



# Simultaneous determination of thirteen organophosphate esters in settled indoor house dust and a comparison between two sampling techniques



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## HIGHLIGHTS

- Thirteen organophosphate esters (OPEs) were simultaneously measured in house dust.
- GC/PCI-MS/MS may be one of the best methods for OPE analysis in house dust.
- Valuable data for potential certification of OPEs in NIST SRM 2585 were generated.
- Use of household vacuum is a cost-effective alternative to standardized sampling.

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## ABSTRACT

An analytical method for the simultaneous determination of 13 organophosphate esters (OPEs) in house dust was developed. The method is based on solvent extraction by sonication, sample cleanup by solid phase extraction (SPE), and analysis by gas chromatography–positive chemical ionization–tandem mass spectrometry (GC/PCI-MS/MS). Method detection limits (MDLs) ranged from 0.03 to 0.43  $\mu\text{g/g}$  and recoveries from 60% to 118%. The inter- and intra-day variations ranged from 3% to 23%. The method was applied to dust samples collected using two vacuum sampling techniques from 134 urban Canadian homes: a sample of fresh or “active” dust (FD) collected by technicians and a composite sample taken from the household vacuum cleaner (HD). Results show that the two sampling methods (i.e., FD vs HD) provided comparable results. Tributyoxyethyl phosphate (TBEP), triphenyl phosphate (TPhP), tris(chloropropyl) phosphate (TCPP), tri(2-chloroethyl) phosphate (TCEP), tris(dichloro-isopropyl) phosphate (TDCPP), tricresyl phosphate (TCrP), and tri-n-butyl phosphate (TnBP) were detected in the majority of samples. The most predominant OPE was TBEP, with median concentrations of 31.9  $\mu\text{g/g}$  and 22.8  $\mu\text{g/g}$  in FD and HD samples, respectively, 1 to 2 orders of magnitude higher than other OPEs. The method was also applied to the analysis of OPEs in the National Institute of Standards and Technology (NIST) standard reference material (NIST SRM 2585, organic contaminants in house dust). The results from SRM 2585 may contribute to the certification of OPE concentration values in this SRM.

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## 1. Introduction

Organophosphate esters (OPEs) (Table 1) represent an important class of commercial additives used as flame retardants, plasticizers, hydraulic fluids, solvents, extraction agents, antifoam agents, adhesives, and coatings for electronic devices (ATSDR, 2009). The mode of use of OPEs (i.e., OPEs are often added into but not chemically bonded to products) makes them more likely evaporate or leach from the products and eventually be released to the environment. OPEs have been detected in many environmental matrices including indoor air (Bergh et al., 2010, 2011; Marklund et al., 2005), airborne particulate matter (Quintana et al., 2007; Reemtsma et al., 2008), and indoor dust (Bergh

et al., 2010, 2011; Brommer et al., 2012; Dodson et al., 2012; Garcia et al., 2007a; Marklund et al., 2003; Stapleton et al., 2009; Van den Eede et al., 2011). A recent review paper summarized toxicity data on selected OPEs, and some human health effects were discussed (van der Veen and de Boer, 2012).

OPEs are often analyzed by gas chromatography (GC) coupled with nitrogen–phosphorous detection (NPD) due to its good selectivity and high sensitivity towards compounds containing phosphorous (Garcia et al., 2007a). However, other phosphorus-containing compounds in the same matrix may co-elute with target analytes, leading to false detection and/or overestimation of target OPE analytes (Bjorklund et al., 2004; Garcia et al., 2007a; Quintana et al., 2007). Mass spectrometry (MS), in general, can provide more structural information, but ionization of most target OPE analytes in electron impact (EI) mode often yields one characteristic mass fragment ion at  $m/z$  99 corresponding to

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**Table 1**  
List of each target analyte: precursor and product ions, collision induced dissociation (CID, v), method detection limit (MDL), limit of quantitation (LOQ), average recovery (Ave. Rec., %), and precision (relative standard deviation, RSD, %).

| Compound (phosphate)      | Comp.  | MW <sup>a</sup> (g/mol) | Pre <sup>b</sup> Ion (m/z) | CID <sup>c</sup> (v) | Product ions <sup>b</sup> (m/z) | IS <sup>d</sup> | MDL (µg/g) | LOQ (µg/g) | Ave. rec. (%) | Precision, RSD (%) |              |              | Total (n = 18) |
|---------------------------|--------|-------------------------|----------------------------|----------------------|---------------------------------|-----------------|------------|------------|---------------|--------------------|--------------|--------------|----------------|
|                           |        |                         |                            |                      |                                 |                 |            |            |               | Day1 (n = 6)       | Day2 (n = 6) | Day3 (n = 6) |                |
| Trimethyl-                | TMP    | 140                     | 141                        | 0.56                 | <b>127</b> 109 99               | IS1             | 0.08       | 0.28       | 118           | 13                 | 12           | 5.0          | 11             |
| Triethyl-                 | TEP    | 182                     | 183                        | 0.43                 | <b>155</b> 127 99               | IS2             | 0.09       | 0.29       | 111           | 18                 | 16           | 23           | 19             |
| Tripropyl-                | TPrP   | 224                     | 225                        | 0.33                 | <b>183</b> 141 99               | IS3             | 0.20       | 0.68       | 90            | 7.0                | 21           | 16           | 18             |
| Tri-iso-butyl-            | TiBP   | 266                     | 267                        | 0.36                 | <b>99</b> 211 155               | IS4             | 0.40       | 1.32       | 79            | 19                 | 21           | 7.8          | 16             |
| Tri-n-butyl-              | TnBP   | 266                     | 267                        | 0.36                 | <b>211</b> 155 99               | IS4             | 0.07       | 0.23       | 83            | 16                 | 9.1          | 17           | 14             |
| Triphenyl-                | TPhP   | 308                     | 309                        | 0.40                 | <b>239</b> 169 99               | IS4             | 0.16       | 0.53       | 84            | 14                 | 17           | 11           | 14             |
| Tri(chloropropyl)-        | TCPP   | 326                     | 327                        | 0.30                 | <b>251</b> 175 99               | IS5             | 0.11       | 0.35       | 94            | 7.4                | 16           | 4.6          | 11             |
| Tri(2-chloroethyl)-       | TCEP   | 284                     | 285                        | 0.46                 | <b>223</b> 161 99               | IS5             | 0.07       | 0.23       | 92            | 7.5                | 6.3          | 12           | 8.3            |
| Tributoxyethyl-           | TBEP   | 398                     | 399                        | 0.43                 | <b>299</b> 199 99               | IS6             | 0.43       | 1.43       | 88            | 13                 | 10           | 12           | 14             |
| 2-Ethylhexyl-diphenyl-    | EHDPP  | 362                     | 251                        | 0.46                 | <b>247</b> 233 153              | IS6             | 0.16       | 0.55       | 60            | 14                 | 19           | 12           | 15             |
| Triphenyl-                | TPhP   | 326                     | 327                        | 0.46                 | <b>247</b> 251 233              | IS6             | 0.13       | 0.42       | 104           | 12                 | 8.9          | 14           | 12             |
| Tris(dichloro-isopropyl)- | TDClPP | 430                     | 431                        | 0.46                 | <b>319</b> 211 209              | IS6             | 0.08       | 0.28       | 102           | 5.7                | 5.7          | 12           | 7.9            |
| Tricresyl-                | TCrP   | 368                     | 369                        | 0.01                 | <b>369</b> 370 355              | IS6             | 0.03       | 0.12       | 112           | 5.4                | 3.1          | 5.9          | 5.7            |

<sup>a</sup> Molecular weight of an analyte.

<sup>b</sup> Precursor ion and product ions are used for qualification. One product ion (in bold) was selected for quantitation.

<sup>c</sup> CID (collision-induced dissociation, in resonant waveform).

<sup>d</sup> IS: internal standard. IS1: TMP-d<sub>6</sub>; IS2: TEP-d<sub>15</sub>; IS3: TPrP-d<sub>21</sub>; IS4: TnBP-d<sub>27</sub>; IS5: DPhMP; IS6: <sup>13</sup>C<sub>18</sub>-TPhP.

protonated phosphoric acid, while molecular ions and other fragments are very low in intensity. This complicates the confirmation and quantitation of OPEs, since *m/z* 99 has no information about the substituents and there is little information in higher mass ions that could help in the qualitative identification (Ma and Hites, 2013). In addition, other compounds in the sample matrix may also contribute to the formation of low-mass fragments such as *m/z* 99.

Recent studies have reported the use of MS operated in positive chemical ionization (PCI) mode, which could provide sensitivity comparable to NPD with enhanced selectivity and confirmation capability, since pseudo molecular ion [M + H]<sup>+</sup> is often formed as the base peak for most OPEs (Bergh et al., 2010, 2012; Bjorklund et al., 2004; Quintana et al., 2007). Such pseudo molecular ions can subsequently undergo collision-induced dissociation (CID) to yield unique product ions, which can then be used for quantitation and confirmation (Bergh et al., 2010, 2012; Bjorklund et al., 2004).

Indoor house dust is a repository for organic compounds released indoors and tracked in from outdoors (Butte and Heinzow, 2002). Once indoors, these compounds are less prone to degradation due to the nature of the indoor environment (e.g., cool temperatures, less direct sunlight) and thus can persist for longer periods, especially when dust is trapped in carpets. Therefore, indoor dust has been analyzed in many studies as an indicator of human exposure to pollutants in the indoor environment (Butte and Heinzow, 2002; Schantz et al., 2007; Wise et al., 2006). House dust is often collected by vacuuming. In this study, two sampling techniques were used: a sample of fresh or "active" dust (FD) collected by technicians following the protocol developed for the Canadian House Dust Study (Rasmussen et al., 2011, 2013) and a composite sample taken from the household vacuum system (HD) (Fan et al., 2010; Kubwabo et al., 2012, 2013). Previous studies have shown that samples collected from household vacuum systems (HD) may provide equivalent results to fresh dust samples (FD) collected by technicians, for a variety of compounds including most synthetic musk compounds (Kubwabo et al., 2013), phthalates (Kubwabo et al., 2013), triclosan and parabens (Fan et al., 2010). Thus, the objectives of this study were to develop an analytical method to simultaneously measure the concentrations of 13 OPEs in indoor house dust, and then to compare the FD and HD sampling methods for the determination of OPEs in settled indoor dust.

## 2. Material and methods

### 2.1. Materials

Thirteen target OPEs and their abbreviations are listed in Table 1. Individual OPE standards were purchased from TCI America (Portland, OR) except TPrP and TCPP (Sigma-Aldrich, Oakville, ON, Canada). Deuterated internal standards (i.e., TMP-d<sub>9</sub>, TEP-d<sub>15</sub>, TPrP-d<sub>12</sub>, and TnBP-d<sub>27</sub>) were purchased from CDN Isotopes Inc. (Pointe-Claire, QC, Canada). Diphenyl methyl phosphate (DPhMP) was purchased from ChemService (West Chester, PA, USA) and <sup>13</sup>C<sub>18</sub>-TPhP from Wellington Laboratory (Guelph, ON, Canada). Individual stock solutions were prepared in toluene and working standard solutions were prepared by mixing individual standard solutions and diluting in toluene to the appropriate concentrations. Solvents (i.e., hexane, acetone, and toluene, and dichloromethane, all GC-grade) were purchased from EMD Chemicals Inc. (Gibbstown, NJ, USA). SRM 2585 was obtained from the National Institute of Standards and Technology (Gaithersburg, MD, USA).

### 2.2. Dust sample collection and preparation

Vacuum samples were collected from randomly selected urban Canadian single family dwellings under the Canadian House Dust Study (CHDS) as described previously (Fan et al., 2010; Kubwabo et al., 2013; Rasmussen et al., 2011, 2013) and briefly summarized here.

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