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Vortex-assisted liquid–liquid microextraction of octylphenol, nonylphenol and bisphenol-A

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ABSTRACT

A new and fast equilibrium-based solvent microextraction technique termed vortex-assisted liquid–liquid microextraction (VALLME) has been developed and used for the trace analysis of octylphenol, nonylphenol and bisphenol-A in water and wastewater samples. According to VALLME, dispersion of microvolumes of a low density extractant organic solvent into the aqueous sample is achieved by using for the first time vortex mixing, a mild emulsification procedure. The fine droplets formed could extract target analytes towards equilibrium faster because of the shorter diffusion distance and larger specific surface area. Upon centrifugation the floating extractant acceptor phase restored its initial single microdrop shape and was used for high-performance liquid chromatographic analysis. Different experimental parameters were controlled and the optimum conditions found were: 50 μl of octanol as the extractant phase; 20 ml aqueous donor samples; a 2 min vortex extraction time with the vortex agitator set at a 2500 rpm rotational speed; centrifugation for 2 min at 3500 rpm; no ionic strength or pH adjustment. The calculated calibration curves gave high levels of linearity yielding correlation coefficients (r^2) greater than 0.9935. The repeatability and reproducibility of the proposed method were found to be good and the limits of the detection were calculated in the low $\mu g\,l^{-1}$ level ranging between 0.01 and 0.07 $\mu g\,l^{-1}$. Matrix effects were determined by applying the proposed method to spiked tap, river water and treated municipal wastewater samples. The proposed method was finally applied to the determination of target pollutants in real wastewater effluent samples using the standard addition method.

1. Introduction

Analytical microextractions represent an important development in the field of sample preparation, addressing issues of simplicity, miniaturization and time efficiency [1]. Although different types of microextraction techniques were initially reported, it was the introduction of solid-phase microextraction (SPME) in 1990 [2] that initiated intensive research efforts in the area. Few years later, solvent microextraction (also known as liquid-phase microextraction or LPME) appeared in the literature [3–6], representing a miniaturization of the traditional liquid–liquid extraction (LLE) procedure whereby the solvent to aqueous phase ratio was greatly reduced. The general requirements for LPME were the use of an acceptor phase immiscible to the aqueous sample donor solution and analytes that were more soluble in the extractant phase than in the sample solution. Hitherto, different methodologies evolved from this approach including amongst others immersion [7] and headspace [8] single-drop microextraction, static and dynamic LPME [9] or even hollow fiber LPME [10,11].

Recently, a new LPME method termed dispersive liquid–liquid microextraction (DLLME), based on a ternary component solvent system similar to the one found in homogeneous liquid–liquid extraction and cloud point extraction, appeared in the literature [12]. For DLLME, a water-immiscible extractant solvent dissolved in a water-miscible dispersive solvent was rapidly injected into an aqueous donor solution leading to the formation of a cloudy solution consisting of fine droplets of the extractant solvent dispersed entirely in the aqueous (continuous) phase. Target analytes were extracted into these fine droplets, which could be subsequently separated by centrifugation and used for analysis. The main drawbacks associated with DLLME were the difficulty to automate and the necessity of using a third component (disperser solvent), which commonly decreased the partition coefficient of analytes into the extractant solvent [13]. Recently, dispersion of the extractant phase into the sample solution was also achieved using the so-called temperature-controlled ionic liquid DLLME method [14]. The method was based on the ability of an ionic liquid drop to disperse in an aqueous phase at higher temperatures, yet return to phase separation upon cooling and centrifugation. Although the method yielded high enrichment factors, analyte losses due to volatilization at higher temperatures were reported. Finally, the possibility of using ultrasound as a mean for dispersing the

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extractant acceptor phase (organic solvent [13,15] or an organic solvent/ionic liquid mixture [16]) into an aqueous donor phase was recently explored. In general, heterogeneous liquid–liquid systems are known to become uniform when subjected to ultrasonic irradiation. The process is also known as "homogenization" or "emulsification" and has been used as an alternative to the conventional LLE method [17]. Moreover, ultrasound was found to speed up this homogenization/emulsification step given that the formation of submicron size droplets greatly increased the contact surface between the two liquids, yielding fast and efficient analyte transfer. Nevertheless, in many cases analytical chemists have been reluctant to test ultrasound as a mean for improving liquid–liquid extraction given that it most often produces stable emulsions that result in long phase separation times. Problems were also encountered due to the use of cleaning baths as ultrasound irradiation production equipment which are notorious for their tendency to decline in power with time and their lack of uniformity in the transmission of ultrasound irradiation [18]. It should also be mentioned that even at these low frequencies and relatively short application times, analyte degradation may occur through large pressure and temperature gradients, high shear forces, or even by free radicals generation [19,20].

The aim of this research was to introduce a new and fast microextraction method whereby dispersion of the extractant phase into the aqueous is achieved for the first time using vortex mixing, a mild emulsification procedure. The resulting methodology was termed vortex-assisted liquid–liquid microextraction (VALLME) and was used for the extraction of trace amounts of alkylphenols (namely: octylphenol (OP) and nonylphenol (NP)) and bisphenol-A (BPA) used here as model compounds from water and wastewater samples. In general, alkylphenols are considered as degradation products of alkylphenolpolyethoxylates, a widely used class of nonionic surfactants with industrial and household applications [21,22]. OP and NP have been classified as endocrine disruptive compounds by several organizations, and are listed as a priority substance in the Water Framework Directive [23]. BPA on the other hand is commonly used as an intermediate in the production of polycarbonate and epoxy resins, flame retardants and other specialty products [24] and was found to exhibit weakly estrogenic activity as well as antiandrogenic activity [25]. Hitherto, different reports based on SPME or LPME coupled to high-performance liquid chromatography (HPLC) deal with the trace analysis of environmental samples containing these target analytes [21,26–32]. For the purpose of the present investigations, several experimental parameters affecting the extraction process (namely: organic solvent, agitation time, rotational speed of the vortex agitator, acceptor phase volume, aqueous sample volume, pH and salt addition) were initially controlled and optimized and the performance of the proposed method was then assessed. Matrix effects upon extraction were evaluated by analyzing spiked tap and river water as well as effluent water samples taken from a municipal wastewater treatment plant.

2. Experimental

2.1. Chemicals and samples

BPA and OP were purchased from Aldrich (Sigma–Aldrich, Gillingham, Dorset, UK). 1-octanol and NP Pestanal® (94% purity) were purchased from Riedel-de Haën (Seelze, Germany). All organic solvents used here were of pesticide grade. Deionized water was prepared on a water purification system (EASYpure®RF) supplied by Barnstead/Thermolyne Corporation (Dubuque, IO, USA). Stock solutions were prepared in methanol and stored at 4 °C in the dark when not in use. Working standards were prepared daily at the concentration levels of interest.

A 100 μl Hamilton (Bellefonte, BA, USA) HPLC 710 SNR model microsyringe was used to introduce the organic solvent into the aqueous sample and then collect it and inject it into the HPLC system for analysis.

River water samples were collected from the River Koiliaris situated in Chania-Crete (pH 7.5; chemical oxygen demand (COD) = 20 mg/l; total dissolved solids (TDS) = 100 mg/l). Wastewater effluent samples were collected from the municipal wastewater treatment plants of Chania (pH 7.6; COD = 15 mg/l; TDS = 508 mg/l) and Rethymno (pH 8.0; COD = 68 mg/l; TDS = 780 mg/l) situated in the North-West part of Crete, serving approximately 70,000 and 25,000 habitants, respectively. All samples were collected the day before being analyzed and were stored in the dark at 4 °C.

2.2. VALLME

Unless otherwise stated within the text, 20 ml aqueous samples spiked at a known concentration with all target analytes were placed in a round-bottom glass vial (diameter: ~2 cm) and 50 μl of octanol were then slowly introduced acting as the extractant solvent. The mixture was then vigorously shaken using a vortex agitator (Reax Control, Heidolph, Germany) for 2 min at 2500 rpm (maximum setting). As a result fine droplets were formed facilitating mass transfer of the target analytes into the organic acceptor phase. Separation of the two phases occurred upon centrifugation at 3500 rpm for 2 min (Labofuge 400 Heraeus, Kendro Laboratory Products, Germany). The floating octanol phase could thus restore its original single microdrop shape and 30 μl could be easily collected with the help of a microsyringe and used for HPLC analysis. During optimization, all experiments were run at least in duplicate.

2.3. HPLC analysis

Separation and quantification was carried out using an HPLC system, manufactured by Shimadzu (Shimadzu Corporation, Kyoto, Japan), equipped with a fluorescence detector (FLD) and two solvent delivery pumps. A Nucleosil 100-5 C18 (250 mm × 4.6 mm × 5 μm; Macherey-Nagel, Duren, Germany) was used to separate the target analytes at 27 °C. The mobile phase was acetonitrile:water (80:20) with a flow rate of 1.0 ml min^{-1}. The excitation and emission wavelengths of the FLD were set at 277 and 300 nm respectively. The total analysis time was 15 min.

3. Results and discussion

3.1. Optimization of VALLME

Initially, several water immiscible solvents (namely: 1-octanol, toluene, *n*-hexane, octane and cyclohexane) were tested, having densities lower than that of water and differing in polarity and water solubility. Each time, 50 μl of the organic solvent to be tested was slowly added to a 20 ml aqueous sample spiked at 1 μg l^{-1} with BPA and OP and 10 μg l^{-1} with NP. Given that all solvents tested had densities lower than that of water, they resided in the top surface of the water sample in the form of a single microdrop. The mixture was then vigorously agitated using a vortex agitator (2 min; 2500 rpm) leading to drop breakage into fine droplets. In the present studies centrifugation (2 min at 3500 rpm) was chosen as a viable mean for separating the two phases of this liquid–liquid dispersion. Amongst the low density solvents tested, 1-octanol had the ability to "restore" its initial single microdrop shape and as such could be easily collected and used for HPLC analysis. Under the present experimental conditions, coalescence of the fine droplets into a coherent phase did not occur for the rest of the tested solvents which were left scattered on the top surface of the aqueous solution in the form of smaller satellite microdrops hindering thus

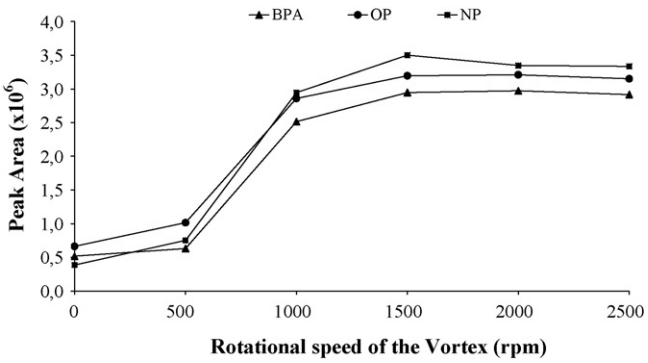

Fig. 1. Effect of the rotational speed of the vortex agitator upon VALLME. Other experimental conditions: 50 μl octanol; 20 ml aqueous samples spiked at 1 μg l^{-1} with BPA and OP and 10 μg l^{-1} with NP; 2 min agitation using a vortex agitator; centrifugation for 2 min at 3500 rpm.

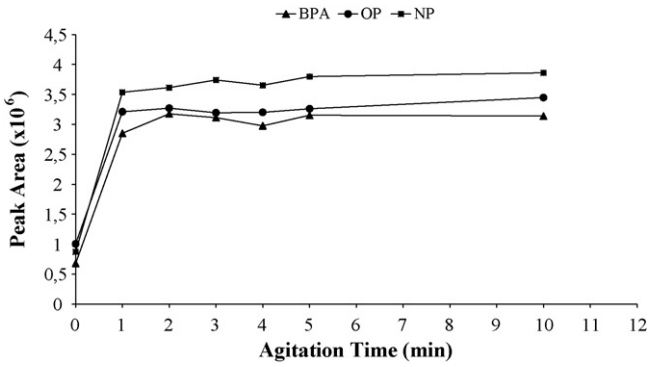

Fig. 2. Effect of vortex extraction time upon VALLME. Other experimental conditions: 50 μl octanol; 20 ml aqueous samples spiked at 1 μg l^{-1} with BPA and OP and 10 μg l^{-1} with NP, vortex agitator set at 2500 rpm rotational speed; centrifugation for 2 min at 3500 rpm.

their collection. Despite the numerous studies in the field separation processes driven by gravity or centrifugal forces are not yet completely understood [33]. In addition the mechanisms involved during drop breakage and formation are rather complex and form part of many ongoing investigations. Nonetheless, they appear to be greatly influenced (amongst others) by the physicochemical properties of the phases involved and the geometry of the apparatus used [34]. It should be mentioned here that the ability of 1-octanol to efficiently extract alkylphenols (NP and 4-*tert*-OP) when compared to ionic liquids and carbon tetrachloride has been demonstrated in the past [27]. Based on the above, 1-octanol was used as the acceptor organic phase for the rest of the experiments.

In general, the effect of a vortex agitator is to swirl the fluids and create a vortex, the size and shape of which depend upon the rotational speed of the rotor. In the case of immiscible liquids and at elevated speeds this generally results into the breakup of one of the two phases into fine droplets. Although such unstable fluid fields would seem unfavorable for operation, solvent microextraction methods are equilibrium methods and mass transfer within the organic acceptor phase is a limit step [6]. These fine droplets could extract analytes towards equilibrium faster because of the shorter diffusion distance and larger specific surface area [35]. Accordingly, in a separate set of experiments, the effect of the rotational speed of the vortex agitator upon VALLME was investigated and the results are depicted in Fig. 1. The "0 rpm" experimental point corresponded to the extraction where the water–octanol mixture was not subjected to vortex agitation and preconcentration of the target analytes was solely due to diffusion during the centrifugation step [36]. Fig. 1 demonstrates the beneficial effect of vortex agitation over centrifugation alone and it appears that the final analyte concentration of the microextract is nearly uniform for speeds greater than 1500 rpm where equilibrium conditions appear to be attained within the 2 min agitation time applied. Based on these observations it was decided to use the maximum speed setting of the vortex agitator (2500 rpm) for all subsequent experiments.

Fig. 2 depicts the results obtained whilst investigating the effect of vortex extraction time upon VALLME. At the experimental point "0 min", samples were only centrifuged and preconcentration was once again solely due to diffusion during centrifugation [36]. As can be seen extraction rates increased for increased vortex extraction times and it appears that equilibrium is attained for all target analytes after only 2 min. Based on the above, a 2 min vortex extraction time was chosen, enabling extraction at equilibrium conditions and resulting in increased precision and sensitivity.

Next, the effect of the acceptor phase volume upon extraction was investigated for volumes ranging between 50 and 80 μl. Octanol volumes lower than 50 μl were avoided, given that final collection of at least 30 μl which could be used for analysis was not always possible. It was assumed that although octanol had the ability to "restore" its initial microdrop shape, the formation of smaller satellite microdrops that could not coalesce with the mother drop was unavoidable. Octanol dissolution into the aqueous phase may have partially contributed to the reduced volumes of the final microdrops used for analysis. In the present investigations an overall 36, 38 and 42% decrease in the response of the instrument was recorded for BPA, OP and NP, respectively, whilst increasing the acceptor phase volume from 50 to 80 μl. This was due to the decreased final concentrations of target analytes in the octanol phase [6]. Thus, for all subsequent extractions, 50 μl octanol volumes were used.

The effect of aqueous sample volume upon VALLME was then investigated. As expected, increasing the volume of the spiked aqueous solution from 5 to 20 ml, increased the total mass of analytes available for extraction [37], resulting in a net increase in the response of the analytical instrument for BPA, OP and NP and the recorded signals were found to be 1.5, 2.4 and 3.4 times higher, respectively. It should be mentioned here that larger volumes were not tested given that the sensitivity of the instrument was found to be satisfactory. Based on the above, 20 ml aqueous samples were used each time for extraction.

It is well known that pH can significantly influence the partitioning of ionizable hydrophobic chemicals to octanol. The pollutants investigated here are considered to be weak acids and are expected to be found mainly in their molecular form for pH values below 8.0 and in their deprotonated form for pH values over 11 [24,27]. During the present studies, a non-significant negative effect of the pH upon VALLME was recorded for pH values ranging from 4 to 8. This is in agreement with a recent report published by Liu et al. [27], who concluded that altering the pH of sample solutions containing 4-*tert*-OP and NP, had a significant effect on the uptake kinetics into the 1-octanol film supported on a hollow fiber, yet no pH effect was observed for the equilibrium distribution, which is the case here. Given that no significant changes in extraction efficiency were observed in the environmentally relevant pH range, it was decided not to alter the pH of the aqueous samples.

Finally, the effect of salt for NaCl concentrations ranging from 0 to 15% (w:v) upon VALLME was investigated and the results are given in Fig. 3. As can be seen the presence of salt restricted the extraction of OP and NP, and was found to be beneficial for BPA. Similar results were obtained by Cai et al. [30], whilst developing an SPME method coupled to HPLC-FLD for the analysis of BPA, NP, and 4-*tert*-OP. In their work, increasing the ionic strength of the samples (up to 20% (w:v) NaCl) resulted in an increase of the extraction efficiency for BPA and a decrease for NP. In the case of 4-

Table 1
Selected method parameters (linear concentration range, r^2 and LOD) and average relative recoveries ($n=3$) for different samples (namely tap water, river water and wastewater (WW)) spiked at 1 μg l^{-1} with BPA and OP and 10 μg l^{-1} with NP (RSD values given in parentheses).

Compound	Conc. range	r^2	LOD	Relative recoveries (% (RSD))		
				Tap	River	WW effluent
BPA	0.05–100	0.9992	0.02	94 (3)	105 (3)	75 (2)
OP	0.05–100	0.9996	0.01	101 (3)	111 (3)	63 (6)
NP	0.50–100	0.9935	0.07	104 (4)	109 (4)	67 (7)

tert-OP, extraction increased reaching a maximum at 5% (w:v) NaCl and then decreased for increased salt concentrations. Recently, Braun et al. [38] developed a method based on SPME coupled to gas chromatography–mass spectrometry. During optimization the authors reported that the response for 4-*tert*-NP decreased significantly as the salt concentration increased, whereas for BPA a slight increase in extraction yield was recorded for increased NaCl concentrations, which was hardly lowered up to the saturated condition. Finally, Rezaee et al. [31] whilst developing a sample preparation method based on DLLME coupled to HPLC-UV reported a non-significant effect on the extraction recovery of BPA when sodium chloride up to 8% (w:v) was added in the sample solution. The authors in this study took into account for their calculations the increase in volume of the sedimented extractant solvent phase. Given that in the present investigations the presence of salt did not result in significant positive changes in the extraction yields of all target analytes, it was decided not to alter the ionic strength of the aqueous samples destined for analysis.

Overall, the optimized experimental conditions found here were: 50 μl octanol; 20 ml aqueous samples; 2 min vortex extraction time; vortex agitator set at 2500 rpm rotational speed; centrifugation for 2 min at 3500 rpm; no ionic strength or pH adjustment.

3.2. Analytical performance of VALLME

The linearity of the proposed method was determined by extracting under the optimized extraction conditions, aqueous solutions spiked at concentrations ranging from 0.05 to 100 μg/l for BPA and OP and 0.5–100 μg/l for NP. The calculated calibration curves gave a high level of linearity, yielding correlation coefficients (r^2) 0.9992, 0.9996 and 0.9935 ($n=5$) for BPA, OP and NP, respectively (Table 1). The repeatability of the method, expressed as relative standard deviation (RSD), was evaluated after extracting at two concentration levels five consecutive aqueous samples each time. Spiking aqueous samples at 1 μg l^{-1} with BPA and OP and 10 μg l^{-1} with NP yielded RSD values of the order of 2.4, 2.1 and 2.2%, respectively. For samples containing 0.1 μg l^{-1} BPA and OP and 1 μg l^{-1} NP, the RSD values found were 5.9, 4.6, 8.0%, respectively. The limits of detection (LOD) defined for a signal-to-noise of three (S/N = 3) were found in the low μg l^{-1} level (Table 1), lower or similar to the ones reported when coupling a liquid- or solid-phase microextraction method coupled to HPLC (Table 2). Enrichment factors defined as the ratio between the final analytes concentration in the organic acceptor phase and the initial aqueous sample concentration were found to be approximately for 450, 690 and 150 for BPA, OP and NP, respectively.

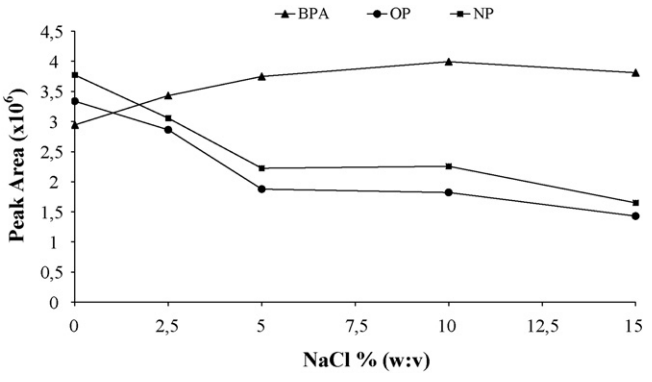

Fig. 3. Effect of ionic strength (% NaCl, w:v) upon VALLME. Other experimental conditions: 50 μl octanol; aqueous samples spiked at 1 μg l^{-1} with BPA and OP and 10 μg l^{-1} with NP; 2 min vortex extraction time; vortex agitator set at 2500 rpm rotational speed; centrifugation for 2 min at 3500 rpm.

It is well known that the efficiency of microextraction methods can be affected by the composition of the sample matrix. Accordingly, tap, river and municipal sewage effluent water samples were spiked at 1 μg l^{-1} with BPA and OP and 10 μg l^{-1} with NP and analyzed under the optimized experimental conditions. The relative recoveries found (defined as the ratio of the concentrations found in environmental and deionized water samples spiked with the same amount of analytes) are given in Table 1. As can be seen, in the case of tap and river water matrix did not affect extraction. However, in the case of effluent wastewater a decrease in extraction yield and as a consequence in sensitivity was observed. A similar observation has been reported in the past [39] and it was decided that for quantification in more complex environmental samples (such as wastewater effluents) the standard addition method should be used. Typical HPLC chromatograms obtained after VALLME of wastewater effluent samples before and after spiking at 1 μg l^{-1} with BPA and OP and 10 μg l^{-1} with NP are given in Fig. 4.

Table 2
Comparison of LOD obtained with VALLME and other published liquid- or solid-phase microextraction methods coupled to HPLC.

Method	LOD (μg l^{-1})	Reference
DLLME coupled to HPLC-UV	BPA: 0.07	[31]
Ionic liquid LPME coupled to HPLC-FLD	4-NP: 0.3 4-*tert*-OP: 0.7	[21]
1-Octanol Thin Film supported on a hollow fiber coupled to HPLC-FLD	4-NP: 0.06 4-*tert*-OP: 0.1	[27]
SPME coupled to HPLC-FLD	BPA: 0.9	[29]
SPME coupled to HPLC-FLD	BPA: 0.43 4-*tert*-OP: 0.16, NP: 0.29	[30]
In-tube SPME coupled to HPLC-UV	BPA: 0.1 OP: 0.8 NP: 0.6	[32]
In-tube SPME coupled to HPLC-UV-FLD	BPA: 2.4	[28]
In-tube SPME coupled to HPLC-FLD	BPA: 0.02	[26]
VALLME coupled to HPLC-FLD	BPA: 0.02 OP: 0.01 NP: 0.07	Present studies

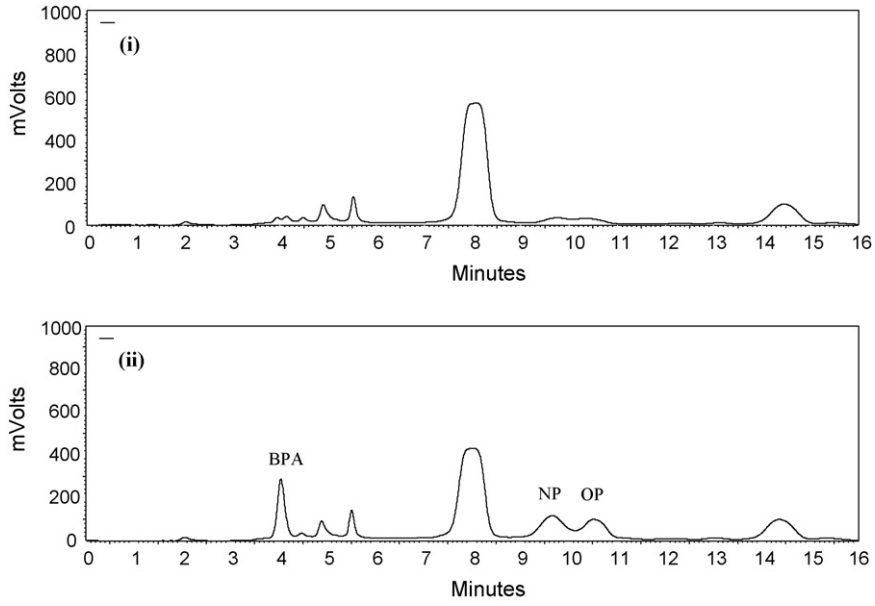

Fig. 4. Typical HPLC chromatograms obtained after VALLME of wastewater effluent samples (i) before and after spiking at 1 $\mu g\,l^{-1}$ with BPA and OP and 10 $\mu g\,l^{-1}$ with NP.

Table 3
Concentrations of target pollutants in wastewater effluent samples originating from two municipal wastewater treatment plants situated in the north part of Crete (Chania and Rethymno). The standard deviations of the measurements are also included.

Compound	WW effluent from Chania ($\mu g\,l^{-1}$)	WW effluent from Rethymno ($\mu g\,l^{-1}$)
BPA	0.14 ± 0.01	0.28 ± 0.03
OP	0.39 ± 0.07	0.21 ± 0.04
NP	3.20 ± 0.25	0.67 ± 0.10

3.3. Analysis of effluent wastewater samples

The presence of BPA, OP and NP in real treated samples taken from two municipal wastewater treatment plants was then quantified using the VALLME. The standard addition method was chosen and samples were multiply extracted. As can be seen (Table 3) the presence of all target pollutants was confirmed, demonstrating the inability of this treatment process to efficiently remove these contaminants [25]. In addition, the contamination levels found in the treated wastewater samples examined here were similar to the ones found in different Mediterranean countries. Gómez et al. studied the contamination levels of effluents samples taken from two municipal wastewater treatment plants located in south-eastern Spain (Almeria), reported a 0.38 $\mu g\,l^{-1}$ mean value for BPA after a 1 year monitoring study [39]. Gonzalez et al., whilst comparing the efficiency of a pilot plant membrane bioreactor working in parallel to a full-scale wastewater treatment plant situated in Rubí (Barcelona-Spain), reported a 2 $\mu g\,l^{-1}$ average value for NP in the effluent samples [40]. Finally, Stasinakis et al. reported 0.18 and 0.15 $\mu g\,l^{-1}$ mean values for NP and BPA respectively for effluent samples taken from six different wastewater treatment plants in Greece [25].

4. Conclusions

A new and fast sample preparation method termed vortex-assisted liquid–liquid microextraction is presented here having the inherent advantage of achieving equilibrium conditions within only a few minutes. For the first time dispersion of the extractant phase into the aqueous was achieved using vortex mixing, a mild emulsification procedure, avoiding thus problems associated with the application of ultrasound. The proposed method was successfully applied to the determination of BPA, OP and NP at trace levels in water samples. For more complicated matrices the standard addition method was found to be suitable for quantification. Overall, this is a promising and fast sample preparation method that can be used for the trace analysis of organic pollutants in aqueous environmental samples.

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