

# Analysis of Organophosphate Esters in Dust, Soil and Sediment Samples Using Gas Chromatography Coupled with Mass Spectrometry

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**Abstract:** Background contamination is a major problem in the analysis of organophosphate esters (OPEs). In this study, the possible sources of OPEs pollution were screened, and several different ways were applied to minimize the blank contamination. Under the strict quality control conditions, the cleanup efficiency of different solid phase extraction (SPE) was investigated. On the basis of this, a method was developed for the determination of 7 OPEs in dust, soil and sediment samples by gas chromatography coupled with mass spectrometry (GC/MS). The target compounds were extracted by hexane-dichloromethane (1:1, *V/V*) followed by aminopropyl silica gel SPE column cleanup for dust, and target compounds in soil and sediment were Soxhlet extracted and cleaned up by two-step SPE. The results showed that aminopropyl silica gel SPE column displayed the best purification performance among the three employed columns. Instrumental detection limits of the 7 OPEs ranged from 2.5 to 25.8  $\mu\text{g L}^{-1}$ , and method limits of quantification (MLOQs) in dust and soil sample ranged from 1.4 to 15.7  $\text{ng g}^{-1}$  and 0.3 to 2.9  $\text{ng g}^{-1}$ , respectively. The average recoveries of 7 OPEs in different matrices (dust and soil) at two spiked concentration levels ranged from 67.9% to 117.4%. The proposed method was successfully applied to analyze OPEs in different environmental samples collected in Shanghai.

**Key Words:** Organophosphate flame retardant; Organophosphate esters; Gas chromatograph-mass spectrometry; Soil; Dust; Sediment

## 1 Introduction

Organophosphate esters (OPEs) are derivatives of phosphoric acid with different substitutes including alkyl chains, aromatic functions, as well as partly halogenated alkyl chains phosphate. Generally, halogenated OPEs are mainly used as flame retardants, whereas non-halogenated OPEs are predominantly used as plasticizers and for other applications such as antifoaming agents and hydraulic fluids<sup>[1]</sup>. In most applications, OPEs are used additively in the material, which

means that they are not fixed in the polymer product through chemical binding and can easily leak into the environment via volatilization, abrasion, and dissolution. OPEs were introduced into the market in the late 1970s, and the analytical methods of OPEs were researched in-depth during 1980s to 1990s. After that, the environmental monitoring studies were almost abandoned during the 1990s, as most aryl and alkyl phosphates were found to be degradable in the environment<sup>[2,3]</sup>. However, the scientific research interest on these chemicals in environment was re-emerged since many of them were found

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in indoor environment. In last decades, the usage of OPEs had been widespread since the Stockholm Convention was enacted for the ban of brominated diphenylethers as flame retardants. Thereafter, the diffusion from host materials resulted in continuous release of OPEs into the environment. Nowadays, OPEs are ubiquitous contaminants detected worldwide in air, dust, soil, sediment, and biological samples<sup>[3–6]</sup>. In China, compared with the legacy pollutants, such as OCPs, PBDEs, and PCBs, environmental contamination of OPEs are sparse and most of the published studies are focused on the contamination in water, sediment, and biota<sup>[7–10]</sup>.

To improve the analytical quality of OPEs, in 2012, Brandsma *et al.*<sup>[11]</sup> organized the first worldwide interlaboratory study on OPEs. Nine laboratories from different countries or regions participated in the alignment. Because of the widely use of OPEs in material, the background contamination became a major problem in the analysis of OPEs. This composition together with the high complex matrix interference made it a challenge for the analysis of OPEs in environment. Thus, some strict quality control measures must be taken to minimize the pollution in the background. For complex samples, an extensive clean-up procedure should be taken to remove or reduce the matrix interference. In general, gel permeation chromatography (GPC), silica/sulfuric acid gel column and concentrated sulfuric acid are normally applied to eliminate the interference. GPC purification is a technique with time-consuming and waste solvent. Since OPEs are sensitive to strong acids, destructive methods (such as the use of sulfuric acid/silica gel columns for preparing biotic samples prior to analysis of e.g. dioxins and PCBs) cannot be utilized. However, solid phase extraction (SPE) with silica was successfully used for the cleanup of persistent organic pollutants from complex matrix. With regard to OPEs, silica-gel columns used for fish samples and amino-propyl-silica columns for eggs were reported<sup>[5,7]</sup>.

In this study, the possible sources of OPEs pollution were screened and several different ways were applied to minimize the blank contamination. Under the strict quality control conditions, the cleanup efficiency of different solid phase extraction (SPE) was investigated for the determination of OPEs in different environmental matrix. A feasible method was developed for the detection of 7 OPEs in dust, soil and sediment samples by gas chromatography coupled with mass spectrometry (GC/MS). The results obtained in this study provided valuable information on the ecological and human health risk assessments of OPEs.

## 2 Experimental

### 2.1 Apparatus and reagents

Agilent 7890 series gas chromatograph coupled to an Agilent 5975C mass spectrometer (USA), PTFE Centrifugal

tube (USA). Buchi (R-114) efficient rotary evaporator (Switzerland), pierce (model1870) nitrogen evaporator, SPE Vacuum Manifolds (Supelclean, USA), HN1006 ultrasonic cleaner (Huanan Ultrasonic Equipment Co. Limited, China), silica gel SPE column (1 g/6 mL, Biotage); aminopropyl silica gel SPE column (1 g/6 mL, CNW) and florisil SPE column (1 g/6 mL, Supelclean) were used in this study.

Seven OPEs standards were purchased from Sigma-Aldrich (Table 1). All solvents and other chemicals, such as *n*-hexane (Hex), dichloromethane(DCM) and acetone(pesticide grade, Fluka, Germany), methyl *tert*-butyl ether (MTBE) and ethyl acetate (EtAc) (HPLC grade, Sigma-Aldrich, Germany), silica, florisil gel and Sodium sulfate (analysis grade, Sino pharm Group Co. Limited, China), were used for the analysis.

All glassware were firstly cleaned by soak detergent water, and washed with hot chromic acid (Including 5% potassium bichromate sulfuric acid solution). After carefully rinsed the glassware with deionized water, the glassware were roasted at 450 °C for 5 h. Silica gel and florisil were baked at 120 °C for 5 h and then stored in sealed containers.

### 2.2 Collection and preparation of samples

Two dust samples (one from a laboratory room, the other from an office room) were collected from Shanghai university in September 2013. 70 mg of the dust sample was accurately weighted and extracted with ultrasonic for twice using 20 mL of Hex/DCM (1:1, *V/V*). The extracts were clean up by aminopropyl silica gel SPE cartridge and concentrated to 50  $\mu$ L under a gentle nitrogen stream before instrument analysis. The sediment samples were collected from Taihu lake in November, 2011. The soil samples were collected from a main traffic road in Shanghai city, 2013. Both the sediment and soil samples were freeze-dried, ground fine, sieved through 80 mesh, and kept in amber glass bottles until extraction. 5 g of solid sample was accurately weighted and Soxhlet extracted with 400 mL of Hex/acetone (1:1, *V/V*) for 72 h. The extracts were cleaned up on a self-assembly silica gel column followed by commercial aminopropyl silica gel SPE cartridge.

### 2.3 Preparation of SPE columns

#### 2.3.1 Preparation of self-assembly SPE columns

Neutral silica/florisil gel was heated at 120 °C for 12 h. When the gel cooled down to room temperature, it was deactivated by 3% water. After balanced in sealed containers overnight, Hex was finally added to separate the air. The self-assembly gel column (20 cm  $\times$  1.2 cm i.d.) was prepared manually, from top to bottom with 2.0 g anhydrous sodium sulfate, 10 g silica/florisil gel and 0.2 g glass wool. The column was prewashed with 30 mL of EtAc. After the sample was loaded, the target compounds were eluted by the

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