

Organophosphate and phthalate esters in Standard Reference Material 2585 “Organic Contaminants in House Dust”

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Abstract

Twenty-two phthalate diesters and organophosphate triesters have been determined in Standard Reference Material (SRM) 2585 Organic Contaminants in House Dust. Ultrasonic assisted solvent extraction and Solid Phase Extraction on a Florisil adsorbent were used as clean-up combined with analysis using gas chromatography - tandem mass spectrometry in positive ion chemical ionization mode. Seven phthalates were detected in the concentration range 1 - 570 $\mu\text{g/g}$. Diethylhexyl phthalate was the major phthalate with a concentration of 570 $\mu\text{g/g}$ dust. Twelve organophosphates were detected in the SRM 2585. Tri(2-butoxyethyl) phosphate was the dominating phosphate with a concentration of 82 $\mu\text{g/g}$ and nine phosphates with concentrations around 1 $\mu\text{g/g}$ dust. Three phosphates were detected but were below LOQ and three were below a MDL of 0.001 $\mu\text{g/g}$. The applied extraction and clean-up method was evaluated for the analysis of SRM 2585. Extraction yield was $\geq 99\%$, except for TCEP (97%) and DEP (98,5 %). The problem of calibration curvature is addressed, and it is shown how to improve the analysis by using deuterated standards. To our knowledge this is the first report of the concentrations of phthalates esters in SRM 2585 House Dust as well as the determination of as many as fourteen organophosphate triesters.

Introduction

Dust is a source of exposure to a variety of organic contaminants in the indoor environment (1, 2). A variety of analytical methods have been applied to assess indoor air as well as house dust with respect to various types of these organic indoor air pollutants (3-10). Thus, the availability of certified reference materials for indoor dust is of interest for estimating the accuracy of data obtained with different sample preparation methods. Standard Reference Material “Organic Contaminants in Indoor Dust” SRM 2585 is available for this kind of assessment with respect to the common indoor air pollutants polycyclic aromatic hydrocarbons (PAH), polychlorinated biphenyls (PCB), polybrominated biphenyl ethers (PBDE) and a number of chlorinated pesticides including DDT. Two other groups of ubiquitous indoor contaminants are organophosphate esters and phthalate esters, hereafter referred to as OPEs and phthalates respectively. These groups of compounds are commonly used as additives in polymeric materials (11), *i.e.* substances added to alter the physical properties, such as mouldability and flame resistance, of polymeric materials. Since these additives are not chemically bonded to the polymer, they can be released to the surrounding air. Most phthalates and OPEs are semi-volatile organic compounds (SVOC) (12), which are substances known to adsorb to solids such as airborne particles and settled dust and to partition between gaseous and particulate phases (13-15). The dynamic distribution between dust and air means that it is important to evaluate their levels in dust as well as air to assess overall inhalation and dermal exposure in indoor environments (1). Dust is also a potential route for ingestion (1). Both OPEs and phthalates are used both in consumer products as well as in building materials and have become ubiquitous indoor air pollutants with higher levels indoors than outdoors. (2, 12, 16-20) Sampling of dust for the determination of phthalates and OPEs is performed in a number of different ways, *e.g.* dust wipes of surfaces, using the content of

vacuum cleaner bags, open dishes for collecting settling dust, and a technique used in recent publications where a filter mounted in a nozzle adapted to a vacuum cleaner was used to collect settled dust from selected surfaces above the floor (21-24). Thus, there is a need for common guidelines for the sampling, as well as for a reference material for evaluating sample pre-treatment and analysis to obtain comparable values (25).

Standard Reference Material 2585 Organic Contaminants in House Dust is provided by the National Institute of Standards and Technology, Gaithersburg, MD, USA. This material originates from material collected from vacuum cleaner bags from homes, motels, hotels and cleaning services in Maryland, Montana, New Jersey, North Carolina, Ohio and Wisconsin during the years 1993 to 1994 (26-28). Concentrations of selected polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), polybrominated biphenyl ethers (PBDEs) and chlorinated pesticides have been certified for this SRM. Homogeneity of the material has been evaluated for PAHs, PCBs and pesticides, and the moisture content has been determined to be 2.11%, and the results are reported on dry-mass basis. Because of the homogeneity and the availability to other laboratories worldwide for comparison, the house dust reference material represents an ideal material for evaluating and testing analytical methods used for the determination of phthalates and organophosphates in indoor dust.

The aim of this work was to determine the concentration of seven phthalates and fifteen OPEs present in SRM 2585 House Dust using exhaustive extraction, clean-up with solid phase extraction (SPE) and analysis by using gas chromatography - tandem mass spectrometry GC-MS/MS and quantification using deuterated internal surrogate standards. To our knowledge these are the first reported values of the concentrations of phthalates in SRM 2585, and our results are compared to measurements of seven OPEs reported in a recent publication by Van den Eede et al. (29)

Experimental

Chemicals

Acetone, cyclohexane and *n*-hexane were used as solvents; all were of Suprasolv quality and were obtained from Merck (Darmstadt, Germany). The reference compounds of phthalates and organophosphates were obtained from a number of different manufacturers. Names, abbreviations and other data regarding these substances are provided in **Table 1**. All reference compounds were of >95% purity.

Standard reference material 2585

SRM 2585 “Organic contaminants in House Dust” was obtained from the National Institute of Standard and Technology Gaithersburg, MD, USA. The SRM was prepared from a composite of dust collected from vacuum cleaner bags from homes, motels, hotels and cleaning services in Maryland, Montana, New Jersey, North Carolina, Ohio and Wisconsin during the years 1993 to 1994. The composite dust material was processed and sieved down to a $\leq 100 \mu\text{m}$ particle size fraction to prepare SRM 2585.

Instrumentation

A GC-MS system, which consisted of a 6890N GC (Agilent Technologies, Palo Alto, CA) connected to a Finnigan TSQ 7000 triple quadrupole mass spectrometer (MS) (Thermo Fisher Corporation, Waltham, MA), was initially used for validation of the extraction and clean-up method and quantification of both OPEs and phthalates in the house dust SRM 2585. The GC was equipped with a Programmable Temperature Vaporizer (PTV) injector and a model 7683 autosampler (both from Agilent Technologies). The PTV temperature program was: 70 °C for 0.5 min followed by a ramp of 700 °C/min to 310 °C, which was

maintained for 8 min. The GC column oven temperature program was: 60 °C for 2 min followed by ramps of 20 °C/min to 270 °C, 3°C/min to 275°C and 20°C/min to 300°C, which was maintained for 3 min. Helium was used as the carrier gas at a linear flow rate of 45 cm/s in constant flow mode. The GC was equipped with a J&W DB5-MS capillary column (length 30 m, i.d. 0.25 mm, 0.25 µm film thickness, Agilent Technologies). The MS was operated in positive chemical ionization mode (PCI) using isobutane as reagent gas and performing the analysis in selected reaction monitoring (SRM) mode. The ion source temperature was set to 165 °C, the electron energy set to 200 eV and finally the filament emission current was 300 µA.

A second GC-MS system was used for validation of the extraction and clean-up method and quantification of both OPEs and phthalates in the SRM 2585. The system consisted of a Varian 450 GC connected to a Varian 320 triple quadrupole MS. The GC was equipped with an CTC Combi Pal autosampler, a S/S injector set to 280°C used in splitless mode for 1 min and a J&W DB5-MS-UI capillary column (length 30 m, i.d. 0.25 mm, film thickness 0.25 µm, Agilent Technologies). Helium was used as the carrier gas at 1 mL/min in constant flow mode. The MS was operated in PCI mode using ammonia as reagent gas (pressure 5.30 Torr) and performing the analysis in SRM mode. The ion source temperature was set to 210 °C, the electron energy set to 150 eV and finally the filament emission current was 100 µA. An analysis protocol using iso-butane as reagent gas has been previously described in detail by Bergh et al. (10). The ionization of OPEs and phthalates with ammonia as reagent gas is similar to the previously published method. In this case the selected ions are listed in **Table 2**. Electrophilic addition $[M+NH_4]^+$ occur for some of the compounds, *i.e.* TCEP, TCiPP, TDCPP; TPP, DPEHP and TToP. Also the phthalates are susceptible to electrophilic addition to some extent, and if the pressure of the reagent gas is increased the electrophilic addition also increases. To get the most of

the $[M+H]^+$ even though a rather high pressure is used, the temperature in the ion source was increased to 220°C that decreased the electrophilic addition and almost solely generated $[M+H]^+$, the limit of quantifications were equivalent as when iso-butane were used as reagent gas (10).

Extraction and clean-up

100 mg of SRM 2585 dust was extracted by ultrasonic assisted solvent extraction in 4 mL of acetone for 10 min in an ultrasonication bath (Sonorex Digital 10 P, BANDELIN electronic, Berlin, Germany). This extraction process was repeated once with fresh solvent and the two extracts were combined and the resulting suspension centrifuged (LABOFUGE 300, Kendro Laboratory products, Osterade, Germany). After recovery of the supernatant the solvent was change from acetone to 2 mL of hexane. An SPE Florisil cartridge (Isolute® SPE-FL 500 mg/3 mL, IST, Hengoed, UK) was conditioned with 3 mL of hexane before the sample was loaded onto the cartridge. The cartridge with the adsorbed sample was washed with 10 mL of hexane and then the OPEs and phthalates where eluted with 6 mL of hexane:acetone (1:1). If any visible particles where still in the sample, it was filtered through a nylon syringe filter (Titan filtration systems, 0.20 µm pore size, diameter 25 mm; pre-cleaned by rinsing with 1 mL of acetone) and the final sample extract solution evaporated down to 5 mL.

Results and Discussion

Extraction and clean-up of SRM 2585

When collecting dust the samples are generally small, around 100 mg, especially when a filter sampling device on a vacuum cleaner nozzle is used for sample collection. For this reason the sample size of SRM 2585 was selected to be 100 mg of dust. Each dust sample

was spiked with deuterated internal surrogate standards (DEP- d_4 , TBP- d_{27} , BzBP- d_4 and DEHP- d_4) and was extracted by ultrasonic assisted solvent extraction using 3 x 4 mL of acetone. The first and second fractions were pooled and the target analytes determined in the combined fraction. The third fraction was used to determine the remaining amount of the target analytes in the dust after extraction.

An initial analysis of the dust showed that the amount of TPeP was $< 0.01 \mu\text{g/g}$ and this compound was subsequently used as internal volumetric standard. Solvent volume of the pooled fractions one and two (extract) and of fraction three (extraction control) was reduced down to 1 mL and the relative amount of the target analytes was determined using the volumetric standard. Efficiency of the extraction as determined by analysis of the third fraction showed that only seven of the twenty-one target analytes could be detected above LOD, three OPE:s and four phthalates. All but one of these compounds had a relative amount $\leq 1.5\%$ in the third fraction, while the seventh compound, TCEP, had a relative amount of 3.0%, **Table 3**. It was concluded that two extraction cycles of 4 mL of acetone were sufficient for complete extraction of OPE:s and phthalates from 100 mg of SRM 2585 with a yield $\geq 99\%$., except for TCEP 97% and DEP 98,5 %.

Clean-up of the SRM 2585 extract using an SPE-FL cartridge was evaluated using spiked solutions. Approximately 1 μg of individual OPE and phthalate target analytes was dissolved in 8 mL of acetone, corresponding to the dust extraction solvent volume. A change of solvent from 8 mL acetone (extraction solvent) to 1 mL of hexane (SPE sample application solvent) was made. The procedure was performed as follows; the 8 mL acetone fraction was evaporated down to 1 mL, 6 mL of hexane was added and the solvent volume was further reduced down to 2 mL. The relatively high volatility of some of the low molecular weight OPEs and phthalates makes evaporation to dryness unsuitable. Changing from acetone to hexane is a critical step, especially for the

phthalates, since even a small amount of acetone left in the solution was shown to give a significant breakthrough on the SPE-FL cartridge. By performing the solvent change in the way described above, the amount of acetone remaining in the solution as well as the loss of low molecular analytes were negligible. The 2 mL hexane solution was loaded on top of the SPE cartridge and the cartridge first rinsed with 3 mL of hexane and the target analytes then eluted with 6 mL of hexane:acetone (1:1). No breakthrough was detected for any of the analytes in the 3 mL of hexane wash fraction and recoveries were between 80-115% (n=3) for the analytes.

A comparison was also made using syringe filtration (n=3) and the SPE-FL clean-up (n=3); the different clean-up techniques gave similar results in terms of determined concentrations in the dust, but the repeatability was significantly better using the SPE Florisil clean-up with hexane wash. Relative standard deviations of the determined concentrations were 1-46% for the syringe filtration, while they were 2-10% for the SPE-FL clean-up. The chromatographic profiles using electron ionization and full scan mode showed a significant improvement with SPE-FL clean-up, **Figure 1**. The same clean-up procedure was later extended to use a 10 mL hexane wash, still with no breakthrough. The OPEs are very sensitive to column degradation and relatively clean sample extracts are preferred. The second GC-MS system was also complemented with the novel “ultra inert” column (J&W Scientific); however the new column did not provide a notable difference in terms of life span and/or less column degradation.

Quantification, curvature and matrix effects

As was described in a previous paper the GC-PICI-SRM-MS method used for the final analysis and quantification is very selective and generates a “clean” chromatographic profile, **Figure 2**, (10). The calibration curves showed significant curvature that could be

compensated for by the internal standard. In the present analysis of SRM 2585 it was evident that at concentration levels around 2 ng/ μ L the internal standards could not fully compensate for the curvature. The quantification of DBP, BzBP and DEHP was made both with relative response factors using both polynomial and linear regression analysis. The results were the same with no significant differences for all compounds regardless of regression analysis provided that a linear calibration system of two adjacent calibration points was used. Two GC-MS systems with different injection systems were used for the analyses, a Thermo GC-MS/MS triple quadrupole system with a PTV injection port and a Varian GC-MS/MS triple quadrupole system with a S/S injection port. The calibration curvature appeared in PICI-SRM mode both with isobutane and ammonia as the ionization reagent, as well as in EI-SIM mode. When using the GC-MS system with a PTV injection port the curvature was slightly less than compared to the GC-MS system with S/S injection port. A suggestion is that the curvature is dependent on the instrument, more specifically the injection system, rather than the mode of ionization. However, the presumed dependence on injection technique needs to be investigated further.

The compounds in the SRM 2585 span a large concentration range and there were indications of matrix enhancement effects in the sample when using too small a final volume of extract, in this case 1 mL. For this reason the final sample extract volume was adjusted to approx. 5 mL where the concentrations of all target compounds were at an acceptable level with respect to calibration and matrix effects. The instrumental LODs and LOQs were defined as the amount of analyte required to produce a signal greater than 3 and 10 times the standard deviation of the baseline noise, respectively. The MQL were calculated as three times the standard deviation of the procedural blanks above the blank mean values. For analytes with no detectable blank levels the MQL was set equal to LOQ

taking into account the amount of sample used for analysis. Values of LOQ and MQL are presented in **Table 4**.

Dust is a complicated matrix and to further investigate possible matrix effects, two subsamples of the SRM 2585 dust sample were analyzed. One subsample was analysed as is and the second subsample was spiked with OPE and phthalates. The results showed indications of response enhancement for six OPEs; TCEP (0-20%), THP (0-20%), DPEHP (0-20%) and TEHP (0-10%). Due to the use of three deuterated phthalate internal standards, the phthalates showed little or no matrix effects (95-109% response) with the exception of DEHP that exhibited a response enhancement of 50%. A repeated experiment for this compound with an extended calibration curve and polynomial regression analysis showed that this was solely a contribution from the external standard calibration curvature and in the final analysis a sample spiked with DEHP showed no matrix effect (a response of 98%). By increasing the wash fraction in the SPE cleaning from the initial 3 mL up to 10 mL of hexane and decreasing the strength of the elution of the target analytes by changing the elution solvent from 3 mL acetone to 6 mL of hexane:acetone (1:1), the matrix effects were slightly reduced but were not completely eliminated. The matrix effects were further investigated by spiking the dust extract with three levels of the target analytes. Calibration curvature makes standard addition uncertain, and with a positive curvature the concentration will be underestimated. Indications of matrix enhancement effects were obtained for TCEP, THP and TEHP where the standard addition showed a significant curvature at 0.1% significance level (*i.e.* the coefficient of the quadratic term of the calibration curve differs significantly from zero). Thus only the first level of the standard addition was used and this only for verification of the amounts quantified by external standard calibration. The concentrations for the three analytes TCEP, THP and TEHP were determined to 0.73 ± 0.06 , 0.26 ± 0.16

and $0.33 \pm 0.04 \mu\text{g/g}$ (95% confidence interval) respectively, verifying that the concentrations determined by external standard quantification are accurate. DPEHP was determined by all three standard addition levels with no significant curvature. The concentration was in this case determined to $1.10 \pm 0.53 \mu\text{g/g}$, which is slightly lower than the value determined with external standard quantification. But, taking into account the relatively large error margins for the standard addition the determined amount is within the precision of the determination, **Table 4**. TBEP is the analyte that is most prone to interact with glass surfaces, and it is susceptible to the degradation in the GC column. The analytical performance of this particular analyte is usually lower, and the results for this compound were verified by a four level standard addition. The external standard calibration curve of this analyte showed no statistical indication of curvature up to a concentration of $3 \text{ ng}/\mu\text{L}$ with a correlation coefficient of 0.9995. Thus, the standard addition was performed with the same spikes as before but with an additional spike with the highest concentration of $2.1 \text{ ng}/\mu\text{L}$, corresponding to approximately double the concentration of this analyte in the SRM 2585. The standard addition calibration had no significant curvature (even a 90 % confidence interval the quadratic coefficient includes zero) and the determined concentration was 73 ± 13 , which is only slightly lower than the concentration determined by an external standard analysis.

Determination of OPEs and Phthalates in SRM 2585

The final analysis of SRM 2585 was performed as seven replicates and three method blanks, and the results are presented in **Table 4**. Two compounds, TDCPP and TToP, were close to the MQL. Concentration determination of these compounds was based on seven replicates and two additional samples with half the normal final solvent volume. In general the OPEs are presentd in lower concentrations compared to the phthalates. The

exception is TBEP which is present in relatively high amounts, 82 $\mu\text{g/g}$ dust. This is consistent a previous study of OPEs and phthalates in dust from indoor environments (21). We also found THP in SRM 2585. THP is not known to be frequently used, and to our knowledge it has not been reported in indoor environments in air as well as in dust. TiPrP and TPrP were not detected in SRM 2585 (MDL < 0.002 $\mu\text{g/g}$). TEP and TiBP were detected, but in very low amounts, above LOD but below LOQ. The two propyl phosphates are in general not found in indoor air samples and the TEP and TiBP usually occur in relatively low amounts in air. These four compounds are all relatively volatile and therefore unlikely to be present in high amounts in dust. A recent study of SRM 2585 by Van den Eede *et al.* (29) allowed comparison of seven of the twelve OPEs found in the SRM 2585 in this study, **Table 5**. The determined concentrations are in relatively good agreement with a difference < +17% for all compounds except TBEP and TToP, which differ +40% and -45%, respectively. TToP was near the LOQ in this study. The relative standard deviation of TBEP in the study by Vand den Eede et al. was relatively large, 20%, **Table 5**. The concentration determined in this study is based on using the standard addition method ($73 \pm 13 \mu\text{g/g}$), and possibly this method provides the best determination of the concentration of TBEP.

Conclusions

Extraction by ultrasonic assisted solvent extraction provides full extraction of OPEs and phthalates from SRM 2585 House Dust. The extraction method gives a relatively clean extract, which is especially important for the OPEs. All target analytes, fourteen organophosphates and seven phthalates, were determined in SRM 2585 House Dust by using linear regression, polynomial regression or standard addition. The phthalates concentrations described here for SRM 2585 are, to our knowledge, the first reported.

Even though there are no certified values for SRM 2585 for concentrations of OPEs and phthalates, the results reported in this study provide the opportunity for other laboratories worldwide to compare their results using this same material. The results reported in this study could ultimately be used in conjunction with additional analyses at the National Institute of Standard and Technology to assign certified values for OPEs and phthalates in SRM 2585 (30)

In general the phthalate concentrations are consistent with published investigations of different indoor environments (3,4,9,31). The exception could be DiBP, which was found in higher concentrations in SRM 2585. A summary of relevant studies of phthalates in indoor dust has been presented by Langer *et al.* (4). The phthalate concentrations in SRM 2585 are very similar to the median values reported from a study in the U.S. in 2003 ($n=120$; DEP 4.98 $\mu\text{g/g}$, DiBP 1.91 $\mu\text{g/g}$, DBP 20.0 $\mu\text{g/g}$, BzBP 45.4 $\mu\text{g/g}$, and DEHP 340 $\mu\text{g/g}$, Cape Cod, MA) (9) and also to our previous study (21). The availability of additional deuterated OPE compounds, only TBP- d_{27} and TPP- d_{15} are currently available, would improve the analytical determination of these compounds significantly, especially for TBEP.

Disclaimer

Certain commercial equipment or materials are identified in this paper to specify adequately the experimental procedure. Such identification does not imply recommendation or endorsement by NIST, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

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Table 1: Names, abbreviations, CAS numbers of the target analytes.

Name ^a	Abbreviation ^b	CAS No.
Phosphates		
Triethyl ¹	TEP	78-40-0
Triisopropyl ¹	TiPrP	513-02-0
Tripropyl ¹	TPrP	513-08-6
Triisobutyl ¹	TiBP	126-71-6
Tributyl ¹	TBP	126-73-8
Tris(2-chloroethyl) ¹	TCEP	115-96-8
Tris(2-chloroisopropyl) ²	TCiPP	13674-84-5
Tripentyl ³	TPeP	2528-38-3
Trihexyl ¹	THP	2528-39-4
Tris(1,3-dichloroisopropyl) ³	TDCPP	13674-87-8
Tri(2-butoxyethyl) ¹	TBEP	78-51-3
Triphenyl ¹	TPP	115-86-6
Diphenyl-ethylhexyl ³	DPEHP	1241-94-7
Tri(2-ethylhexyl) ¹	TEHP	78-42-2
Tritolyl ¹	TToP	1330-78-5
Tributyl- <i>d</i> ₂₇ ⁵	TBP- <i>d</i> ₂₇ (IS)	-
Phthalates		
Dimethyl ⁴	DMP	131-11-3
Diethyl ⁴	DEP	84-66-2
Diisobutyl ⁴	DiBP	84-69-5
Dibutyl ⁴	DBP	84-74-2
Benzylbutyl ⁴	BzBP	85-68-7
Diethylhexyl ⁴	DEHP	117-81-7
Di- <i>n</i> -octyl ⁴	DnOP	3115-39-7
Diethyl- <i>d</i> ₄ ⁵	DEP- <i>d</i> ₄ (IS)	-
Benzylbutyl- <i>d</i> ₄ ⁵	BzBP- <i>d</i> ₄ (IS)	-
Diethylhexyl- <i>d</i> ₄ ⁵	DEHP- <i>d</i> ₄ (IS)	-

^a Suppliers were: ¹Aldrich Chemicals, Milwaukee, USA; ²Akzo Nobel, Herkenbosch The Netherlands; ³TCl, Tokyo, Japan; ⁴Sigma Aldrich, Steinheim, Germany; ⁵Cambridge Isotope Laboratories Inc, Andover, USA. ^b IS, Internal Standard.

Table 2: Precursor ion, collision energy and product ion used with ammonia as reagent gas

	Molecular weight	Precursor Ion [m/z]	Product Ion [m/z]	Collision Energy [eV]
Phosphates				
TEP	182	183	99	15
TiPrP	224	225	99	15
TPrP	224	225	99	15
TiBP	266	267	99	20
TBP	266	267	99	20
TCEP	284	302 (285)*	99	25
TCiPP	326	327 (344)*	99	20
TPeP	308	309	99	15
THP	350	351	99	15
TDCPP	430	448/(431)*	99	20
TBEP	398	399	199/(299)*	10
TPP	326	327/(344)*	327	10
DPEHP	362	363/380	251	15
TEHP	434	435	99	15
TToP	368	386/(369)*	369	10
TBP- <i>d</i> ₂₇ (IS)	293	294	102	20
Phthalates				
DMP	194	195	163	5
DEP	222	223	149	15
DiBP	278	279	149	15
DBP	278	279	149	20
BzBP	312	313	149	10
DEHP	390	391	149	15
DnOP	390	391	149	20
DEP- <i>d</i> ₄ (IS)	226	227	153	15
BzBP- <i>d</i> ₄ (IS)	316	317	153	10
DEHP- <i>d</i> ₄ (IS)	394	395	153	25

* = The ions in brackets are used for verification and not quantification.

Table 3: Exhaustive extraction of 100 mg of SRM 2585 dust (3 × 4 mL solvent)

Phosphates	% remaining in 3 rd fraction	Phthalates	% remaining in 3 rd fraction
TCEP	3.0	DEP	1.5
TCiPP	1.0	DBP	0.3
TBEP	1.0	BzBP	0.1
		DEHP	0.4

Table 4: Concentration levels in µg/g of phthalates and organophosphates in SRM 2585

	Detection limits		Blank level (n=3)	SRM 2585 (n=7)		
	LOQ (µg)	MQL	Mean	Mean	SD	RSD %
Phosphates						
TEP	0.5	0.23	-	> MQL	-	-
TiPrP	0.1	0.005	-	n.d.	-	-
TPrP	0.1	0.004	-	n.d.	-	-
TiBP	3.6	0.97	-	> MQL	-	-
TBP	6.2	0.01	-	0.19	0.02	13
TCEP	5.4	0.27	-	0.84 (0.73)	0.06	7
TCiPP	9.2	0.61	0.09	0.88*	0.14	16
TPeP	4.6	0.023	-	n.d.	-	-
THP	2.0	0.17	0.07	0.25 (0.26)*	0.03	13
TDCPP	46	2.3	-	2.3 ^a	0.28	12
TBEP	19	0.93	-	82 (73)	6.5	8
TPP	3.9	0.20	-	1.1	0.10	9
DPEHP	2.0	0.10	-	1.3 (1.0)	0.12	9
TEHP	7.1	0.36	-	0.37 (0.33)	0.04	11
TToP	14	0.68	-	0.74 ^a	0.11	14
Phthalates						
DMP	1.0	0.6	0.15	1.0*	0.03	3
DEP	1.8	0.9	0.64	6.7*	0.34	5
DiBP	0.5	3.4	1.1	6.0*	0.26	4
DBP	18	1.6	0.82	31*	1.1	4
BzBP	1.0	0.1	0.08	93*	1.9	2
DEHP	5.3	1.1	1.1	570*	11	2
DOP	3.5	0.2	-	17*	0.92	5

* Values are reduced by its equivalent blank value.

^a n=9. Values include two additional samples with a decreased final volume of the sample extract. TCEP, THP, DPEHP, TEHP and TBEP were also determined by standard addition, values given in brackets.

Table 5: Comparison of concentrations in µg/g of seven organophosphates present in SRM 2585.

	Van den Eede et. al. (2011) GC-EI-MS			This study GC-PICI-SRM			Difference
	Mean	SD	RSD %	Mean	SD	RSD %	[%]
TBP	0.18	0.02	11	0.19	0.02	13	5.3
TCEP	0.70	0.17	24	0.84	0.06	7	17
TCiPP	0.82	0.10	12	0.88	0.14	16	6.8
TDCPP	2.0	0.26	13	2.3	0.28	12	13
TBEP	49	9.6	20	82 (73)	6.5	8	40 (33)
TPP	0.99	0.07	7	1.1	0.10	9	10
TTToP (TCP)	1.07	0.11	10	0.74	0.11	14	-45

The determined value of TBEP in brackets value determined by four level standard addition. TTToP are abbreviated by TCP (Tri-cresyl phosphate) in the study by Van den Eede *et al.*

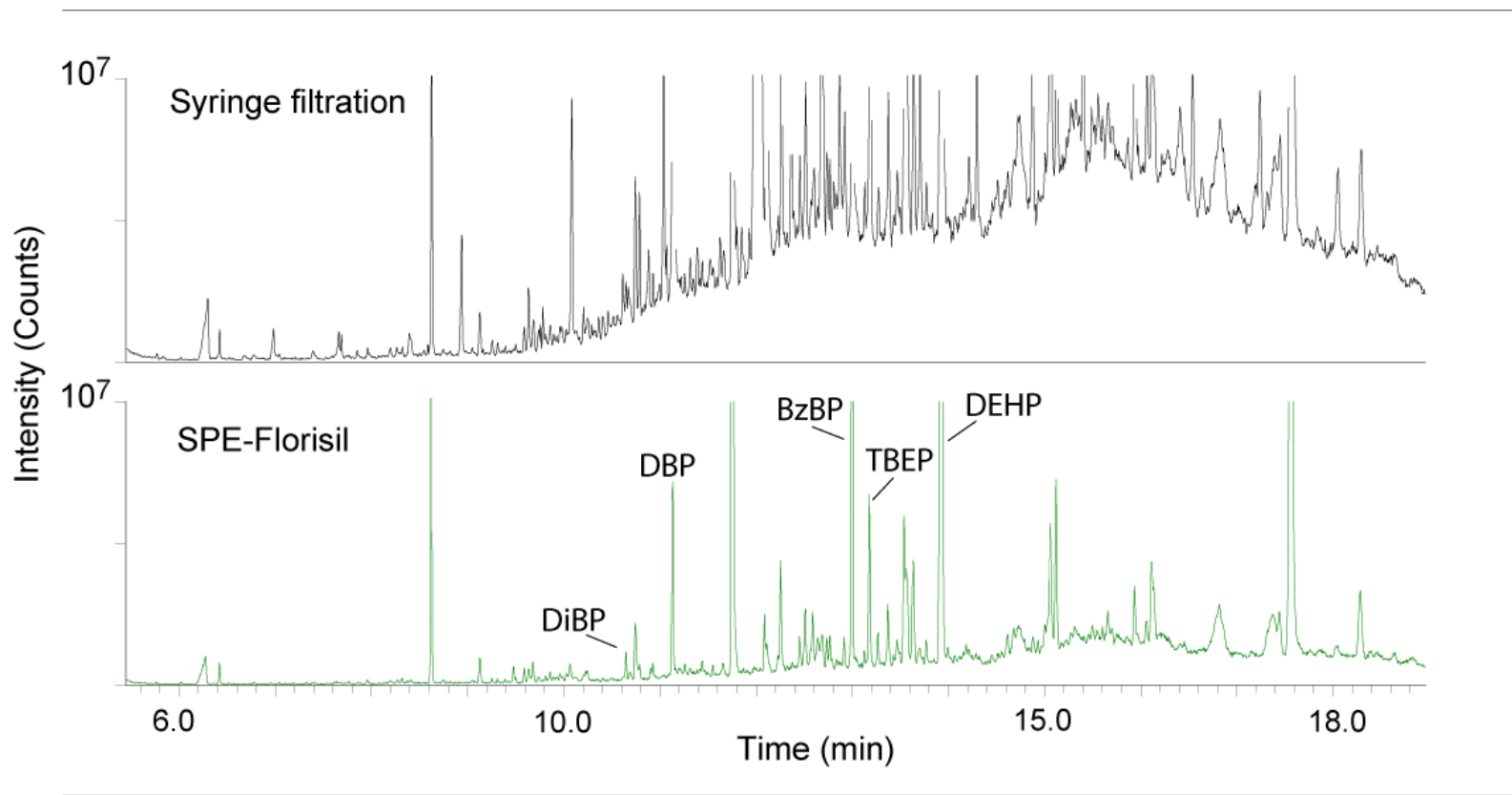


Figure 1: EI-MS chromatogram of SRM 2585 dust extract using syringe filtration and SPE-Florisor clean-up.

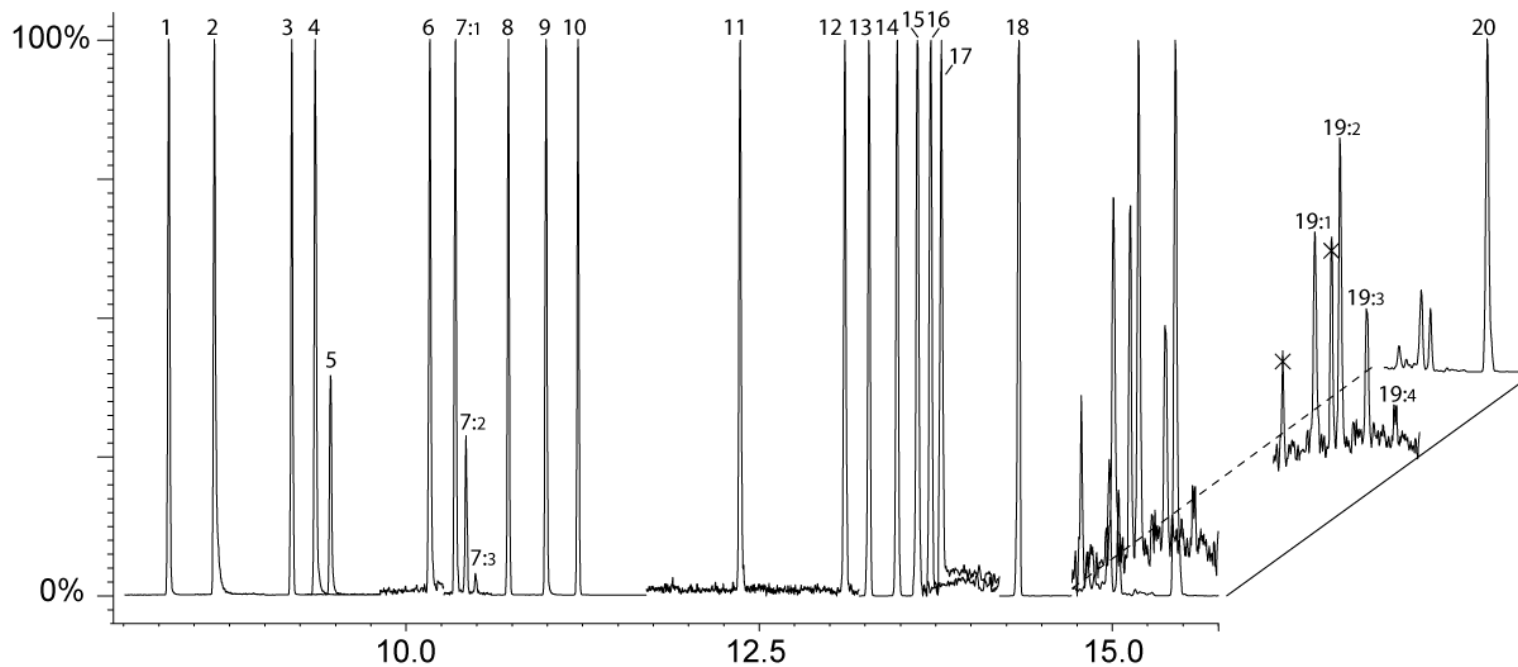


Figure 2: PICI-SRM chromatogram of the SRM 2585 House Dust extract. All scan intervals are normalized to 100%. 1:DMP, 2:TiBP, 3:DEP, 4:TBP- d_{27} , 5:TBP, 6:TCEP, 7:TCiPP (3 isomers), 8:DiBP, 9:TPeP (spiked), 10:THP, 11:DBP, 12:TDCPP, 13:BzBP, 14:TBEP, 15:TPP, 16:DPEHP, 17:TEHP, 18:DEHP, 19:TToP (4 isomers), 20:DnOP

