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Simultaneous derivatization and dispersive liquid–liquid microextraction of anilines in different samples followed by gas chromatography–flame ionization detection

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ABSTRACT

A new method based on simultaneous derivatization and dispersive liquid–liquid microextraction in one step is developed for determination of five anilines in different aqueous samples. In this method, acetonitrile containing microlitre-level of butylchloroformate was rapidly injected into aqueous sample by a syringe. After centrifugation of the cloudy solution, the fine droplets of the butylchloroformate containing the derivatized analytes were sedimented in the bottom of the conical test tube. Then, 0.5 μL of the settled phase was injected into gas chromatography–flame ionization detector. Under optimum conditions the enrichment factors, extraction recoveries and enhancement factors were high and ranged between 197 and 298, 47 and 69%, and 4.7and 6.2, respectively. Linearity was observed in the range of 10–10,000 $\mu g\,L^{-1}$ (except for 4-chloroaniline), and the relative standard deviations (RSD %) were lower than 5.2% ($n=6$). The limits of detection of the six anilines ranged from 1 to 3 $\mu g\,L^{-1}$. Different aqueous samples including tap, river and well waters as well as wastewaters were successfully analyzed. In this method the extraction solvent and derivatization agent are the same and the derivatization reaction was carried out under mild conditions. This method has several advantages over other reported techniques, being very simple, rapid and less hazardous for the environment.

1. Introduction

Anilines are widely used in the polymer, rubber, pharmaceutical, and dye industries. The high consumption of these compounds in industrial processes leads to their release into the aquatic environment. Due to the toxicity and potential carcinogenicity, determination of aromatic amines has been paid much attention [1]. A variety of analytical methods have been reported, including gas chromatography (GC) [2–4] and high performance liquid chromatography (HPLC) [5,6]. Capillary electrophoresis (CE) [7] and spectrophotometric methods [8] have been reported as well. Sample preparation is one of the most important steps in an analytical process. For the analysis of anilines, several sample preparation methods have been developed such as solid phase extraction (SPE) [9,10], solid phase microextraction (SPME) [11,12], and liquid–liquid–liquid microextraction (LLLME) [13,14].

SPE is a sample preparation technique that has been applied to a wide range of compounds [15–17]. However, it is time-consuming and has a relatively low enrichment factor. Also SPE cartridges need conditioning and require further toxic organic solvents for washing and elution steps. SPME introduced in 1990 by Pawliszyn [18,19] is based on equilibrium of analytes between the sample matrix and a fused silica fiber coated with an adsorbent phase. It has been widely applied to extract different analytes from environmental samples due to its solvent-free nature, simplicity and rapidity. Despite the advantages provided by this method, the extractant fiber is expensive and fragile, and sample carry-over is also a problem [20]. Recently, a novel liquid phase microextraction (LPME) method termed dispersive liquid–liquid microextraction (DLLME) was introduced by Assadi and co-workers [21,22]. In DLLME, the mixture of extraction and disperser solvents is rapidly injected into an aqueous sample. A cloudy solution containing fine droplets of extraction solvent is formed. Finally the dispersion is removed by centrifugation and the enriched analytes in the sedimented phase are determined by either chromatographic or spectrometry methods. Some advantages of DLLME are simplicity of operation, rapidity, low sample volume, low cost and high enrichment factor. DLLME has been successfully applied to extraction and concentration of a wide variety of organic compounds such as

Abbreviations: DLLME, dispersive liquid–liquid microextraction; EF, enrichment factor; EnF, enhancement factor; FID, flame ionization detection; LLLE, liquid–liquid–liquid microextraction (LLLME)

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antioxidants [23], polycyclic aromatic hydrocarbons [24], and sulfonylurea herbicides [25] in food and environmental samples. Anilines are polar compounds which can cause tailing and irreversible adsorption. Hence, derivatization step is often required to obtain a good GC performance. Several derivatization reagents such as dimethyl chloro thiophosphate [26], heptafluorobutyric anhydride [27], trifluoroacetic anhydride [28], N-allyl-N′-arylthiourea formation [29] and iodine [30] have been developed for sensitive determination of anilines. However, the derivatization procedure requires more time and efforts. Chemical derivatization is an approach that most analytical chemists would like to avoid because of several reasons. First, the additional reagent and operation may lead to potential uncertainty in quantitation. Second, the need for derivatization introduces an additional step to the sample preparation procedure, indicating operational inconvenience. Third, the exposure to derivatization reagents is undesirable. In order to resolve the above-mentioned problems, in situ derivatization was developed, which simply adds a reagent into a liquid sample [31]. Simultaneous DLLME and derivatization is an efficient extraction technique to analyze different compounds in aqueous samples [32–34]. Rapidity, high extraction recovery, simplicity of operation, good repeatability and low cost are some advantages of this method. Also, sample preparation time as well as consumption of toxic organic solvents is minimized.

In this study, we have proposed a new method based on simultaneous DLLME and derivatization in one step for the analysis of anilines in aqueous samples. Figures of merit for the proposed approach are reported using GC with flame ionization detection or mass spectrometry. The effects of different parameters on the derivatization/extraction procedure are thoroughly discussed. In this method, the extraction solvent and derivatization agent are the same and the derivatization procedure has been carried out under mild conditions.

2. Material and methods

2.1. Reagents and solutions

Aniline (purity > 99.5%), *o*-anisidine (purity > 99%), 4-chloroaniline (purity > 99%) and 2-chloroaniline (purity > 98%) were obtained from Merck (Darmstadt, Germany), and *o*-toluidine (purity 99.5%) was purchased from Fluka (Buchs, Switzerland). Analytical grade methanol, acetone and acetonitrile (as disperser solvents), butylchloroformate (as derivatization agent/extraction solvent), hydrochloric acid and sodium hydroxide were obtained from Merck. A stock solution of aromatic amines (each 2000 mg L^{-1}) was prepared in methanol and working standard solutions were prepared daily by appropriate dilutions of stock solution with de-ionized water (Ghazi Company, Tabriz, Iran). A standard solution of analytes (each 250 mg L^{-1}) in butylchloroformate was injected into the separation system each day (three times) for quality control and the obtained peaks areas were used in calculation of enrichment factors and recoveries. An acetate buffer (C=0.01 mol L^{-1}, pH=4) was prepared and used in back extraction of anilines from wastewater of a paint factory.

2.2. Samples

Tap water was collected from our laboratory just before analysis. Well water was picked up from a local area (Tabriz, Iran). Other samples including river water (Talkherood, Tabriz, Iran), municipality wastewater, paint factory wastewater (Tabriz, Iran) and leather processing unit wastewater (Tabriz, Iran) were also tested. All the samples except wastewater of the paint factory were directly subjected to the derivatization/extraction procedure. The paint wastewater (non-aqueous phase) was mixed with acetate buffer (1:1, v/v) in an extraction funnel and shaken manually for 2 min. During this step analytes were protonated and back extracted into aqueous phase. Finally 5 mL of the aqueous phase was used with the above-mentioned samples.

2.3. Instrumentation

A gas chromatograph (GC-2014, Shimadzu, Japan) equipped with a split/splitless injector system, and a flame ionization detector was used for separation and determination of the selected aromatic amines. Helium (99.999%, Gulf Cryo, United Arab Emirates) was used as the carrier gas at a constant linear velocity of 30 cm s^{-1}. The injection port was held at 250 °C and used in the splitless mode with a purge time of 1 min. Separation was carried out on a CP-Sil 8 CB capillary column (30 m × 0.25 mm i.d., and film thickness 0.25 μm) (poly (5%-diphenyl- 95%-dimethylsiloxane) (Chrompack, Milan, Italy). The oven temperature was programmed as follows: initial temperature 50 °C (held for 2 min) then was raised to 250 °C at a rate of 7 °C min^{-1}, and held at 250 °C for 1 min. The total time for one GC run was less than 32 min. The FID temperature was maintained at 250 °C. Hydrogen gas was generated with a hydrogen generator (OPGU-1500S, Shimadzu, Japan) for FID at a flow rate of 40 mL min^{-1}. The flow rate of air for FID was 300 mL min^{-1}. Gas chromatography–mass spectrometry (GC–MS) analysis was carried out on an Agilent 6890N gas chromatograph with a 5973 mass-selective detector (Agilent Technologies, CA, USA).The separation was carried out on an HP-5 MS capillary column (30 m × 0.25 mm i.d. and film thickness 0.25 μm) (poly (5%-diphenyl-95%-dimethylsiloxane) (Hewlett-Packard, Santa Clara, USA). Helium was used as carrier gas at a flow rate of 1.0 mL min^{-1}. The oven temperature program was the same as GC–FID analysis mentioned above. pH measurements were performed with a Metrohm pH meter model 654 (Herisau, Switzerland). A D-7200 centrifuge from Hettich (Kirchlengern, Germany) was used in DLLME.

2.4. Derivatization/extraction procedure

5 mL of sample, back-extracted sample or standard solution was placed into a 10-mL glass test tube with a conical bottom. An aliquot of 0.75 mL of acetonitrile (disperser solvent) containing 25 μL butylchloroformate (derivatization agent/extraction solvent) was injected rapidly into the aqueous solution by a 1-mL syringe. After centrifuging of cloudy solution for 5 min at 5000 rpm, an aliquot (0.5 μL) of the sedimented organic phase was removed using a 1-μL GC microsyringe (zero dead volume, Hamilton, Switzerland) and injected into the GC system for analysis.

2.5. Calculation of enrichment factor, extraction recovery and enhancement factor

The enrichment factor (*EF*) is defined as the ratio between the analyte concentration in the sedimented phase (C_{sed}) and the initial concentration of analyte (C_0) within the sample:

$$EF = C_{sed}/C_0 \quad (1)$$

C_{sed} is obtained from calibration curves plotted by direct injection of standard solutions of the selected amines in butylchloroformate (derivatization agent/extraction solvent).

The extraction recovery (*ER*) is defined as the percentage of the total analyte amount (n_0) which is extracted into the sedimented phase (n_{sed}):

$$ER = (n_{sed}/n_0) \times 100 = [(C_{sed}\, V_{sed})/(C_0\, V_{aq}) \times 100]$$
$$ER = (V_{sed}/V_{aq})\, EF \times 100 \quad (2)$$

where V_{sed} and V_{aq} are the volumes of the sedimented phase and aqueous solution, respectively.

The enhancement factors were determined from the ratio of the slopes of two calibration curves. These curves were plotted by direct injection of standard solutions of the target anilines prepared in butylchloroformate and methanol. These factors indicate the improvement of FID signals due to butylated amino groups of analytes.

3. Results and discussion

Several factors such as selection of a suitable disperser and its volume, volume of derivatization agent/extraction solvent, salt addition, pH and centrifugation time and speed affect the process. So all these parameters were optimized in order to obtain good performance and are discussed in detail in the following sections.

3.1. Selection of disperser solvent

Miscibility in both extraction solvent and aqueous phase is an essential factor in the selection of a disperser solvent. In addition, dispersive solvent should disperse extraction solvent as very fine droplets into aqueous phase to obtain fast transfer of analytes from aqueous phase (sample) into the extraction phase. Acetonitrile, methanol, and acetone have these properties. So 1 mL of each of them was tested for this purpose. By using 50 μL butylchloroformate, the volume of sedimented phase for acetone, methanol and acetonitrile was 18, 22 and 24 μL, respectively. The results indicated that the maximum extraction efficiency was achieved by using acetonitrile as disperser solvent (Fig. 1). Thus, acetonitrile was chosen as the disperser solvent for subsequent experiments.

3.2. Optimization of derivatization agent/extraction solvent volume

The volume of derivatizing agent/extraction solvent plays a key role, because it affects the final extraction yield. Its increasing would increase the extracted amounts of analytes, however the concentration of analytes in the sedimented phase were also diluted which led to decrease in analytical signals. In order to study the effect of derivatization agent/extraction solvent volume on the performance of the presented DLLME procedure, different volumes of butylchloroformate (20, 25, 30, 40, and 50 μL) and a constant volume of dispersive solvent (acetonitrile, 1 mL) were tested. By increasing the volume of extraction solvent from 20 to 50 μL the analytical signals decreased rapidly. In the case of 20 μL butylchloroformate, the volume of sedimented phase was 5 μL, where its retrieval was difficult and repeatability was not good (Fig. 2). Therefore, 25 μL was selected as the optimized volume of butylchloroformate to obtain the sedimented phase volume of 10 ± 1 μL.

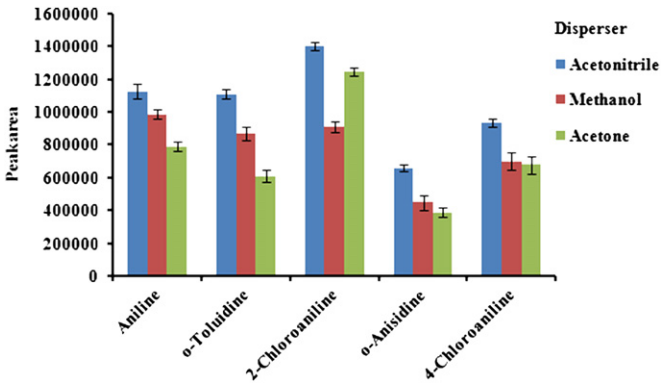

Fig. 1. Effect of disperser kind on the microextraction efficiency. Extraction conditions: aqueous sample volume, 5 mL; analytes concentrations, 1 mg L^{-1} of each anilines; disperser solvent, methanol, acetone or acetonitrile, 1 mL; derivatization agent/extraction solvent, 50 μL butylchloroformate; centrifuging time, 5 min and centrifuging speed, 4000 rpm. The bars indicate the maximum and minimum of three determinations.

3.3. Effect of disperser solvent volume

The dispersive solvent volume is another important factor that affects extraction efficiency in DLLME. At low volumes of the disperser, the organic extractant droplets cannot form properly which leads to low enrichment factors (*EFs*). On the other hand, at high volumes of the disperser, the polarity of the aqueous phase is reduced which leads to increase in the solubility of analytes into the aqueous phase and decrease in extraction efficiency. In order to study the effect of acetonitrile volume, its volume was varied in the range 0.25–1.25 mL at a 0.25-mL interval. By increasing the volume of disperser, the sedimented phase volume decreased due to increase in the solubility of butylchloroformate into the aqueous phase. With volumes higher than 1 mL the sedimented phase volume was very low, so its retrieval was impossible. According to the obtained results (Fig. 3), 0.75 mL was chosen as an optimum volume for the dispersive solvent.

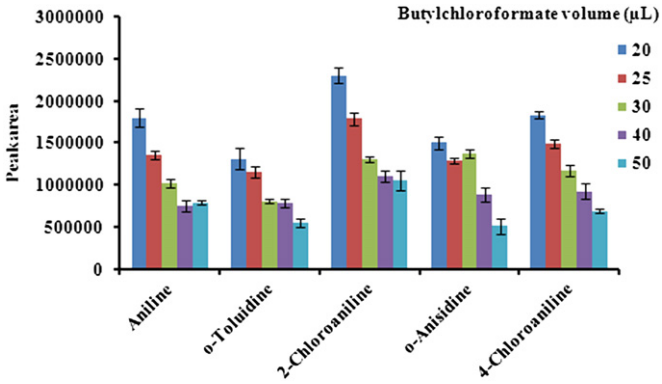

Fig. 2. Optimization of derivatizing agent/extraction solvent volume. Extraction conditions: the same as Fig. 1, except 1 mL acetonitrile was used as dispersive solvent. The bars indicate the maximum and minimum of three determinations.

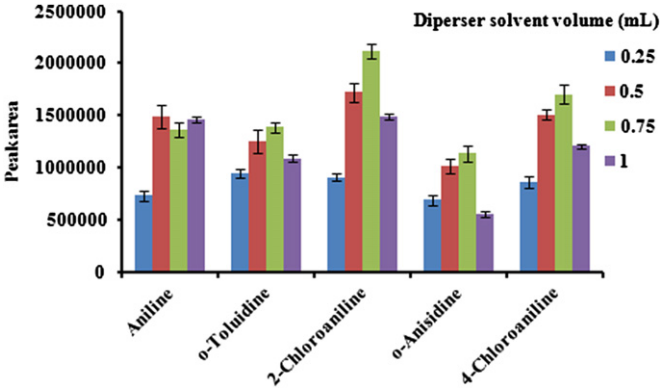

Fig. 3. Effect of disperser solvent volume on the microextraction efficiency. Extraction conditions: the same as Fig. 2, except 25 μL butylchloroformate was used as extraction solvent. The bars indicate the maximum and minimum of three determinations.

3.4. Effect of solution pH

The effect of aqueous solution pH was examined within the range 2–12 (at 2-units intervals) using pH adjusting by HCl or NaOH solutions. The results in Fig. 4 indicate that the peaks' areas increase with the pH increasing from 2 to 4 and remain constant up to pH 10. At higher pHs, the peaks' areas decreased noticeably. Decrease in extraction efficiencies of target analytes can be attributed to protonation of amines (pK_b: 9.37–11.35) and hydrolysis of derivatization agent at highly acidic or alkaline pHs, respectively. It is noted that by increasing pH from 2 to 10, the volume of the sedimented phase was constant at about 10 μL. At pH 12 due to the hydrolysis of derivatization agent, the volume of the sedimented phase decreased to 4 μL. It should be mentioned that butylchloroformate might produce toxic products under hydrolysis. Its use at pHs higher than 10 is not advisable or special precautions such as using ventilation must be considered. The pH of working solution was 6.8; therefore there is no need for pH adjustment in the following studies. However in the cases of real samples, pH should be considered and it should be adjusted between 4 and 10.

3.5. Salt addition effect

The salt addition was studied by adding NaCl in the range 0–10% (w/v) to the sample solution. By increasing NaCl concentration from 0% to 2.5%, analytical signals were regularly increased. It seems that salting out effect is the reason of this phenomenon. By increasing NaCl amount from 0% to 2.5% (w/v), the sedimented phase volume decreased from 10 to 4 μL. Because the density of aqueous sample increases with addition of the salt, thus butylchloroformate ($d=1.06\ kg\ L^{-1}$) is divided into two sections. One section is sedimented in the bottom of test tube whereas the other is collected on the surface of aqueous phase. It is noted that in the presence of 5% NaCl or higher, the organic phase did not settle. Therefore no salt was added in the following experiments to obtain 10 μL sedimented phase volume.

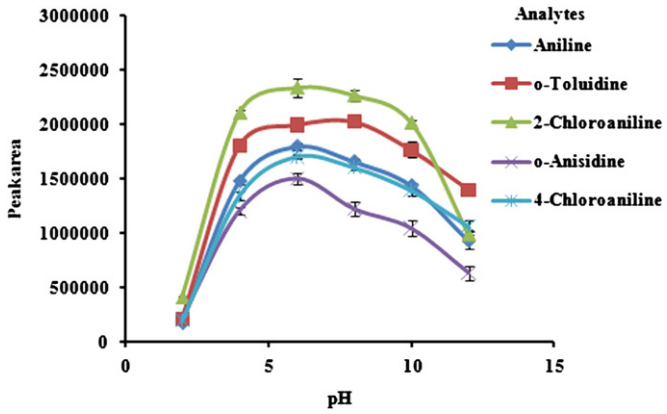

Fig. 4. Effect of sample solution pH on the microextraction efficiency. Extraction conditions: all conditions are the same as Fig. 3 except pH. The bars indicate the maximum and minimum of three determinations.

3.6. Optimization of centrifuging time and speed

Centrifugation is a mandatory process to achieve separation of extractant droplets from aqueous phase. The effect of time and speed of centrifuging were examined in the ranges of 1–7 min and 1000–6000 rpm, respectively. These parameters had no obvious effects on the extraction efficiency. However 5 min and 4000 rpm had a little better effect on the repeatability. So they were selected as centrifuging time and speed, respectively, in the following studies.

3.7. Quantitative features of the method

The optimum experimental conditions were used to assess the applicability of the proposed method for quantitative determination of target analytes by GC–FID. Under the selected conditions, the proposed method was evaluated in terms of linear range, squared correlation coefficient (R^2), precision (*RSD*%), enrichment factor (*EF*), enhancement factor (*EnF*), limit of detection (*LOD*), and limit of quantification (LOQ). A calibration study was performed by spiking de-ionized water with analytes over the concentration range of 10–10,000 $\mu g\ L^{-1}$. The results obtained demonstrate a good linearity for all of the analytes with squared correlation coefficients always equal or higher than 0.993 (Table 1). The repeatability of the proposed method, expressed as relative standard deviation (RSD%), was evaluated by extracting six consecutive aqueous samples at three concentration levels (100, 500 and 5000 $\mu g\ L^{-1}$) and was found to vary between 2.9 and 5.2%. Relatively high enrichment factors ranging from 197 to 298 and good enhancement factors ranging from 4.7 to 6.2 were obtained. Limits of detection and quantification were in the ranges 1–3 and 3–12 $\mu g\ L^{-1}$, respectively.

3.8. Comparison of the proposed method with others

To test the feasibility of the new method, its analytical parameters were compared with those of other methods used in the analysis of target analytes. For this purpose, relative standard deviation, linear range, limit of detection, limit of quantification, and enrichment factor of these methods were listed in Table 2. The repeatability of the method is good and RSDs for the proposed method are lower than or comparable with those of the mentioned methods. Detection limits of the method are much lower than those of the second method whereas both of them used the

Table 1
Quantitative features of simultaneous derivatization/DLLME followed by GC–FID in determination of the selected anilines.

Analyte	LR^a ($\mu g\ L^{-1}$)	R^{2b}	LOD^c ($\mu g\ L^{-1}$)	LOQ^d ($\mu g\ L^{-1}$)	$EF \pm SD^e$	$EnF \pm SD^f$	$ER\ (\%) \pm SD^g$
Aniline	10–10,000	0.993	2	7	251 ± 12	5.2 ± 0.1	50 ± 1
o-Toluidine	10–10,000	0.996	2	5	225 ± 16	5.4 ± 0.1	54 ± 1
2-Chloroaniline	10–10,000	0.995	1	3	298 ± 14	6.2 ± 0.6	67 ± 1
o-Anisidine	10–10,000	0.996	2	7	286 ± 14	5.3 ± 0.4	69 ± 1
4-Chloroaniline	20–10,000	0.995	3	12	197 ± 8	4.7 ± 01	47 ± 1

[a] Linear range.
[b] Square of correlation coefficient.
[c] Limit of detection, $S/N=3$.
[d] Limit of quantification, $S/N=10$.
[e] Mean enrichment factor ± standard deviation, $EF=C_{sed}/C_0$ ($n=3$).
[f] Mean enhancement factor ± standard deviation ($n=3$).
[g] Mean extraction recovery ± standard deviation ($n=3$).

Table 2
Comparison of the presented simultaneous derivatization/DLLME method with other methods used in preconcentration and determination of the target analysts.

Analytes	Sample	*RSD* (%)[a]	*LOD*[b] (μg L^{-1})	*LOQ*[c] (μg L^{-1})	R^2[d]	Method	References
Aniline	Wastewater samples	3.23	0.96	–	–	SPME–GC–FID[e]	[35]
Aniline	Water samples	–	28	–	0.9967	SDME–GC–FID[f]	[36]
o-Toluidine		–	21	–	0.9948		
2-Chloroaniline		–	12	–	0.9929		
4-Chloroaniline		–	19		0.9908		
Aniline	Serum	3.61	100	–	0.99	LLE–GC–MS[g]	[37]
o-Toluidine	Ground water	5.6	0.025	–	0.99908	SPME–GC–MS[h]	[38]
Aniline	Water samples	8.4	–	1.4	–	SPME–GC–MS[i]	[30]
2-Chloroaniline		12	–	1.8	–		
o-Anisidine		6.3		1.7	–		
Aniline	Water samples	3.9	2	7	0.993	Simultaneous	This method
o-Toluidine		3.1	2	5	0.996	derivatization/DLLME–GC–FID[j]	
2-Chloroaniline		2.9	1	3	0.995		
o-Anisidine		3.7	2	7	0.996		
4-Chloroaniline		5.2	3	12	0.995		

[a] Relative standard deviation.
[b] Limit of detection.
[c] Limit of quantification.
[d] Square of correlation coefficient.
[e] Solid phase microextraction–gas chromatography–flame ionization detection.
[f] Single drop microextraction–gas chromatography–flame ionization detection.
[g] Liquid–liquid extraction–gas chromatography–mass spectrometry.
[h] Solid phase microextraction–gas chromatography–mass spectrometry.
[i] Solid phase microextraction–gas chromatography–mass spectrometry.

similar detection system, e.g. FID. It should be noted that in some of the techniques mentioned (for example the forth method), the high sensitive detection system such as the mass spectrometry was used which is inherently more sensitive than FID. These results reveal that the presented technique is very simple, rapid, sensitive and repeatable and can be used for anilines preconcentration from aqueous samples. The main advantage of the developed procedure is that the derivatization reaction and extraction process are performed in a single step. Also, derivatization agent and extraction solvent are the same so the consumption of organic solvent is much lesser. The other advantage is that the derivatization reaction has been carried out in mild conditions, so this method is easy to use, faster and no time is needed for derivatization and no heating is required.

3.9. Real samples analysis

The utility of the proposed method was tested by analyzing tap, river and well waters and different wastewaters. None of the analytes were detected in tap, river (Talkherood, Tabriz, Iran), well waters and municipality wastewater sample. The proposed method was also applied for analysis of anilines contents of two industrial wastewaters. Two suspected peaks in retention times belonging to aniline and *o*-toluidine were observed in the chromatogram obtained from leather processing unit wastewater. One peak in retention time of aniline was found in the chromatogram of paint factory wastewater. Typical GC–FID chromatograms of these samples are shown in Fig. 5. The concentrations of aniline and *o*-toluidine in wastewater of the leather processing unit were 159 and 109 μg L^{-1}, respectively, and the concentration determined for *o*-toluidine in paint factory wastewater was 221 μg L^{-1}. The presented derivatization/extraction procedure followed by GC–MS was performed on the wastewaters of leather processing unit and paint factory to identify the observed peaks in these samples (Fig. 6). The mass data confirmed the presence of aniline and *o*-toluidine in leather processing unit wastewater and *o*-toluidine in paint factory wastewater. Anilines standards were added to each sample at three concentration levels (100, 500, and 1000 μg L^{-1} of each aniline) prior to performing the method to evaluate the matrix effect. The obtained recoveries were within the range of 72–106%. These results demonstrate that the matrices of the analyzed samples have a little effect on the performance of the method in determination of aromatic amines from aqueous samples (Table 3).

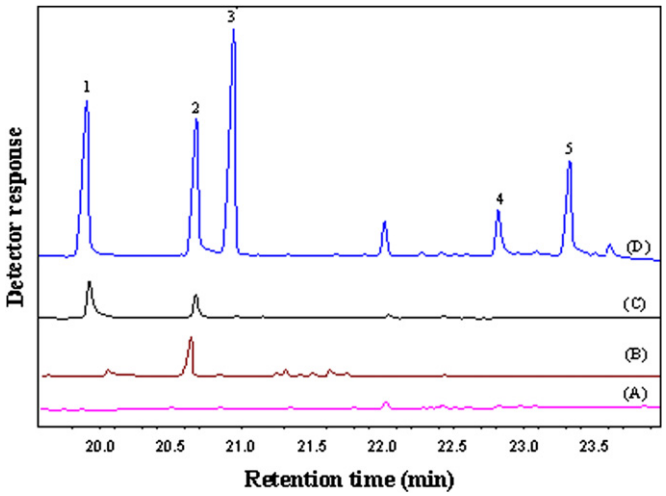

Fig. 5. GC–FID chromatograms of (A) blank, (B) wastewater of a paint factory, (C) wastewater of a leather processing unit, and (D) spiked deionized water (with 1 μg mL^{-1} of each analyte). In all cases, the derivatization/microextraction method was performed and 0.5 μL of the sedimented phase was injected into GC. Peaks identification: 1 – aniline; 2 – *o*-toluidine; 3 – 2-chloroaniline; 4 – *o*-anisidine; and 5 – 4-chloroaniline.

4. Conclusions

In this study, a fast and simple pretreatment method using simultaneous derivatization and DLLME was established for the preconcentration of five aromatic amines followed by GC–FID

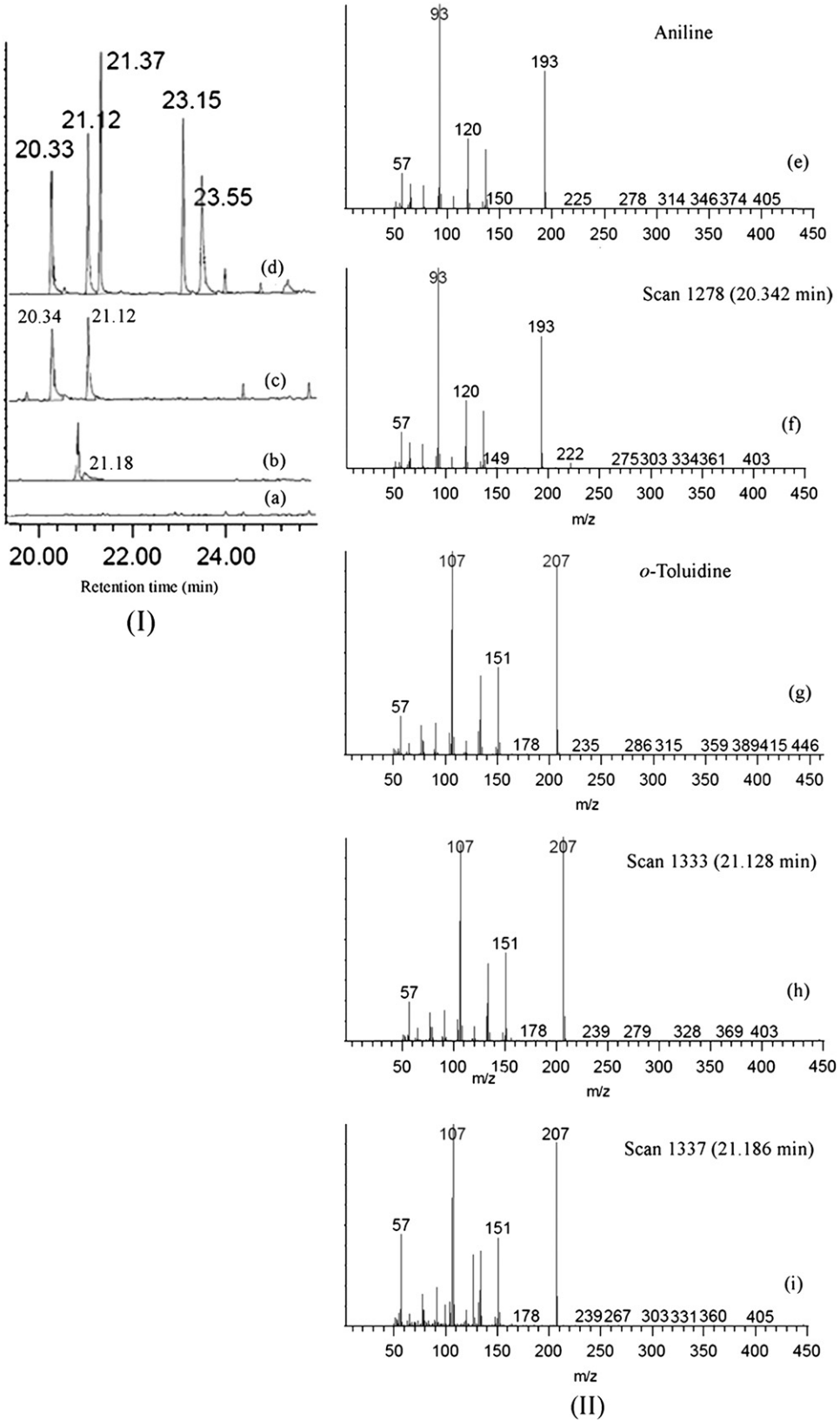

Fig. 6. (I) Total ion chromatograms (TIC) of (a) blank, (b) a paint factory wastewater, (c) leather processing unit wastewater, and (d) spiked deionized water (with 1 μg mL^{-1} of each analyte). In all cases, the derivatization/microextraction method was performed and 0.5 μL of the sedimented phase was injected into GC–MS. (II) Mass spectra of (e) aniline, (f) scan 1270 (retention time 20.342 min) in wastewater of leather processing unit, (g) *o*-toluidine, (h) scan 1333 (retention time 21.128 min) in wastewater of leather processing unit, and (i) scan 1337 (retention time 21.180 min) in wastewater of paint factory. Peaks identification: aniline (t_R=20.33 min), *o*-toluidine (t_R=21.12 min), 2-chloroaniline (t_R=21.37 min), *o*-anisidine (t_R=23.15 min), and 4-chloroaniline (t_R=23.5 min).

Table 3
Recoveries obtained by simultaneous derivatization/DLLME in real samples spiked at 100, 500 and 1000 μg L^{-1}, and analyzed by GC–FID.

Analyte	Recovery (%)					
	Tap water	Well water	Talkherood water	Municipality wastewater	Paint factory wastewater	Leather processing unit wastewater
Aniline	94–105	91–93	81–94	82–95	76–82	78–97
o-Toluidine	96–98	89–94	88–89	82–91	73–89	81–86
2-Chloroaniline	97–106	86–88	81–97	85–89	75–89	81–93
o-Anisidine	93–104	92–104	89–92	86–92	77–97	72–94
4-Chloroaniline	85–93	96–106	96–102	88–91	81–91	87–91

determination. This method has been successfully applied for derivatization and preconcentration of the target compounds in a few minutes, with high efficiency and using low-cost reagents. The detection and quantification limits of the selected anilines were obtained in the ranges 1–3 and 3–12 μg L^{-1}, respectively. In addition, the present method is linear over a broad concentration range and shows high correlation coefficients. Analysis of real samples revealed the potential of the method in environmental analysis even for relatively complex samples. The developed method provided several advantages including simplicity, less solvent and time-consuming, low detection limits, and excellent repeatability.

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