

## An ultrasonic extraction method for quantification of phthalates in poly (vinyl chloride) and polypropylene by gas-chromatography time of flight mass spectrometry (GC-TOFMS)

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**Abstract:** Phthalates are used as plasticizers in the manufacturing of plastics to increase their flexibility. Phthalates are endocrine disruptors and given their potential toxicity and widespread use, many countries have implemented strict regulations on their usage. A rapid gas chromatography time-of-flight mass spectrometry (GC-TOFMS) analytical method was developed for the determination and quantification of six regulated phthalates. Three extraction methods were investigated including two standard techniques; a dissolution method and a Soxhlet method (EN 14372:2004E). These two standard methods were compared to a simpler ultrasonic extraction method. The recoveries and accuracy of the measurements were assessed by analyzing a polypropylene (PP) certified reference material (matrix CRM) and spiked polyvinyl chloride (PVC) samples. The ultrasonic extraction method resulted in better recoveries (>80%) when compared to the dissolution method. The results obtained from extracting the CRM using the ultrasonic, dissolution and Soxhlet extraction methods were within the certified ranges. The dissolution method occasionally retains the phthalates during precipitation, leading to lower recoveries and inconsistent performance. The ultrasonic extraction method is simpler, uses less solvent and is less time consuming when compared to the conventional Soxhlet extraction method. The ultrasonic extraction method can confidently be used for the accurate quantification of the regulated phthalates in plastics at concentration levels ten times below the European Union regulated limits.

**Keywords:** Phthalates; poly (vinyl chloride); polypropylene; ultrasonic extraction; gas-chromatography time of flight mass spectrometry. © 2018 ACG Publications. All rights reserved.

### 1. Introduction

Phthalates are a family of compounds synthetically obtained by esterification of phthalic acid with different alcohols and are often referred to as phthalic acids of esters (PAEs) [1]. Numerous variations of phthalates have been developed differing in the number of carbon atoms in the alcohol chain [2]. Phthalates make up a group of industrial chemicals with high global production volumes and are commonly used as plasticizers in the production of a variety of plastics, with poly (vinyl chloride) (PVC) incorporating the largest share of the market [3-4]. The primary purpose for the addition of phthalates to PVC is to soften the plastic and to improve the properties of the plastic such as flexibility, elasticity,

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transparency, durability and longevity [5]. These plastic materials are used in a wide range of products such as food packaging, textiles, toys, medical devices and electro-technical products [6-9]. In addition to their use in polymers and plastics, phthalates are also added to printing inks and lacquers, to improve surface adhesion, flexibility and wrinkle resistance [10].

Phthalates do not chemically bind to plastic, and can easily migrate into the environment [5,11]. Studies have also shown the presence and migration of phthalates from plastics such as PVC, polypropylene (PP), polystyrene (PS), polyethylene (PE) and polyethylene terephthalate (PET) [3,5,12-14]. As the plastic ages and breaks down, or when heat is applied, migration of phthalates into the environment accelerates [1,11,15]. Phthalates are present in many household products and therefore the probability of exposure is high. The presence of phthalates in plastic toys and plastic packaging products is of particular concern due to their toxicological effects on human health [5,11].

Phthalates are endocrine disruptors and are therefore associated with adverse developmental and reproductive effects. Certain phthalates such as di-2-ethylhexylphthalate (DEHP), benzyl butyl phthalate (BBP) and dibutyl phthalate (DBP) are classified as a category 1B with the hazard notation H360 [16]: “reproductive toxicant for both fertility and developmental effects”. While other phthalates are classified as carcinogenic and are thus classified as substances of high concern in Europe [3,7,17]. Given the aforementioned potential toxicity of the phthalates, many countries and some economic communities such as the European Union have implemented laws to control the use of phthalates mainly in children products [1,18]. Consequently, the plasticizer market is now demanding phthalate free products with the same performance. As a result, several studies have been conducted to identify safer, alternative plasticizers for PVC that will yield an equivalent or even better quality product to those produced with phthalates [18-22].

These regulations encourage industries, which use phthalates as plasticizers to produce child care articles and plastic packaging, to consider the protection of human health [6] by monitoring the presence and quantity of specific phthalates in their products [16] to ensure compliance and minimize human exposure [23]. Section 108 of the US Consumer Product Safety Improvement Act of 2008 mandated all manufacturers of child care articles to test their products for specific phthalates [2]. According to Annexure XIV of REACH regulations, production of certain low molecular weight phthalates is restricted, thus these will only be produced and sold after specific authorization has been granted. European Union (EU) and Korean regulations have set a minimum required limit to a level less than 0.1% by weight for benzyl butyl phthalate (BBP), bis(2-ethylhexyl)phthalate (DEHP), di-*n*-octyl phthalate (DNOP), diisononyl phthalate (DINP) and diisodecyl phthalate DIDP in children toys [16, 24]. According to the Directives 2007/47/EC and 67/548/EEC, manufacturers must indicate the presence of any compound carcinogenic, mutagenic or toxic to reproduction on the product label [17].

Human exposure to phthalates can be by ingestion, inhalation of house dust and/or indoor air, dermal contact and medical devices [25-26]. Recent studies on human exposure suggests medical devices such as blood transfusion bags, hospital PVC tubing materials as well as ingestion of phthalate contaminated food, as the major sources of exposure [7,17,23,25]. Packed food, particularly fatty foods, are the most affected in particular by DEHP [23]. For house hold products, recycling has also been identified as a possible source of phthalate contamination in the recycled plastic. In a study by Pivnenko et al. [3], it is suggested that phthalates are not removed following plastic recycling and could potentially persist in the recycling process resulting in phthalates spreading and accumulating due to the difficulty the recyclers face in achieving 100% sorting [3].

The analysis of plasticizers from polymer matrices involves extraction, identification and quantification [27]. The standard extraction methods such as EN 14372:2004E [28], ASTM D7823-13 [29] and CPSC-CH-C1001-09.3 [30] as well as many literature-reported methods commonly use Soxhlet extraction with dichloromethane, diethylether or tetrachloroethane: carbinol (2:1) and tetrahydrofuran (THF) dissolution to extract phthalates from the polymer matrices [6,11,27]. Although Soxhlet extraction is known as the standardized high precision and robust method, it requires large solvent volumes; large sample amounts; long extraction and drying times; and occasionally results in loss of analyte in the pre-concentration step [5-6,27,31]. Other methods have been reported for extracting phthalates from environmental samples including water, soils, tissue and plasma as well as cardboard [10-11, 26,32].

To ensure the quality control of plastic products and to protect human health [5], it is necessary to investigate and compare the methods routinely used to quantify plasticizers in plastic products with

updated, more efficient extraction and analysis approaches. Furthermore, allowable concentration limits are continuously decreasing, and the performance of these methods at these lower concentrations needs to be evaluated. Although researchers have investigated the extraction of phthalates from PVC, limited information is available on the rapid extraction and quantification of phthalates at concentration levels that are ten times below the regulated limit.

In the present study, a rapid ultrasonic extraction method was used for the determination and quantification of phthalates in PVC using GC-TOFMS. The ultrasonic extraction method was compared with the standard THF dissolution [30] and Soxhlet extraction [28] methods. The standard Soxhlet extraction method typically uses a 1 g sample size (or more) for the extraction and analysis from a PVC matrix [10-11,23,33-34]. In the present study a smaller matrix sample size (0.1 g), reduced extraction solvent volume; and various extraction solvents (hexane and toluene) were investigated. Other solvents have also been used to extract the phthalates from the PVC matrix such as methanol [35], dichloromethane [36], methyl *tert*-butyl ether [37], chloroform [8], acetone: hexane mixture [32] acetone, methanol and ethyl ether [34]. However, methanol and methyl *tert*-butyl ether were reported to have the lowest extraction efficiency [34,37]. In the present study phthalate extraction from a PP matrix was also evaluated using all three extraction methods by analyzing spiked matrix samples as well as the PP matrix certified reference material. The effect of extraction time on phthalate recoveries for the ultrasonic extraction method was also explored. Phthalates targeted in this study are namely: benzyl butyl phthalate (BBP), diethyl phthalate (DEP), dimethyl phthalate (DMP), bis (2-ethylhexyl) phthalate (DEHP), di-*n*-octyl phthalate (DNOP) and di-*n*-butyl phthalate (DBP) in PVC and in PP. Other commonly used phthalates were also evaluated to ensure method selectivity and specificity.

For comparison purposes, as well as to cross validate the ultrasonic extraction method described in this manuscript, THF dissolution and Soxhlet extraction methods were carried out. Other solvents have also been used in literature for precipitating the polymer after dissolving such as methanol [38] and acetonitrile [6]. In the present study the results from precipitating PVC or PP in hexane are compared to those obtained from precipitating in ethanol. Soxhlet extraction was carried out as described in [28]. However, other solvents such as dichloromethane have also been reported [5]. PP matrix CRM as well as the spiked PVC samples were used to assess the accuracy of the extraction methods. Commercial PVC was also evaluated to test for the presence of phthalates.

## 2. Experimental

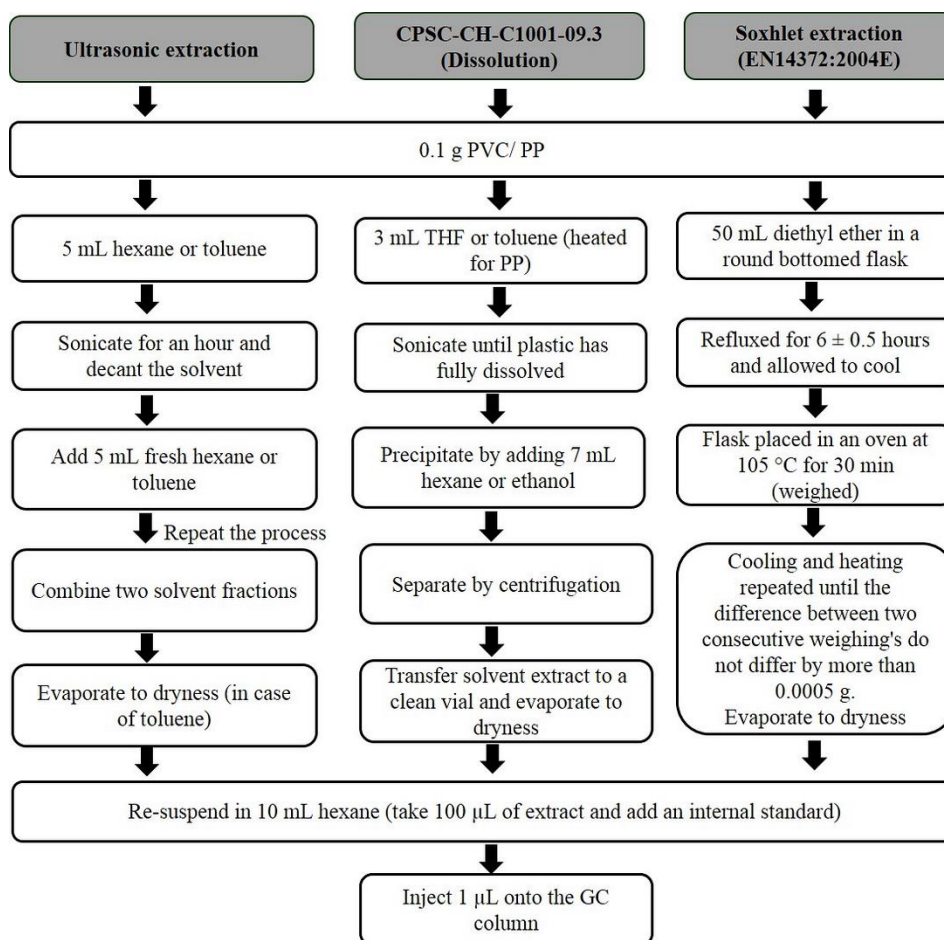
### 2.1. Materials and methods

Phthalate EPA 606 CRM calibration mixture containing BBP, DEHP, DBP, DEP, DMP and DNOP at 2000 µg/ mL and deuterated BBP internal standard at 100 µg/ mL in methanol were used for stock solution preparation and dilutions (all from Restek, Bellefonte, Germany). Individual phthalate reagents, HPLC grade tetrahydrofuran, diethyl ether, ethanol and neat PP were used in extractions (all from Sigma Aldrich, Darmstadt, Germany). Neat Sasol grade S6721 PVC was used in the spiking experiments (from Sasol, Randburg, South Africa). PP matrix CRM was supplied by the National Metrology Institute of Japan, NMIJ CRM 8151-a (Tsukuba, Japan). HPLC grade hexane, acetone, toluene and dichloromethane were all supplied by Burdick and Jackson (Morristown, New Jersey, United States) and methanol by Romil (Waterbeach, Cambridge, United Kingdom).

All the glassware was decontaminated before use by first thoroughly washing with Millipore Milli-Q water (18.2 MΩ) (from Merck, Darmstadt, Germany), followed by rinsing each three times with acetone, methanol and hexane respectively. Glassware was then baked out in an oven at 120 °C for at least 24 hours prior to use. Upon removal from the oven, all glassware was covered with pre-cleaned aluminum foil. Native and isotope labelled stock solutions were prepared in hexane. Isotope labelled deuterated BBP was used as an isotope dilution standard for the native BBP and used as an internal standard for DMP, DEP, DBP, DEHP and DNOP. Calibration solutions were prepared by serial dilutions of the native stock covering the concentration range of the calibration curve, 0.5 µg/ g to 200 µg/g. Aliquots of the diluted calibration solutions were spiked with the same volume of the isotope labelled stock solution to achieve a final concentration of 50 µg/ g, the mixture was vortexed and 1 µL was injected onto the GC column.

## 2.2. GC-TOFMS analysis conditions

The data was collected on a LECO Pegasus III or IV GC-TOFMS instrument using ChromaTOF software for data acquisition and processing. Chromatographic separation was achieved on a Restek Rxi-5SilMS column (30 m x 25 mm (i.d.) x 25  $\mu$ m film thickness). The oven temperature gradient began at 150 °C, held for 1 min, ramped to 230 °C at 30 °C/ min, followed by a ramp to 260 °C at 5 °C/ min where it was held for 1 min and a final ramp to 300 °C at 20 °C/ min which was held for 5 min. A 1  $\mu$ L volume of each sample was injected in split mode at a split ratio of 30:1. The inlet and the transfer line temperatures were both set at 290 °C. Ion source temperature was set at 250 °C and helium carrier gas flow rate at 1.2 mL/ min. Acquisition delay was set at 120 seconds and the mass spectrometer set to scan from 50 to 550 mass units with mass spectra collected at 10 spectra/ second. Retention time and identity of each phthalate was determined by injecting individual standard solutions. To avoid contamination or carryover, the syringe was washed and primed with dichloromethane and hexane pre- and post-injection, and hexane solvent blanks were injected in between the sample injections.



**Figure 1.** Schematic presentation of ultrasonic, dissolution and Soxhlet extraction methods

## 2.3. Extraction

To ensure maximum extraction efficiency, polymer pellets were soaked in liquid nitrogen and ground to 40  $\mu$ m size using a Retsch ZM 200 centrifugal mill. Neat PVC and neat PP samples were gravimetrically spiked with phthalate natives at the concentration levels that match the regulated limit (0.1% by weight) as well as ten times below the regulated limit (0.01% by weight). The spiked samples

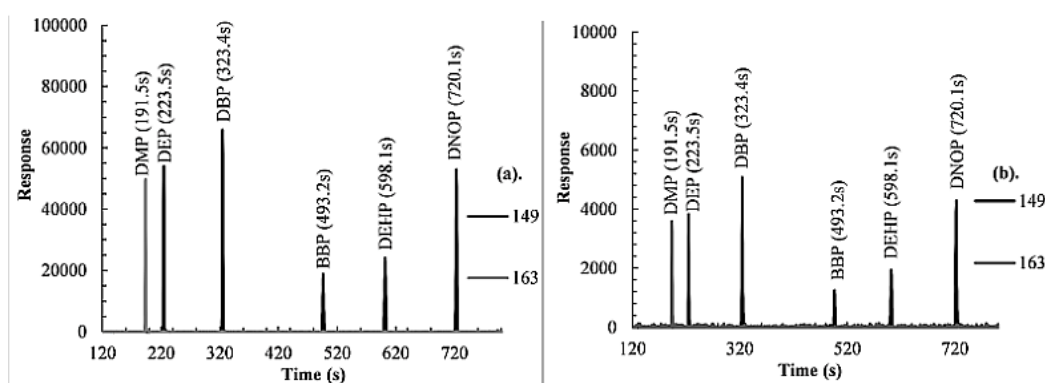
were allowed to equilibrate for 24 to 48 hours prior to extraction at 4°C. Commercial PVC and PP matrix CRM samples were gravimetrically spiked with the same volume of the isotope labelled stock solution used in the preparation of the calibration blends, prior to injection. A seven or eight-point calibration curve was used for quantification.

Extraction methods were carried out as illustrated in Figure 1. Ultrasonic extraction (UE) method was modified from the methods described in literature for extracting phthalates from PVC [33, 39-40]. THF dissolution was followed as described in literature with THF at room temperature for PVC [17,30,37,40-41] and with heated THF for the PP matrix. The dissolution was also performed in toluene for the PP matrix. Soxhlet extraction method was carried out as described in [28].

### 3. Results and discussion

#### 3.1. Chromatographic separation

Pure phthalate standards were run individually to optimize separation, verify the retention time of the target analytes and to ensure that the target phthalates were free of interferences. Both retention time and mass spectra were monitored to ensure accurate identification and subsequent quantification of the phthalates in the samples. Chromatographic separation of the phthalates was achieved in 12 minutes as displayed in Figure 2. Phthalate isomers, DEHP and DNOP, that are considered to co-elute and are subjected to different treatment by the European Legislation [2], were adequately separated on the Rxi-5Sil MS column. Thus, simultaneous analysis and quantification of DEHP and DNOP was easily achieved without the usage of a specialized chromatographic phthalate column. Quantification ions selected for the deuterated BBP internal standard were distinctly different from the ions selected for the natives.



**Figure 2.** Extracted ion chromatogram (149 and 163) of the PVC sample that was spiked at the regulated limit (a) and at ten times below the regulated limit (b)

The common problem in phthalate analysis is the possibility of contamination that might occur in any step of the extraction and or analysis procedure resulting in an over-estimated analyte concentration or enhanced analyte peaks. Organic solvents, glassware and septum bleeding are reported as possible sources of phthalate contamination [42]. Therefore, in the present study a blank PVC, blank PP, as well as a solvent and method blanks (glassware) were included to determine whether there was any background contamination originating from matrix, glassware and or extraction solvents. No phthalates were detected in the blank PVC, blank PP, toluene and hexane solvents and the method blanks. This confirmed that there was no background contamination from the glassware, extraction solvent, PVC and PP matrices or the instrument. Thus, no blank response correction was applied to the data.

### 3.2. Limit of detection and quantification (LOD and LOQ)

Calibration curves were found to be linear in the concentration range 0.5 µg/ g to 200 µg/ g from three independent calibration curves generated on three different days. The correlation coefficients of the target phthalates were all greater than 0.99 (Table 1) which indicated good positive linearity [43-44]. There was a slight improvement on the correlation coefficient values with the addition of an internal standard on five of the six phthalates. The standard error in the intercept ( $S_a$ ) and the standard error in the gradient ( $S_b$ ) were less than the standard error of the calibration curve ( $S_a$  and  $S_b < S_{y/x}$ ) which indicated good general precision and selection of standards. Standard error in the gradient was less than the standard error in the intercept ( $S_b < S_a$ ) which indicated an acceptable working range. The value of the slope was not zero ( $m \neq 0$ ) for all the phthalate analytes which indicated satisfactory calibration sensitivity [43-44]. The aforementioned statistical parameters indicated that all the calibration curves could confidently be used for the quantification of six phthalate analytes of interest.

Different approaches exist for the determination of detection limits. A linear regression of a seven or eight point calibration curve of the native phthalates that were spiked with an internal standard was used for quantification. The limit of detection (LOD) and quantification (LOQ) were defined as three and ten times the standard error of the calibration curve at y-intercept respectively. The average instrument LOD and LOQ was calculated as 0.043 pg and 0.145 pg on column, respectively (Table 1). The average method LOD and LOQ was determined as 0.103 µg/ g and 0.435 µg/ g respectively. The values were determined with relative standard deviation below 5% for all six phthalates.

**Table 1.** Correlation coefficients, instrument and method limit of detection (LOD) and limit of quantification (LOQ)

	Phthalate analytes					
	DMP	DEP	DBP	BBP	DEHP	DNOP
*R <sup>2</sup>	0.9976	0.9976	0.9980	0.9977	0.9943	0.9973
**R <sup>2</sup>	0.9972	0.9978	0.9987	0.9998	0.9988	0.9986
Instrument LOD (pg on column)	0.040	0.040	0.040	0.040	0.050	0.040
Instrument LOQ (pg on column)	0.15	0.15	0.14	0.14	0.14	0.14
Method LOD (mg/kg)	0.13	0.13	0.12	0.13	0.14	0.13
Method LOQ (mg/kg)	0.44	0.44	0.42	0.43	0.45	0.42

\*External calibration and \*\*calibration with an internal standard.

### 3.3. Measurement accuracy and traceability with estimated uncertainty of measurement

The accuracy of the measurement was determined through analysis of a traceable PP matrix CRM. Measurement uncertainty was estimated and expressed using ISO/IEC *Guide to the Expression of Uncertainty of Measurement* (GUM) [44-45]. All the individual uncertainty contributors were identified, combined and the effective degrees of freedom calculated using Welch Satterthwaite equation [45]. The coverage factor (k) was then determined from the *t-distribution table* at 95% level of confidence [44-45] as displayed as a number in bracket in Table 2. Uncertainty sources were reduced to PP matrix CRM, calibration mix, isotope stock, bias and precision as displayed in Table 3. Bias contribution was calculated as detailed in ISO/IEC GUM document [45]. Precision was determined as the experimental standard deviation of the mean calculated from the repeat measurements for each set of experiments analysed [44-45]. Precision was found to be the largest uncertainty contributor across all the phthalate analytes and across all methods. This is the best case UoM for analysis from PP, while from PVC UoM is expected to be larger due to the use of spikes for accuracy assessment and not the use of a matrix CRM that was unavailable at the time and still not available commercially.

All calibrants and sample spikes were prepared gravimetrically. Metrological traceability was therefore established to the kilogram and amount of substance, through the use of NMI calibrated analytical mass balances and certified reference material calibrants obtained from ISO 17034 accredited suppliers, respectively. The NMI PP matrix CRM is also traceable to SI and therefore a reliable measure of the measurement accuracy.

**Table 2.** Experimentally determined quantities of each of the phthalate analytes in the PP matrix CRM and their associated expanded uncertainty of measurement calculated at 95% level of confidence and a coverage factor indicated in the bracket, for each of the extraction methods used

Method	Phthalate analytes			
	DBP (mg/ kg)	BBP (mg/ kg)	DEHP (mg/ kg)	DNOP (mg/ kg)
UE in hexane	960 ± 28 (2.03)	956 ± 33 (1.99)	1022 ± 24 (1.96)	1034 ± 43 (2.45)
UE in hexane 8h	961 ± 30 (2.07)	964 ± 42 (2.09)	1020 ± 26 (1.98)	1080 ± 90 (2.78)
UE in toluene	960 ± 44 (2.31)	960 ± 42 (2.09)	1026 ± 41 (2.57)	1083 ± 81 (2.26)
UE in toluene 8h	960 ± 26 (1.99)	972 ± 47 (2.16)	1015 ± 23 (1.96)	940 ± 112 (2.78)
THF (hexane)	969 ± 101 (2.78)	940 ± 103 (2.57)	1020 ± 149 (2.78)	929 ± 155 (2.78)
THF (ethanol)	955 ± 70 (2.57)	939 ± 77 (2.45)	1008 ± 137 (2.78)	1071 ± 146 (2.78)
Toluene (hexane)	948 ± 59 (2.45)	970 ± 42 (2.10)	1012 ± 63 (2.45)	1012 ± 80 (2.36)
Soxhlet	952 ± 23 (1.97)	964 ± 90 (2.57)	1005 ± 105 (2.78)	1021 ± 111 (2.31)

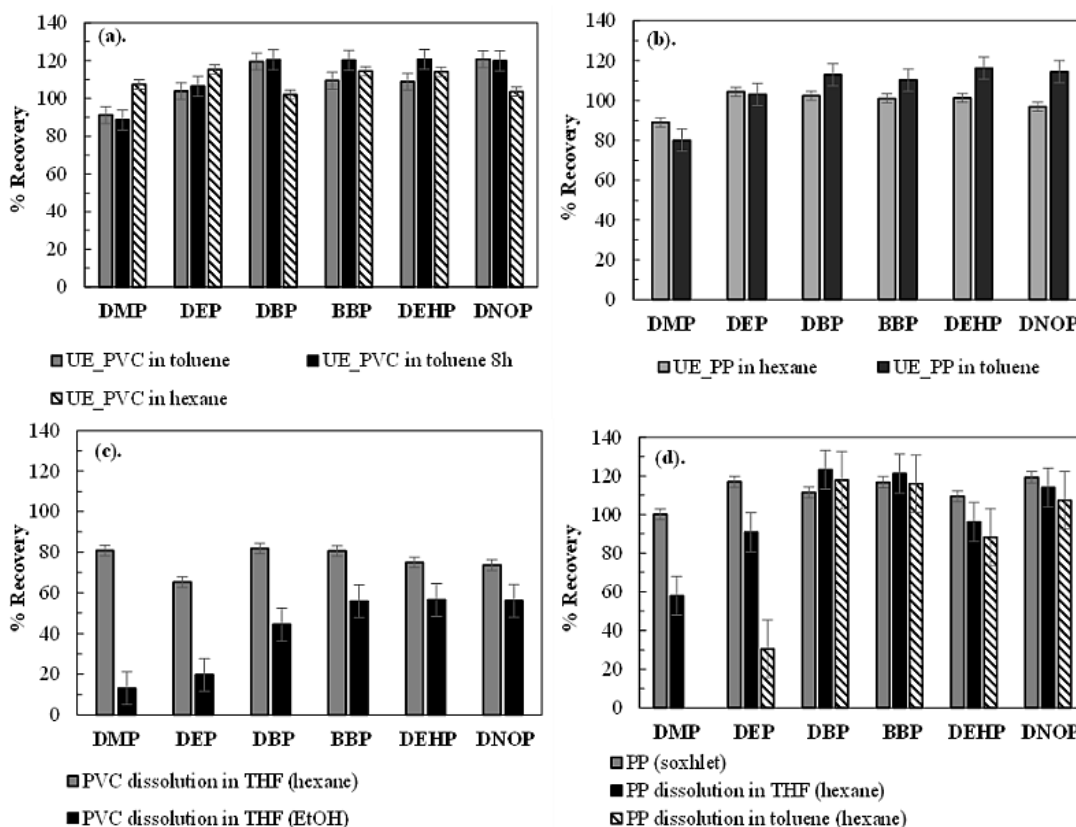
UE refers to ultrasonic extraction; THF (hexane) and THF (ethanol) a method where polymer was dissolved in THF and precipitated in hexane and ethanol respectively; toluene (hexane) refers to a method where the polymer was dissolved in toluene and precipitated in hexane. The number in the bracket is the calculated coverage factor, *k*.

**Table 3.** The uncertainty of measurement budget for the determination of DPB in PP/PVC, listing the main uncertainty contributors

	DBP analyte extracted using ultrasonic method			
	<i>x</i> (mean)	<i>u</i>	<i>u/x</i>	( <i>u/x</i> ) <sup>2</sup>
Matrix CRM (mg/ kg)	963	8.00	0.008307	6.9012E-05
Calibration mix (mg/ kg)	2525.25	7.32323	0.002900	8.4100E-06
Isotope stock (mg/ kg)	126.26	0.89532	0.007091	5.0281E-05
Precision (mg/ kg)	959.78	4.49943	0.004688	2.1977E-05
Bias CRM	0.997	0.0050	0.004688	2.1977E-05
			<i>u<sub>c</sub></i> (combined)	1.3102E-02
			<i>u</i> (standard)	12.58
			<i>U</i> (Expanded)	25.15
			% <i>U</i> <sub>relative</sub>	2.6

### 3.4. Recoveries

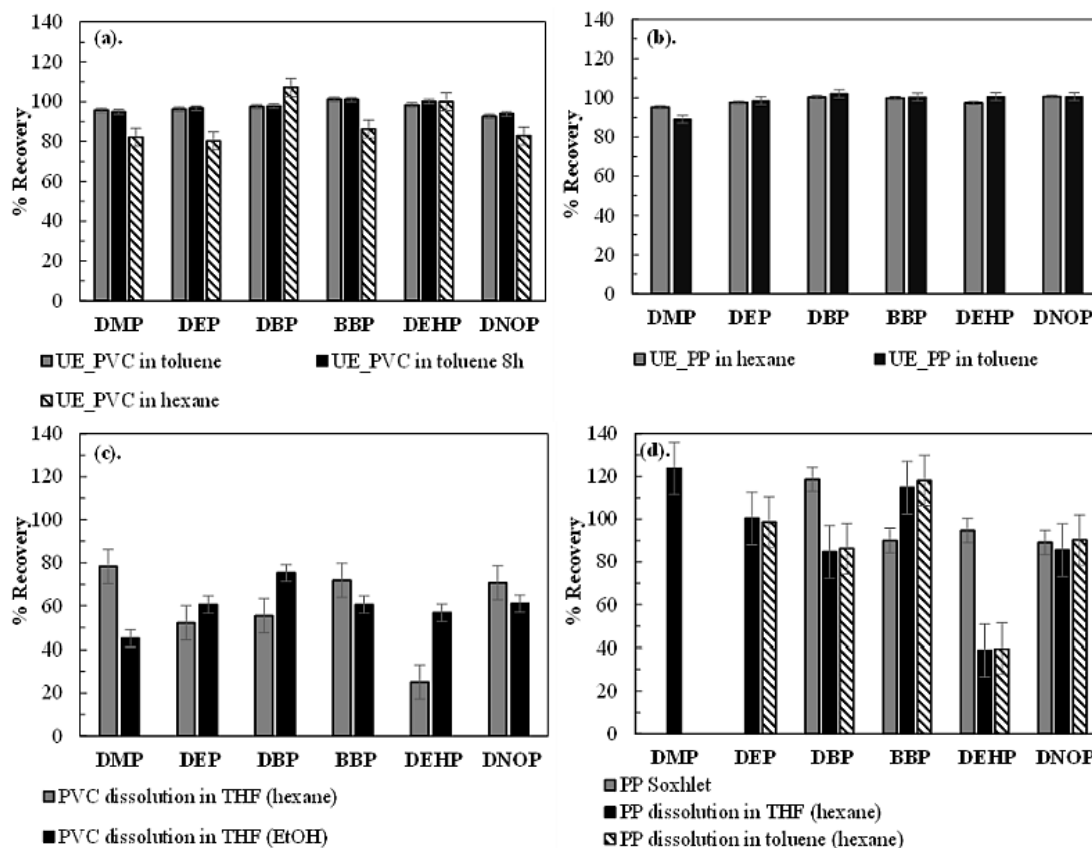
Recoveries were determined using the blank PVC and PP samples spiked with known concentrations of the phthalates, as well as the PP matrix CRM. Recovery of the phthalate compounds was calculated as the ratio between the experimentally determined concentration and the theoretical phthalates concentration added to the PVC, PP and or PP certified value. The methods were carried out under repeatability and reproducibility conditions. The repeatability %RSD and reproducibility %RSD for the measurements was less than 10% respectively for all six phthalate analytes in both the spiked PVC and PP samples; and less than 5% respectively for all three analytes in the PP matrix CRM.



**Figure 3.** %Recoveries for the ultrasonic extraction method (denoted UE) sonicated in hexane and toluene for the PVC and PP matrices respectively (a) and (b); and the dissolution extraction method for the PVC and PP matrices compared with Soxhlet (c) and (d) respectively for the samples that were spiked at the regulated limit. The error bars indicate the expanded uncertainty determined at 95% confidence level and a coverage factor of 2

Figure 3, 4 and 5 compare the percentage recoveries obtained from the ultrasonic, dissolution and Soxhlet extraction (EN 14372: 2004E) methods. Recoveries of greater than 80% were achieved using the ultrasonic extraction method irrespective of the matrix (PVC or PP) and the extraction solvent used (hexane or toluene), at both the regulated limit and ten times below the regulated limit as illustrated in Figure 3. Although the difference is not statistically significant, when closely comparing the two extraction solvents, toluene yielded slightly higher recoveries for all six phthalate analytes of interest whilst hexane gave slightly lower recoveries for DMP, DEP, BBP, DEHP and DNOP. Furthermore, no significant improvement in recovery was observed when the samples were sonicated for a longer period as displayed in Figure 3a and 4a. Thus, a two-hour (one hour per cycle) extraction time proved to be sufficient for the phthalates extraction from PVC or PP to reach equilibrium as there was no significant improvement in recoveries with extraction times of up to eight hours (four hours per cycle) (Figure 3a and 4a). The present results are in agreement with literature, where the extraction time ranged from 10 minutes to 80 minutes and the amount of phthalates extracted was found to increase with the extraction time and later reached equilibrium [35, 37]. For two analytes, DMP and DEP equilibrium was reached at 60 minutes whilst the amount of DBP, DEHP and DNOP increased gradually with increase in extraction time [35]. Literature has also reported an effect on extraction efficiency due to temperature (30 °C and 65 °C) [35, 37]. The current ultrasonic extraction method efficiently extracted both short alkyl chain phthalates DMP and DEP; and longer alkyl chain phthalates DBP, BBP, DEHP and DNOP at ambient temperature for both PVC and PP matrices.

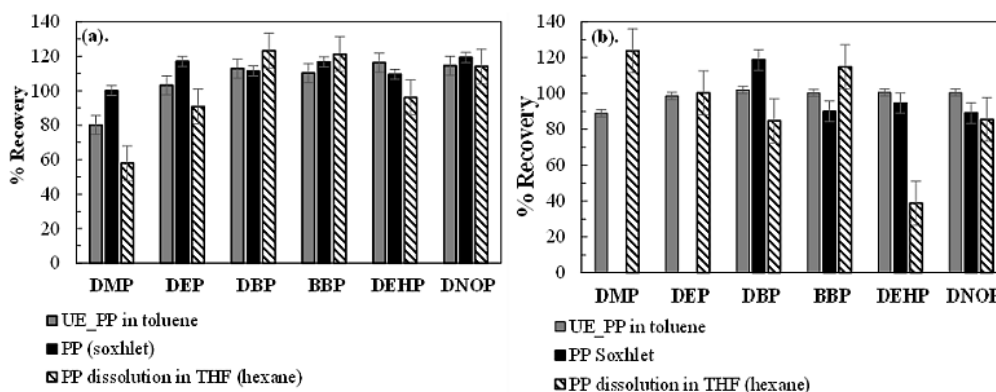




**Figure 4.** % Recoveries for the ultrasonic extraction method (denoted UE) sonicated in hexane and toluene for the PVC and PP matrices respectively (a) and (b); and the dissolution extraction method for the PVC and PP matrices compared with Soxhlet (c) and (d) respectively for the samples that were spiked ten times below the regulated limit. The error bars indicate the expanded uncertainty determined at 95% confidence level and a coverage factor of 2

Using the standard EN 14372: 2004E (Soxhlet) method with samples that were spiked below the regulated limit, only four of the six phthalates were detected DBP, BBP, DEHP and DNOP as illustrated in Figure 4d. The recoveries of these phthalates were greater than 80% but lower than the recoveries obtained using ultrasonic the extraction in toluene for the BBP, DEHP and DNOP analytes. DMP and DEP were not detected in the Soxhlet extract and their degradation products were also not visible on the GC-TOFMS.

A similar result was obtained for the standard dissolution method where PP was dissolved in heated toluene, DMP was not detected (Figure 4d). In addition, heated THF dissolution also resulted in lower recoveries for DMP and DEP. These losses may be attributed to the analytes volatilizing during the polymer dissolution step when heat is applied [46]. This was also supported by the fact that when PVC samples were dissolved at room temperature, without heat, these two analytes were detected with greater than 50% recovery (Figure 3c and 4c). In addition, although it is widely accepted that the polymer fully dissolves in THF [17], studies have indicated that some plasticizers either co-precipitate with the polymer or are retained by the polymer [38] during the precipitation step, which might explain the variable percentage recoveries obtained when applying the standard dissolution method (Figure 4d). This was also experimentally confirmed in the present study where the PP and PVC matrix samples were re-extracted using the THF dissolution procedure and the chromatographic peaks as well as the mass spectrum fragments from phthalate analytes were noticeable on a GC-TOFMS.

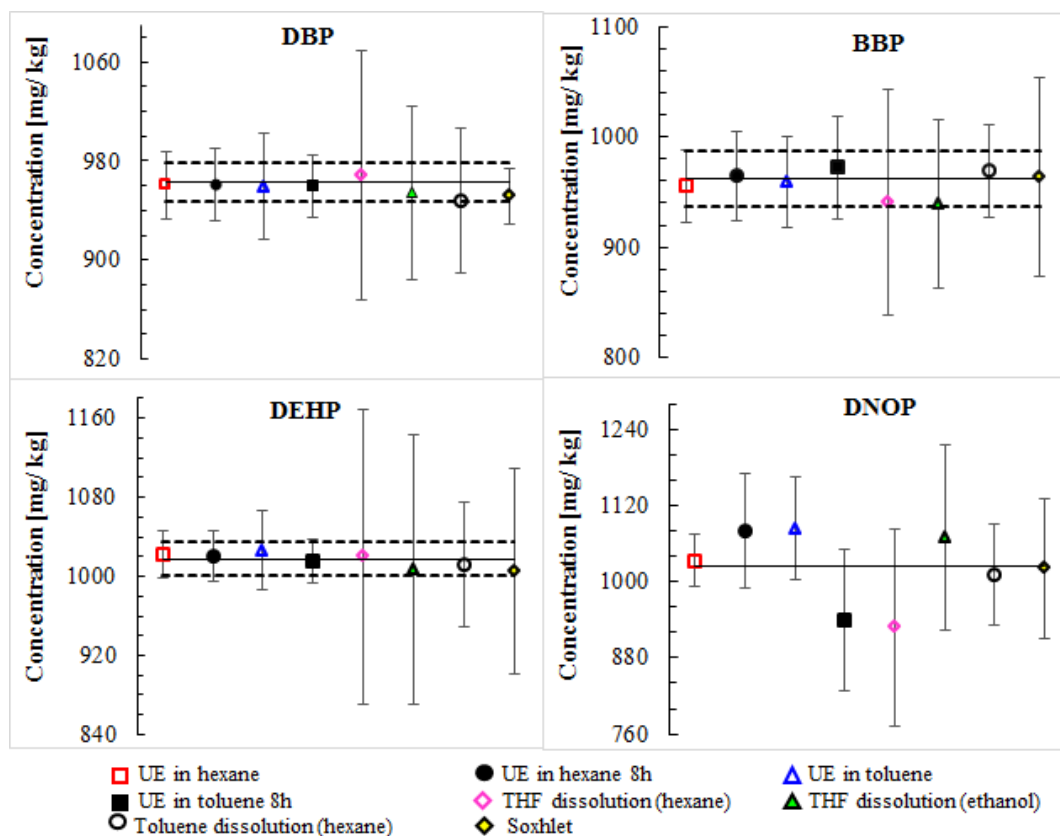


**Figure 5.** Comparison of the best performing UE, dissolution and Soxhlet recoveries for the PP matrix at the regulated limit (a) and ten times below the regulated limit (b)

When the PP matrix CRM sample was dissolved in heated THF and precipitated in hexane, the method's experimental mean was closer to the certified value for DBP and DEHP, compared to BBP which was at the certified value's lower limit of uncertainty as displayed in Figure 6. Similar results were obtained when PP was precipitated in ethanol. When heated in toluene, the experimental mean was closer to the certified value for BBP and DEHP whilst the mean was at the lower limit for DBP. With Soxhlet extraction the experimental means for DEHP and DBP were at the lower limits of the certified value's uncertainty whilst BBP was slightly closer to the certified value.

The DNOP was also successfully extracted from the PP matrix CRM with all the methods. The experimentally determined mean for each of the methods were closer to the information value and the associated estimated uncertainty of measurement overlapped well with the provided information value. Soxhlet, ultrasonic extraction in hexane and toluene dissolution methods all resulted in experimental mean values that were much closer to the information value provided for DNOP.

The ultrasonic extraction method gave results that were closer to the certified value for all three phthalate analytes when compared to the other two standard methods (Figure 6) at the regulated limit and ten times below the regulated limit. The standard dissolution method gave recovery values that differ significantly (Figures 3d and 4d). For samples that were spiked at concentration levels ten times below the regulated limit (Figure 3d, 4d and 5), irrespective of the solvent used for dissolving or precipitating the polymer, the method resulted in poor recoveries for DEHP, (less than 55%) and some analytes were not detected (Figure 5). In contrast, the simpler ultrasonic extraction method yielded good recoveries between 80% and 120% for all the six phthalate analytes, from both matrices, that were spiked at the regulated limit and at ten times below the regulated limit using either extraction solvent (hexane and toluene) as displayed in Figure 3a and 4a. In accordance with recommended method specifications [47-48], the current results indicate no significant losses of analytes from PVC and or PP matrices during the preparation and extraction steps. The percentage recoveries calculated from the analysis of the PP matrix CRM analysis of the PP matrix CRM extracted using different extraction methods are captured in Table 4. Percent recovery values were in the range of 98% to 105%.



**Figure 6.** PP matrix CRM analysis where the solid lines indicate the certified value (for DBP, BBP and DEHP) and information value for DNOP; dashed lines and error bars indicates the expanded uncertainty associated with the CRM and the measurement (at 95% and  $k$  values indicated in Table 2) respectively.

**Table 4.** Comparison of the recoveries obtained from extracting and analyzing the matrix CRM using the different extraction methods. The certified values were  $963 \pm 16$  mg/ kg,  $962 \pm 25$  mg/kg and  $1018 \pm 17$  mg/ kg respectively. The information value for DNOP was 1024 mg/ kg

	% Recovery of phthalate analytes			
	DBP	BBP	DEHP	DNOP
UE in hexane	99.66	99.33	100.4	100.9
UE in hexane 8h	99.80	100.25	100.2	93.86
UE in toluene	99.63	101.7	100.8	105.8
UE in toluene 8h	99.67	101.1	99.72	91.67
THF (hexane)	100.6	97.70	100.2	90.68
THF (ethanol)	99.12	97.61	98.98	104.6
Toluene (hexane)	98.47	100.78	99.38	101.2
Soxhlet	98.80	100.17	98.76	99.70

UE refers to ultrasonic extraction; THF (hexane) and THF (ethanol) a method where polymer was dissolved in THF and precipitated in hexane and ethanol respectively; toluene (hexane) refers to a method where the polymer was dissolved in toluene and precipitated in hexane.

Evaluation of trueness was performed by comparing the measured values of the phthalates to the values of the PP matrix certified reference material. Student  $t$ -tests (95% confidence level) were applied to determine whether the experimental mean obtained from the methods agreed with the certified value and no significant difference was observed. All phthalate concentrations calculated using all three methods were within the certified value's uncertainty limits (Figure 6). However, it is clear from the uncertainty estimation (Table 2 and Figure 6), that the variation in recovery of the dissolution method

(approx. % $U_{relative}$  = 15%), yielded a much larger uncertainty in the measurement result. While the uncertainty of measurement estimated from the ultrasonic extraction method is much smaller due to consistent precision and recoveries (approx. % $U_{relative}$  = 4%). The results of the present study indicate that ultrasonic extraction method can confidently be used for the efficient extraction of phthalates at low concentrations across plastic matrices.

The ultrasonic extraction method was validated by evaluating parameters such as working range, linearity, limit of detection and limit of quantification as detailed in Section 3.2; measurement uncertainty, repeatability, reproducibility and trueness as detailed in Section 3.3. Trueness was evaluated through the use of both a PP matrix CRM and spiked PP samples whilst for PVC it was evaluated through gravimetrically spiked samples. The robustness of the method was evaluated by changing the solvents, solvent volume and the extraction time as discussed in Section 3.4.

A commercial PVC sample was also analyzed and found to contain amongst others, phthalate plasticizers such as butyl octyl phthalate, bis (6-methylheptyl) phthalate, heptyl pentyl ester and DEHP. DEHP was detected to be below the regulated limit.

## 4. Conclusions

The ultrasonic extraction method with GC-TOFMS analysis described in the present study was compared to the standard methods described in literature namely; the dissolution and the Soxhlet extraction EN 14372: 2004 (E) method. Toluene and hexane were able to efficiently extract phthalates from both the PP and PVC matrices using the standard ultrasonic extraction approach. THF dissolution with both hexane and ethanol can be used to extract the phthalates from PVC but additional considerations are required when applying this method to the PP matrix. Variation in recovery was more pronounced in the dissolution method. Both the standard extraction methods worked well when phthalates were present in high concentrations, however some phthalates were not detected at lower concentrations, and those that were detected had low, variable recoveries. The ultrasonic extraction method was demonstrated to be robust across both matrices when analytes are present at both high and low concentrations and reflected a smaller measurement uncertainty. The ultrasonic extraction method can therefore be confidently used for the accurate quantification of the regulated phthalates in plastics.

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