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Determination of diethylhexyladipate and acetyltributylcitrate in aqueous extracts after cloud point extraction coupled with microwave assisted back extraction and gas chromatographic separation

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Abstract

The determination of commercial plasticizers (di-(2-ethylhexyl)adipate (DEHA) and acetyl tributyl citrate (ATBC)) in aqueous solutions is described. The newly proposed technique of applying microwaves to cloud point extracts in order to enable combination with gas chromatographic analysis has been used for this purpose. Both plasticizers were entrapped in the micelles of the non-ionic surfactant Triton X-114 and removed from the bulk phase by centrifugation. Micellization was enhanced by increasing the ionic strength of the solution with concentrated NaCl. Extraction recoveries of the proposed method were over 95% for water and 3% (w/v) aqueous acetic acid and over 85% for 10% (v/v) aqueous ethanol, respectively. The calibration curves obtained, following the proposed methodology have a linear range between 50 and 2000 μg/L for each analyte while the detection limits were as low as 15 and 19 μg/L for DEHA and ATBC, respectively, with an RSD below 5% even for low concentrations. As an analytical demonstration the proposed methodology was applied for the determination of the migration levels of the selected plasticizers from a PVC food packaging film into aqueous simulants.

Keywords: Cloud point extraction; DEHA; ATBC; Microwave back extraction; Gas chromatography

1. Introduction

Polyvinyl chloride (PVC) film is still widely used as a food wrapping material due to its flexibility, transparency and low water permeability [1]. In the form of thin film, also known as "cling film" it is used for retail packaging of food, such as red meat, poultry, cheese, fruit and vegetables [1–5]. High levels of plasticizers are added to the majority of PVC films in order to improve their properties in terms of flexibility, elasticity and processibility. The most widely employed plasticizers in PVC and vinylidene chloride copolymer (PVdC) films destined for food packaging applications are di-(2-ethylhexyl)adipate (DEHA) and to a lesser extent acetyl tributyl citrate (ATBC) [6,7].

These plasticizers have a low molecular mass, which increases their tendency to migrate from the packaging material into the packaged food acting as indirect food additives [2–4,8,9]. The migration of phthalate and adipate plasticizers into fatty foods is well documented in the literature and regulations have been set by US EPA to establish a maximum allowed limit in foodstuffs [10].

In order to determine the migration of plasticizers into food without actually employing a food substrate, the use of food simulants was introduced. Isooctane is employed to simulate fatty foods while water, 3% (w/v) aqueous acetic acid as well as 10% (v/v) aqueous ethanol are used for non-fatty substrates [11].

The migration potential of plasticizers into isooctane (fatty food simulant) is high, due to their hydrophobic nature. Therefore, their concentration levels are high enough (well over 1 mg/L) and can be determined by direct injection into

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a liquid or gas chromatographic system equipped with conventional FID or UV detectors [12]. On the other hand, the migration of such plasticizers into water and aqueous solutions is limited yielding final concentrations in the low μg/L. Thus, a preconcentration-enrichment step is necessary to precede analysis.

Various liquid–liquid extraction techniques employing solvents such as dichloromethane, hexane and isooctane have been widely used for the isolation of various plasticizers (mainly phthalates) from aqueous environments. These procedures have proved time consuming, laborious with several evaporation and re-dissolution steps in order to accomplish sufficient preconcentration. This prolonged analysis accompanied by poor recovery and lack of reproducibility render these methods inadequate for routine analysis [13,14].

A useful alternative to the classical approach is microextraction. Unfortunately, this technique cannot be applied universally because it requires analytes with a high partition coefficient, which is not always the case for polar plasticizers [14,15]. A solution to this problem is given by the use of solid phase extraction and solid phase microextraction techniques which presented high enhancement factors and low detection limits with increased reproducibility [16–19]. Most of the methods used have been applied for the extraction and determination of phthalic acid esters, while the determination of DEHA and ATBC has been limited or even neglected. In every case, detection and quantification of the target analyte has been performed with a suitable detector after GC separation.

Application of the cloud point phase separation behavior of surfactants in aqueous media for the analytical determination of trace organic analytes has received growing attention in recent years [20–22]. Cloud point phase separation is the procedure during which aqueous solutions of several surfactants undergo phase separation under specific conditions such as temperature [23–25] and addition of salts or acids [26,27]. The result is the formation of two distinct phases: a surfactant-rich phase and an aqueous phase with concentration of surfactant close to the critical micellar concentration (CMC) [20,23]. It has been demonstrated that the surfactant-rich phase, thus separated under the cloud point conditions, is able to extract and preconcentrate a wide range of organic compounds such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated compounds, synthetic pesticides, hydroxyaromatic compounds, vitamins, etc., from the aqueous phase [22–33].

The use of preconcentration schemes based on surfactant mediated phase separation offers an interesting alternative to conventional extraction systems. The small volume of the surfactant-rich phase stemming from this methodology and its compatibility with hydroorganic mobile phases have been exploited in the past few years for the extraction and preconcentration of organic compounds prior to high performance liquid chromatography (HPLC) [22], flow injection analysis (FIA) [28] and capillary electrophoresis (CE) [22,29]. The use of cloud point extraction (CPE) schemes for the preconcentration of analytes prior to gas chromatography has not been reported in the literature and therefore volatile organic compounds have been banned from this preconcentration approach. Liquid–liquid extraction is the most popular of the methods applied in order for these compounds to be collected from aqueous solutions while the use of solid phase extraction (SPE) and microextraction (SPME) is gaining nowadays substantial attention solving the problems of irreproducibility and poor recoveries. Recently, Sikalos and Paleologos [34] have proposed a technique based on microwave assisted back extraction of the target analytes from the micellar extracts into a water immiscible solvent thus allowing for the first time the injection of micellar extracts into a GC apparatus.

Bearing in mind that the conventional techniques used for the determination of commercial plasticizers in aqueous solution suffer from a serious of problems we set forth an experiment in which the cloud point extraction approach is combined with this innovative back extraction technique in order to capitalize from their combination in the determination of these plasticizers. More specifically, we applied cloud point extraction for the isolation of the plasticizers DEHA and ATBC from aqueous simulants and their preconcentration into the micelles of the non-ionic surfactant Triton X-114. The obtained surfactant-rich phase was treated with isooctane and the preconcentrated analytes were back extracted by short-term microwave application. The isooctane extract was subsequently injected into the GC with FID detection. Both analytes were effectively determined, yielding detection limits in the low μg/L area, which represent their concentration levels in non-fatty foods in contact with PVC films. Although the whole process may seem arduous, the ability of the CPE procedure to be applied simultaneously to multiple samples, reduces the average time of analysis, thus enabling its use in routine analysis. The proposed methodology was developed with a view to enable the determination of ATBC and DEHA at the low concentration levels, obtained after migration tests with aqueous food simulants, and generally in aqueous solutions where no literature exists, apart from those referring to phthalate plasticizers.

2. Experimental section

2.1. Apparatus

For qualitative and quantitative analysis of the selected analytes, a gas chromatograph HP 5890 series II (Hewlett-Packard, Wilmington, USA) with a flame ionization detector (FID) was used, equipped with a 30 m × 0.32 mm fused silica capillary column, coated with 0.25 μm film (HP-5, J. & W. Scientific, Folsom, USA). The carrier gas was Helium at 75 kPa.

A Shimadzu CTO-10A oven was used for temperature control of the water bath in which the separator vessels were placed. A Hettich, Universal centrifuge was used for separation of the surfactant-rich phase.

2.2. Reagents

DEHA and the internal standard (octadecane) were of analytical grade purchased from Fluka (Buchs, Switzerland). Analytical grade ATBC was purchased from Unitex Chemical, NC, USA. Appropriate amounts were diluted with methanol to prepare 100 mg/L stock solutions, which were further diluted with double distilled water to prepare working solutions. Thus, the methanol content, that usually hampers clouding, was less than 1%. Isooctane, hexane and chloroform used for extractions were HPLC grade. Triton X-114 (Aldrich, Cat. No. 36,934-9) was used, without further purification, to prepare a 100 g/L aqueous solution.

2.3. Procedures

2.3.1. Cloud point extraction from aqueous samples

In a typical cloud point experiment of non-ionic surfactants, 9 mL of the standard or sample solution were placed in a Hach centrifugal vial. 80 μL of Triton X-114 stock solution, 1 mL of 1M phosphate buffer pH 7.0 and 100 μL of concentrated NaCl solution were subsequently added and the mixture was left to stand for 10 min in a water bath at 50 °C.

Centrifugation for 10 min at 4000 rpm was performed to separate the surfactant rich phase from the bulk aqueous supernatant. The vials were then placed in an icebath for 5 min to increase viscosity of the micellar phase and the aqueous supernatant was decanted by inverting the tube. One hundred and fifty microliters of isooctane containing 0.1 mg/L of the internal standard (octadecane) were added and the preconcentrated analytes were extracted by applying microwaves (700 W) for 2 min. Two distinct layers were formed: the surfactant rich phase containing some water remnants (130–160 μL, lower) and the isooctane phase (150 μL, upper). One microliter of this supernatant isooctane phase was injected into the gas chromatograph.

2.3.2. Conventional solvent extraction

In order to compare our proposed methodology with a conventional technique (solvent extraction) the aqueous solution was treated three times with 50 mL of hexane in a separator funnel. The organic extracts were concentrated in a spherical flask, 15 g of anhydrous Na_2SO_4 were added and the mixture was left overnight in order for all remaining water to be removed. The mixture was then filtered to remove Na_2SO_4 and the filtrate was subsequently evaporated to dryness with the aid of a flash evaporator. The extracted plasticizers were finally collected with 10 mL of isooctane and 1 μL of this isooctane extract was injected into the GC.

2.3.3. Preparation of real sample extracts

For the analysis of real samples a 6 cm × 10 cm films of PVC with a thickness of 10 μm were stretched on a stainless steel screen and subsequently immersed into 200 mL of each of the aforementioned simulants. The film remained in each simulant for 10 days at 40 °C in order for the migration of each plasticizer to be completed and equilibrium to be reached [11,35–38]. Samples were then collected at predetermined intervals.

2.4. Gas chromatographic conditions

The GC analysis of the selected compounds was carried out according to the following conditions [11,38,39]: the temperature of the injector was maintained at 250 °C while the detector was set at 300 °C. The column temperature was raised from 200 to 280 °C at 20 °C/min where it remained for 8 min. Detection was performed at a split (1:20) mode.

3. Results and discussion

3.1. Optimization experiments

The parameters that require optimization in a typical non-ionic surfactant based cloud point experiment are sample pH, added surfactant volume, heating temperature and incubation time. On the other hand much attention has been paid to the microwave accelerated back-extraction parameters such as volume of organic solvent and duration for the application of microwaves.

3.1.1. Effect of pH

The pH of the initial solution was optimized for the non-ionic CPE in order to obtain the optimum signal for the selected plasticizers. In 9 mL of a solution containing 0.1 mg/L of both DEHA and ATBC, 1 mL of 1 M phosphate solution was added and the pH was adjusted to the desired value by addition of HCl (146 g/L) or NaOH (160 g/L). Following the experimental process described in the procedure section it was found that the extraction efficiency is almost independent of pH conditions for the pH range of 3–11 (Fig. 1) giving a plateau in the area of 5–11. This behavior is anticipated due to the hydrophobic, non-ionizable nature of

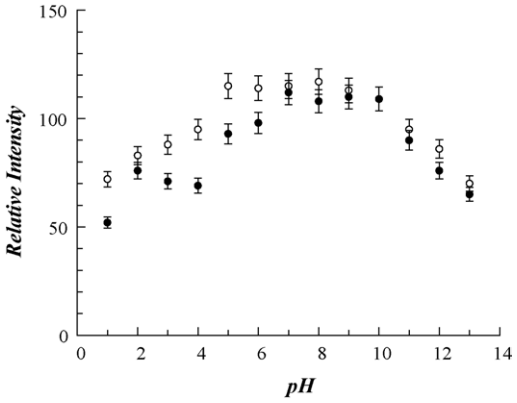

Fig. 1. Effect of pH on the extraction and preconcentration of DEHA (◯) and ATBC (●) with the proposed method (80 μL Triton X-114, 150 μL isooctane, microwave at 700 W for 2 min). Other conditions as described in the text.

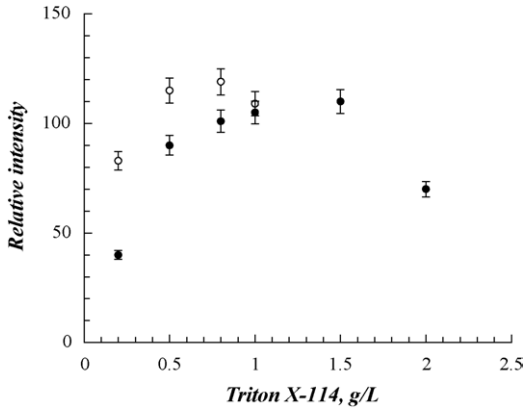

Fig. 2. Effect of surfactant concentration on the extraction and preconcentration of DEHA (◯) and ATBC (●) with the proposed method (pH 6, 150 μL isooctane, microwave at 700 W for 2 min). Other conditions as described in the text.

the analytes, which is not affected by the presence of acids or bases. A more remarkable decrease is observed for pH values below 3 and over 11. This behavior is attributed to the impairment of the clouding phenomenon, which is more pronounced in alkaline solutions. As a result of the above observations the pH of the phosphate buffer was adjusted to 7.0 and 1 mL of buffer solution was added to all standard and sample solutions.

3.1.2. Effect of surfactant concentration

The optimization of the amount of surfactant is an important parameter in the present work because its amount should be sufficient for the quantitative extraction of the target analytes, but not excessive in order not to interfere with the back-extraction process. As can be seen from Fig. 2 a volume of 50–150 μL of the 100 g/L stock solution, corresponding to 5–15 mg of surfactant in 10 mL of sample (corresponding to 0.5–1.5 g/L final surfactant concentration), produced optimum results when 150 μL of isooctane are used for back-extraction. Smaller amounts lead to a reduction of the analytical response due to incomplete partitioning of the analytes in the surfactant micelles, while larger amounts of surfactant lead to an incomplete separation of the surfactant and the isooctane layer (formation of slurry). A surfactant volume of 80 μL (8 mg, 0.8 g/L) was finally selected with a view of further optimizing the volume of the organic solvent used for back-extraction. In all cases, the volume of the surfactant rich phase along with remaining water ranged between 130 and 160 μL. In contrast with conventional cloud point procedures, the volume of the surfactant rich phase is not critical for the calculation of the theoretical preconcentration factor as this is actually determined by the isooctane volume applied for back extraction.

3.1.3. Effect of incubation-equilibration temperature and time

In agreement with the literature referring to CPE of hydrophobic analytes, the incubation-equilibration temperature and time as well as the centrifugation parameters showed no significant alteration in the obtained analytical signals for both DEHA and ATBC. Although the cloud point for Triton X-114 is approximately 25 °C an incubation temperature of 50 °C was adopted, especially in the case of acetic acid and ethanol, to ensure micelle formation, while centrifugation for 10 min at 4000 rpm ensured phase separation. Increased temperature was used not only to accelerate phase formation but also to decrease hydration of micelles and to eliminate any drawbacks deriving from the presence of acetic acid and ethanol.

3.1.4. Effect of organic solvent

Three water immiscible solvents (hexane, isooctane and chloroform) were applied in order to evaluate their efficiency for extracting 0.1 mg/L of the target analytes from 10 mL of aqueous solution. As can be seen from Table 1 they all perform adequately for microwave assisted back-extraction from 8 mg of surfactant rich phase. Isooctane was finally selected because hexane and chloroform have poor reproducibility due to their increased volatility.

The volume of isooctane was finally optimized with a view to recover the target analyte from the surfactant rich phase yielding a high preconcentration factor. As can be seen from Fig. 3, the optimum results are produced when 100 or 150 μL of isooctane are used. Larger volumes result in a gradual decrease of the analytical response due to subsequent dilution (reduction of the theoretical preconcentration factor) while smaller amounts produce slurries perhaps due to the formation of partially miscible ternary mixtures among water, surfactant and organic solvent. For this reason a volume of 150 μL was finally selected as optimum because although 100 or 125 μL seem to yield better signals they often gave hazy solutions and slurries thus resulting in poor reproducibility. It should be noted here that for chemists less experienced with the manipulation of micellar extracts and when the plasticizers are not present in extremely low levels, a larger isooctane volume can be used allowing for less delicate han-

Table 1
Relative intensities of 0.1 mg/L DEHA and ATBC after cloud point extraction into Triton X-114 micelles and back extraction into isooctane, hexane and chloroform

Extraction technique	Relative intensity[a]		
	Isooctane	Hexane	Chloroform
DEHA			
Non assisted	120	120	120
Microwave 1 min	613	610	598
Microwave 2 min	625	620	612
Microwave 5 min	627	618	614
ATB			
Non assisted	110	112	112
Microwave 1 min	590	600	592
Microwave 2 min	605	607	598
Microwave 5 min	603	603	599

[a] Analyte/octadecane (internal standard) peak area $\times 10^{-3}$.

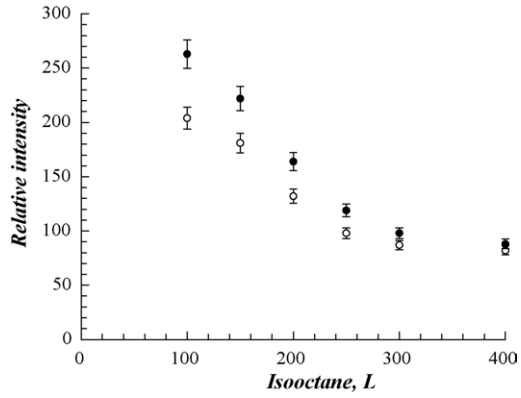

Fig. 3. Effect of eluent volume on the extraction and preconcentration of DEHA (◯) and ATBC (●) with the proposed method (80 μL Triton X-114, pH 6, microwave at 700 W for 2 min). Other conditions as described in the text.

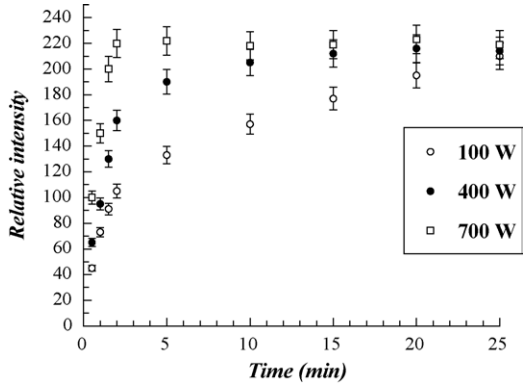

Fig. 4. Profile of the analytical signals obtained by applying three different microwave powers over a time period of 25 min.

dling but always in expense of sensitivity and enhancement factor.

3.1.5. Effect of microwave parameters

Since the cloud point extraction technique is known to produce high (practically quantitative) recoveries, the most important task of this study was, probably, the evaluation of the effect of microwave application to the quantitative back-extraction of the preconcentrated analytes from the surfactant-rich phase into the organic solvent. For this reason the micellar extract along with isooctane (150 μL) was treated with microwaves in a microwave oven. It was found (Table 1) that when the power of microwaves reached 700 W the preconcentrated plasticizers were quantitatively extracted into isooctane within 1 min producing an analytical signal five times greater than the non microwave-treated extracts. Further application of microwaves up to 4 min gave no significant difference in the analytical response. Therefore, a 2 min application was finally selected.

In order to further assess the impact of microwave application on the extraction a two level factorial design was set forward, with the microwave power and duration as variables. Table 2 shows the coded values assigned to each variable. By the signals obtained from each of the 11 combinations [8 + 3 repetitions for the central (0, 0) value] it became obvious that there was no point of curvature, instead the signal increased with increased power and time obtaining a plateau. The time plateau was reached decreases (exponentially) with the increase in microwave power. This is more or less expected since neither of the two plasticizers is thermo-degradable, while in contrast with the micellar assisted microwave extraction procedures [40–42] the analytes are extracted inside a homogenous environment of the single solvent instead of the micro-heterogeneous environment of a micelle which properties, in addition, are temperature depended.

In order to support our findings, we have monitored the extraction recoveries of 0.1 mg/L DEHA solution into isooctane following the described methodology applying microwaves of 100, 400 and 700 W until a plateau was reached. The results depicted in Fig. 4 show that in all cases the same maxima are reached but at times exponentially increased with decreasing microwave power. The obtained figures (Fig. 4) resemble those of kinetic curves further supporting the idea of non-interacting parameters.

Table 2
Coded values for the two level factorial design

Coded Level	Time (min)	Power (W)
−1	2	100
0	8	400
1	20	700

3.2. Analytical features of the method

Under the selected optimum experimental conditions the proposed methodology was applied to a series of standard solutions containing various concentrations of both analytes,

Table 3
Analytical characteristics of the method

Parameter	DEHA	ATBC
Phase volume ratio[a]	0.015	0.015
Preconcentration factor[b]	60	60
Retention time (min)	6.25 ± 0.05	5.50 ± 0.05
Linear range (μg/L)	48–2000	60–2500
LOD[c] (μg/L)	15	19
LOQ[d] (μg/L)	48	60
RSD[e] (%)	3.5	4.2
Regression equation	$E = 4 \times 10^{-4}$ C(μg/L) + 6.5×10^{-3} [f]	$E = 3 \times 10^{-4}$ C (μg/L) − 2.5×10^{-3}
Correlation coefficient	0.9997	0.9997

[a] Phase volume ratio: the ratio of the final volume of surfactant-rich phase to that of the aqueous phase.
[b] Enhancement factor: the ratio of the concentration of analyte after preconcentration to that without preconcentration giving the same absorbance peak area.
[c] Limit of detection, defined as three times the signal-to-noise ratio.
[d] Limit of quantitation, defined as ten times the signal-to-noise ratio.
[e] Relative standard deviation obtained from three extractions and three injections each.
[f] Peak area (arbitrary units).

Table 4
Recoveries of ATBC and DEHA from aqueous simulants after CPE and microwave back extraction compared to conventional liquid extraction

Plasticizer	Simulant	Added (μg/L)	Determined[a] (μg/L)		Recovery %	
			Solvent Extraction	CPE	Solvent Extraction	CPE
ATBC	Water	100	75 ± 10	99 ± 4	75 ± 10	99 ± 4
		200	158 ± 20	190 ± 6	79 ± 10	95 ± 3
		500	400 ± 50	480 ± 10	80 ± 10	96 ± 2
	3% (w/v) CH_3COOH	100	71 ± 10	95 ± 3	71 ± 10	95 ± 3
		200	140 ± 24	186 ± 8	70 ± 12	93 ± 4
		500	380 ± 50	450 ± 10	76 ± 10	90 ± 2
	10% (v/v) CH_3CH_2OH	100	68 ± 8	93 ± 5	68 ± 8	93 ± 5
		200	130 ± 18	190 ± 4	65 ± 9	90 ± 4
		500	330 ± 50	440 ± 15	66 ± 10	88 ± 3
DEHA	Water	100	77 ± 8	100 ± 4	77 ± 8	100 ± 4
		200	164 ± 16	194 ± 6	82 ± 8	97 ± 3
		500	415 ± 30	490 ± 10	83 ± 6	98 ± 2
	3% (w/v) CH_3COOH	100	73 ± 8	96 ± 3	73 ± 8	96 ± 3
		200	146 ± 10	184 ± 8	73 ± 5	92 ± 4
		500	395 ± 45	480 ± 15	79 ± 9	96 ± 3
	10% (v/v) CH_3CH_2OH	100	68 ± 10	95 ± 3	68 ± 10	95 ± 3
		200	136 ± 24	188 ± 10	68 ± 12	94 ± 5
		500	340 ± 55	450 ± 15	68 ± 11	90 ± 3

[a] The values are average of two experiments and three injections of each extract.

in order to develop the respective calibration curves. Table 3 shows the figures of merit of the proposed methodology. It is obvious that both analytes can be determined satisfactorily at μg/L levels, yielding actual preconcentration factors of over 50. Therefore, the proposed method can be applied directly to aqueous simulants, which are often used for testing the migration of plasticizers from packaging materials into foods and which usually demonstrate too low concentrations to be analyzed directly, while conventional liquid extraction into organic solvents suffers from low recoveries (ca. 70%) and poor reproducibility.

3.3. Analysis of real and spiked samples

In order to evaluate the efficiency of the proposed methodology to extract and preconcentrate DEHA and ATBC from aqueous simulants, a recovery test was carried out. Two hundred milliliters of distilled water, 3% (w/v) aqueous acetic acid and 10% (v/v) aqueous ethanol, which are the typical simulants used to investigate migration of plasticizers from plastics films, were spiked with different volumes of a standard solution containing both ATBC and DEHA at a concentration of 100 mg/L. The extraction and subsequent analysis of both plasticizers was performed as described under Section 2.3. Table 4 shows the recoveries obtained for all three simulants. It is obvious that for water and acetic acid the recoveries remain over 95% for all tested concentrations of ATBC and DEHA, while for aqueous ethanol recoveries are somewhat lower especially at high plasticizer concentrations. This is expected because it has been noted in the literature that increased amounts of organic solvents impair micellization and extraction efficiency of surfactant aggregates [43]. A solution to this problem is the increase in the ionic strength of the solution by the addition of concentrated NaCl but still high concentrations of plasticizers show recoveries in the vicinity of 85%. It is interesting to note that when the conventional solvent extraction method was applied recoveries never exceeded 85% while the RSD was well over 10%. Therefore, it became clear that the conventional approach cannot be trustworthy for such low concentrations as such expected in aqueous extracts.

Table 5 shows the results obtained after applying the proposed methodology to the extracts obtained from the contact of the PVC films with the simulants described under "Preparation of real sample extracts" for days 1 and 7 of simulant in contact with the film. It is obvious that although the migration of both DEHA and ATBC in all cases is low, the method

Table 5
Amounts of DEHA and ATBC determined in aqueous simulants after 10 days of simulant/PVC film contact at 40 °C using the proposed methodology

Simulant	DEHA[a] (μg/L)	ATBC[a] (μg/L)
Water		
1 day of contact	52 ± 6	89 ± 7
7 days of contact	85 ± 4	132 ± 4
3% (w/v) CH_3COOH		
1 day of contact	105 ± 5	123 ± 3
7 days of contact	160 ± 5	189 ± 6
10% (v/v) CH_3CH_2OH		
1 day of contact	145 ± 7	184 ± 6
7 days of contact	200 ± 6	242 ± 8

[a] The values are average of two experiments and three injections of each extract.

is effective for the determination of plasticizers even at such low levels. The increased irreproducibility and low recoveries of the solvent extraction approach do not permit a reliable comparison with the proposed methodology and this is the reason why no solvent extraction work is described in the literature for determining plasticizers at such low levels in aqueous solution. In addition, our attempt to apply solvent extraction prior to GC determination for reasons of comparison hardly gave a measurable value. Therefore, no results having analytical significance can be presented.

4. Conclusions

The application of CPE proved to be effective for the extraction and preconcentration of ATBC and DEHA at very low concentrations from aqueous solutions simulating real life conditions. Back extraction into isooctane was an efficient clean-up step prior to injection into the gas chromatograph yielding very low (μg/L) detection limits without impairing the separation efficiency of the column. Since it is the first time that CPE is applied for the extraction of analytes such as plasticizers, this work can provide the necessary impetus for further research in this direction, while the capability of applying the proposed methodology to multiple samples simultaneously can compensate for the complex procedure, which at a first glance would discourage the researcher, thus allowing for massive and routine analysis' applications.

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