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Estimation of measurement uncertainty of polychlorinated biphenyls, polycyclic aromatic hydrocarbons and organochlorine pesticides in the atmosphere using gas chromatography–mass spectrometry and gas chromatography–electron capture detector

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ABSTRACT

Estimation of uncertainty of measurement is a crucial issue to achieve accurate measurement results. When the target has adverse environmental and health effects, accuracy of the results become more important. POPs are the pollutants that have toxic effects and unfortunately, there is a lack of information about uncertainty of the method for determining POPs in air samples. In this work, uncertainty calculations were carried out for PCBs, OCPs, and PAHs in air samples analyzed by using GC–MS and GC–ECD. The main dominant sources for combined uncertainty were calibration curve, recovery and repeatability. The relative uncertainties were found to be in the range of 23–52% for PCBs, 24–59% for OCPs and 23–90% for PAHs.

1. Introduction

Persistent organic compounds (POPs) are the most important class of organic pollutants that consist of three important groups which are polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs) and polycyclic aromatic hydrocarbons (PAHs). Because of their semi-volatility, POPs are transported at low concentrations over long distances in the atmosphere. POPs are characterized by low water solubility and high lipid solubility, resulting in their bioaccumulation in fatty tissues of living organisms. Therefore, both humans and environmental organisms are exposed to POPs around the world which has chronic and acute toxic effects.

PCBs are persistent organic pollutants that have been widely used in the environment that bioaccumulate and biomagnify in the food chain and resist biodegradation. Health hazard of PCBs were identified in a number of reports and due to their persistent nature in the environment they can easily transported one medium to another such as soil and food [1–5].

OCPs are bioaccumulative persistent, and have adverse health effects on human and animal health, causing nervous system damage, diseases of the immune system, reproductive and developmental disorders, and cancers [6–8]. Thus, it is still detected and reported in different compartments of the environment all over the world [9,10].

PAHs are generated during incomplete combustion of organic matter and released into the urban environment mainly through anthropogenic activities such as vehicle emissions, coal and fossil fuel combustion for power generation, petroleum refining, industrial processing, chemical manufacturing, oil spills and coal tars [11–13]. Several PAHs are known carcinogens and many studies have been performed about the health effects of PAHs on human also for environment [14–18].

Many analysis methods were developed to measure persistent organic pollutants in the environment. Analysis of PCBs, PAHs and OCPs in air samples currently performed by gas chromatography (GC) coupled to mass spectrometry (MS) and electron capture detector (ECD). Two main important steps, extraction and clean-up procedure in this study are optimized before quantification by chromatographic techniques [19].

Estimation of measurement uncertainties should be taken into consideration for the determination of POPs due to their adverse

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effects on humans and environment even at low concentrations. According to the international vocabulary of basic and general terms in metrology [20], the uncertainty of a measurement is defined as “a parameter associated with the result of a measurement that characterizes the dispersion of the values that could reasonably be attributed to the measurand”. The interest of calculating the measurement uncertainties is to show the data quality that is fundamentally important for laboratories, their clients and all institutions using these results for comparative purposes [21,22]. However, there is no published paper about a comprehensive evaluation of uncertainty associated to the determination of POPs in air samples. The aim of this study is to determine the uncertainty measurement calculation of the PCBs, OCPs and PAHs in the atmosphere using bottom-up approach.

2. Experimental

2.1. Target PAH, PCB and OCP compounds

The PCB (with IUPAC nomenclature), OCP and PAH compounds investigated in the atmosphere as follows: PCB-18, PCB-20, PCB-28, PCB-31, PCB-44, PCB-52, PCB-101, PCB-105, PCB-118, PCB-138, PCB-149, PCB-153, PCB-170, PCB-180, and PCB-194; Alpha-Hexachlorocyclohexane (Alpha-HCH), Beta-Hexachlorocyclohexane (Beta-HCH), Gamma-Hexachlorocyclohexane (Gamma-HCH) (Lindane), Delta-Hexachlorocyclohexane (Delta-HCH), Dieldrin, 4,4′-DDT, Heptachlor epoxide, Endosulfan I, 4,4′-DDE, Endrin, Endosulfan II, 4,4′-DDD, Endrin aldehyde, Endosulfan sulfate, Endrin ketone, and Methoxychlor; Acenaphtylene (Acy), Acenapthene (Ace), Fluorene (Flu), Anthracene (Ant), Phenanthrene (Phe), Fluoranthene (Flt), Pyrene (Pyr), Benzo(a)anthracene (BaA), Chrysene (Chr), Benzo(b)fluoranthene (BbF), Benzo(k)fluoranthene (BkF), Benzo(a)pyrene (BaP), Dibenzo[*a,h*]anthracene (DahA), Indeno[1,2,3-*c,d*]pyrene (Ind), Benzo[*g,h,i*]perylene (BghiP).

2.2. Sample preparation

In this study, high volume PUF sampler (Andersen PUF sampler, USA) was used with a flow of 0.225 $\mathrm{m}^3\,\mathrm{min}^{-1}$. After twenty-four hours, the samples were taken and wrapped with aluminum foil and stored in desiccators until the extraction time. Particle phase organics were collected by a 90-mm diameter glass fiber filter (GFF), while gaseous phase organics were captured by a two-piece polyurethane foam (PUF) cartridge. The samples were collected in two phases, during two summer months (June 25–August 23, 2007) and two winter months (December 13, 2007–February 12, 2008). A total of 120 samples were collected and analyzed in both seasons. Twelve field blank samples (6 for GFF, 6 for PUF) were collected to determine any contamination during sampling, sample handling, sample preparation, and analyses. Pre-baked GFF and pre-cleaned PUF cartridges were brought to the sampling location in sealed vessels and then placed into the sampler. They were kept in the sampler for several minutes prior to operation.

GFF and PUF samples were soxhlet-extracted with a mixture of dichloromethane (DCM) and petroleum ether (PE) (1:4) with volumes of 150 mL and 650 mL, respectively, for 24 h, at 4 cycles per hour. The volume of the extracts was reduced to 10 mL by rotary evaporator at 500 mbar and 40 °C. They were transferred to 15 mL vials by washing the walls of the balloons with solvent mixture (DCM:PE, 1:4) several times for further volume reduction to 1 mL under a gentle stream of nitrogen. Extracts were transferred to aluminum oxide–florisil columns for cleanup and fractionation of the analytes.

The adsorption column was 10 cm long and 0.5 cm width (diameter), and prepared by placing glass wool in the tip of the column to support sorbent material. Aluminum oxide, florisil, and sodium sulfate (1 g each) were put in to the column. The sodium sulfate was used to reduce water and moisture content in the samples on the top of the column. The analytical procedure after the extraction procedure is illustrated in Fig. 1.

2.3. Chemicals and materials

All solvents and reagents used in the study were of chromatographic grade. PCB congener standard (100 $\mu\mathrm{g\,mL}^{-1}$), internal standard (PCB-30 and PCB-204, 100 $\mu\mathrm{g\,mL}^{-1}$), and surrogate standard (PCB-14, PCB-65, PCB-166, 100 $\mu\mathrm{g\,mL}^{-1}$) were purchased from Absolute Standards (USA). OCP standard solution (2000 $\mu\mathrm{g\,mL}^{-1}$) was obtained from Dr. Ehrenstorfer (Germany). OCP internal standard (Pentachloronitrobenzene, 100 $\mu\mathrm{g\,mL}^{-1}$) and OCP surrogate solution (2,4,5,6-Tetrachloro-m-xylene and Dibutyl chlorendate, 2000 $\mu\mathrm{g\,mL}^{-1}$) were obtained from Absolute Standards (USA) and Fisher Scientific (UK), respectively. PAH standards (PM 610, 100 $\mu\mathrm{g\,mL}^{-1}$) were purchased from AccuStandards (USA). PAH surrogate solution (Acenaphthene-d10, Crysene-d12, Perylene-d12, Phenanthrene-d10, 1000 $\mu\mathrm{g\,mL}^{-1}$) was from Ultra Scientific (USA).

Sodium sulfate, florisil (0.150–0.250 mm) and neutral aluminum oxide (0.063–0.2 mm) were purchased from Merck Company (USA). The granulated sodium sulfate was anhydrous and of 99% purity. Glass microfiber filters (90 mm dia., pore size: 2.7 μm) were from Whatman Company (USA). All of the samples were spiked with surrogate standards prior to their extraction. Prior to extraction, 20 μL of 32 $\mu\mathrm{g\,mL}^{-1}$ deuterated PAH mixture, 40 $\mu\mathrm{g\,mL}^{-1}$ OCP surrogates, and 50 $\mu\mathrm{g\,mL}^{-1}$ PCB surrogates were added to the samples in order to determine the recovery efficiencies for checking the internal quality control.

Calibration standards were prepared from the main stock standards with appropriate dilutions with *n*-hexane. The calibration curve with intercept, the coefficient of determination (r^2), residual standard deviation (S) and slope (B_1) data were reported in Table 1. All of the stock, intermediate and standard solutions were stored in the refrigerator.

The standard solutions were prepared for the PCBs, OCPs and PAHs at five points. For PCBs calibration, 5, 10, 25, 50, and 100 ppb standard solutions were used. PCB-30 and PCB-204 were used as internal standards. PCB-30 as an internal standard was used for the calculation of PCB-18, PCB-20, PCB-28, PCB-31, PCB-44, PCB-52, PCB-101, PCB-105 and PCB-118. The rest of the PCBs were calculated by using PCB-204 responses. The calibration points were 0.01, 0.05, 0.1, 0.2, and 0.5 ppm for OCPs. Pentachloronitrobenzene was used as an internal standard for OCPs and 20 μL from 1 ppm added into standard solutions and samples. The OCPs were analyzed with GC–ECD. The internal standard calibrations were performed for both PCBs and OCPs, however external calibration was used for PAHs since internal standards were not available in our laboratory for PAHs. GC–MS was calibrated with for standard mixtures of PAHs using the concentrations of 0.1, 0.25, 0.5, 1 and 2 ppm.

2.4. Instrumentation and applied methods

A Hewlett Packard (HP) 6890N series gas chromatograph equipped with the electron capture detector (Agilent, USA) was utilized for analysis of the OCPs. A 60 m, 0.25 mm id., 0.25 μm film thickness, cross linked 5% phenyl methyl siloxane, HP 1MS, capillary column (Agilent Tech.) and 15 mCi of nickel 63 type ECD detector was used for separation and detection of OCPs.

A HP 6890N series gas chromatograph (Agilent, USA) coupled with HP 5973 mass spectrometer (Agilent, USA) was used for the