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Determination of organophosphate esters in air samples by dynamic sonication-assisted solvent extraction coupled on-line with large-volume injection gas chromatography utilizing a programmed-temperature vaporizer

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Abstract

An on-line method for the determination of airborne organophosphate esters based on dynamic sonication-assisted solvent extraction and large-volume injection (LVI) gas chromatography with nitrogen–phosphorous detection is introduced. The LVI is performed with a programmed-temperature vaporizer. The entire extracted fraction of 800 μl (hexane–methyl-tert.-butyl ether, 7:3, v/v) is introduced directly into the GC system without any clean-up step following extraction. The extraction and analysis step were completed in less than 15 min. The limit of detection of the investigated organophosphate esters was established to be in the range of 5–32 pg/filter. The correlation coefficients (r^2) were investigated in the linear range study of the entire system and established to be ~0.9900 for all the investigated organophosphates esters. Applications of the method was demonstrated with the extraction of air samples collected onto glass fiber filters from different indoor environments. Six organophosphate esters were found at the levels 0.4–138 ng/m^3.
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1. Introduction

During the last decade there has been increased interest in the development of various techniques for the extraction of solid samples. Several instrumental extraction techniques including pressurized liquid extraction (PLE) [1–3], microwave-assisted extraction (MAE) [4,5] and supercritical fluid extraction (SFE) [6] have been developed. However, other techniques like Soxhlet extraction [7] and sonication-assisted extraction [8–12] are still widely used and can have considerable advantages. For instance, sonication-assisted extraction of soil samples has been reported to be a rapid and simple procedure for the determination of fungicides in soil [13], while Babic et al. [14] reported that the extracts from sonicated soil samples containing pesticides were chromatographically determined without a sub-

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sequent clean-up step. Thus, the analysis time is considerably reduced in comparison to techniques where such a step is required.

When developing an extraction method, care must be taken to avoid degradation of the analytes. Dynamic extraction can be advantageous in this respect, since the analytes are removed as soon as they are transferred from the solid sample to the solvent. Furthermore, in a dynamic system the sample is continuously exposed to fresh solvent, which favors the transfer of analytes from the sample matrix to the solvent.

Large-volume injection gas chromatography (LVI-GC) using a programmed-temperature vaporizer (PTV), has previously been used as a GC interface for the on-line coupling of dynamic microwave-assisted extraction (DMAE) coupled with solid-phase extraction (SPE) [15]. This system was evaluated for organophosphate esters in air samples. The transferred fraction eluted from the SPE consisted of 840 μl of methyl tert.-butyl ether (MtBE). This is to our knowledge the only application so far that involve solid sample extraction and LVI-PTV-GC. Other applications have been performed with supercritical fluid extraction PTV-GC [16,17]. However, these systems did not involve large volume injections since the effluent was gaseous carbon dioxide.

The target analytes in this study are organophosphate esters, which are considered to be ubiquitous priority pollutants in indoor air. Organophosphate esters are a heterogeneous group, with widely varying structural variations amongst their substituents and, thus, wide variations in their chemical and physical properties. These compounds are used as additive flame retardants and plasticisers in a wide range of products, i.e. they are not covalently bonded to the main material (frequently plastics). Therefore, depending on their vapor pressure, organophosphate esters may migrate out from the material and into the surrounding air [18–20].

Several accounts of investigations into the occurrence of organophosphate esters in indoor environments have been published previously. Weschler et al. [21] has identified tris(2-butoxyethyl) and tris(2-chloroethyl) phosphate in office building air at concentrations in the range 5–25 ng/m^3, and Wilkins et al. [22] reported the presence of tri(*n*-butyl) and tris(2-chloroethyl) phosphates in dust from office floors. Nine different organophosphate esters were identified and studied in air samples collected in common indoor work environments by Carlsson et al. [23]. Furthermore, it has been shown that a substantial source of triphenyl phosphate in indoor environments housing computers is the plastic material in the outer cover of computer video display units (VDUs) [20].

Several biological effects of exposure to organophosphate esters have been reported. For example, triphenyl phosphate, widely used as a plasticiser, as well as a flame retardant in electronic equipment, has been shown to be a powerful inhibitor of the monocyte carboxylase in human blood [24]. Moreover, cases of contact allergy when exposed to triphenyl phosphate have been reported [9,25]. In studies of rats and mice, tris(2-chloroethyl) phosphate has shown neurotoxic and carcinogenic properties [26].

Sanchez et al. [27] recently introduced a continuous solvent flow through extraction method based on sonication, entitled dynamic sonication-assisted solvent extraction (DSASE). The extraction method was evaluated for organophosphates in indoor air.

In this study, the DSASE is further developed to include on-line transfer of the DSASE effluent to a gas chromatograph equipped with a PTV injector. The determination of organophosphate esters in various indoor air samples collected on glass fiber filters is demonstrated.

2. Experimental

2.1. Chemicals and standards

Tri(*n*-butyl), tris(2-chloroethyl), triphenyl, tris(2-butoxyethyl), tris(2-ethylhexyl), and tritolyl phosphates were obtained from Aldrich Germany. Tri-(chloropropyl) phosphate was provided by Akzo Nobel, Sweden. All reference substances were of analytical grade (>98%) except methyl diphenyl phosphate (Aldrich), which was of technical grade (80%), this chemical was further purified to 99% using semi-preparative HPLC with an octadecylsilica column (Macherey–Nagel, Düren, Germany).

All standard substances were dissolved in a 7:3 (v/v) mixture of hexane–MtBE, supplied by Merck

(Darmstadt, Germany) and Rathburn (Walkerburn, UK), respectively.

2.2. DSASE and the effluent transfer to LVI-GC

The system was assembled in our laboratory. The DSASE set-up is described in a previous paper [27]. In brief, samples to be extracted were inserted into the extraction cell: an in-line preparative refillable guard column (Alltech, Deerfield, IL, USA) with an internal volume of 0.25 ml. The solvent was pumped through this cartridge by means of a Varian 220 HPLC pump (Varian, Walnut Creek, CA, USA). Extraction was performed inside a Bransonic 52 ultrasonic bath (120 W, 35 kHz). To enable experiments to be performed at different temperatures, a Tempunit TU-16A heater was immersed in the ultrasonic bath.

DSASE was coupled on-line to a GC system (Agilent Technologies, Wilmington, DE, USA) equipped with a PTV inlet using a six-port injection valve (VICI, Valco International, Switzerland) and a deactivated fused-silica transfer line 50×0.25 mm (Micro-Tech Scientific, Sunnyvale, CA, USA).

To remove any possible solvent and solutes remaining in the transfer line following injection, the valve was equipped with a fused-silica leak, 300×0.05 mm I.D. The PTV-GC was equipped with a nitrogen–phosphorous detection (NPD) system (Agilent). The PTV was utilized in solvent vent mode and the parameters were adjusted as follows: solvent vent flow, 200 ml/min; solvent vent time, 4.10 min; temperature program, 70 °C (5.30 min) followed by 700 °C/min to 400 °C (5 min) and purge flow was 33.1 ml/min for 6 min. The PTV liner was packed by the manufacturer, with deactivated glass fiber wool (Agilent).

The column oven temperature was programmed as follows: 50 °C, isothermally for 5.50 min during injection, followed by a temperature increase of 50 °C/min to 190 °C and then 10 °C/min to 230 °C and 40 °C/min up to a final temperature of 300 °C, which was kept for 5 min. The analytical column used was a DB-5 column (30 m×0.32 mm I.D., 0.10 μm film thickness; J&W Scientific, Folsom, CA, USA) and the linear velocity of the nitrogen carrier gas was 40 cm/s. The NPD system was set at temperature of 325 °C and the gas flow-rates were: air, 60 ml/min; hydrogen, 5 ml/min, and nitrogen make-up, 4 ml/min. The NPD system probe was powered by an external current supplier (Detector Engineering & Technology, Walnut Creek, CA, USA) set at 2.7 A, and a bias voltage set at 5 V. The detector bead selected was a ‘‘black bead’’ supplied by Agilent Technologies since it offers improved peak shape for phosphorus-containing compounds and lower nitrogen sensitivity compared to the standard white bead.

All tubing and finger-tight fittings were made of PEEK (polyether ether ketone). The tubing prior to the extraction cell had an internal diameter of 0.25 mm, while after the extraction cell there was a 60-mm length of tubing with an internal diameter of 0.064 mm. The narrow-bore PEEK tubing following the extraction cell served as a restrictor to maintain the solvent in the liquid state during the extraction step. A personal computer-based laboratory data system (ELDS Pro, Chromatography Data Systems, Svartsjö, Sweden) was used to program a relay card for switching the valves and to start the GC. HP-Chemstation software (Agilent Technologies) was used to register the detector signal and to control all GC parameters.

2.3. Cleaning procedures for the glass fiber filters and the DSASE system

Since organophosphates are ubiquitous indoor air pollutants, extensive cleaning procedures had to be applied. Prior to sampling the glass fiber filters were ultrasonicated successively for 20 min in methanol, acetone and dichloromethane and then stored in dichloromethane rinsed aluminum foil. Subsequent to extraction the cell was removed from the holder and cleaned for 5 min with sonication of the cell parts immersed in the extraction solvent.

Prior to the next extraction, fresh extraction solvent was pumped through the system for 5 min at flow-rate of 0.5 ml/min.

2.4. Air sampling and spiked samples

Stationary air sampling was performed with a personal sampler holder [28] made from anodized aluminum. A 25-mm binder-free borosilicate glass fiber filters (Gelman Science, Ann Arbor, MI, USA)

and two 15×15 mm cylindrical polyurethane foam (PUF) plugs (Specialplats, Gillinge, Sweden) were use to trap the analytes. Air was pumped through the sampler using a battery-operated personal sampler pump (224-PCXR7, SKC, Eighty Four, PA, USA). In previous work [23], it was shown that organophosphate esters are retained only in the filters and no breakthrough was observed, so in this study, only the glass fiber filters were analyzed.

The flow-rate was set to 3 L/min and the samples were collected for 60 min in a library with new furniture, a brand-new car and a private home, yielding a total air volume of 180 l in each case. Samples were also collected in the laboratory during half a working day, using a pocket pump (210-1002, SKC) with a flow-rate set to 250 ml/min for 240 min, yielding a total air volume of 60 l. The samples were wrapped in aluminum foil and stored in a freezer at −18 °C until analysis. Analysis of blank samples showed no traces of organophosphate esters.

Filters were spiked with 20 μl of a standard solution containing seven organophosphate esters with a concentration of approximately 0.05 ng/μl of each compound for the initial PTV parameter investigation. A solution of 0.05 ng/μl of methyl diphenyl phosphate was used as an internal standard for both the spiking studies and for the real samples. Prior to extraction, 20 μl of the internal standard solution was added to the filter. The spiked filters were then kept inside a box for 30 min in order to allow the solvent to evaporate. The inside of this box was covered with aluminum foil and rinsed with dichloromethane prior to use.

2.5. Analytical procedure for DSASE–LVI-GC

The glass fiber filters were cut into small pieces and inserted into the extraction cell. The conditions for DSASE were kept at the optimum settings identified in the previous work [27]. These conditions were as follows: temperature of the ultrasonic bath, 70 °C; duration of extraction, 3 min; flow-rate of the extraction solvent, 200 μl/min. However, the duration of the DSASE was extended to 4 min (1 min more than the previous optimum). This is further discussed in the section transfer of the extract and the large-volume injection.

To ensure that the cell had the same temperature as the water in the ultrasonic bath, the holder with

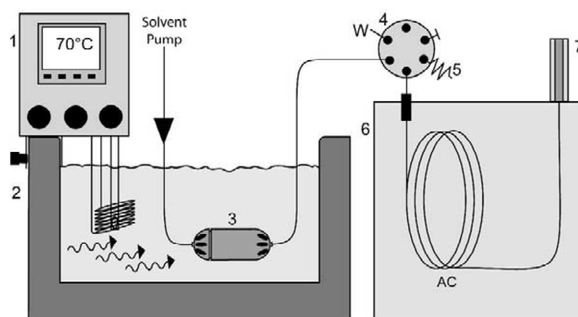

Fig. 1. General scheme of DSASE–PTV-GC–NPD system: 1 = heater, 2 = ultrasonic bath, 3 = extraction cell, 4 = six-port injection valve, 5 = fused-silica leak, 6 = GC system equipped with a PTV inlet, 7 = NPD system, W = waste, AC = analytical column.

the extraction cell was immersed in the ultrasonic bath 1 min prior to start of the extraction process. Simultaneously the pump was started to assure that the system was filled with extraction solvent. The pressure over the extraction cell during the extraction was about 30 bar. The ultrasound bath and the relay program were started at the same time, and thus the GC and the data acquisition. A schematic diagram of the on-line system is shown in Fig. 1.

Following extraction the valve was switched and the extraction step was finished. At this stage in the analysis procedure, clean up of the extraction system was performed, i.e. extraction cell, tubing and the valve.

3. Results and discussion

In the development of the DSASE–LVI-GC method, the extraction step was optimized off-line for organophosphate esters in a previous work [27]. The entire method was evaluated by a system performance test including the following parameters: limit of detection (LOD), linear range, retention time and the normalized peak area. The on-line method was applied to air samples collected in indoor environments.

3.1. Transfer of the extract and the large-volume injection

The PTV was used in solvent vent mode in which

the vapor of the solvent is discarded through the solvent vent line during sample introduction. However, it is not desirable to remove all the solvent unless a suitable adsorbent with sufficient retentive power for the target analytes is used, since the residual solvent acts as a finite stationary phase in the liner and, thus, both as a carrier and as a trap for the analytes.

The deactivated glass wool, packed in the liner in this study, also yields retention, but acts more as an extensive surface from which the evaporation of the solvent occurs. Inefficient trapping would cause losses of the more volatile analytes. Therefore, to supply the PTV with solvent to maintain the retentive power throughout the introduction of the sample, the rate of sample introduction must be slightly higher than the rate of solvent evaporation. This was achieved with the selected PTV settings. Recently the liner used was tested successfully for the PTV injection of organophosphate esters eluted in MtBE [15].

The entire extracted fraction of 800 μl was introduced into the GC system without any clean-up step. This is 200 μl more than the 600 μl that was found to be optimal in the previous study [27]. The reason for the enlarged extraction fraction was to avoid carry-over effects. In this study a six-port valve was used as an injection valve. This allows flushing of the valve channel not only during the transfer of the analytes, but also after the extraction, i.e. during cleaning of the system. This cleaning procedure is very important since the standard valve channel can be very adsorptive and carry over can easily occur [15]. With a three-port valve this cleaning procedure following the extraction would not be possible. However, the design and operational parameters of the system ensured that there was no detectable carry-over. The system cleaning was performed during the GC analysis step.

Large-volume injection utilizing PTV in the solvent vent mode pre-concentrates the analytes in the injector. Although the solvent should be evaporated without significant loss of analytes, in this study 10% loss of the analyte, tri(*n*-butyl) phosphate was discovered. This loss was due to the settings of the PTV, but adjustments to milder injection conditions resulted in flooding of the PTV and hence loss of all analytes. However a reduced flow-rate of the extraction solvent would maybe solve the problem but the flow-rate was optimized for the extraction step. However, the loss was found to be reproducible, and therefore accepted. The solvent evaporation process was ongoing during the extraction process that was 4 min. In addition 0.1 min was required after the extraction to complete the solvent removal. Thus, the time needed for extraction and introduction onto the GC was 4.1 min.

The solvent evaporation temperature was set to 70 °C. Lower temperatures caused flooding while higher temperatures discriminated against analytes with low boiling points. The column temperature during transfer of the solutes is important for the peak shapes of the analytes. An initial column temperature of 50 °C during solute transfer was found to yield narrow peaks for all compounds investigated. When working at higher temperatures the peaks broadened, due to inefficient refocusing in the column.

In general, minor adjustments of the PTV parameters will not yield any major change of the chromatography or the recovery, but care must be taken. However the whole method was robust especially concerning that no clean-up step was utilized. The only system maintenance needed was exchange of the PTV liner after 30–40 extractions due to activation of the glass wool and the liner, and accumulated dirt from the extraction. The liner was activated most likely due to the large amounts of solvent introduced in combination with steep and frequent temperature gradients.

3.2. System performance and method linear range

The system performance was investigated by extracting spiked glass fiber filters. Recoveries of the analytes were not evaluated in this study, since they were determined in a previous study, which found the levels to be more than 95% for all of the compounds investigated [27]. However, as the loss of the tri(*n*-butyl) phosphate was established to be 10%, the total recovery of this specific compound was 86%.

The LODs for the overall method, the reproducibility of the peak areas, retention times and linear range study are illustrated by the data for spiked glass fiber filters listed in Table 1.

The first column of Table 1 shows the LODs of the organophosphate esters trapped onto the filters.

Table 1
System performance and method linearity by using spiked filters

Organophosphate ester	LOD[a] (pg/filter)	Peak area repeatability[b] RSD (%)	Peak area reproducibility[c] RSD (%)	Retention time[d] RSD (%)	Correlation coefficient[e]	Calibration line	Linearity range (ng/filter)
Tri(n-butyl) phosphate	31.8	5.1	14.3	0.01	0.9990	$y=0.175x+0.031$	0.05–10
Tris(2-chloroethyl) phosphate	13.4	11.7	9.2	0.01	0.9994	$y=0.227x-0.024$	0.05–10
Tris(2-chloropropyl) phosphate[f]	5.6	3.2	6.2	0.02	0.9969	$y=0.264x-0.046$	0.05–25
Tris(2-butoxyethyl) phosphate	20.3	4.1	5.9	0.01	0.9961	$y=0.163x-0.051$	0.05–10
Triphenyl phosphate	9.5	6.2	8.0	0.01	0.9998	$y=0.183x+0.027$	0.05–25
Tris(2-ethylhexyl) phosphate	16.2	3.8	5.8	0.01	0.9900	$y=0.197x-0.087$	0.05–25
Tritolyl phosphate[g]	6.7	6.1	7.5	0.01	0.9995	$y=0.241x+0.011$	0.05–25

[a] LOD for the amount of analyte trapped onto the filters for detection by the DSASE–LVI-GC method.
[b] Repeatability of normalized peak area determined with five ($n=5$) consecutive analyses of spiked filters at the 1000 pg level.
[c] Reproducibility of the normalized peak area determined with four ($n=4$) analyses of spiked filters at the 1000 pg level during 4 days.
[d] Reproducibility of the retention times determined with four ($n=4$) analyses of spiked filters at the 1000 pg level during 4 days.
[e] Linearity was investigated at seven levels with triplicate in each point.
[f] Integrated as a sum of three isomers.
[g] Includes only the first isomer of tritolyl phosphate.

LODs were calculated according to the criteria of the International Union of Pure and Applied Chemistry and the American Chemical Society, i.e. the amount that produce signals that are three times the standard deviation of the noise signal. These results were calculated from the linear range study (column 5 and 6). The LODs are in the range of 5–20 pg/filter for all compounds except tri(n-butyl) phosphate, which had a LOD of 31.8 pg/filter.

In columns 2 and 3 the normalized peak area repeatability and reproducibility of each compound in the overall process are shown, respectively. These experiments involved the extraction of five and four spiked filters at the 1 ng/filter level. The RSDs of the normalized peak areas were in the ranges of 3.2–11.7% for the five consecutive experiments and 5.9–14.3% for the reproducibility study. In column 4 the reproducibility of the retention times are presented. The determined range was 0.01–0.02% (RSD). Low variations in the retention times are essential, since identification of the organophosphate esters in real samples relies on comparison of their retention times to those of external standards. These results were compared with the equivalent ones obtained when developing DSASE and the extracts were injected off-line in a GC–NPD system by using a split/splitless injector [27]. In that study the RSDs were in the range of 5–8%.

Data related to the linear range study of the method are also presented in Table 1, columns 5–7. Filters were spiked with the standard mixture at seven different levels in the range of 0.05–25 ng/filter, and analyzed in triplicate. The correlation coefficients were in the range of 0.9900–0.9998. The determined linearity was within acceptable limits.

3.3. Determination of organophosphate esters in air samples

Sample peak area and retention time reproducibility were investigated to be sure of the sample homogeneity. An air sample collected in a library for 180 min with a flow-rate of 3 ml/min, was divided into three equal portions for this experiment and each portion was analyzed independently. The RSD of the peak areas ranged from 6.4% for tris(2-chloropropyl) phosphate up to 15.6% for tris(2-ethylhexyl) phosphate. Triphenyl phosphate had an RSD of 7.3% and tris(2-chloropropyl) phosphate 6.4%. These results were in the same range as the spiked filter study discussed above. With these results it is most likely that the assumption, that the air sample is homogeneously retained over the filter is true. The RSD for the retention times were also in the same range as determined in the spiking study, 0.01–0.02%.

Using the described analytical method a number of indoor environments were investigated, including a library with new furniture, a brand-new car, a private

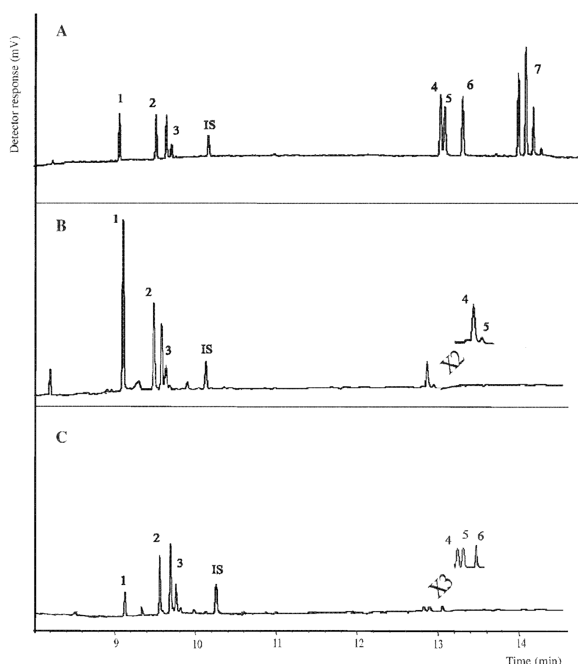

Fig. 2. Chromatograms of organophosphate esters of air samples extracted and analyzed with DSASE coupled on-line with LVI-GC utilizing a PTV. (A) Standard mixture, (B) brand-new car, (C) library with new furniture. The identity of the organophosphate esters are as follows: 1 = tri(*n*-butyl)-, 2 = tris(2-chloroethyl)-, 3 = three isomers of trichloropropyl-phosphate ester, with unknown chlorine positions, I.S. = methyldiphenyl-, 4 = tris(2-butoxyethyl)-, 5 = triphenyl-, 6 = tris(2-ethylhexyl), and 7 = four isomers of tritolyl phosphate ester.

home built in the 1960s and a laboratory. The samples were quantified using the calibration lines included in Table 1. The laboratory samples were collected using a personal air sampling pocket pump during half a working day. Organophosphates could be identified in all air samples from the indoor environments. In all samples, tri(*n*-butyl) phosphate, was present, as well as tris(2-chloroethyl) phosphate, three isomers of tris(chloropropyl) phosphate, triphenyl phosphate, and tris(2-butoxyethyl) phosphate. Tris(2-ethylhexyl) phosphate was only detected in the library samples. DSASE–LVI-GC–NPD chromatograms from samples collected in the library with new furniture and the brand-new car are shown in Fig. 2.

There were significant differences in concentration profiles between the sampling locations (Table 2). Obvious reasons for these differences in emissions are variations in the amounts of the individual plasticizers/flame retardant additives added during the manufacture of the various emitting materials present in the indoor environment, together with differences in the mass and surface area of these materials. Thus, every indoor environment has a unique concentration profile of emitted plasticizers/flame retardants, depending on the present furniture, building materials, electronic equipment, etc.

The most abundant compound in the air at any of the investigated sampling locations was tri(*n*-butyl) phosphate collected in the car, for which the con-

Table 2
Levels of organophosphate esters found in air samples

Organophosphate ester	Library[a] ng/m^3 (SD)	New car[b] ng/m^3 (SD)	Private home[c] ng/m^3 (SD)	Laboratory[d] ng/m^3 (SD)
Tri(*n*-butyl) phosphate	4.10 (0.12)	138 (0.12)	14.2 (0.45)	11.9 (0.01)
Tris(2-chloroethyl) phosphate	35.1(1.95)	109.5 (0.51)	11.4 (0.72)	20.25 (0.02)
Tris(2-chloropropyl) phosphate[e]	47.3 (0.76)	61.4 (0.20)	10.0 (0.26)	112 (0.01)
Tris(2-butoxyethyl) phosphate	0.77 (0.03)	36.4 (0.06)	42.5 (1.39)	45.8 (0.01)
Triphenyl phosphate	0.494 (0.02)	1.44 (0.01)	11.7 (0.26)	35.3 (0.03)
Tris(2-ethylhexyl) phosphate	2.75 (0.01)	–	–	–

[a] New furniture installed, $n = 3$.
[b] $n = 3$.
[c] Built during the 1960s, $n = 3$.
[d] Personal monitoring in a laboratory during half a working day, $n = 2$.
[e] Integrated as the sum of three isomers.

centration was 138 ng/m^3. Isetun et al. [29] found strong polar interactions between organophosphate esters and the glass fiber absorbent, but the most volatile compounds like tri(*n*-butyl) phosphate are not fully retained on it, implying that the real amount of tri(*n*-butyl) phosphate is probably even higher.

Compared to other triphosphate esters, triphenyl phosphate was found at significantly higher concentrations in samples collected in the private home and at the laboratory, approximately 12 and 35 ng/m^3, respectively. These samples were taken in the vicinity of electronic equipment. Carlsson et al. [23] report that the arylated organophosphate esters, e.g. triphenyl phosphate, emanate from electronic equipment, while the identified alkylated organophosphate esters probably have different origins. This is a possible reason for the higher concentrations of this compound found in the private home and the laboratory.

4. Conclusions

Dynamic sonication-assisted solvent extraction coupled to large volume injection gas chromatography proved to be an effective tool for the analysis of organophosphate esters in air samples. The extraction set-up is simple and inexpensive compared to other commercial extraction systems. Due to the low limit of detection and the fact that the whole sample is introduced into the GC, only short sampling times were required. Furthermore, the low limit of detection for the method opens the possibility to use personal sampling equipment in the breathing-zone of exposed workers. No clean-up step is needed, so the analysis time is reduced considerably. The time required for a complete analysis was less than 15 min.

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