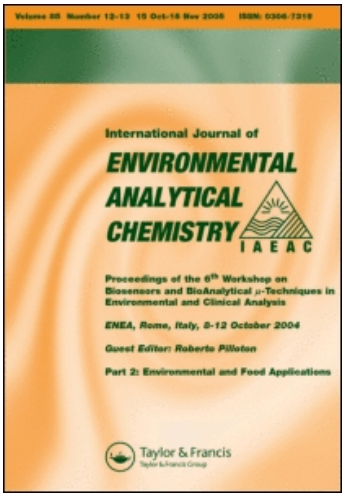

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Determination of trace amounts of some low molecular weight alcohols in aqueous samples using liquid-phase microextraction and gas chromatography

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Determination of trace amounts of some low molecular weight alcohols in aqueous samples using liquid-phase microextraction and gas chromatography

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A new and versatile liquid-phase microextraction method combined with gas chromatography (GC) analysis was applied for the extraction and determination of some aliphatic alcohols. Microlitre volumes of 1-undecanol were delivered on to the surface of the aqueous sample and the sample was agitated for a desired time. Then, the sample vial was cooled by inserting it into an ice bath for 5 min. The solidified solvent was transferred into a suitable vial and immediately melted, of which 1.0 μL was injected into GC for analysis. The parameters affecting the microextraction efficiency such as sampling temperature, stirring rate, nature and volume of the extracting solvent, salt addition and extraction time were investigated. The optimal microextraction conditions were established as: sample solution temperature, 60°C; stirring rate, 1250 rpm; volume of the extracting solvent, 8.0 μL (1-undecanol); salt concentration, 4 M NaCl and extraction time of 20 min. Under the optimal conditions, detection limits of the method were in the range of 3–56 μg L^{-1} and the relative standard deviations for determination of the alcohols were in the range of 2.2–11.9. Dynamic linearity of the alcohols was found to be in the range of 60–800 μg L^{-1}. After 20 min of extraction period, the pre-concentration factors for the alcohols were in the range of 13–358. Finally, the method was applied for determination of trace amounts of the alcohols in several real aqueous samples and satisfactory results were obtained.

Keywords: liquid-phase microextraction; low molecular weight alcohols; gas chromatography

1. Introduction

Alcohols are widely used in pharmaceutical and cosmetic industries and as raw materials in manufacturing of surfactants. Thus, determination of alcohols is of great importance in clinical, food and beverage industries [1,2]. Moreover, in an examination of the alcohols level due to emission from plants as well as their ambient level due to alcohol-fuel vehicles, quantitative analysis of the alcohols in the environment is required [2].

The most commonly used extraction techniques such as liquid–liquid and solid-phase extractions have several significant disadvantages. The major disadvantage of liquid–liquid extraction is the use of large volumes of expensive and toxic solvents. Also, it is

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extremely time consuming. The requirements for solid-phase extraction solvents are less stringent than those for liquid–liquid extraction [3].

Solid-phase microextraction (SPME) has the potential to overcome many difficulties associated with the conventional extraction methods [4]. SPME is a solvent-free, simple and fast extraction method. It has been extensively used in different fields such as food, environmental, clinical and forensic sciences. However, there are still some drawbacks in the method, including damage of fibre during the sampling, limited lifetime of the fibre, bleeding of the SPME coating into GC injector and sample carry-over [5,6].

Liquid-phase microextraction (LPME) has been developed as an alternative extraction technique [7–15]. This method provides analyte extraction in a few microlitres of extracting solvents. LPME avoids some problems of SPME such as fibre degradation. It is also fast, inexpensive and requires very simple equipments. Moreover, although a variety of SPME fibres are commercially available, the choice of solvents for LPME is much broader and organic phase is renewable at negligible cost. There are two modes of LPME sampling: direct LPME and headspace LPME (HS-LPME). Direct LPME consists of suspending a microdrop of extracting solvent at the tip of a microsyringe, which is immersed into the aqueous sample [16,17] whereas, in HS-LPME, microdrop of high boiling extracting solvent is exposed to the headspace of the sample. HS-LPME is a good extraction technique to analyse volatile and semi-volatile compounds in different matrices. In addition, because of availability of wide range of polar and non-polar as well as water miscible solvents, HS-LPME seems to be an attractive extraction technique. However, the use of microdrop LPME for headspace analysis is relatively difficult, since most suitable extracting solvents used in GC are of high vapour pressure, which might be lost during the extraction process. Moreover, when using water miscible solvents, due to increase in drop size during the sampling, it may fall off the needle [18]. There are a few reports concerning the application of the mentioned method for headspace analysis of some aliphatic alcohols into single organic drop [18,19]. A semi-automatic dynamic mode of HS-LPME system has also been developed in order to improve the operation and to achieve greater reproducibility in the sample extraction [17]. Recently, a relatively novel liquid–liquid microextraction technique based on solidification of floating organic drop was applied for the extraction and determination of some poly aromatic heterocyclic compounds as well as lead ion by graphite furnace atomic absorption spectrometry and three fat-soluble vitamins in aqueous samples [21–24]. In this work, an attempt was made to apply the latter method for the extraction and determination of some aliphatic alcohols namely as, 2-methyl propanol, 1-butanol, 2-butanol, 1-pentanol, 2-pentanol, 3-pentanol, 1-hexanol, 3-hexanol, 1-heptanol and 4-heptanol in several aqueous samples.

2. Experimental

2.1 *Reagents and materials*

A kit of standards containing aliphatic alcohols was purchased from Merck Company (Darmstadt, Germany). Stock standard solutions ($1000\,mg\,L^{-1}$) were prepared in methanol. All of the standard solutions were kept in the fridge at 4°C. 1-undecanol (98%, b.p.: 248–250°C), 1-dodecanol (98%, b.p.: 261–263°C), 2-dodecanol (95%, b.p.: 249–250°C), *n*-hexadecane (98%, b.p.: 283–286°C), reagent grade methanol and sodium chloride were also purchased from Merck. Double distilled water was used for preparing the working solutions.

2.2 *Apparatus*

Injection of the solutions into gas chromatograph was carried out using a 5 μL SGE microsyringe (Code: 5B-7, Switzerland). Stirring of the solutions was carried out using a Heidolph MR 3001 K magnetic heater-stirrer (Kelheim, Germany) and an 8 mm × 4 mm stirring bar. A simple water bath was placed on the heater-stirrer to control the temperature of the samples. Separation and identification of the alcohols were performed using a Shimadzu 17-A GC (Tokyo, Japan) equipped with a flame ionisation detector (FID) and CPB-10 (14% cyanopropyl + 86% methyl polysiloxane) fused-silica capillary column with a 25 m × 0.22 mm i.d. and 1.5 μm film thickness manufactured under the license of Hewlett–Packard Company (Australia). Separation conditions were as follows: The temperature of both injector and detector was set at 270°C. The GC split ratio was 1 : 10 and helium was used as carrier gas with the flow rate of 1 mL min^{-1}. The column temperature was held at 40°C for 3 min, then raised to 210°C at 10°C min^{-1}, held for 1 min, finally raised to 250°C at 20°C min^{-1} and again held for 1 min. In all cases, one of the organic solvent peaks was used as internal standard in order to correct variable injection volumes [18]. The analytical signal was taken as the ratio of relative peak area of each alcohol to the internal standard and the overall response is shown in each diagram.

2.3 *Extraction procedure*

A 500 μg L^{-1} solution of the alcohols, prepared in double distilled water, was used in the extraction studies. A 20 mL of an aqueous solution containing the alcohols was transferred into a 21 mL vial and the desirable volume of 1-undecanol was placed on the surface of solution using a microlitre syringe. Then, the vial was sealed and the stirrer was turned on. Once the desirable extraction time reached, the sample vial was put into an ice beaker and the extracting solvent was solidified after 5 min. Having used a simple spatula, the solidified solvent was transferred into the conical vial, in which the melting took place. Finally, 1.0 μL of the extractant was injected into the GC for quantification. A simple diagram of the used apparatus is shown in elsewhere [21].

3. Results and discussion

3.1 *Selection of extracting solvent*

In this study, the applied solvent should not only meet all of the common features for selection as an extracting solvent, but also its melting point should be near room temperature (10–30°C). Accordingly, several solvents such as 1-undecanol, 1-dodecanol, 2-dodecanol and *n*-hexadecane were investigated. Based on the obtained results, 1-undecanol was found to get the best extraction efficiency, while its chromatographic peak was easily separated from the analyte peaks. Also because of its low vapour pressure under the extraction conditions, the extractant was stable at the extraction period. Therefore, 1-undecanol was selected as the extracting solvent.

3.2 *Effect of sample solution temperature*

The effect of sample solution temperature was studied by exposing an extracting drop, located on the surface of aqueous sample, for 30 min in the range of 20–70°C.

Analytical measurements were performed on the aqueous solutions containing 500 μg L^{-1} of each analyte. Figure 1 shows that by increasing of the sample solution temperature, the extraction efficiency increased probably because the partition coefficients of the analytes increase. At higher temperatures (>60°C), the extraction system became unstable due to over-pressurisation of the sample vial. Thus, in the subsequent experiments, the sample vial temperature was held at 60°C.

3.3 *Effect of extracting solvent volume*

The effect of the extracting solvent volume on analytical signal was studied in the range of 6.0–16.0 μL. Figure 1 also shows that the analytical signals of the alcohols increased slowly by increasing of the solvent volume in the range of 6–8 μL. Then, it decreased when the solvent volume increased to 16.0 μL. Based on the following LLE equation:

$$\frac{dC_o}{dt} = A_i\beta/V_o(KC_{aq}C_o) \quad (1)$$

where, K is the distribution coefficient; C_o and C_{aq} are analyte concentrations in the organic and aqueous phases at time t, respectively; A_i is the interfacial area; and β is the overall mass transfer coefficient with respect to the organic phase [9,25]; the rate of the analytes transfer into microdrop is directly related to the interfacial area between the two liquid phases and inversely related to the organic-phase volume. Thus, by increasing of the drop volume, the effect of the interfacial area predominates and the analytical signal increases. By further increasing of the microdrop volume, the effect of the solvent volume predominates and the analytical signal decreases. In the present study, a constant volume (8.0 μL) of the extracting solvent was located on the surface of the aqueous sample for the rest of the study.

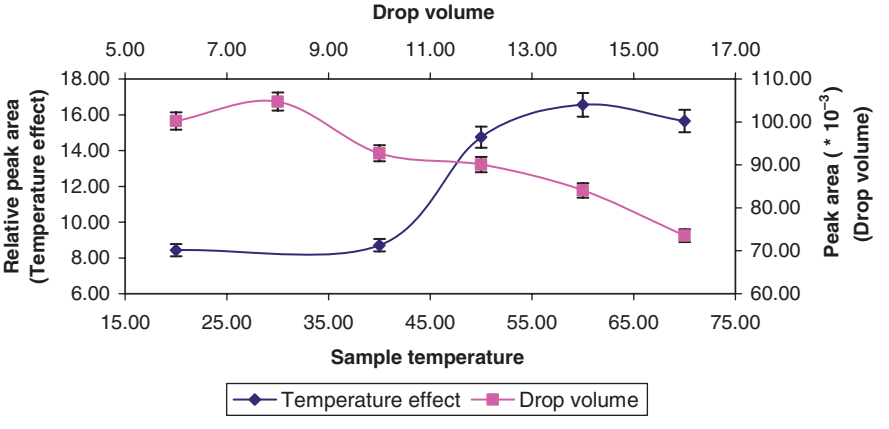

Figure 1. The effect of aqueous sample temperature on the relative peak area (—◆—). Conditions: extracting solvent volume, 10 μL; sample volume, 20 mL; stirring rate: 1250 rpm; extraction time, 30 min and without salt addition. The effect of extracting solvent volume on the peak area (—■—). Conditions: sample solution temperature: 60°C; stirring rate, 1250 rpm; sample volume, 20 mL; extraction time, 30 min and without salt addition.

3.4 *Effect of stirring rate*

Agitation of the sample solution enhances the rate of extraction. The stirring rate has a direct influence on extraction efficiency in limited times due to an increase in mass transfer into the organic drop. In this work, the samples with a volume of 20 mL were stirred at different stirring rates (300, 700, 1000, 1250 rpm) on a stirrer plate. According to Figure 2, the relative peak area increases with increasing of the stirring rate up to 1250 rpm, which is the highest stirring rate attainable with the stirrer. Hence, a stirring rate of 1250 rpm was chosen for further studies.

3.5 *Effects of salt addition*

To monitor the effect of salt addition on the extraction efficiency, the concentration of NaCl was changed in the range of 0.0–4.0 M, while the concentration of the alcohols was kept at the level of 500 μg L^{-1}. The results showed that extraction efficiency of the alcohols sharply increased with an increase in the salt concentration as shown in Figure 2. It is evident that the addition of NaCl promotes the transfer of the analytes into the extracting solvent. This can be explained by the fact that water molecules form hydration spheres around the salt ions. These hydration spheres reduce the concentration of water available to dissolve analyte molecules; thus it was expected that this would drive additional analytes into the extracting solvent [26]. Therefore, saturated salt condition with a NaCl concentration of 4 M was selected for further works.

3.6 *Extraction time*

To increase the precision and sensitivity of the LPME method, it is necessary to select an exposure time that guarantees the equilibrium between the aqueous and organic phases.

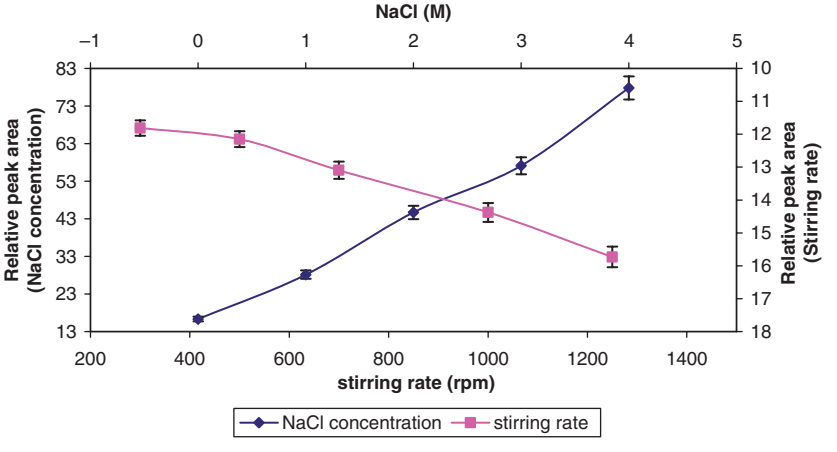

Figure 2. The effect of stirring rate on the extraction efficiency (—◆—). Conditions: sample solution temperature, 60°C; extracting solvent volume, 8 μL; sample volume, 20 mL; extraction time, 30 min and without salt addition. The effect of salt addition on the relative peak area (—■—). Conditions: sample solution temperature: 60°C, extracting solvent volume, 8 μL; sample volume, 20 mL; extraction time, 30 min; stirring rate, 1250 rpm.

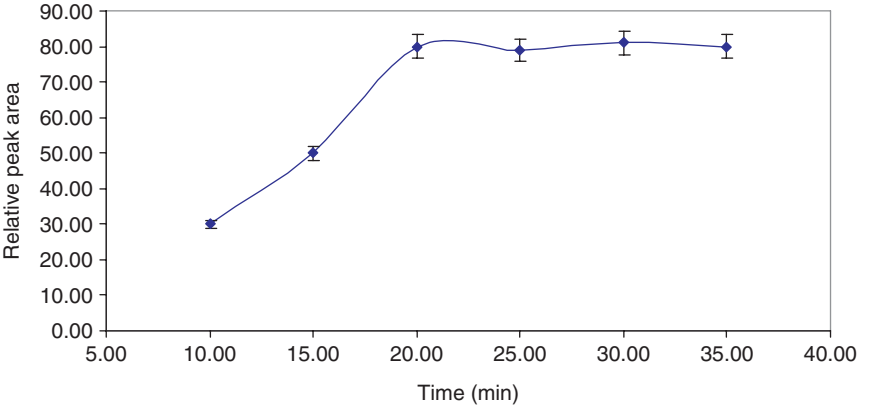

Figure 3. The effect of extraction time on the relative peak area. Conditions: sample solution temperature, 60°C; extracting solvent volume, 8 μL; sample volume, 20 mL; extraction time, 30 min; stirring rate, 1250 rpm and NaCl concentration, 4 M.

A series of experiments were performed and the extraction time profile was obtained by plotting the relative peak area against the extraction time evaluated in the range of 10–30 min. As Figure 3 shows, the relative peak areas increased by increasing of the exposure time up to 20 min and then remained relatively constant. Thus, the exposure time of 20 min was selected for the subsequent experiments.

3.7 *Evaluation of the method performance*

The pre-concentration factor (PF) can be calculated based on the following equation:

$$\mathrm{PF} = \frac{C_{o,f}}{C_{aq,i}} \tag{2}$$

where, $C_{aq,i}$ was selected as $200\,\mu g\,L^{-1}$ and $C_{o,f}$ was calculated from a suitable calibration curve, obtained from the direct injection of the standards in 1-undecanol into GC. Pre-concentration factors in the range of 24–358 were achieved for the alcohols (Table 1). The dynamic linearity of the proposed method was investigated in the concentration range of 60–800 $\mu g\,L^{-1}$ and relatively good linearities with the correlation of determinations (r^2) in the range of 0.9830–0.9990 were observed. The corresponding regression equations, correlation of determinations, linear dynamic ranges (LDRs) and the limit of detections (LODs) based on the signal-to-noise ratio of 3.0 were calculated (Table 1).

Applicability of the extraction method was investigated in five different spiked aqueous samples. A tap water sample was collected freshly from our laboratory (University of Tehran, Tehran, Iran) and a wastewater sample was taken from the sewage of a leather company in the west of Tehran (Iran). The other samples including grape juice, apple juice and Delester (an Iranian soft drink brand belonging to beer family) were obtained from Sundis Company (Uremia, Iran). Except for tap water, all the mentioned samples were diluted two times and then filtered through 0.45 μm pore size cellulose acetate membrane filters prior to the extraction.

Table 1. Figures of merit of the proposed method in determination of the alcohols.

Alcohol	[a]LDR ($\mu g\,L^{-1}$)	Regression equation	r^2	LOD ($\mu g\,L^{-1}$)	[b]PF
2-Butanol	200–800	$Y=0.001x-0.1003$	0.9888	21	24
2-Methyl propanol	200–800	$Y=0.001x-0.1022$	0.9830	56	32
1-Butanol	200–800	$Y=0.0021x-0.2433$	0.9836	40	29
3-Pentanol	200–800	$Y=0.0012x-0.1333$	0.9940	41	111
2-Pentanol	100–800	$Y=0.0065x-0.5591$	0.9977	5	103
1-Pentanol	100–800	$Y=0.0076x-0.7106$	0.9927	3	222
3-Hexanol	100–800	$Y=0.0093x-1.0446$	0.9930	5	358
1-Hexanol	60–800	$Y=0.0244x-0.9034$	0.9930	3	278
4-Heptanol	60–800	$Y=0.0208x-2.6037$	0.9990	3	353
1-Heptanol	60–800	$Y=0.0396x+1.4403$	0.9935	3	116

[a]Linear dynamic range; [b]Pre-concentration factor.

Table 2. The results obtained from the analysis of some real samples (each number refers to the corresponding alcohol, as in Figure 4).

[a]Sample		1	2	3	4	5	6	7	8	9	10
Tap water	Recovery (%)	108	109	105	109	110	97	107	83	106	80
	RSD (%)	6.6	8.0	7.4	6.1	10.0	3.4	5.8	10.3	8.3	7.0
	[b]Found	324	327	315	327	330	291	321	249	318	240
	[c]RE%	8	9	5	9	10	−3	7	−17	6	20
Apple juice	Recovery (%)	106	112	116	105	101	97	98	89	99	83
	RSD (%)	8.0	6.7	4.9	4.1	6.7	5.7	3.0	7.8	2.6	6.6
	Found	318	336	348	315	303	291	294	267	297	249
	RE%	6	12	16	5	1	−3	−2	−11	−1	−17
Grape juice	Recovery (%)	102	85	91	81	90	104	84	115	108	106
	RSD (%)	9.3	6.1	3.1	3.5	6.8	6.7	6.0	6.4	2.2	6.5
	Found	306	255	273	243	270	312	252	345	324	318
	RE%	2	−15	−9	−19	−10	4	−16	15	8	6
Wastewater	Recovery (%)	104	114	91	108	102	110	107	119	101	81
	RSD (%)	6.1	8.3	7.8	4.2	5.3	4.8	9.6	8.6	8.1	11.9
	Found	312	342	273	324	306	330	321	357	303	243
	RE%	4	14	−9	8	2	10	7	19	1	−19
Delester	Recovery (%)	101	84	86	82	84	102	89	104	94	84
	RSD (%)	4.5	5.9	3.3	4.2	5.9	3.3	6.7	5.2	4.6	7.8
	Found	303	252	258	246	252	306	267	312	282	252
	RE%	1	−16	−14	−18	−16	2	−11	4	−6	−16

[a]To each sample, the concentration level of 300 $\mu g\,L^{-1}$ was added; [b]$\mu g\,L^{-1}$; [c]Percent of relative error.

The results of relative standard deviations (RSDs) for LPME of the alcohols from the real samples based on four replicate measurements are shown in Table 2. The data demonstrated a good recovery in the range of 80–119%. The RSDs for determination of the alcohols in the examined real samples were located in the range of 2.2–11.9%. Figure 4 depicts the chromatograms of the alcohols at the spiked concentration level of 300 $\mu g\,L^{-1}$ in tap and wastewater samples before and after spiking. Finally, the present

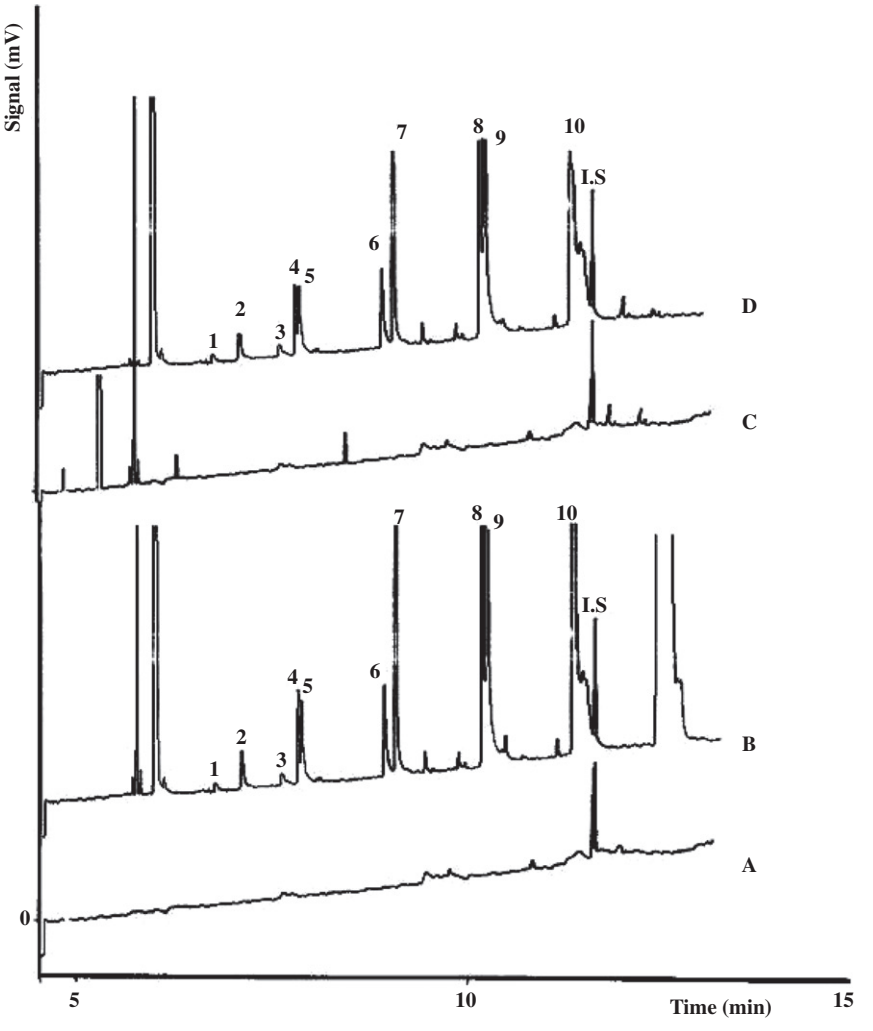

Figure 4. The chromatograms resulted from the extraction of the alcohols under optimum conditions from tap water (A, before spiking; B, after spiking) and wastewater (C, before spiking; D, after spiking) samples before and after spiking at the concentration level of 300 μg L^{-1}. Column temperature programming: 40°C for 3 min, then raised to 150°C at 10°C min^{-1}, held for 1 min, finally raised to 250°C at 20°C min^{-1} and once again held for 1 min. **1**: 2-butanol, **2**: 2-methyl propanol, **3**: 1-butanol, **4**: 3-pentanol, **5**: 2-pentanol, **6**: 1-pentanol, **7**: 3-hexanol, **8**: 1-hexanol, **9**: 4-heptanol, **10**: 1-heptanol, **I.S.**: Internal standard.

method was compared to the other methods in terms of validation, precision, etc. As shown in Table 3, the present work has got superiority over HSME (headspace solvent microextraction) and DSME (direct solvent microextraction) techniques in terms of LODs and DLRs. When it comes to the comparison of the other parameters such as the RSDs and correlation of determinations (r^2) the method is relatively comparable. Nevertheless, in terms of extraction time and volume of extracting organic solvent, it seems not to be interesting.

Table 3. Comparison of the proposed method with the others for determination of the alcohols.

Extraction method	Detection system	LOD ($\mu g\,L^{-1}$)	DLR ($\mu g\,L^{-1}$)	r^2	RSD (%)	V[a] (μL)	Time[b] (min)	Ref.
Proposed	GC–FID	2.6–56.4	60–800	>0.983	2.2–11.9	8	20	–
DSME[c]	GC–FID	1100–43600	Within 10,00,000	>0.980	<7	3	15	19
HSME[d]	GC–MS	2–97	100–20,000	>0.987	5.5–9.3	0.9	9.5	20
HSME	GC–FID	6400–11800	Within 15,00,000	>0.987	<–10	1	15	18

[a]Volume of the extracting solvent; [b]Extraction time; [c]Direct solvent microextraction; [d]Headspace solvent microextraction.

4. Conclusions

A modified, simple and flexible method of LPME referred to as solidification of floating organic drop was applied to fulfill the objective of the study, which was efficient extraction and trace determination of 10 different low molecular weight alcohols in some aqueous samples. The proposed method has advantages such as simplicity, good accuracy, high precision, low cost, and relatively low organic solvent consumption. Further, since fresh organic solvent was used for each extraction, there was no memory effect. On the other hand, as no special apparatus was required for holding the organic solvent, it was convenient to agitate the sample solution at the highest stirring rate attainable (about 1250 rpm). It is worth to note that since no attention is needed to pay during the extraction period thus, several extraction vials can be stirred simultaneously.

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