Determination of adipate plasticizers in poly(vinyl chloride) by microwave-assisted extraction

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Abstract

A new method based on the application of microwave radiation to the extraction of adipate plasticizers from poly(vinyl chloride) PVC plastics is described. The experimental conditions for microwave-assisted extraction (i.e. extracting solvent, temperature, time and microwave power) were evaluated in terms of recovery. The optimisation was carried out with pastes of PVC plastified with di-2-ethylhexyl adipate, and extracts were measured by gas chromatography with flame ionization detection. Six different adipate plasticizers were studied, and microwave-assisted extraction was compared with supercritical fluid extraction for the extraction of adipates and phthalates from PVC matrices. It has been observed that the microwave-assisted extraction parameters evaluated are tightly interconnected. It has been shown that the efficiency of microwave-assisted extraction depends on the kind of solvent, the temperature achieved and the heating time. Moreover, the final temperature reached depends on the microwave power, the number of vessels and the irradiation time. On the other hand, microwave-assisted extraction provides higher recovery values than supercritical fluid extraction for both phthalate and adipate plasticizers.   © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Microwave-assisted extraction; Extraction methods; Plasticizers; Adipates; Poly(vinyl chloride); Phthalates; Diethylhexyl adipate

1. Introduction

The materials and substances usually employed in the toy industry for manufacturing toys and infantile use articles can be potentially dangerous for children, as well as for factory workers' health, and are susceptible to produce environmental contamination. Some organic compounds that are used as additives in plastics (e.g. plasticizers such as phthalates and adipates, among others) can be toxic by contact with skin, ingestion or inhalation [1,2]. Recently, some European Union Directives have limited the use of these substances [3–5], warning of their risks. Since the limits established for total content and migration of these species are close to the limits of detection of the analytical techniques commonly used for these determinations, development of new, simpler and efficient methods of analysis, that enable us to determine toxic species within the established limits, is advisable.

Poly(vinyl chloride) (PVC) is one of the most widely used thermoplastic materials in the plastic industry, due to the wide range of properties (i.e. high chemical and mechanical endurance) and the large number of applications they can find through the use of suitable additives. The role of additives is to alter the polymer properties or to prolong the polymer life [6]. Plasticizers are the most common

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additives. A plasticizer is a substance which is added to a material to improve its processability, flexibility and stretchability [7]. Phthalates and adipates are the most frequently used plasticizers, especially di-2-ethylhexyl and diisononyl phthalates (DEHP and DINP, respectively) and di-2-ethylhexyl adipate (DEHA). The properties of a plasticized polymer strongly depend on the concentration and chemical structure of the plasticizer [8].

The determination of plasticizers and other additives in plastics is carried out in two steps: (i) sample treatment, in which additives must be separated from the polymer and isolated from other interferent components that are present in plastic matrix; and (ii) measurement, in which additives are measured using a suitable technique. The analytical techniques applied to the determination of these compounds, mainly gas chromatography (GC) [9–13] and high-performance liquid chromatography (HPLC), are well established. Nevertheless, conventional methods for sample treatment show serious drawbacks, such as low analysis throughput and risk of losses and contamination.

Separation and isolation of plastic additives are carried out using extraction methods [14], usually Soxhlet extraction or supercritical fluid extraction (SFE), the latter being more efficient than the former in extracting a wide range of additives from plastic matrices [9,15–18]. The applications of SFE to the extraction of organic compounds have been continuously growing over the last years [17–20]. Carbon dioxide is the common extraction solvent in SFE because of its favourable characteristics, such as relatively low critical temperature and pressure, low cost, high purity and low toxicity.

Currently, microwave radiation is widely used in the field of sample preparation for many applications in chemistry laboratories [21–24]. The use of microwave radiation for treatment of solid and liquid samples enables the analyst to adapt the sample characteristics to the requirements of the analytical technique easily and quickly. Among other applications, microwave has been used for digestion of inorganic [25–29], biological [30–33] and food [34–37] samples, affording better results (i.e. shorter digestion time and lower risk of losses or contamination) than conventional methods. Microwave radiation has also been employed for the extraction of a variety of analytes from several matrices [38–51], thus reducing treatment time and solvent consumption with respect to other extraction techniques [52]. Nevertheless, the development of microwave-assisted extraction (MAE) methods is still in progress.

The aim of the present work is the development of a MAE method for the extraction of adipate plasticizers in the analysis of PVC. A comparison with a well established extraction method, SFE, is included.

2. Experimental

2.1. Reagents

A Vestolit B 7021 (Hüls, Germany) PVC resin has been used for the preparation of plastisols. This is a non prestabilized homopolymer, capable of forming low viscosity pastes easily.

All the plasticizers used are listed in Table 1. Adipate plasticizers were supplied by Sigma (St Louis, MO, USA), except DEA, supplied by Fluka (Germany). The phthalate plasticizers used to compare extraction methods were DEHP (BASF, Germany), DINP (BASF) and DIDP (diisodecyl phthalate, Hüls, Germany). For PVC pastes with low concentration of DEHA, TBAC (tributyl acetyl citrate, Merck, Germany) was used as auxiliary plasticizer. Standard solutions of plasticizers were prepared in methanol (Baker analyzed, J.T. Baker, Netherlands) and cyclohexane (Supra Solv, Merck).

2.2. Instrumentation

MAE was carried out using a MSP-1000 microwave sample preparation system (CEM, Matthews, NC, USA). Lined vessels made of PTFE PFA and Ultem polyetherimide and specifically designed for extraction mode operation were used, whereas temperature was controlled by means of an armored fiberoptic probe ATP-2 (CEM, P/N 113718).

The SFE system employed for comparison was a SFX 220 (ISCO, UK) supercritical fluid extractor, equipped with a SFX 200 controller and type D syringe pump. The extractor is composed of two identical extraction chambers placed inside a heater

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Table 1
List of plasticizers used

Abbreviation	Chemical name	Molecular mass (g/mol)	CAS no.
Adipates			
DMA	Dimethyl adipate	174	627-93-0
DEA	Diethyl adipate	202	141-28-6
DBA	Di-*n*-butyl adipate	258	105-99-7
DIBA	Diisobutyl adipate	258	141-04-8
DEHA	Di-2-ethylhexyl adipate	371	103-23-1
DIDA	Diisodecyl adipate	427	27178-16-1
Phthalates			
DEHP	Di-2-ethylhexyl phthalate	391	117-81-7
DINP	Diisononyl phthalate	419	28553-12-0
DIDP	Diisodecyl phthalate	447	26761-40-0
Citrates			
TBAC	Tributyl acetyl citrate	402	77-90-7

block. Temperature and pressure are controlled from a command board.

The extracts were analyzed by means of a Shimadzu GC-9A (Shimadzu, Kyoto, Japan) gas chromatograph equipped with a split/splitless injection system and a flame injection detection system (FID). A capillary column 15 m×0.53 mm I.D., 0.50 μm film thickness with SPB-5 as stationary phase from Supelco (Supelco, Bellefonte, PA, USA) was used.

2.3. Procedure

Plastisols were prepared by mixing powdered PVC with plasticizer. After removing the air in a vacuum chamber, they were cured at 150 °C for 15 min. DEHA concentration was 50 parts per hundred of resin (mass fraction 33%) in plastisols prepared for optimization, except in multiadipate paste, in which the concentration was six parts of each adipate plasticizer per hundred of resin. In plastisols prepared for evaluating the influence of the DEHA concentration, in which the adipate plasticizer was in low concentrations, TBAC was used as principal plasticizer, in a concentration of 50 parts per hundred of resin. Samples for extraction were prepared by cutting thin films (240–270 μm thick, approximately) from PVC plasticized pastes with a cleaver.

MAE was carried out in sets of three replicates,

arranging three lined extraction vessels (LEVs) symmetrically on the microwave cavity turntable. In all cases, each vessel contained 0.5 g of sample and 25 ml of solvent. One of them was the control vessel, equipped with a special cap to connect temperature and pressure probes.

SFE extractions were also made in sets of three. Approximately 0.2 g of sample were placed inside the extraction cartridge. The extraction was carried out at 95 °C and 7000 p.s.i. for 2 min of static time and then 30 min of dynamic time (1 p.s.i.=6894.76 Pa). Analytes were directly collected in methanol from the restrictor output. Operating conditions have been taken from a previous work in which the parameters for extraction of phthalate plasticizers were optimized [9]. The selected conditions are thought to be valid for the extraction of adipate plasticizers, too.

Quantitative determinations of the extracted plasticizers were carried out by calibration plots. Reference standard solutions were prepared by dissolving pure adipates in cyclohexane and methanol. Chromatographic conditions were as follows: column temperature program was initiated at 110 °C and held for 1 min, increased at 10°/min for 15 min and held at 260 °C for 20 min. The work was done in split mode; 1.0 μl of sample solution was injected manually by means of a microsyringe into the injector, which was heated at 300 °C. In chromatographic measurements, peak area was considered.

3. Results and discussion

3.1. MAE conditions

The factors that must be taken into account when a MAE method is going to be developed are, mainly, the nature of the organic solvent used as extractant and the instrumental conditions of the microwave system, i.e. microwave heating time, temperature at which extraction must be carried out and microwave irradiation power. The extraction temperature was optimised first, since it seems to be the most critical parameter. Then, extraction time and microwave irradiation power were adjusted, trying to gather maximum recovery, minimum operation time and soft instrumental conditions. Finally, the influence of the amount of sample in each vessel and of the plasticizer concentration in PVC plastisol on the DEHA extraction recovery were also evaluated.

3.2. Extracting solvent

The first step in the optimization process of MAE method was to select the solvent that could be employed as the most efficient extractant. Non-polar solvents cannot be used because they do not absorb microwave radiation. A solvent with polar groups in its structure is required (i.e. alcohols, ketones, ethers, esters, halides), or a mixture of polar and non-polar solvents, so that solvent molecules are capable of interacting with the electric field of the microwave radiation [21–23].

In the present study, four solvents were evaluated: methanol, ethanol, 2-propanol and a mixture of cyclohexane–acetone (1:1). After the first series of experiments, the acetone–cyclohexane mixture was

immediately discarded, since, under MAE conditions, PVC is dissolved in acetone. Thus, the chromatograms obtained from these extracts contain residual noise and the S/N ratio decreases.

Table 2 shows the recoveries obtained by gravimetric and chromatographic measurements for the three alcoholic solvents evaluated. It can be observed that gravimetric data show an opposite behaviour with respect to chromatographic data: methanol is the solvent that gives the highest gravimetric recovery but the lowest chromatographic recovery. Taking into account that DEHA standards have been prepared using cyclohexane as solvent, new standards in methanol were prepared. Methanol chromatographic data, interpolated to the new calibration curve, lead to recovery values similar to the gravimetric ones (Table 2). This can be explained by taking into account that the sensitivity of the DEHA chromatographic response is a function, among others, of the solvent used.

From the results obtained, methanol was the solvent selected as extractant.

3.3. Extraction temperature and time

Five temperatures were selected, 40, 60, 80, 100 and 120 °C for MAE experiments. Fig. 1 shows the influence of temperature on DEHA recovery using 5 and 10 min as extraction times. It can be seen that recovery increases with temperature, for both series, the values being always higher for 10-min than for 5-min extraction. A recovery value close to 100% is reached at 120 °C extracting for 10 min. Five-minute extraction would require a higher temperature to achieve 100% recovery. Assuming that extraction is based on diffusion, this process is dependent on the

Table 2
DEHA recoveries obtained by MAE for different solvents

Solvent	Gravimetry		Standards in cyclohexane		Standards in methanol	
	Recovery (%)[a,b]	RSD (%)[c]	Recovery (%)[a,b]	RSD (%)[c]	Recovery (%)[a,b]	RSD (%)[c]
Methanol	93±3	1.4	71±2	0.9	93±2	1.0
Ethanol	88±1	0.4	78±1	0.4		
2-Propanol	81±1	0.7	84±4	2.0		

[a] MAE conditions: $T_{ext} = 120$ °C; $t_{ext} = 10$ min; microwave power = 20%; no. of vessels = 3; sample mass = 0.5 g; solvent volume = 25 ml.
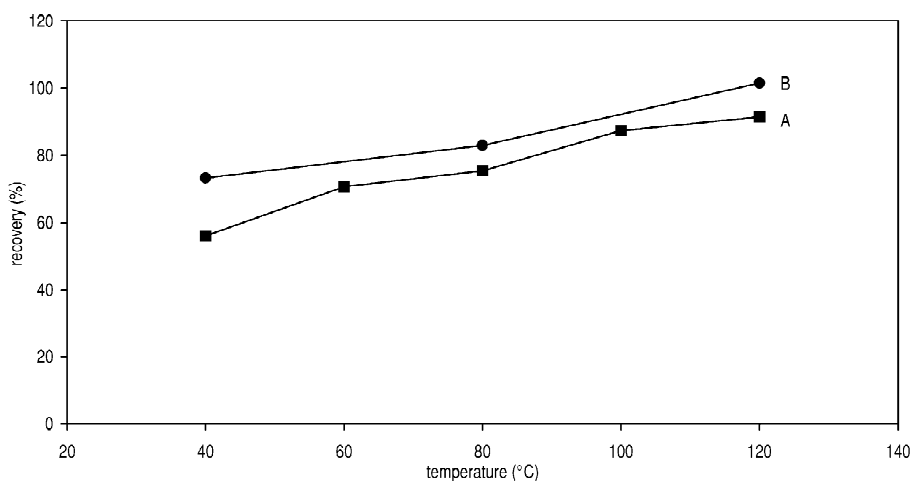[b] Confidence level: 95%.
[c] Calculated from three replicates.

Fig. 1. Effect of the extraction time and temperature on the DEHA recovery using MAE. (A) $t_{ext} = 5$ min; (B) $t_{ext} = 10$ min. Microwave power $= 20\%$; no. of vessels $= 3$; solvent: 25 ml methanol; sample mass $= 0.5$ g.

ability of the analyte molecules to migrate from the polymer to the solvent and the ability of the solvent molecules to diffuse inside the matrix structure and interact with the analyte. Analyte and solvent migration are enhanced by temperature. Therefore, high temperatures and long times improve the extraction. In our case, 120 °C temperature and 10-min extraction time represent suitable conditions for an efficient extraction of the whole content of DEHA plasticizer from PVC.

3.4. Microwave power

Microwave power is a critical factor that determines whether the desired extraction temperature is going to be reached efficiently or not. On the other hand, the number of vessels introduced into the microwave cavity may alter the distribution of the microwave radiation inside the cavity, thus influencing the amount of microwave radiation that is going to be absorbed for each vessel.

Fig. 2 shows the results obtained for two series of microwave extractions carried out at two different microwave powers, 20 and 30% of system nominal power (960 W), and setting six vessels on the turntable inside the microwave cavity. It can be seen that at 20% microwave power, recovery values obtained are around 80% for all the vessels. Nevertheless, by increasing the microwave power up to

30%, the recoveries obtained are close to 100%. To compare these results, the relation between number of vessels, microwave power and temperature should be taken into account. This is considered in Fig. 3, which shows the variation of temperature inside the vessel with the extraction time for different series of experiments. At 20% power and working with three vessels, 120 °C extraction temperature is reached in 4 min of irradiation, but when six vessels are arranged at the same microwave power, this temperature is not reached during the extraction time. At 20% microwave power, sufficient microwave radiation is supplied so that three vessels can reach the selected temperature in a short time, but not for six vessels. In this case, when microwave power is increased up to 30%, 120 °C temperature is reached, but only after 8 min of microwave irradiation.

Therefore, microwave power should be modified and adjusted depending on the number of vessels introduced into microwave cavity and on the extraction temperature.

3.5. Other adipate plasticizers

MAE conditions previously optimised were applied to the determination of six different adipate plasticizers. Fig. 4 shows a chromatogram corresponding to an extraction carried out on a multiadipate plasticized PVC paste. It can be observed that
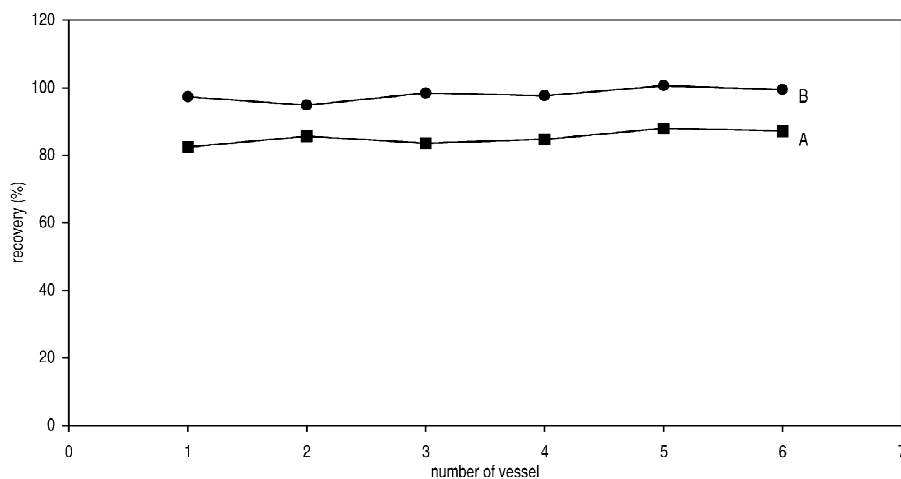
Fig. 2. Effect of the microwave irradiation power on the DEHA recovery using MAE; (A) 20% microwave power; (B) 30% microwave power. $T_{ext} = 120$ °C; $t_{ext} = 10$ min; no. of vessels = 6; solvent: 25 ml methanol; sample mass = 0.5 g.

all but DIDA plasticizers give well-defined chromatographic peaks. Since DIDA is composed of a mixture of isomers, just as occurs with phthalate plasticizer DIDP, its chromatographic signal is more irregular, and it is not possible to distinguish a lonely peak for measurement. Therefore, DIDA peak areas were calculated by setting manually the start and end peak points.

Table 3 shows the recoveries obtained for each

adipate plasticizer. It can be observed that, except for DEA, in all the cases the recovery obtained is over 90%. So, the optimised conditions are acceptable for the extraction of different adipate plasticizers.

3.6. Plasticizer concentration

Table 4 shows the DEHA recoveries for extractions carried out on plastisols of low concentration in
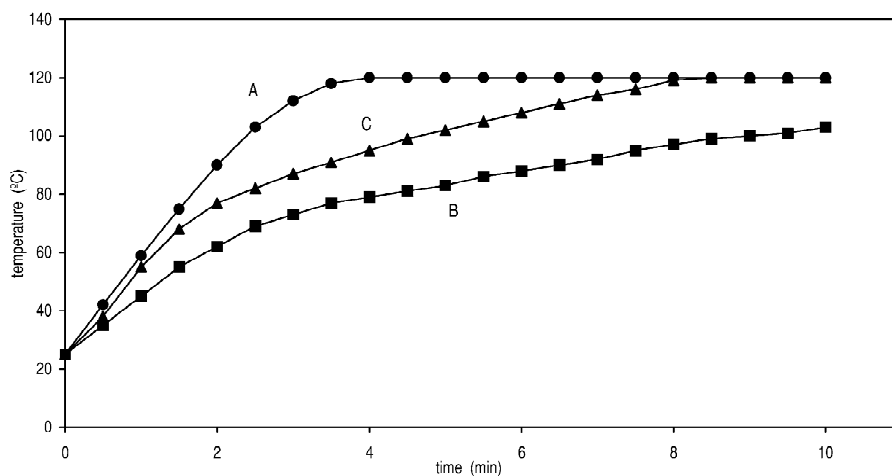

Fig. 3. Variation of extraction vessels temperature with time under different MAE conditions. (A) Three vessels, 20% microwave power; (B) six vessels, 20% microwave power; (C) six vessels, 30% microwave power. $T_{ext} = 120$ °C; $t_{ext} = 10$ min; solvent: 25 ml methanol; sample mass = 0.5 g.
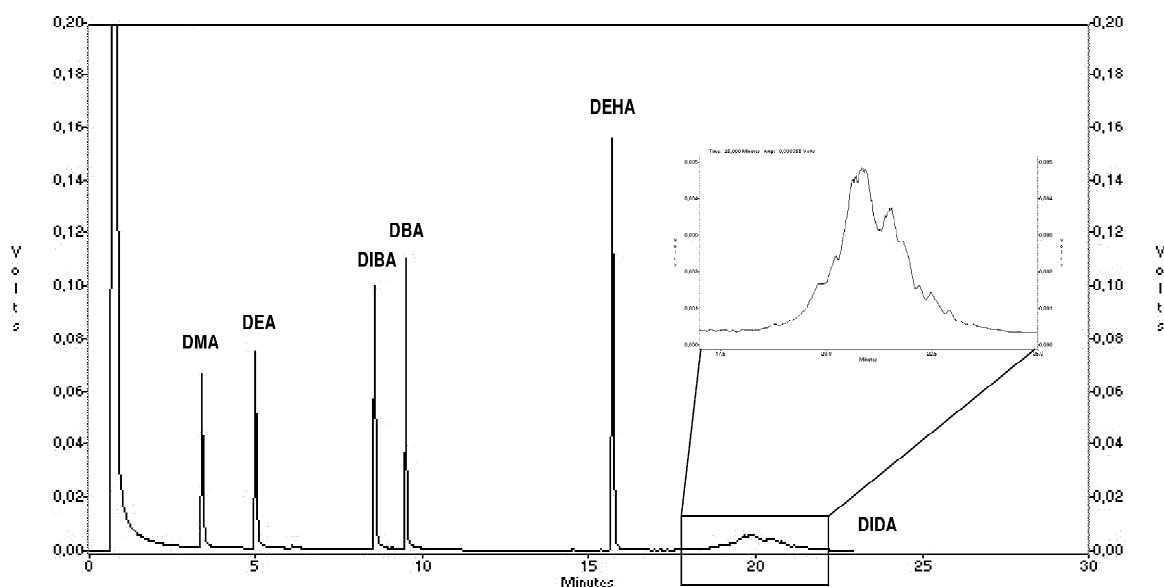
Fig. 4. Chromatogram of a multiadipate standard solution.

Table 3
Recoveries obtained by MAE for different adipate plasticizers

Adipate	Recovery (%)[a,b]	RSD (%)[c]
DMA	89±6	2.9
DEA	75±14	7.4
DBA	92±9	4.0
DIBA	98±9	3.7
DEHA	90±10	4.7
DIDA	86±6	3.0

[a] MAE conditions: $T_{ext} = 120$ °C; $t_{ext} = 10$ min; microwave power$=20$%; no. of vessels$=3$; solvent: 25 ml methanol; sample mass$=0.5$ g.

[b] Confidence level: 95%.

[c] Calculated from three replicates.

Table 4
DEHA recoveries by MAE for different plasticizer concentrations

DEHA concentration (%)	Recovery (%)[a,b]	RSD (%)[c]
1.07	86±1	0.5
0.33	93±4	1.7
0.11	104±15	5.9
0.036	125±17	5.5

[a] MAE conditions: $T_{ext} = 120$ °C; $t_{ext} = 10$ min; microwave power$=20$%; no. of vessels$=3$; solvent: 25 ml methanol; sample mass$=0.5$ g.

[b] Confidence level: 95%.

[c] Calculated from three replicates.

DEHA. Results indicate that MAE is suitable for the determination of small amounts of adipate plasticizers present in plastics. The deviation observed for the lowest concentrations of DEHA can be attributed to the chromatographic measurements. For low concentrations, measurements should be carried out in splitless mode. This way, the amount of injected sample would be larger than in split mode, so that the sensitivity would be higher.

3.7. Amount of sample

Table 5 summarizes the results corresponding to the recoveries obtained from the MAEs carried out by changing the amount of plastisol introduced into

Table 5
DEHA recoveries by MAE for different amounts of sample

Mass of plastisol (g)	Recovery (%)[a,b]	RSD (%)[c]
0.5	101±4	1.6
1.0	92±2	1.0
1.5	94±7	3.3
2.0	93±7	3.2

[a] MAE conditions: $T_{ext} = 120$ °C; $t_{ext} = 10$ min; microwave power$=20$%; no. of vessels$=3$; solvent: 25 ml methanol.

[b] Confidence level: 95%.

[c] Calculated from three replicates.

Table 6
Comparison between MAE and SFE for different adipate plasticizers

Adipate	MAE		SFE	
	Recovery (%)[a,c]	RSD (%)[d]	Recovery (%)[b,c]	RSD (%)[d]
DMA	84±6	3.1	62±5	3.5
DEA	86±3	1.4	65±8	4.8
DBA	96±5	2.2	81±9	4.3
DIBA	96±8	3.4	81±8	3.8
DEHA	94±5	2.0	80±7	3.7
DIDA	78±7	3.7	84±7	3.3

[a] MAE conditions: $T_{ext} = 120$ °C; $t_{ext} = 10$ min; microwave power = 20%; no. of vessels = 3; solvent: 25 ml methanol; sample mass = 0.5 g.
[b] SFE conditions: $T_{ext} = 95$ °C; $t_{ext} = 30$ min; $P = 7000$ p.s.i.; solvent: methanol.
[c] Confidence level: 95%.
[d] Calculated from three replicates.

each vessel. It can be observed that, in all the cases, the recoveries are close to 100%, irrespective of the amount of sample employed. The low values of the relative standard deviation mean that the extraction reproducibility is good.

3.8. Comparison between extraction techniques

MAE has been compared with another technique commonly employed for the extraction of this kind of organic compounds, viz. SFE. Table 6 shows the recoveries obtained for MAE and SFE of six adipate plasticizers. It can be observed that, in all cases, MAE gives better results than SFE. Moreover, the reproducibility of the results seems to be slightly better for MAE than for SFE, three replicates having been carried out at the same time.

Finally, Table 7 shows the recoveries obtained for one adipate plasticizer (DEHA) and three different phthalate plasticizers (DEHP, DINP, DIDP) by MAE and SFE. For all the plasticizers, the recoveries

obtained using MAE are better than those obtained using SFE.

4. Conclusions

MAE is a rapid and easy technique for the sample pretreatment step in the determination of plasticizers in PVC. Several samples can be extracted simultaneously and, in comparison with SFE, the analysis time is greatly reduced. The MAE recovery values are high and reproducible, and when working under optimised conditions, they are better than those obtained using SFE.

Table 7
Comparison between MAE and SFE for different phthalate and adipate plasticizers

Plasticizer	MAE		SFE	
	Recovery (%)[a,c]	RSD (%)[d]	Recovery (%)[b,c]	RSD (%)[d]
DEHA	103±4	1.4	88±14	6.3
DEHP	103±9	3.4	88±9	4.3
DINP	93±8	3.5	84±9	4.2
DIDP	95±9	4.9	86±7	3.2

[a] MAE conditions: $T_{ext} = 120$ °C; $t_{ext} = 10$ min; microwave power = 20%; no. of vessels = 3; solvent: 25 ml methanol; sample mass = 0.5 g.
[b] SFE conditions: $T_{ext} = 95$ °C; $t_{ext} = 30$ min; $P = 7000$ p.s.i.; solvent: methanol.
[c] Confidence level: 95%.
[d] Calculated from three replicates.

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