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An innovative ultrasound assisted extraction micro-scale cell combined with gas chromatography/mass spectrometry in negative chemical ionization to determine persistent organic pollutants in air particulate matter

E. Beristain-Montiel, R. Villalobos-Pietrini, G.E. Arias-Loaiza, S.L. Gómez-Arroyo, O. Amador-Muñoz*

Centro de Ciencias de la Atmósfera, Universidad Nacional Autónoma de México, Circuito exterior, 04510, México City, Distrito Federal, Mexico

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ABSTRACT

New clean technologies are needed to determine concentration of organic pollutants without generating more pollution. A method to extract Persistent Organic Pollutants (POPs) from airborne particulate matter was developed using a novel technology recently patented called ultrasound assisted extraction micro-scale cell (UAE-MSC). This technology extracts, filters, collects the sample, and evaporates the solvent, on-line. No sample transfer is needed. The cell minimizes sample manipulation, solvent consumption, waste generation, time, and energy; fulfilling most of the analytical green chemistry protocol. The methodology was optimized applying a centred 2^3 factorial experimental design. Optimum conditions were used to validate and determine concentration of 16 organochlorine pesticides (OCls) and 6 polybrominated diphenyl ethers (PBDEs). The best conditions achieved were 2 extractions with 5 mL (each) of dichloromethane over 5 min (each) at 60 °C and 80% ultrasound potency. POPs were determined by gas chromatography/mass spectrometry in negative chemical ionization (GC/MS-NCI). Analytical method validation was carried out on airborne particles spiked with POPs at seven concentration levels between 0.5 and 26.9 pg m^{-3}. This procedure was done by triplicate (N = 21). Recovery, ranged between 65.5 ± 2.3% and 107.5 ± 3.0% for OCls and between 79.1 ± 6.5% and 105.2 ± 3.8% for PBDEs. Linearity (r^2) was ≥0.94 for all compounds. Method detection limits, ranged from 0.5 to 2.7 pg m^{-3}, while limits of quantification (LOQ), ranged from 1.7 to 9.0 pg m^{-3}. A Bias from −18.6% to 9% for PBDEs was observed in the Standard Reference Material (SRM) 2787. SRM 2787 did not contain OCls. OCls recoveries were equivalent by UAE-MSC and Soxhlet methods UAE-MSC optimized extraction conditions reduced 30 times less solvent and decreased the extraction time from several hours to ten minutes, respect to Soxhlet. UAE-MSC was applied to 15 samples of particles less than 2.5 μm ($PM_{2.5}$) from three seasons (warm dry, rainy, and cold dry) collected in five sites around Mexico City. OCls (4,4′-DDE and endrin aldehyde) concentrations ranged from <LOQ to 12.6 pg m^{-3}, while PBDEs levels were below the quantification limit, although BDE-99 was detected in all samples. UAE-MSC is a novel technology to determine organic compounds present in trace concentrations in particulate matter. This technology can be extended to extract organic compounds in different solid matrices to minimize time extraction and solvent consumption.

1. Introduction

Persistent Organic Pollutants (POPs) are a group of synthetic organic compounds that are highly toxic, persistent and globally distributed in the environment. POPs are soluble in adipose tissue. They can be bioaccumulated and biomagnified in living organisms across the food chain [1]. Some of the effects afforded by POP exposure include diabetes, thyroid disruption, hormonal diseases, reproductive problems and even cancer [2]. The Stockholm Convention is a global effort to regulate and eliminate POPs to decrease the damage to human health and to the environment. POPs include organochlorine pesticides (OCls), industrial chemical substances like polychlorinated biphenyls (PCBs), polybrominated

* Corresponding author.
E-mail address: oam@atmosfera.unam.mx (O. Amador-Muñoz).

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biphenyl ethers (PBDEs) and oxidation products like polyhalogenated dibenzo dioxins and furans (PCDDs/Fs).

In October 2013, the International Agency for Research on Cancer as part of the World Health Organization classified to outdoor air pollution as carcinogenic to humans (Group 1). Particulate matter is one of the major constituents of air pollution, and was also classified as carcinogenic to humans (Group 1) [3]. The chemical composition of particulate matter is largely responsible for the adverse effects on human health [4,5]. Several studies have identified POPs in particulate matter [6,7].

Because POP concentrations are typically in the pg m^{-3} range, efficient and reproducible analytical methodologies are needed to guarantee their adequate detection and quantification. Soxhlet extraction has been the conventional technique to recover POPs from aerosol [8]. However, high amounts of extraction solvents (>150 mL) and long extraction times (12–72 h) are usually required for this technique. Instead, more environment friendly techniques have been developed to extract POPs from aerosol. These include Pressurized Liquid Extraction (PLE) [6], Ultrasonic Assisted Extraction (UAE) [9], Microwave Extraction (MAE) [10] and Supercritical Fluid Extraction (SFE) [11], which use small solvent volumes, and Solid Phase Microextraction (SPME) [12] which do not require the use of organic solvents.

Green Chemistry is a field focused at the molecular level on achieving sustainability in an integrated system, and is guided by twelve principles [13]. It is defined as the "design of chemical products and processes to reduce or eliminate the use and generation of hazardous substances". Green Analytical Chemistry (GAC) has emerged as an extension of Green Chemistry to change the use of existing analytical methodologies by favourable environmental methodologies [14]. The main objectives of GAC are to measure chemicals without generating waste, the use of smaller amounts of harmful solvents and reagents, less energy consumption and produce an overall high cost benefit. The miniaturization of the chemical analysis equipment [15] or micro-scale technology is a technique which fulfills these objectives. The term "'micro total analysis system"' refers to reducing the size of the analytical systems [16]. Miniaturization is focused on decreasing costs, the consumption of reagents, the analysis time and sample volumes [17]. The risk of accidents and the exposure to toxic and hazardous waste generation is also reduced. The micro-scale technology can be implemented in analytical procedures with no loss of quality in the analysis by using conventional analytical methodologies.

In this study, we develop a methodology to determine organochlorine pesticides (OCPs) and polybrominated biphenyl ethers (PBDEs) in airborne particulate matter ≤2.5 μm ($PM_{2.5}$). The methodology uses a novel microscale technology design which was recently patented [18–20] to extract, filter, collect the sample and evaporate the solvent excess on-line. This technology is more environmentally friendly than traditional analytical chemistry since minimize the sample manipulation, organic solvent consumption, waste generation, energy and time extraction, fulfilling most of the principles adopted by the GAC [14].

2. Experimental

2.1. Chemicals

Organochlorine pesticides (OCls) mix (purity, 97.5–99.5%): 4,4′-DDD; 4,4′-DDE; 4,4′-DDT; endosulfan I; Aldrin; endosulfan II; α-HCH; β-HCH; γ-HCH; δ-HCH; dieldrin; endosulfan sulfate; endrin; endrin aldehyde; heptachlor and heptachlor epoxide, were purchased from Chem Service (West Chester PA, USA). Polybrominated biphenyl ethers (PBDEs): 2,2′,4,4′-tetraBDE (BDE-47); 2,2′,4,4′,5-pentaBDE (BDE-99); 2,2′,4,4′,6-pentaBDE (BDE-100), 2,2′,4,4′,5,5′-hexaBDE (BDE-153); 2,2′,4,4′,5,6′-hexaBDE (BDE-154) and decaBDE (BDE-209) were purchased from Chiron, AS (purity 99.8%, Chiron, Norway). Decaclorobiphenyl (purity 99.3%), 4,4′-dibromooctafluorobiphenyl (purity 99.8%) and 4,4′-dibromobiphenyl (purity 99.8%), used as internal standards, were acquired from Chem Service (ChemService, USA). Honeywell-Burdick & Jackson (Muskegon MI, USA) supplied acetone, *n*-hexane and dichloromethane (HPLC grade).

2.2. Ultrasound assisted extraction micro-scale cell (UAE-MSC)

Ultrasound-assisted extraction (UAE) is a technique that is greener than more classical techniques that use large amounts of solvents and long operation times [21]. Cavitation increases analyte solubility and solvent diffusivity inside the matrix. In this study, we used UAE as power source for POPs extraction with a frequency of 40 kHz. Fig. 1A shows the components of the UAE-MSC. This technology extracts, filters, and collects analytes on-line. No sample transfer is needed as in conventional ultrasound extraction or other extraction techniques where solvents are used. It was recently patented by Amador-Muñoz et al. [18]. The design consisted of a glass micro-scale cell (MSC) (1) that contained the sample and the solvent. The MSC was connected on the bottom side to a PTFE filter holder (2) and a Teflon rotatory valve (3). On the top, the MSC was connected to a condenser (4) to avoid analyte loss by evaporation. The MSC, the filter holder, and the valve were protected by a glass jacket (5). All components were immersed in an ultrasound bath (6). Time, temperature and ultrasound potency were controlled. After the extraction process, the rotatory valve was opened and the solvent was evaporated with the Baffled Liner System.

2.3. Baffled liner system (BLS)

BLS (Fig. 1B) is a technology used to evaporate the organic solvent. The system consisted of a container (7) with a screw-on cap with two orifices; one of which was used to introduce nitrogen gas flow (8). The second orifice contained a PTV (programmable temperature vaporizing) chromatographic baffled liner (9). A soft nitrogen flow entered the container, reaching the solvent surface and carrying the solvent vapours into the baffled liner. During this process, some organic compounds can also be evaporated together with the solvent and carried into the liner; however, due to sub-ambient temperatures naturally produced by the nitrogen flow, the organic compounds condense and stick to the internal walls of the liner [19]. This process is similar to that developed in the PTV injector of a gas chromatograph when solvent mode is used. At the end of the evaporation process, the compounds stuck in the baffled liner walls were turned to the remaining organic extract by rinsing the liner with drops of the solvent. Finally, the volume of the extract was adjusted to 1 mL with dichloromethane, making it ready for gas chromatography–mass spectrometry analysis.

2.4. UAE-MSC optimization

In this study, recovery tests were carried out with the spiking method. This procedure has been extensively applied in different environmental matrix [22,23], including airborne particles [24,25]. Recovery experiments used the slurry spiking method with 22 native POPs spiked on $PM_{2.5}$. Particles were previously collected on glass fibre filters. Particle-native compound interaction was overnight to allow the sorption process between particles and native POPs.

The first extraction condition used in this study was based on our previous procedure to determine polycyclic aromatic hydrocarbons (PAHs) in particulate matter using only UAE [26,27]. In this study, we evaluated solvent type, number of consecutive extrac-