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Dynamic headspace liquid-phase microextraction of alcohols

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Abstract

A method was developed using dynamic headspace liquid-phase microextraction and gas chromatography-mass spectrometry for extraction and determination of 9 alcohols from water samples. Four different solvents, hexyl acetate, *n*-octanol, *o*-xylene and *n*-decane were studied as extractants. The analytes were extracted using 0.8 μl of *n*-octanol from the headspace of a 2 ml sample solution. The effect of sampling volume, solvent volume, sample temperature, syringe plunger withdrawal rate and ionic strength of the solution on the extraction performance were studied. A semiautomated system including a variable speed stirring motor was used to ensure a uniform movement of syringe plunger through the barrel. The method provided a fairly good precision for all compounds (5.5–9.3%), except methanol (16.4%). Detection limits were found to be between 1 and 97 μg/l within an extraction time of ∼9.5 min under GC–MS in full scan mode.

Keywords: Headspace liquid-phase microextraction; Extraction method; Food analysis; Alcohols

1. Introduction

Conventional sample preparation techniques such as liquid–liquid extraction (LLE) and solid-phase extraction (SPE) have several disadvantages. LLE is time consuming and requires large volume of expensive and toxic solvents. On the other hand, although SPE uses low amounts of organic solvent, it is applicable only to non-volatile and semivolatile compounds [1].

Solid-phase microextraction (SPME) has the potential to overcome many difficulties associated with conventional extraction methods [2]. SPME is a solvent free, simple and fast extraction method. The technique has been extensively used in different fields of application such as food, environmental, clinical and forensic science. However, there are still some drawbacks in this method, including damage of fibre during sampling, limited life time of the fibre, bleeding of the SPME coating into the GC injector and sample carry-over [3,4].

Direct SPME, that is placing the fiber directly into the sample to extract organic compounds, is recommended for relatively clean samples and extraction of semivolatile and non-volatile compounds. However, for analysis of volatile analytes, especially in complex samples, direct SPME is not recommended, sampling of the analytes from the headspace above the sample matrix (HS-SPME) [5] being more adequate. However, because of the greater availability of non-polar or slightly polar fiber coatings, HS-SPME applications are mostly limited to non-polar or medium-polar analytes [6,7] and there are a few reports concerning SPME of polar compounds [8].

Liquid-phase microextraction (LPME) has been developed as an alternative extraction technique [9–11]. This method provides analyte extraction in a few microliters of organic solvents. LPME avoids some problems of the SPME method such as fibre degradation; it is also fast, inexpensive and uses very simple equipment. Moreover, although a variety, SPME fibres is commercially available, the choice of solvents for LPME is much broader and the organic phase is renewable at negligible cost.

Similar to SPME, there are two modes of LPME sampling: direct LPME and headspace LPME (HS-LPME). The direct LPME consists of suspending a microdrop of organic solvent at the tip of a syringe, which is immersed in the aqueous sam-

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ple. HS-LPME is very similar to LPME except that microdrop of high boiling extracting solvent is exposed to the headspace of a sample. Like HS-SPME, headspace LPME is a good extraction technique to analyze volatile and semivolatile 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, use of microdrop LPME for headspace analysis it is relatively difficult, because most suitable organic solvents in GC have high vapour pressure, which result in them evaporating too quickly in headspace during extraction. Moreover, when using water miscible solvents, because of increase in drop size during sampling, it may drop from needle [12]. There are a few reports concerning application of a drop of solvent suspended from the tip of a syringe needle for headspace analysis [12–18]. Recently, Lee and Shen [19] have introduced dynamic HS-LPME that overcomes some limitation of static microdrop HS-LPME. In this technique the extraction is performed within the microsyringe barrel and the syringe is employed as both a separatory funnel for extraction and a syringe for direct injection into a GC column. When the syringe plunger is withdrawn, a very thin organic solvent film (OSF) is generated on the inner syringe wall. Mass transfer of the analytes occur between the gaseous sample and OSF. In each extraction cycle a fresh gaseous sample contacts with a new OSF. In comparison to droplet LPME, the described dynamic LPME provides a larger enrichment factor within a shorter analysis time and selection of solvent is more flexible [19,20].

Lee and Shen [19] used dynamic HS-LPME to analyze chlorobenzenes in a solid matrix such as soil. Because they used a manually operated extraction system the precision of the method was relatively poor (relative standard deviation, R.S.D. were between 5.7 and 17.7%).

In the present study, a semiautomatic dynamic HS-LPME system was developed in order to improve ease of operation and to achieve greater reproducibility in the sample extraction. A variable speed stirring motor was used for automation of sample extraction step. Low molecular weight alcohols were used as model compounds. The experimental parameters that affect the extraction efficiency of studied compounds from aqueous samples were evaluated and optimized. Relatively good precision and high sensitivity were obtained with the proposed method.

2. Experimental

2.1. Chemicals

Methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, *tert*-butanol, 1-pentanol, 2-pentanol and ethyl methyl ketone (used as internal standard) were purchased from Merck (Darmstadt, Germany). A stock standard solution of nine alcohols studied was prepared in water at concentration level of ~4000 mg/l for methanol and ethanol; and ~2000 mg/l for the rest of compounds. A mixture of these compounds was prepared weekly by diluting the standard solution with double distilled water, and more diluted working solutions were prepared daily by diluting this solution with water. The standard solutions were stored refrigerated at 4 °C.

Hexyl acetate, *n*-octanol, *o*-xylene and *n*-decane (Merck) containing a fixed concentration of ethyl methyl ketone (IS), were used as extraction solvents.

2.2. Instrumentation

A 10 μl GC microsyringe model 701N (gauge 26s and point style 2) from Hamilton (Reno, NV, USA) was used to perform LPME experiments. The sample vial was placed in a water-bath on a magnetic stirrer (CB162, Bibby, UK). A circulating water-bath (Fanazma, Iran) was used to maintain the sample at desirable temperature. The basic extraction apparatus is shown in Fig. 1. A variable speed stirring motor was attached to a circular plate (6). Rotation of the plate causes movement of syringe plunger through the barrel.

Gas chromatographic analysis was carried out using a Fisons Instrument (Rodano, Italy) model 8060 fitted with a split/splitless injector and Trio 1000 mass spectrometer (Fisons Instruments, Manchester, England) detector. Helium was used as the carrier gas with a flow rate of 0.6 ml/min. The components were separated on a 60 m × 0.25 mm i.d., 0.1 μm film thickness DB-5MS column from J&W Scientific (Folsom, CA, USA). The injector temperature was set at 220 °C and all injections were made in split mode (split ratio, 40:1). The column was initially maintained at 40 °C for 7 min; subsequently, the temperature was increased to 100 °C at a rate of 15 °C/min (1 min hold) then was increased to 240 °C (30 °C/min, 10 min hold). The mass spectra were acquired as full scans from *m*/*z* 20 to *m*/*z* 90 (2 scans/s), with a source temperature of 200 °C under a 70 eV ionization potential.

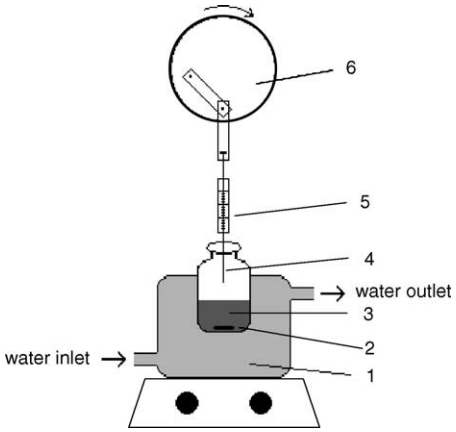

Fig. 1. Schematic diagram of the HS-LPME system. (1) water bath; (2) magnetic stirrer bar; (3) sample solution; (4) syringe needle tip; (5) microsyringe; (6) circular plate connected to a variable speed stirring motor.

2.3. Extraction procedure

Sample solution (2 ml) spiked with an appropriate amount of studied compounds was introduced in a 4 ml vial with a screw top/silicone septum. The sample vial was placed in a water-jacketed vessel on a magnetic stirrer (1500 rpm). The vial was thermostated at 60 °C (unless otherwise indicated) for 10 min before extraction and during the extraction. A 0.8 μl volume of organic solvent was withdrawn into the microsyringe (unless otherwise indicated). Then, the syringe needle was inserted through the silicone septum and the end of needle was located about 1 cm above the surface of the solution. During the extraction, the plunger moves in and out of the syringe barrel at a constant rate between 0.7 and 4 μl/s. Therefore, the gaseous sample withdraws into and discharges from the syringe barrel. The above cycle was then repeated 80 times (unless otherwise indicated). After extraction, the syringe needle was removed from the vial and the sample was injected into the GC.

In order to achieve the optimal conditions (maximum recovery), the effect of parameters such as; sample temperature, sampling volume (volume of gaseous sample taken by syringe), solvent volume (volume of organic solvent withdrawn in syringe), number of extraction cycles, syringe plunger withdrawal rate and salt addition were studied.

3. Results and discussion

3.1. Headspace liquid-phase microextraction

Dynamic HS-LPME [19] as previously described provides a simple, inexpensive and fast extraction technique. However, its manual operation provides relatively poor precision. Automation of the system can improve precision and sensitivity of the technique. In this study a semi-automated dynamic HS-LPME was developed so that this method could be more accurate and more easily operated. In the proposed set-up (Fig. 1) circular motion of a stirring motor converts to a piston like movement as can be seen in the figure. Position of the connector on the circular plate defines displacement distance of the syringe barrel, and hence, sampling volume. To achieve reproducible results, plunger movement speed must be constant during the extraction. The rotation speed of the motor was set and kept constant by a power supply controller.

3.1.1. Selection of organic solvent

To reduce the risk of evaporation and avoid overlapping of solvent with analytes peaks, the choice of organic solvent is limited to those having relatively high boiling points. Four solvents, hexyl acetate, *n*-octanol, *o*-xylene and *n*-decane were tested to select the best one for the extraction of alcohols in water samples with this technique. Ethyl methyl ketone was used as internal standard to correct for variation in injection volumes. Peak area ratio of analytes to IS was used as the analytical signal. Preliminary experiments showed that

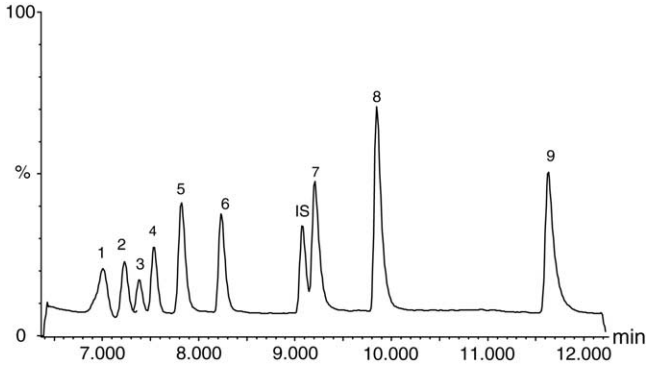

Fig. 2. Chromatogram of the standard solution spiked with 40–80 mg/l of alcohols after HS-LPME at optimum conditions. (1) methanol; (2) ethanol; (3) 2-propanol; (4) *tert*-butanol; (5) 1-propanol; (6) 2-butanol; (7) 1-butanol; (8) 2-pentanol; (9) 1-pentanol.

n-octanol gave the best extraction efficiency. Fig. 2 shows a chromatogram of the standard solution of alcohols after HS-LPME using *n*-octanol as extraction solvent.

3.1.2. Effect of plunger withdrawal rate

The extraction efficiency of the method greatly depends on movement speed of the plunger in the syringe barrel [19–21]. When the syringe plunger is withdrawn, a very thin organic solvent film is formed on the inner surface of microsyringe barrel and sample headspace is drawn in. The analytes in the gaseous phase equilibrate between the organic film and the gaseous sample. The thickness of OSF can affect extraction efficiency of the system [19]. The film thickness (d_f, cm) is given by [21,22]:

$$d_f = AR\left(\frac{u\eta}{\gamma}\right)^k$$

where A is a constant; R, inner diameter of the barrel in cm; u, flow rate (cm/s); η, viscosity of the solvent (P); γ, surface tension of the organic film (dyn/cm); and k is an empirical constant equal to 1/2 or 2/3. Using a given solvent, film thickness depends only upon the flow rate of the syringe barrel. As can be seen from the equation, faster movement of the plunger leads to thicker film. Fig. 3 shows effect of syringe plunger moving speed on extraction efficiency. At high moving speed (more than 1.5 μl/s) the extraction efficiency was very low. This may be because the time available for the analytes to reach the equilibrium condition was short. Also, at low plunger moving speed (less than 0.7 μl/s) a weak enrichment of all analytes was obtained. The maximum peak area of all analytes was obtained a plunger moving speed of about 1.4 μl/s. Therefore, this movement speed was selected in further experiments.

3.1.3. Effect of temperature

The effect of sampling temperature was studied by extraction of a fortified water sample (at a level of about 40–80 mg/l for each alcohol), at 30–70 °C. The dependence of the relative peak area of analytes on temperature was shown in Fig. 4,

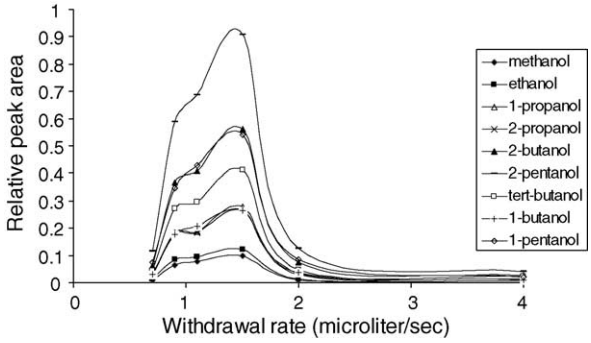

Fig. 3. Effect of withdrawal rate of syringe plunger on the relative peak areas of alcohols. Concentration of analytes is 40–80 mg/l. Sample temperature: 40 °C, sampling volume: 5 μl, solvent volume: 0.8 μl, number of extraction cycles: 80, salt addition: no NaCl added.

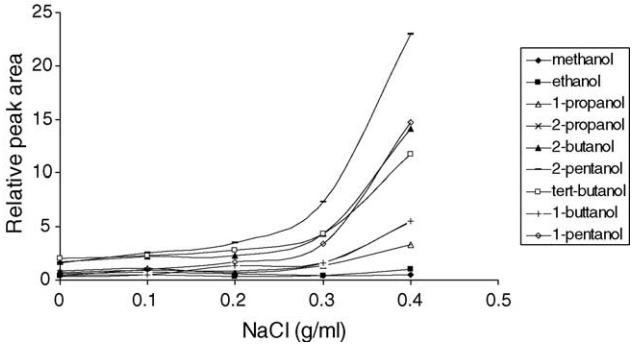

Fig. 5. Effect of addition of NaCl on the relative peak areas of alcohols. Concentration of analytes is 40–80 mg/l. Sample temperature: 60 °C, sampling volume: 5 μl, solvent volume: 0.8 μl, number of extraction cycles: 80, syringe plunger movement speed: 1.4 μl/s.

for all tested compounds. The linear increase of the response is observed up to 50 °C for each analyte. Over this temperature the increased rate becomes smaller for 1 and 2-pentanol. The response for other compounds seems to be constant over 50 °C. Temperature has a significant effect on both kinetics and thermodynamics of the extraction process. There are two opposing effects, which influence LPME process. Firstly, at higher temperature Henry's constant and diffusion coefficient of analyte in the headspace are increased. However, the distribution constant of analytes to the organic phase are decreased with increasing temperature. This is especially observed for the compounds with small distribution constant. In further measurements, the sample vial temperature was held at 60 °C.

3.1.4. Effect of salt addition

The effect of increasing the ionic strength of the water sample was evaluated by adding NaCl. An amount between 0.1 and 0.4 g/ml of NaCl was added to the spiked water samples at concentration level of about 40–80 mg/l for each analyte studied. Fig. 5 shows dependence of analytes signals versus salt concentration. The largest peaks were obtained when salt was added in an amount that caused saturation at the extraction temperature. The addition of salt to the sample matrix decreases the solubility of the analytes in the sample matrix, allowing more analytes to move to the sample headspace and enhancing the extraction efficiency.

3.1.5. Number of extraction cycles

The influence of number of extraction cycles (withdrawal of sample vapour into the syringe followed by discharge) on the extraction efficiency of the method was studied. As can be seen in Fig. 6, the amount of extracted analyte for methanol, ethanol, 1-propanol, 2-propanol and *tert*-butanol linearly ($R > 0.98$) increase with number of extraction cycles (n). On the other hand, the compounds 1-butanol, 1-pentanol, 2-butanol and 2-pentanol with relatively high partition coefficient in OSF show a nearly constant concentration in organic phase over $n > 80$.

It has been shown mathematically [20] there is a linear relationship between the number of extraction cycles and amount of analytes enriched from aqueous samples. In the proposed equation, it was assumed that after each extraction cycle, the OSF is completely renewed and trace amount of analyte left in the renewed OSF is negligible. With this assumption, when n is relatively small, the transported amount

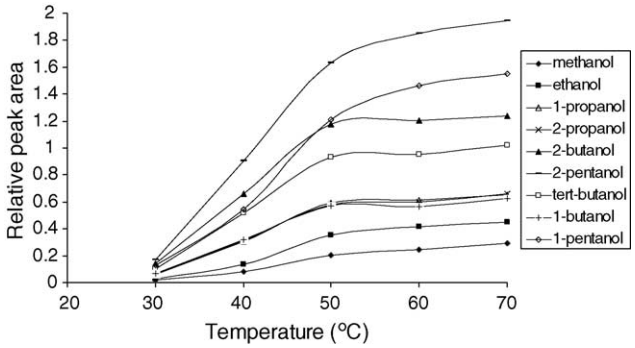

Fig. 4. Effect of sample temperature on the relative peak areas of alcohols. Concentration of analytes is 40–80 mg/l. Sampling volume: 5 μl, solvent volume: 0.8 μl, number of extraction cycles: 80, syringe plunger movement speed: 1.4 μl/s, salt addition: no NaCl added.

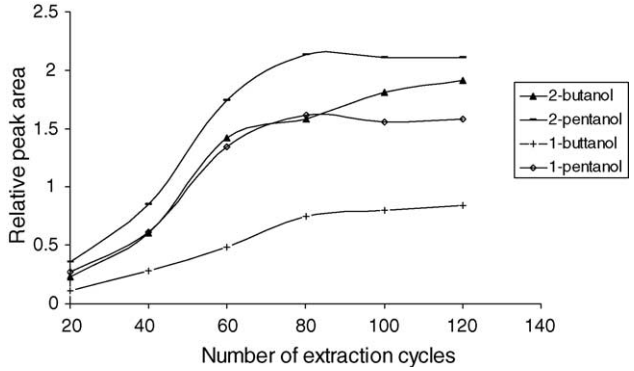

Fig. 6. Effect of number of extraction cycles on the relative peak areas of alcohols. Concentration of analytes is 4–8 mg/l. Sample temperature: 60 °C, sampling volume: 5 μl, solvent volume: 0.8 μl, syringe plunger movement speed: 1.4 μl/s, salt addition: saturated with NaCl.

Table 1
Correlation coefficient, linear dynamic range, limit of detection and relative standard deviation for dynamic HS-LPME of alcohols

Compound	Spiking level (mg/l)	r	LDR (mg/l)	LOD[a] (μg/l)	R.S.D. (%)
Methanol	0.2–20	0.9723	0.2–20	97	16.4
	20–2000	0.9968	20–400		
Ethanol	0.2–20	0.9855	0.2–20	67	9.3
	20–2000	0.9988	20–400		
2-Propanol	0.1–10	0.9942	0.1–10	11	7.4
	10–1000	0.9999	10–500		
tert-Butanol	0.1–10	0.9952	0.1–10	5	6.8
	10–1000	0.9995	10–200		
1-Propanol	0.1–10	0.9954	0.1–10	20	7.1
	10–1000	0.9998	10–500		
2-Butanol	0.1–10	0.9945	0.1–10	3	5.5
	10–1000	0.9987	10–500		
1-Butanol	0.1–10	0.9841	0.1–10	5	6.1
	10–1000	0.9984	10–500		
2-Pentanol	0.1–10	0.9895	0.1–10	1	5.6
	10–1000	0.9987	10–200		
1-Pentanol	0.1–10	0.9875	0.1–10	2	6.8
	10–1000	0.9998	10–200		

[a] LODs calculated from $S/N = 3$.

of analyte during each sampling cycle is approximately the same. However, rate of increase in analyte concentration in organic phase decrease gradually with n, because organic film is not completely renewed in each cycle. This may be one reason why curves are not linear in higher n value for some compounds. In addition, in the offered equation [20] initial concentration of analyte in headspace assumed to be constant during the extraction. Whereas, analyte concentration in headspace gradually decrease with increase in number of sampling cycle. This will be more remarkable for the compounds that have a large partition coefficient between OSF and headspace. In this case, the relationship between extracted analyte and n is no longer linear at higher n value.

3.1.6. Sampling and solvent volume

According to the theoretical equations [19] a linear relationship between sampling volume (volume of gaseous sample withdrawn into the syringe) and amount of analytes extracted is expected:

$$C_{\text{org}} = \frac{K_{\text{osf-hs}} C^0_{\text{hs}}}{K_{\text{osf-hs}} + r^2/(R^2 - r^2)} \frac{V_{\text{hs}}}{V_{\text{org}}}$$

where C_{org} is concentration in organic solvent; $K_{\text{osf-hs}}$, partition coefficient between the OSF and the headspace; C^0_{hs}, the original concentration of the analyte in the headspace; R, the radius of the syringe inner barrel; r, the radius of the gaseous sample plug in the syringe; V_{hs} and V_{org} are sampling and solvent volume, respectively.

The effect of sampling volume is shown in Fig. 7. The curves indicate that the concentration of analytes in organic phase is not directly proportional to sampling volume. This may be because of partial evaporation of organic solvent as sampling volume increased. Although a sampling volume of 10 μl provided higher sensitivity, a 5 μl sampling volume was chosen in further experiments to diminish the extraction time.

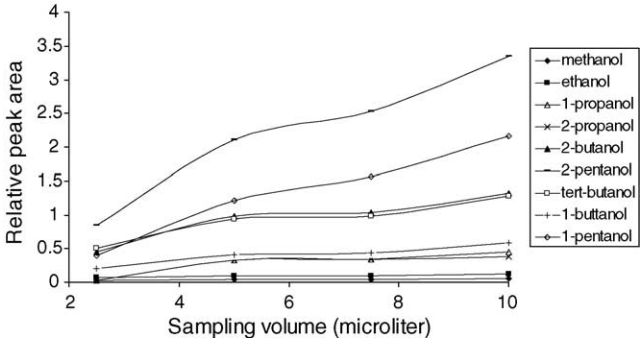

Fig. 7. Effect of sampling volume on the relative peak areas of alcohols. Concentration of analytes is 4–8 mg/l. Sample temperature: 60 °C, solvent volume: 0.8 μl, number of extraction cycles: 80, syringe plunger movement speed: 1.4 μl/s, salt addition: saturated with NaCl.

To study the effect of solvent volume, four different volume of solvent; 0.8, 1.3, 1.8 and 2.3 μl was checked. As it can be seen from the above equation, C_{org} varies linearly with

Table 2
Results of analysis of two different beers

Compound	Alcoholic beer (mg/ml)	Non-alcoholic beer (mg/ml)
Ethanol	83.1	2.28
1-Propanol	0.214	–
2-Propanol	0.008	–
1-Butanol	0.004	–
2-Pentanol	0.04	–

Table 3
Recoveries and relative standard deviations of studied compounds in spiked beer samples

Compound	Alcoholic beer		Non-alcoholic beer	
	Recovery (%)	R.S.D. (%)	Recovery	R.S.D.
Methanol	114.4	18.2	110.7	14.3
Ethanol	103	8.6	106	8.3
2-Propanol	90.4	12.4	102.3	6.2
tert-Butanol	91.2	10.3	105.6	5.7
1-Propanol	105.1	6.3	103.2	4.5
2-Butanol	98.7	4.9	100.2	5.8
1-Butanol	97.1	6.9	98.3	6.4
2-Pentanol	103	7.5	101.8	4.6
1-Pentanol	96.5	7.4	97.1	5.3

$n = 3$ determination.

$1/V_{org}$. The results of this experiment showed that there is a linear relationship between concentrations of all analytes in organic solvent and $1/V_{org}$ in the solvent volume of 0.8–2.3 μl ($R > 0.96$).

3.2. Method evaluation

The calibration graphs were calculated using six spiking levels of all analytes in the concentration range of 0.1–20 mg/l (80 mg/l IS concentration in octanol) and 10–2000 mg/l (800 mg/l IS concentration in octanol). For each point three replicate extractions were performed. The extraction conditions were as follows: number of extraction cycles: 80, sample solution: 2 ml, stirring rate: 1500 rpm, sample temperature: 60 °C, sampling volume: 5 μl, solvent volume: 0.8 μl, added NaCl: saturated. Table 1 shows relative standard deviation, dynamic linear range (DLR), limit of detection (LOD) and correlation coefficient (r) obtained by the method. The reproducibility study was carried out by extracting a spiked (about 2–4 mg/l of each compound) water sample, by performing five repeated extraction. The relative standard deviations were from 5.5 to 9.3%, except 16.4% for methanol. The reproducibility of the method is comparable with those obtained by static HS-LPME [12]. Also, in comparison with manually operated dynamic HS-LPME [19] an improvement in the precision is observed.

In order to test applicability of the method to real sample analysis, the recovery of the method was determined by a single point standard addition technique with two alcoholic and non-alcoholic beers. Samples were diluted 20-fold before extractions. In the case of alcoholic beer, ethanol was determined after 1250-fold dilution. For each sample three extractions were performed. The analytes were added to the diluted real samples at 50 mg/l for ethanol and 5 mg/l for other compounds. The results are shown in Tables 2 and 3. The recovery of all extractions was between 90.4 and 114.4% for alcoholic beer and 97.1–110.7 for non-alcoholic beer (Table 3). The relative standard deviations were relatively acceptable. In comparison with HS-SPME [23,24] and static HS-LPME [12] analysis of alcohols in alcoholic beverages by GC-FID, it appears that there is no great difference between R.S.D. values of the methods. The dynamic linear range of all compounds studied in the proposed method (Table 1) was extended to higher concentration compared to HS-SPME analysis [23,24]. It may be because just a small portion of sample is extracted into the solvent drop.

4. Conclusions

In the present work, a semiautomatic dynamic HS-LPME was developed and applied to extract volatile alcohols from aqueous solutions. Compared to other extraction methods, HS-LPME has numerous advantages such as: simplicity, low cost, ease of operation, high sensitivity, no possibility of sample carry-over, extremely low consumption of toxic solvents and short analysis time. In the other hand, in dynamic HS-LPME the selection of solvent is more flexible and lost of droplet during analysis is eliminated. In comparison to manually operated extraction, semiautomation of the method led to the better precision. Good linearity and sensitivity, as well as short analysis time are additional advantages of the method for measurement of the alcohols in aqueous samples.

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