldrich.

Analysis of PAHs and PCBs by GC-MS

Preparation of standard solutions

Preparation of stock solution for individual PAHs and PCBs: 50 mg of each analytical grade PAHs were weighed, transferred separately into a 50 mL capacity volumetric flask and dissolved in ~5 mL HPLC grade acetonitrile. The volume was made up to the mark with additional acetonitrile. This gave a stock solution of 1000 µg/mL for each PAH.

Preparation of stock solution for PAHs and PCBs mixture: 5mL of each individual stock solution (1000 µg/mL) were taken in a 50mL volumetric flask and volume was made up to 50mL with HPLC grade acetonitrile to get 100 µg/mL PAHs mixture stock solution.

Working standard of PAHs and PCBs mixture: Working standard solution of 10, 1, 0.5, 0.25, 0.1, 0.01, 0.005 µg/mL concentration were prepared from the stock solution of mixture by serial dilution.

GC/MS Conditions, LOD and linearity range

GC/MS (Perkin Elmer CLARUS 500) equipped Phase ELITE-1 capillary column (30 m × 0.25mm × 0.25 µm) was used. The injector temperature was set at 270^{0}C. Helium was used as carrier gas with a flow rate of 2 mL/min. The oven programming was set empirically and standard solution of each individual PAH and PCB was injected separately. The retention time of each PAHs and PCBs was recorded and separation of peaks of different PAHs and PCBs was assessed. The oven temperature programming was modified to get proper separation. Suitability of standardized GC/MS condition for analysis was assessed by injecting the extract of the fortified sample. The lowest concentration of the compound with peak area more than three times the noise level was considered as limit of detection of the instrument. The linearity range was determined by plotting a graph of peak area vs concentration.

Extraction and clean up

Distilled water (250 mL) was fortified with 125µg (0.5 µg/mL level) and 62.5 µg (0.25 µg/mL level) of SDS and SDBS mixture. For extraction of organic contaminant from water, hexane: dichloromethane (85:15) mixture and ethyl acetate was tried for liquid-liquid extraction as per the procedure described under section 3.6.2 of Materials and Methods.

Method Recovery and LOQ

Distilled water (250 mL) was fortified with 0.1 µg (0.001 µg/mL level) and 1µg (0.002 µg/mL level) and 1.25 µg (0.004 µg/mL) of PAHs and PCBs and processed as per standardised procedure. The method of recovery was calculated from the amount recovered from water sample. For determination limit of quantification the cleaned extract was spiked with different concentration of PAHs and PCBs mixture and analysed. The lowest concentration giving peak area 10 times that of noise level was identified as estimate of LOQ. LOQ was determined by spiking the water sample at level equivalent to half, double and LOQ estimate and processed by standardised method for residue analysis.

Analysis of surfactants by LC-MS-MS

Preparation of standard solutions of surfactants

Preparation of stock solution of SDS and SDBS: 50 mg of each analytical grade SDS and SDBS were weighed, transferred separately into a 50 mL capacity volumetric flask and dissolved in 25 mL acetonitrile. The volume was made up to the mark with additional HPLC grade Millipore water. This gave a stock solution of 1000 µg/mL for each SDS and SDBS.

Preparation of stock solution for SDS and SDBS mixture: 5 mL of each individual stock solution (1000 µg/mL) were taken in a 50 mL volumetric flask and volume was made up with mixture of acetonitrile and water (1:1) to give 100 µg/mL SDS and SDBS mixture stock solution.

Working standard of SDS and SDBS mixture: Working standard solution of 20, 10, 5, 1, 0.5, 0.1, 0.25, µg/mL concentration were prepared from the stock solution of mixture by serial dilution**.**

Standardization of LC/MS/MS conditions, Linearity Range and LOD

LC/MS/MS (Shimadzu model 8030 triple quadrapole) equipped Eclipse plus C-18 (3 mm × 100 mm × 3.5 µm) and auto sampler with the volume of injection set to 10 µl was used. The solvent gradient was set empirically and standard solution of each individual surfactant was injected separately. The retention time of each surfactant was recorded and separation of peaks of different surfactants was assessed. Then the standard solutions of the surfactants mixture were injected in LC/MS.MS.

Standard solutions of mixture with concentration 50, 10, 5, 1, 0.5, 0.25, 0.01 µg/mL were injected in LC/MS/MS using standardized conditions and the detector response v/s concentration graph were drawn and linearity range and Limit of Detection (LOD) for each surfactant was calculated.

Standardization of extraction and clean-up methodology

Distilled water (250 mL) was fortified with 125 µg (0.5 µg/mL level) and 62.5 µg (0.25 µg/mL level) of SDS and

SDBS mixture. For extraction of organic contaminant from water, hexane: dichloromethane (85:15) mixture and ethyl acetate was tried for liquid-liquid extraction as per the procedure described under section 3.6.2 of Materials and Methods.

Method Recovery and LOQ

In order to measure the total method recovery, the fortified water samples (1L) was processed through the selected extraction and clean-up procedure and analysed for added SDS and SDBS and processed as per standardised procedure. The method of recovery was calculated from the amount recovered from water sample. For determination limit of quantification the cleaned extract was spiked with different concentration of surfactant mixture and analysed. The lowest concentration giving peak area 10 times that of noise level was identified as estimate of LOQ. LOQ was determined by spiking the water sample at level equivalent to half, double and LOQ estimate and processed by standardised method for residue analysis.

Calculations and Data analysis

After analysis with, based on the area of the peaks corresponding to each PAHs and PCBs the residue amount was calculated as follows:

$$\underset{(\mu g\ mL^{-1})}{\text{Concentration}} = \frac{\text{Peak area of sample x concentration of standard } (\mu g\ mL^{-1}) \text{ x Vol. of extract (ml)}}{\text{Peak Area of standard x Volume of sample processed (mL)}}$$

Results and discussion

Standardization of Conditions of GC/MS

GC–MS parameter for the analysis of PAHs and PCBs were standardised. The oven programming was initially set empirically and standard solution of each individual PAH and PCB was analysed. The retention time of each PAHs and PCBs was compared to assess separation of peaks of different PAHs and PCBs. The oven temperature programming was modified to get proper separation.

Under the standardised conditions, the retention time of PAHs naphthalene, phenanthrene, pyrene and Benzo(a)anthracene was 7.72, 15.34, 18.54 and 21.54 min and PCBs code 52 and 44 was 16.87 and 17.24 min (Figure 1).

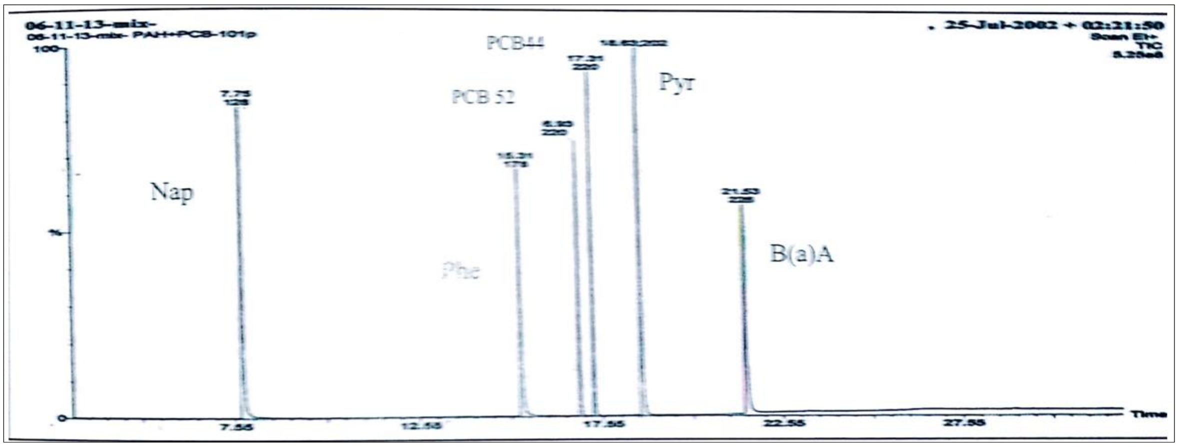

Fig 1: GC-MS chromatogram of PCBs and PAHs

The GC-MS response was found to be linear in the range from 0.001 to 0.50 µg/mL for PCBs and PAHs (Figure 2).

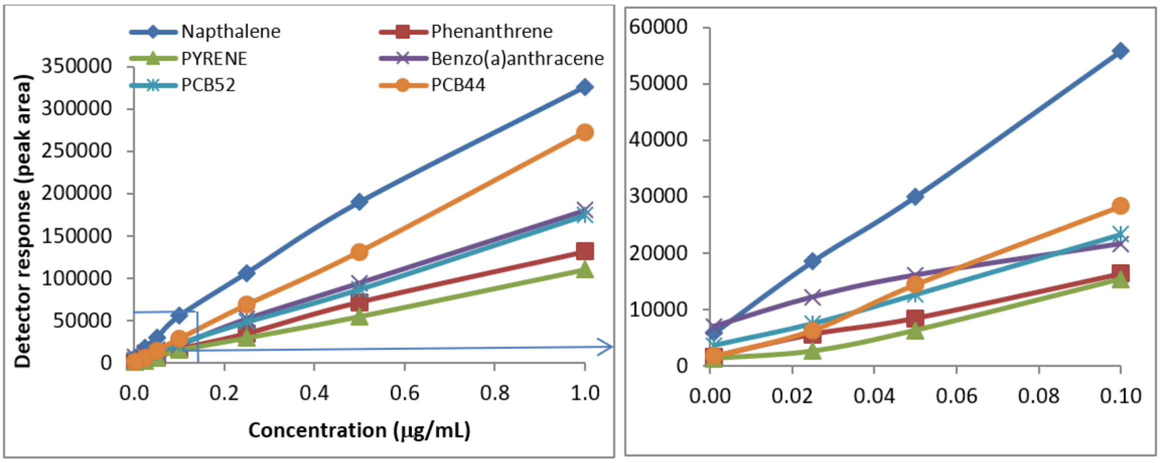

Fig 2: Linearity range of PCBs and PAHs in GC-MS analysis

The limit of detection as per the criteria 'peak area three times noise level' was found to be 0.001 µg/mL for all the compounds.

Under the standardised conditions, the retention time of SDS and SDBS was 4.51 and 4.96 min (Figure 3).

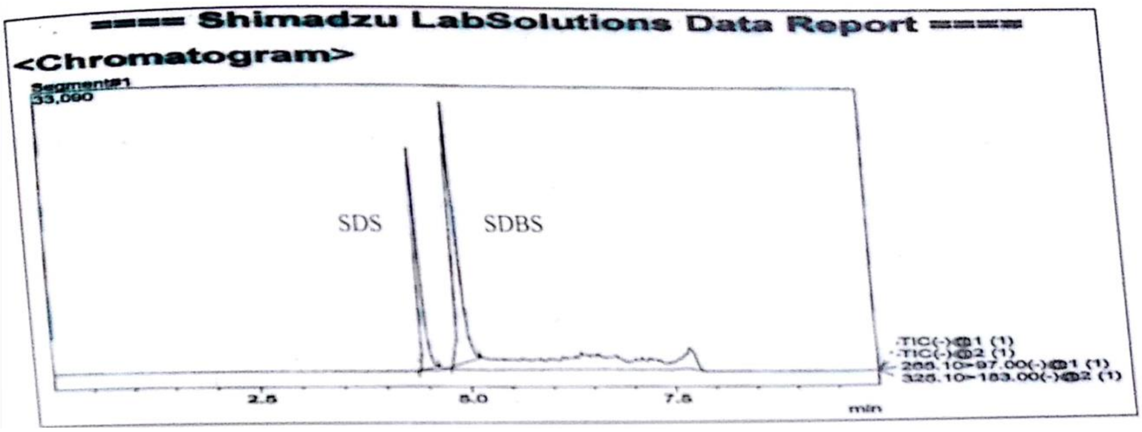

Fig 3: LC-MS-MS chromatogram of surfactants SDS and SDBS

Similarly, the LC-MS-MS response was found to be linear in the range from 0.4 to 20.0 µg/mL for both the surfactants.

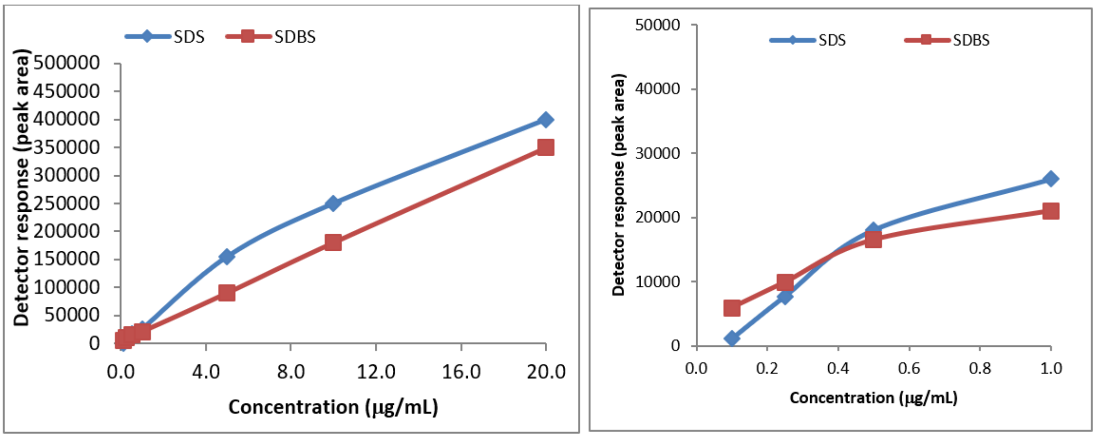

Fig 4: Linearity range of SDS and SDBS in LC-MS-MS analysis

The limit of detection was found to be 0.1 µg/mL for SDS and SDBS.

Standardization of extraction protocol: For extraction of PAHs, PCBs and surfactants, mixture of dichloromethane: hexane (85:15) and ethyl acetate were tried at 0.25 and 0.5 µg/mL fortification levels. The recovery data is presented in Table 4 and figure 5.

The recoveries of PAHs and PCBs varied from 46.4-84.8% at 025 µg/mL fortification level, 60.8-80.8% at 0.5 µg/mL fortification level. Among PAHs, highest recovery was recorded for benzo(a)anthracene (73.6-84.8%) and among PCBs, PCB 52 recorded the highest recovery (68.8-73.6). The recoveries of surfactants SDS and SDBS varied from 42.0-91.2% at 0.25 µg/mL fortification level and 68.0-88.0% at 0.5 µg/mL fortification level. Among the two surfactants, highest recovery was recorded for SDBS. Among the two solvents tried for extraction, dichloromethane: hexane (85:15) mixture gave higher recoveries for PAHs and PCBs and ethyl acetate for surfactants.

Since dichloromethane: hexane (85:15) mixture gave higher recoveries for PAHs and PCBs, it was selected for extraction of PAHs and PCBs for the sewage water in the experiment. Similarly ethyl acetate, which gave higher recoveries for surfactants, was selected for the sewage water in the experiment. GC-MS has been used for analysis of PAHs and PCBs by several researchers (Anyakora, 2005; Filipkowska, 2005; Hossam *et al*., 2009). DCM: Hexane mixture has been used for extraction of PAHs (Blanchard *et al*., 2001) [1] and PCBs (Berset and Holzer 1995) and ethyl acetate for extraction of surfactants (Petrovic *et al.*, 2001). For determination of Limit of quantification (LOQ), the recovery experiments were carried out at 0.0025, 0.005 and 0.01 µg/mL fortification levels using standardised protocol. The lowest concentration 0.0025 µg/mL was observed to give the response more than 10 times that of noise level and was considered as LOQ.

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