New Analytical Method for Determination of Phthalates in Wastewater by on Line LC-GC-MS Using the TOTAD Interface and Fraction Collector

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Abstract: There is an increasing demand for automatic, reliable and sensitive analytical methods for determining trace levels of phthalic acid esters (PAEs) in environmental samples. While on line coupled liquid chromatography-gas chromatography (LC-GC) has been proof to be a powerful tool for trace-level analyses in complex matrices, the present work presents a new totally automated on line LC-GC method, using the Through Oven Transfer Adsorption Desorption (TOTAD) interface, for the analysis of four of the main phthalates, dibuthyl phthalate (DBP), diethyl phthalate (DEP), dimethyl phthalate (DMP) and diethylhexyl phthalate (DEHP), in a matrix as complex as leachate. The sample is directly injected into the LC injector valve with no sample pretreatment other than simple filtration. The LC step separates the target analytes from matrix interference. Two different LC fractions are collected in a purposely designed fraction collector and then transferred to the TOTAD interface, which concentrates the analytes, totally eliminates the solvent and transfers the analytes to the GC-MS system, where the analysis is carried out. The LOD of the method varied from 0.1 μg/L (DEHP) to 1.4 μg/L (DMP), RSD for retention time below 0.14% and for absolute peak areas below 12% and linearity from 1 μg/L to 1000 μg/L (R^2 > 0.99), except in the case of DEHP (linearity from 1 to 250 μg/L, R^2 = 0.94). The method was applied to the analysis of the target analytes in samples collected from a municipal solid waste (MSW) landfill in Rosario (Argentina).

Keywords: new analytical method; phthalates; landfill leachates; on line LC-GC; TOTAD interface

1. Introduction

PAEs are mostly used as plasticizers, especially in polyvinyl chloride (PVC) and as additives in a variety of products (among them, cosmetics, medical equipment, paints, lubricants, adhesives) [1]. PAEs are categorized as non-persistent organic pollutants however, because they are continuously being introduced into the environment, present a risk to human health and ecosystems. Low molecular weight PAEs, which means that contain between one and four carbon atoms in their alcohol side chain, such as DBP, DEP and DMP, are used in cosmetic and personal care product [2,3]. High molecular weight PAEs, such as DEHP, are used as plasticizers and are added to polymers to increase the flexibility, workability and toughness of the product [4]. The amount of PAEs in plastic products ranges from 10% to 60% by weight [5] and around 87% of PAEs produced are used in PVC [6]. DEHP and DBP are phthalates more frequently used plasticizer in PVC [7]. PAEs are not chemically bound to the polymeric matrix and may be released to the environment by leaching, migrating or evaporating from the final products [8,9]. PAEs have been detected in many environmental samples, including surface runoff [10], river sediment [11], wastewater [12], sewage sludge [10] and landfill leachate [13]. PAEs are

considered to be endocrine disruptors and have been proved to present estrogenic and antiandrogenic action [14,15], making them dangerous to human health [16]. DEHP and DBP are classified as highly dangerous substances in EU regulations [17] and six PAEs (DBP, DEP, DMP, di-n-octyl phthalate (DOP), DEHP and benzyl butyl phthalate (BBP)) have been included in the lists of priority pollutants by the European Union [18]. In the case of DEHP, Directive 2008/105/EC establishes a limit value of 1.3 µg/L for surface water and 8 µg/L in drinking water [19]. Some countries have banned phthalates in products designed for children [20,21].

Landfills are one of the most common disposal methods for MSW [22]. Water infiltration and percolation through the water layer of landfills produces leachates with high concentrations of organic and inorganic pollutants [23]. PAEs are present in leachates in very different concentrations [24]. Many studies worldwide have been carried out to determine PAEs in leachates [25–27]. Jonsson et al. (2003) found PAEs in 11 of 17 landfill leachates analyzed in Europe [26], and Bauer et al. (1997) in all the leachates analyzed from Bavarian landfills [24]. In leachates from landfill in Japan [25] and in Poland [28], PAEs were found in all the leachates measured, DEHP being found in the highest most concentrations. Gao and Wen (2016) also pointed out that DEHP concentrations were the highest, while DEP and DMP were presented in a relatively low concentration [29]. The data point to the need to analyze PAEs in leachates from all over the word, since they are a major source of PAEs in the environment.

The analysis of PAEs in leachates is a complex task, chromatographic techniques such as gas (GC) or liquid chromatography (LC) coupled to mass-spectrometry (MS) are the most frequently used [30]; but the samples require pretreatment before chromatographic analysis. Pretreatment usually include an extraction procedure followed by concentration and clean-up steps. Liquid-liquid extraction (LLE) is the most widely used extraction procedure [25,26], although solid phase extraction (SPE) [13], solid phase micro extraction (SPME) [31], liquid phase microextraction (LPME) [32], stir bar sportive extraction (SBSE) [33]; dispersive liquid-liquid microextraction (DLLME) [34] and microextraction by packed sorbent (MEPS) [35] have also been used. Frequently used methods to analyze PAEs in leachates are those developed for the analysis of drinking, waste or ground water [28,36] although leachates are more complex matrices [37]. As the extraction procedures are usually non-specific, components other than analytes are co-extracted and a clean-up step is sometimes necessary and must ensure that the interfering compounds from the matrix are eliminated, while the extract must be concentrated in order to reach lower detection limits. For the purpose to enhance the sensitivity of the methods, large volume injection (LVI) in GC-MS using a programmable temperature vaporizer (PTV) has been used to analyze organic pollutants, including PAEs, in wastewater [35,38]. Beldean-Galea et al. (2013) developed a comprehensive two-dimensional gas chromatography coupled with quadrupole mass spectrometry (GC × GC-qMS) for the identification of organic pollutants in landfill leachates, including PAEs, with preliminary solvent extraction [37]. Later, the same author used SPME [39] and DLLME [40] for the extraction procedure. Reliable and sensitive analytical methods are necessary for the determination and quantification of PAEs in leachate samples. There is increasing interest in developing on line hyphenated techniques for environmental PAEs analysis that combine the sample preparation, separation and detection steps [36].

On line coupled LC-GC is a very powerful technique for the analysis of compounds at very low concentration in complex matrices. The use of LC eliminates or decreases the time-consuming sample preparation step and minimizes sample manipulation and the risk of contamination or analyte loss [41,42]. The TOTAD interface used in the on line LC-GC is totally automated and can be used with water-sensitive detector as MS. The operation mode of the TOTAD interface has been described elsewhere [43]. TOTAD interface has been used to analyze pesticide residues in water by LVI [44] and by on line LC-GC [45] and other environmental pollutants in environmental samples [46–48]. The TOTAD interface can be coupled to a fraction collector, allowing the different fractions obtained in the LC

separations be collected [49]. The separation of the analytes into different LC fractions results in cleaner fractions with fewer interfering compounds, which is desirable in the analysis of very complex matrices such as leachates. Moreover, the sensitivity of the analysis increases because almost all the analyte reaches the GC detector as the whole volume of each collected LC fraction is transferred to the GC system through the TOTAD interface.

The aim of present work was to develop an analytical method for the determination of PAEs in leachates by on line LC-GC coupled to MS, using the TOTAD interface and a fraction collector. Two LC fractions were determined, and the fraction collector was constructed according to the volume of each of the fractions to be collected. The method was applied to the analysis of leachates samples from a landfill in Argentina.

2. Materials and Methods

2.1. Materials

The PAEs used in this study are among the most frequently detected in leachates: DMP, DEP, DBP and DEHP showed in Figure 1. Standards of the same were obtained from HPC Standards GmbH (Cunnerdorf, Borsdorf, Germany). The acetonitrile and water used as LC mobile phase were HPLC grade of Lab-Scan Analytical Sciences (Gliwice, Poland). Acetonitrile was also used to prepare stock solutions of each PAE at a concentration of 500 mg/L. Working solutions at 1 mg/L and 0.1 mg/L were prepared by dilution of the stock solutions. All solutions were stored in glass flasks covered with foil paper at 4 °C. These solutions were used to spike the leachates at concentrations ranging from 1 µg/L to 1000 µg/L to validate the analytical method.
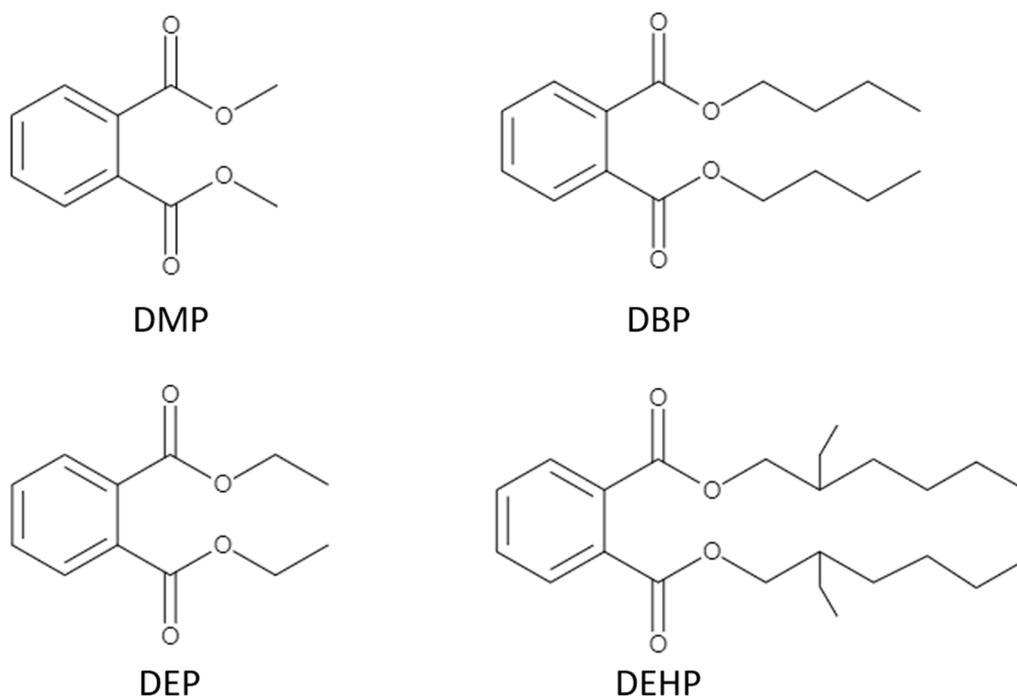

Figure 1. Chemical formula of the four PAEs analyzed.

Tenax TA 80–100 mesh (Supelco, Bellefonte, PA, USA), located between two blocks of glass wool to hold it in place, was used to pack the liner of the TOTAD interface. Once the liner was filled it was conditioned passing a helium stream, while was heated from 50 to 350 °C at 50 °C/min. The final temperature was held for 60 min.

Leachate samples were manually collected from the raw leachate tanks at a MSW landfill site on the outskirts of Rosario (Argentina) at half of the depth to avoid sedimented material from the bottom, using stainless-steel containers. The samples were then

transferred to clean glass vials and covered with foil. The landfill receives approximately 1200 tons per day (t/d) of MSW. The treatment plant consists of an equalization and separation of solids followed by two anaerobic sequential reactors, an aerobic reactor and a final chlorination treatment. The raw leachate samples were sampled at the entrance of the first anaerobic reactor and the leachate sample used as blank at the exit of the aerobic reactor. No plastic materials were used during sampling and analysis, and the leachate samples were simply filtered through a 0.2 μm filter of nylon (Chromatography Research Supplies, Inc) prior to LC-GC-MS analysis.

2.2. Instrumentation

The analyses were carried out using an on line LC-GC system with a TOTAD interface (US patent 6,402,947 B1 exclusive rights assigned to Gibnik Analytical Solutions S.L., Barberá del Valles, Barcelona, Spain) and a fraction collector. The HPLC was a Konik 560 provided with a manual injection valve (model 7725 from Rheodyne, CA, USA), a 50 μL loop, column oven and UV-Vis detector. The LC column, 100 mm × 4.6 mm i.d. (internal diameter), was a modified silica-packed column (C8, ACE, Aberdeen, Scotland). The liner inside the body of the interface was filled with a 1 cm length of previously conditioned Tenax TA, plugged with glass wool at both ends. The fraction collector was constructed using two eight-port valves provided with a multi-position microelectric valve activator (Valco, Houston, TX, USA) to select the position of the multiport valves. Two loops placed between the two eight-port valves allows the two LC fractions containing the PAEs to be collected. The GC (Konik 5000B) was coupled to a mass spectrometer (MS Q12 Konik). An HP-5MS (30 m × 0.25 mm i.d., 0.25 μm thickness) (Agilent J&W GC columns, Santa Clara, CA, USA) column was used for chromatographic separation. The Konikrom plus program (Konik, Sant Cugat del Vallés, Barcelona, Spain) was used for the process and data acquisition.

2.3. LC conditions and Fraction Collection

The LC column (ACE 10 C8; 100 mm × 4.6 mm i.d.) was kept at 25 °C throughout the experiment. The UV detector operated at 235 nm. Acetonitrile/water (65/35; *v/v*) was used as mobile phase, rising to 100% acetonitrile in 4 min and maintained for 5 min. The flow rate was 1 mL/min. The LC fraction to transfer to the loops of the fraction collector were selected by injecting 50 μL of the four PAEs solutions at 10 mg/L. Having fixed the volume of LC fractions to be analyzed, the fraction collector was constructed using two multiport valves, each with one entrance and several exit ports and stainless-steel tubes of 0.75 mm i.d. For leachate analysis, 50 μL of the leachate samples were injected into the LC injector under the same LC conditions as indicated previously. When each fraction began to elute, the double valve was turned, directing the LC fraction to the corresponding loop. Once the transfer to the loop was completed, a six port valve situated immediately after the UV detector was switched to send the LC eluent to waste. Afterwards, the HPLC pump was changed to a flow rate to 0.1 mL/min to propel the two LC fractions collected to the GC by means of the TOTAD interface. Both fractions were successively sent to the GC.

2.4. TOTAD Interface Operation Mode

First, the TOTAD temperature was stabilized at 100 °C, and the LC fractions collected in each loop were propelled by the LC pump to the TOTAD. For this, the double valve was turned and the eluent was changed to acetonitrile at a flow rate of 0.1 mL/min. The helium flow entering A and B in the body of the interface was 500 mL/min during the transfer step. After transfer of the whole fraction, these conditions were maintained for 1 min to ensure the total elimination of the solvent. Then, the flow of gas through B was closed and the TOTAD interface was quickly heated up to 300 °C for the thermal desorption of the analytes, which were transferred to the GC column. This temperature was maintained for 5 min. Between runs, the interface was cleaned by passing the helium flow for 5 min and

heating to 350 °C, before cooling the interface to the initial temperature to start another analysis.

2.5. GC Analysis

A J&W HP-5MS column (30 m × 0.25 mm and film thickness 0.25 μm) was used for the GC analysis. Helium was used as carrier gas at 1 mL/min. During the transfer and the solvent elimination steps of the TOTAD interface the GC oven temperature was kept at 60 °C. This temperature was maintained for another 3 min once the TOTAD interface was heated. Then, the temperature was raised at 15 °C/min up to 295 °C and maintained at this final temperature for 5 min. An MS was used as detector in electron impact mode at 70 eV, with an ion source temperature of 200 °C, full scan mode from 100 to 300 u. Three characteristic ions corresponding to each PAEs were monitored for identification. Finally, an extracted ion chromatogram (EIC) was used, ion 149 was used to quantify DEP, DBP and DEHP and ion 163 was used for DMP.

3. Results and Discussion

There is an increasing demand for reliable and sensitive analytical methods for determining trace levels of PAEs in environmental samples. However, because of the high risk of contamination during manipulation of the sample and blank problems, which may result in false positives or overestimated determinations, reducing sample preparation to a minimum is of great interest [50]. Ideally the use of extraction solvents, plastics and glassware should be avoided, and, to this end, it was thought that the on line coupling of sample preparation would be of great interest. The method developed in the present work involves the on line LC-GC by means of the TOTAD interface using a fraction collector. Four phthalate esters, among the most frequently used (DMP, DEP, DBP and DEHP), were chosen as model analytes to test the feasibility of using the method. DMP, DEP and DBP are all low molecular weight phthalates of high water solubility, and DEHP has a high molecular weight and is poorly soluble in water. Figure 2 shows a scheme of the LC-GC-MS system with the TOTAD interface and the fraction collector enlarged. The TOTAD interface has been described previously, along with the five steps included in its operation mode [51]. The sample is directly injected into the LC injector with no other pretreatment than simple filtration and is automatically analyzed without any manual manipulation. The first dimension of the system (the LC) acts as extraction and clean-up step and the second dimension (the GC) as the analytical step.

LC has a higher separation capacity than other conventional sample extraction procedures and gives a much cleaner extract. The use of on line LC-GC integrates the sample extraction and fractionation steps into the analysis, avoiding manipulation of the sample and in this way minimize the risk of contamination. Even though on line LC-GC is more difficult when the LC step is carried out in reversed phase (RPLC-GC) rather than in normal phase (NPLC-GC), we decided to use acetonitrile/water as LC eluent due to the aqueous nature of the sample. It should be noted that, unlike other interfaces, the TOTAD interface has demonstrated its suitability for on line NPLC-GC as well RPLC-GC [52,53]. A solution of each phthalate in acetonitrile at 10 mg/L was used to set up the LC fractions to be transferred to the GC. It is necessary to use a sufficiently concentrated solution in order to obtain a LC chromatogram in which the elution time of each PAEs can be well stablished. Figure 3 shows the LC chromatogram obtained in this conditions.
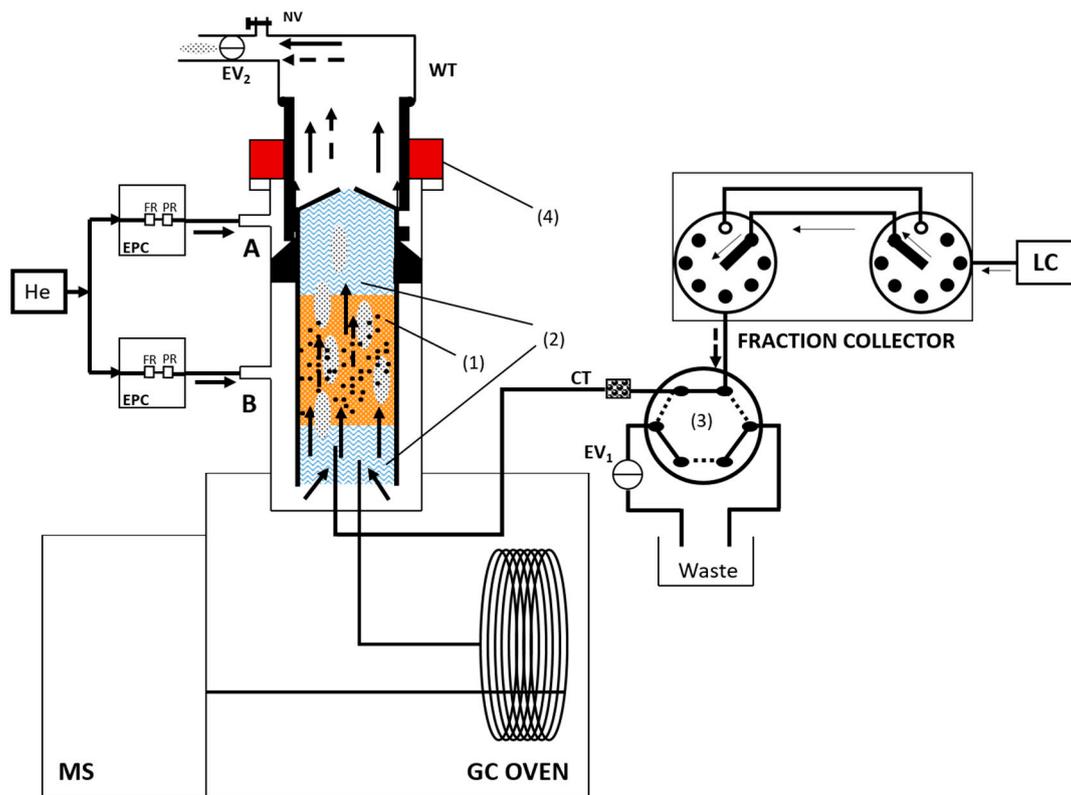
Figure 2. Scheme of the TOTAD interface with fraction collector during the transfer step. Symbols: (1) sorbent (Tenax TA); (2) glass wool; (3) six-port valve; (4) heated cover; (EV1 and EV2) electro-valves 1 and 2; (EPC) electronic pressure control; (PR) pressure regulator; (FR) flow regulator; (solid arrows) gas flow; (dotted arrows) liquid flow; (CT) silica capillary tubing, 0.32 mm i.d.; (WT) waste tubing; (W) waste; (⬭) solvent; (⠿) analytes; (NV) needle valve.
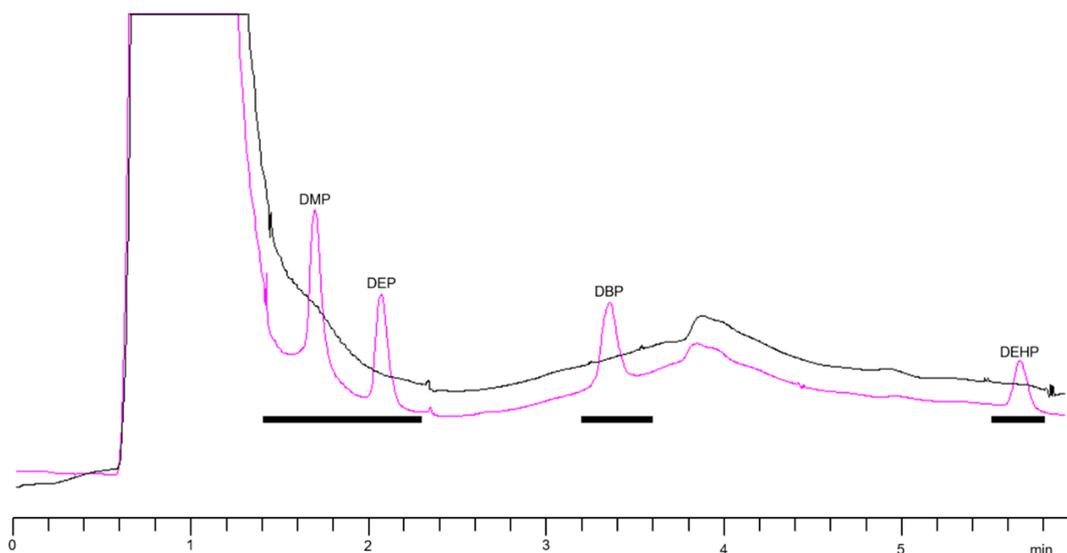

Figure 3. LC chromatograms from an unfortified leachate sample (black) and the leached sample fortified at 1 mg/L of each phthalate (pink). The thick black lines correspond to the LC fractions transferred to the fraction collector.

The chemical composition of a landfill leachate depends on the composition of the waste, climatic conditions and the age and degradation rate of the solid waste, which will commonly include a wide variety of inorganic and organic compounds, most of them pollutants of a varying chemical nature, such as organic acids, aromatic hydrocarbons

phenols, chlorinated aliphatic, pesticides, pharmaceutical and heavy metals [25,54]. The LC conditions must be carefully selected to guarantee that the target analytes do not overlap the main components of the leachate. Different eluent compositions were tested (40:60, 45:55, 50:50, 60:40, 65:35 and 70:30, *v/v*) and 65:35 *v/v* was chosen as eluent initial composition. The composition was changed to 100% acetonitrile in four minutes to elute the four PAEs chosen, being the most hydrophobic, DEHP, the last PAE to elute from the LC column. This eluent composition was maintained for 15 min to assure the complete removal of the retained compounds from the LC column. Using this eluent composition, three LC fractions were selected: the first one (fraction 1) contained DMP and DEP, which eluted from 1.4 to 2.3 min, the second fraction (fraction 2a) contained DBP eluted from 3.2 to 3.6 min and the last fraction (fraction 2b), which eluted from 5.5 to 5.8 min, contained DEHP. The first fraction was collected in the first loop of the fraction collector and the other two were both collected in the second loop of the fraction collector. Bearing in mind that the flow rate applied during the LC separation was 1 mL/min, the volumes of the two fractions were 900 μL and 700 μL, respectively. Separation into two fractions gives a cleaner extract since the interferences are also fractionated. In order to store these two fractions it was necessary to design a collector, which, in our case, consisted of a set of two multiport valves and several stainless steel tubes (used to connect the collector to the LC system or to the TOTAD interface, or to store the LC fractions with the PAEs of interest). Each multiport valve has one entrance and several exit ports. The entrance port of multiport valve 1 is connected to the exit of the LC detector. Multiport valve 2 is connected in the opposite way, so that the exit port connects the collector with the TOTAD interface. The rest of the ports of both multiport valves are connected by means of the corresponding stainless steel tubes, which are set up to collect the fractions containing the PAEs of interest. Individual ports can be selected by simultaneously modifying the position of both valves automatically. The analytical method developed means that two fractions can be collected, one containing DMP and DEP and the other DBP and DEHP, so only two loops were used. The fraction collector was fitted with a loop of 900 μL internal volume, which was made using a stainless steel tube of 0.75 mm i.d. of 2.04 m length, connected to position "1" of each multiport valve, which was used for the isolation of DMP and DEP. Another stainless steel tube of 1.58 m length and 700 μL internal volume, connected to position "2" of each valve, was used for the isolation of DBP and DEHP. After the LC analysis, both LC fractions collected were transferred to the GC-MS by means of the TOTAD interface. As a lower transfer speed results in higher sensitivity [55], the LC pump was set at 0.1 mL/min to transfer each fraction. Due to the volume of each fraction, transfer took 9 and 7 min, respectively (total time 16 min). Table 1 shows the two LC fractions transferred to the GC, the PAEs isolated in each, the initial and final time of the fractions, the volume of each fraction and the time needed to transfer them.

Table 1. Characteristics of LC fractions.

Fraction	PAEs Contained	Initial Time (min)	Final Time (min)	Volume (μL)	Transfer Time (min)
1	DMP	1.4	2.0	900	9 min
	DEP	2.0	2.3		
2a	DBP	3.2	3.6	700	7 min
2b	DEHP	5.5	5.8		

Figure 4 shows the GC chromatogram obtained in the analysis of a leachate sample spiked at 250 μg/L. As can be seen, although compounds other than PAEs are detected, the four PAEs are properly resolved and can be quantified with no problem. While the chromatograms obtained in the analysis of PAEs frequently suffer from high noise due to cross contamination from sample preparation products [35], the proposed method involves no sample manipulation as the process is fully automated, and so this problem is avoided. It should be pointed out that to properly establish the window of the LC fraction to be

transferred, it is very important in order to obtain fairly clear GC chromatograms, which will facilitate the identification and quantification of the GC peaks. The transfer of only one LC fraction containing the four PAEs, that is, an LC fraction from 1.4 to 5.8 min, with a volume of 4.4 mL, could have been possible as the TOTAD interface effectively eliminates the solvent. The volume to be transferred is not a problem, but more interfering compounds would have appeared in the GC chromatogram and the analysis time would be longer because transfer at a flow rate of 0.1 mL/min would take 44 min rather than 16 min. Using an MS detector in on line RPLC-GC could present difficulties because the polar eluent used in the RPLC step that must be completely removed before GC analysis to avoid damaging the MS detector.
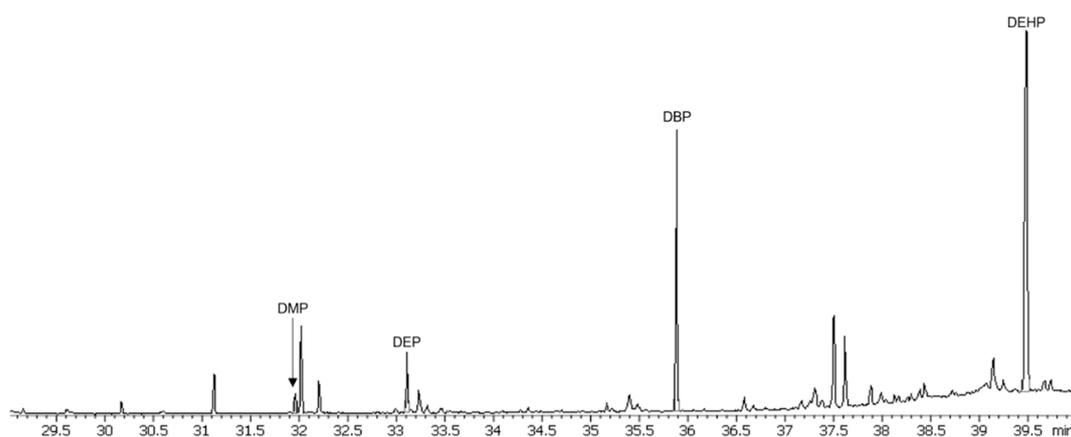

Figure 4. GC-MS chromatogram obtained from the analysis of a leachate sample spiked at 250 µg/L by on line RPLC-GC-MS using a fraction collector.

3.1. Validation of the Method

The newly developed analytical method was validated by determining repeatability, linearity and sensitivity. Table 2 shows the relative standard deviations (RSDs) of the absolute peak areas and the retention time for five injections, the limit of detection (LOD) and quantification (LOQ) and correlation coefficients (R^2).

Table 2. RSD from the absolute peak area and from the retention time ($n = 5$). Ions selected, LOD, LOQ and R^2 for the linear range studied.

PAE	RSD Area (%)	RSD Tr (%)	Ions Selected	LOD (µg/L)	LOQ (µg/L)	R^2
DMP	10.1	0.04	135,163,194	1.4	2.3	0.9993
DEP	11.5	0.07	149,177,222	0.4	0.7	0.9991
DBP	8.6	0.1	149,205,223	0.2	0.3	0.99
DEHP	11.9	0.14	149,169,279	0.1	0.2	0.94

3.1.1. Repeatability

The repeatability was determined by injecting 50 µL of the leachates spiked at 250 µg/L of each PAEs. The RSDs for absolute peak area ($n = 5$) ranged from 11.9% (DEHP) to 8.6% (DBP), respectively. It is worth noting that, besides the RSD values for the absolute peak areas obtained may be considered fairly high, the figures correspond to the overall analysis, including extraction, clean-up and concentration (in the LC step of the analysis), the isolation of the two fractions in the fraction collector and the GC analysis. No variability in the retention time was observed as the RSDs for the retention time ranged from 0.14% to 0.04%. This is an advantage of the TOTAD interface over other interfaces, in which retention times may vary widely. This problem does not arise with the TOTAD interface because the analytes are refocused in the packed material inside the liner [45].

3.1.2. Linearity

Before testing the linearity of the method, the leachate blank sample used to spike with different concentration of the target PAEs was analyzed, and only DEHP was detected. The leachate sample was spiked with different concentrations of DEHP and analyzed, plotting the peak areas versus concentration. The initial concentration of this PAE in the sample can be calculated as the intercept divided by the slope of the linear regression line adjusted to the data points. The DEHP concentration calculated was 22.27 μg/L. The linearity ranged from 1 to 1000 μg/L for DMP, DEP and DBP and from 1 to 250 μg/L for DEHP. The upper value of the linearity range tested for DEHP was much lower than for the other PAEs (low molecular PAEs) as DEHP is a highly lipophilic molecule and poorly soluble in water. A wide range of values for the water solubility of DEHP is mentioned in the literature (from 0.0006 to 1.3 mg/L at 20–25 °C). The probable explanation of this variability is that DEHP readily forms more or less colloidal dispersion in water. The linearity range for DEHP was based on the value (0.27 mg/L) given by Defoe et al. [56]. The correlation coefficients (R^2) were greater than 0.99 for the three low molecular weight PAEs in the range 1 μg/L to 1000 μg/L and 0.94 for DEHP in the range 1 μg/L to 250 μg/L.

3.1.3. Sensitivity

The detection limits were calculated as the amount of product that gave a signal equal to three times the background noise in the analysis of the leachate spiked at 250 μg/L. As can be observed the LOD for DMP was higher than those obtained for the other PAEs, which were similar to that reported by Clara et al. (2010) and Asakura et al. (2004) in leachates and in wastewater [10,24]. The LODs obtained are much lower than those showed by Otero and coworkers (2015) [57] and slightly higher than those reported by Clavijo et al. (2014) for drinking water (tap water and bottled water) and ground water [58].

There is no limitation concerning the concentration of PAEs in wastewater. According to Directive 2008/105/EC [59], the DEHP concentration in surface water is limited to 1.3 μg/L, but there is no limit set for the other PAEs [60]. The LOD obtained for DEHP was lower than this value.

3.2. Analysis of Real Samples

The developed method was applied in the analysis of leachate samples from a MSW landfill. The data obtained (Table 3) are only reported to demonstrate the applicability of the developed method and not as a characterization of the landfill leachate, which had been characterized in a previous work [61].

Table 3. PAE concentrations in leachate samples from a MSW landfill.

PAE	Concentration (μg/L)				
	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
DMP	41.53	174.76	209.07	24.21	60.03
DEP	240.08	221.3	545.99	116.85	340.37
DBP	41.88	70.96	178.79	n.d.	44.39
DEHP	>250	>250	>250	>250	>250

The four PAEs were detected in all the samples, except in one sample where DBP was not detected. The concentrations of DEHP could not be quantified in any sample, as they were higher than 250 μg/L. Some authors have demonstrated that DEHP is normally present in higher concentration than other PAEs [30,62]. Our analysis found the DMP, DEP and DBP values to be higher than those reported in China [29,63], United States [64] and most of Europe [26], but similar to those reported in Poland [28,65], Thailand [66] and Brazil [67]. Since the phthalate content in landfill leachate relies upon numerous factors, it may vary among countries as well as among landfill sites. The chemical composition of leachates will depend on several factors such as the composition, compaction of the

deposited waste, the storage method, how fast a new layer is formatted, the age of the landfill, the technology, construction or the operation methodology of the landfill, in addition to the water content [68]. In Argentina recycling and sorting household solid waste is not common practice and, as a result, large amounts of plastic containing PAEs may be dumped in MSW landfill sites. This could explain the high values obtained.

4. Conclusions

A new on line LC-GC method using the TOTAD interface and a fraction collector has been developed. The method permits the analysis of four PAEs in complex matrices such as wastewater and landfill leachate. No sample pretreatment is necessary other than simple filtration. The method is totally automatic and avoids sample manipulation, reducing the risk of contamination. The method shows good linearity and repeatability and has low detection limits. The applicability of the method has been demonstrated by the analysis of leachate samples from a landfill site in Argentina.

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