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Ultrasound-Assisted Emulsification Microextraction for Fetermination of Volatile Fatty Acids in Agricultural Wastewater Samples by Gas Chromatography Flame Ionization Detector

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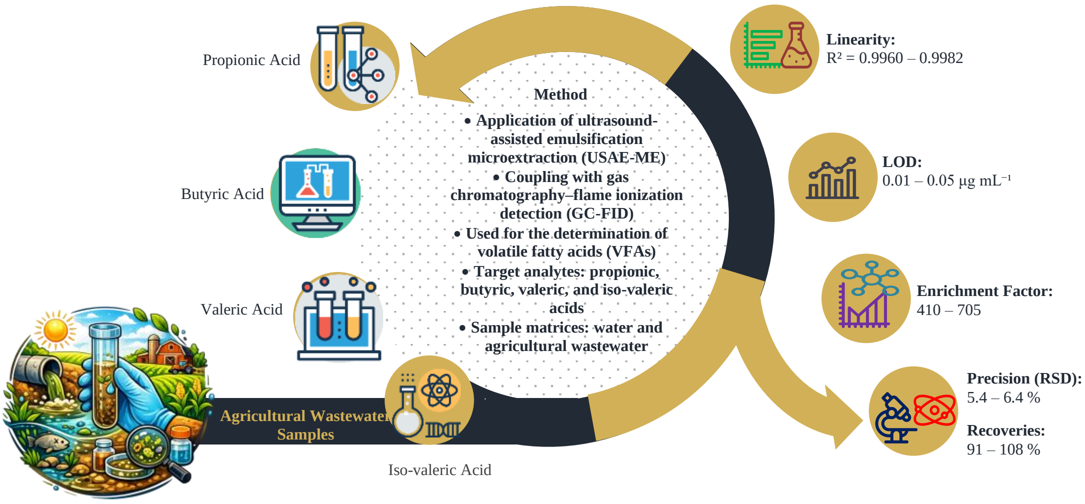
ABSTRACT

Ultrasound-assisted emulsification microextraction (USAE-ME) procedure coupled with gas chromatography–flame ionization detection (GC-FID) was applied for the determination of four volatile fatty acids (VFAs), including Propionic acid, butyric acid, valeric acid, and iso-valeric acid, in water and agricultural wastewater samples. The method is based on the dispersion of microvolumes of an organic solvent in the aqueous phase and subsequent extraction of target analytes into the fine droplets of the organic phase. After centrifugation, the sedimented phase is separated and directly injected to the GC system. The effect of experimental parameters, such as type and volume of extraction solvent, equilibrium time, pH and ionic strength of the aqueous solution were investigated and optimized. Under the optimum conditions a relatively broad dynamic linear range with a good linearity (R2) ranging from 0.9960 to 0.9982 were obtained for all target analytes. The limit of detection (S/N=3) and the enrichment factors were in the range of 0.01-0.05 µg mL−1 and 410-705, respectively. The relative standard deviations (RSD %) for 2 µg mL−1 of VFAs were in the range of 5.4–6.4% (n=5). Finally, the purposed method has been successfully applied to the determination of target VFAs in different water samples and good spiked recoveries over the range of 91–108% were obtained.


Propionic Acid
Butyric Acid
Valeric Acid
Agricultural Wastewater Samples
Iso-valeric Acid
Method
• Application of ultrasound-assisted emulsification microextraction (USAE-ME)
• Coupling with gas chromatography–flame ionization detection (GC-FID)
• Used for the determination of volatile fatty acids (VFAs)
• Target analytes: propionic, butyric, valeric, and iso-valeric acids
• Sample matrices: water and agricultural wastewater
Linearity:
R² = 0.9960 – 0.9982
LOD:
0.01 – 0.05 µg mL⁻¹
Enrichment Factor:
410 – 705
Precision (RSD):
5.4 – 6.4 %
Recoveries:
91 – 108 %

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1. Introduction

Volatile fatty acids (VFAs) compromise a variety of low molecular weight aliphatic monocarboxylic acids with a strong hydrophilic character [1]. They originate from anaerobic bio degradation of carbohydrates, proteins and fats. Therefore, they are widely present in raw sewage, activated sludge [1-4], waste and landfill leachates [5-8], and waste waters. Also, these compounds are involved in different processes, for example in biological removal of phosphorus from waters [9-10] or nitrification–denitrification in activated sludge [11-12].

These VFAs with sulphur compounds and volatile amines are responsible for unpleasant odor generation in waste-waters or during composting operations. On the other hand, they may have some profitable effects since they act as a source of carbon for microorganisms involved in the removal of phosphorus from waters [9]. They play an important role in the maintenance of the hindgut health [13-14]. Determination of VFAs in different types of matrix for medicinal [15], nutritional [16-17], bacterial, and environmental [18-19] purposes has attracted much interest, because they are excellent indicators of bacterial activity. Therefore the development of inexpensive and accurate analytical methods for identification and quantification of these compounds is important.

Determination of VFAs is most often carried out by gas chromatography (GC) coupled with flame ionization detector (FID) or mass spectrometry [20]. Since the matrices of environmental samples are complex, and the concentration of analytes is also often very low, sample preparation plays an important role in the determination of these species. Liquid-liquid extraction (LLE) [21], solid phase extraction (SPE) [22] and purge and trap (P&T) [23] are the widely used methods for extraction and preconcentration of these volatile species. However, LLE is time consuming, tedious and requires large amounts of high cost and potentially hazardous organic solvents. SPE uses much less solvent than LLE, but requires column conditioning and is relatively expensive. P&T can also suffer from severe losses of volatile compounds.

In last decade, liquid phase microextraction (LPME) has been introduced as an efficient alternative to traditional methods for sample preparation and extraction of organic and inorganic compounds. LPME is a single-step extraction method that has a very high sample to solvent ratio which leads to a higher enrichment factor of target analytes. LPME is fast, simple, inexpensive and since very little solvent is used, there is minimal exposure to toxic organic solvent. LPME has different types such as single drope microextraction (SDME), hollow fiber liquid phase microextraction (HF-LPME), dispersive liquid-liquid microextraction (DLLME) and ultrasound assisted emulsification extraction (USAE-ME). Among them, SDME and hollow fiber supported liquid membrane extraction have been applied for separation and preconcentration of VFAs from aqueous phase prior to GC [24, 25]. However, SDME suffers from some disadvantages such as Long extraction time, instability of microdrop and sometimes low precision. Also, in HF–LLME, extraction needs to excessive amount of sample and is limited by the small surface of the fiber.

In the other hand, use of emulsions generated by ultrasound radiation has found interest in analytical chemistry. In this way, a microextraction technique for aqueous samples, known as ultrasound-assisted emulsification–microextraction (USAE-ME) has been proposed [26]. This approach is based on the emulsification of a micro volume of organic extractant in an aqueous sample by ultrasound radiation and further separation of both liquid phases using centrifugation. The application of ultrasound radiation accelerates the mass-transfer process between two immiscible phases, and moreover, with a large contact surface between both phases lead to an increment in the extraction efficiency in a minimum time. Thus, USAE-ME can be employed as a simple and efficient extraction and preconcentration procedure. Up to now, this method has been successfully applied for determination of organic and inorganic speices using proper detection methods such as gas chromatography [27], high performance liquid chromatography [28], UV-Vis spectrophotometry [29], graphite furnace atomic absorption spectrometry [30] and flame atomic absorption spectrometry [31].

The aim of the present work is to investigate the applicability of the USAE-ME for the extraction and determination of VFAs in real water samples by GC–FID. All the experimental parameters affecting the extraction procedure are intensively investigated and analytical characteristics of the method are evaluated and compared with other methods. Real water samples, including tap water and agricultural wastewater are analyzed to demonstrate the applicability of the proposed method.

2. Experimental

2.1. Reagents and Materials

Propionic acid (99%), butyric acid (99%), valeric acid (99%), iso-valeric acid (99%) and all other organic solvents and analytical reagents including nitrobenzene, chloroform, dichloromethane, carbon tetrachloride, hydrochloric acid and sodium chloride were purchased from Merck (Darmstadt, Germany). All of these reagents were of analytical grade. Stock solutions of VFAs (1000 μg mL^{-1}) were prepared by dissolving calculated amounts of each them in double distilled water. Stock solutions were stored at 4 ºC in the refrigerator. Fresh working solutions were prepared daily by diluting the different amounts of the standard stock solutions in the doubly distilled water to required concentrations. Doubly distilled water was used for preparation of aqueous solution.

2.2. Instrumentation

Separation and detection of VFAs compounds were carried out using a Shimadzu 10148 gas chromatograph system (Kyoto, Japan) equipped with a flame ionization detector (FID) and a CBPS fused silica capillary column (25 m × 0.25 mm i.d., 3μm film thickness). The injection port was operated at splitless mode and nitrogen was employed as carrier gas at a constant flow rate of 1.0 mL min^{-1}. The temperature of injector and detector were set as 220 ºC and 280 ºC, respectively. The oven temperature program was: 120 ºC, held for 2 min; rating 20 ºC min^{-1} to 130 ºC, held for 1 min; rating 20 ºC min^{-1} to 160 ºC, held for 1 min; rating 40 ºC min^{-1} to a final temperature of 210 ºC and held for 2min. The flow of Zero Air (99.99%, Sabalan Co, Tehran, Iran) for FID was 50 mL min^{-1} and flow rate of hydrogen was 65 mL min^{-1}. A 40 KHz ultrasonic water bath (Parsonic 2600s, Parsnahand, Iran) was applied for emulsification process. A centrifuge of Farayand 16105 (Iran) was used for centrifugation.

2.3. Ultrasound-assisted emulsification microextraction (USAE-ME)

5.0 ml of water sample containing 10% (m/v) NaCl and acidified by HCl (6.0 M) to pH 0.5 was placed in a 10.0 ml conic tube and then 20 μL of nitrobenzene (as extraction solvent) was rapidly injected into the sample solution by syringe. The mixture solution was then immersed into an ultrasonic water bath in such a way that the levels of both liquids (bath and sample) were the same and ultrasonicated for 1.0 min to form a homogeneous cloudy solution. The phase separation was performed by a rapid centrifugation at 3500 rpm for 10.0 min. Accordingly, the dispersed fine droplets of extracting solvent were sedimented at the bottom of conical test tube. Then, 1.0 μL of the sedimented phase was withdrawn from the bottom of the conical test tube by using a 5.0 μL Hamilton syringe and injected directly into GC-FID for final analysis.

3. Results and discussion

3.1. Optimization of extraction conditions

In order to obtain a high extraction efficiency, the effect of different parameters affecting the extraction conditions such as the type and volume of the extraction solvent, the pH, the equilibrium time, sonication time, centrifuging time and the salt effect were optimized. One variable at a time optimization was used to obtain the optimum conditions for the USAE-ME.

3.2. Selection of extracting solvent

The selection of a suitable extracting solvent is of great importance for the optimization of USAE-ME process. An extracting solvent must have several characteristics: it should have good emulsification efficiency in the aqueous samples, high affinity for the target compounds, low solubility in water and an excellent gas chromatography behavior. In the present study, the usefulness of several solvents, including dichloromethane, carbon tetrachloride, chloroform, and nitrobenzene was investigated. In the preliminary experiments, aliquots of 5.0 mL of sample solutions and 20.0 μL of each solvent were sonicated for 2.0 min. No emulsification was observed with chloroform and dichloromethane. Probably, the higher water solubility of these solvents prevents the emulsion formation under investigated experimental conditions, so they were not considered for further studies. Carbon tetrachloride and nitrobenzene were able to form a stable emulsion during sonication, leading a biphasic system after centrifuging the solution. However, carbon tetrachloride showed a band overlapping with the target analyst. Beside this, the extraction efficiencies achieved by nitrobenzene were higher than those achieved by carbon tetrachloride. Therefore, nitrobenzene was selected as extracting solvent for subsequent experiments. Fig. 1 shows the chromatogram of VFAs obtained after USAE-ME with nitrobenzene in preliminary studies.

3.3. Effect of extracting solvent volume

Variations in volumes of extraction solvent cause change in the volume of the sedimented phase. For optimization of extraction solvent volume, different volumes of nitrobenzene were added to 5.0 mL of sample solution and these mixtures were subjected to the same USAE-ME procedures. Results show that by increasing the volume of nitrobenzene, and therefore, sedimented phase volume, the peak area decreases. For the volumes less than 20.0 μL the sedimented phase volume was so little, and the collection of it was too difficult. Therefore, the volume 20.0 μL was selected as optimal volume.

3.4. Effect of pH

Since free C_2-C_{10} acids are polar, at neutral pH, many of them are still in the ionic form and therefore are more soluble in water than in the extraction solvent. Upon lowering the pH of the sample matrix, the acid-base equilibrium shifts toward the neutral forms of the acids which have a greater affinity for the extraction solvent, and the amount extracted increases. Results show that at acidified media the amount of fatty acids extracted by nitrobenzene increased depending on the pK_a of the different acids. For most of the acids, the smaller pK_a, the larger effect on the extraction [30].

So, the pH of the sample solutions was changed in the range of 0.5 – 4.0 with addition of HCl (6.0 M) solution. Results (Fig. 2) showed that by decrease in the pH of the matrix, the larger amount of VFAs can be extracted by nitrobenzene. Therefore, the pH 0.5 was selected as an optimal pH for further studies.

3.5. Effect of equilibrium time

Equilibrium time is usually an important factor in the most of microextraction procedures. In this work, equilibrium time is defined as interval time from the occurrence of the cloudy state and just before centrifugation. The effect of the equilibrium time was investigated in the range of 0.5-10 min. The results showed that the equilibrium time has no significant effect on the extraction efficiency of VFAs. In fact, the surface area between microdrops of organic phase and aqueous sample solution is infinitely large and consequently, the mass transfer from sample solution to extracting solvent is very fast. Therefore, the equilibrium state is achieved quickly and extraction time is very short. This is the most important advantage of this method. Thus the minimum time of 0.5 min was selected as equilibrium time for subsequent experiments.

3.6. Effect of sonication time

Sonication time plays an important role in the emulsification and mass transfer phenomena. As the sonication time increases, the fraction of dispersed phase increases. This can lead to a greater surface contact between two phases and therefore provide efficient mass transfer and better extraction efficiency. However, long sonication time may also result in the volatilization loss of the analytes and extracting solvent, which reduces the extraction recovery. The effect of sonication time on the extraction efficiency was studied in the range of 0.5 – 5.0 min under constant ultrasound power. The results showed that the peak areas of analytes increased with increasing of sonication time up to 1.0 min and then decreased with further increases in the sonication time. Therefore, 1.0 min was enough to form a stable cloudy solution.

3.7. Effect of salt concentration

In the extraction methods, the solubility of many analytes in aqueous solutions decreases with increasing ionic strength due to salting out effect [32]. Since the water molecules prefer to solvate the salt ions, the addition of saturated salt into the sample matrix will decrease the solubility of the acids of the neutral form, which results in an increase in the amount extracted. The magnitude of the increase depends on the solubility of the acids [30]. Different amounts of sodium were added to investigate the influence of ionic strength on extraction performance. The presence of sodium chloride increased the ionic strength of sample solution and decreased the solubility of extraction solvent in water, which increased the volume of sediment phase. In this work, the effect of salt addition on the extraction efficiency was investigated by addition of different amounts of NaCl (0.5 – 15 % m/v) into the samples. As can be seen in Fig. 3, the extraction efficiency of VFAs increased in the range of 0.5 – 10 % and then decreased at higher salt concentrations. According to the obtained results, 10% (m/v) NaCl concentration was selected for further studies.

3.8. Effect of centrifugation time

Centrifugation was required to break down the emulsion and accelerate the phase separation process. The effect of centrifugation time at 3600 rpm was examined in the range of 5 - 15 min. The results showed that the best extraction efficiency was achieved with a centrifuging time of 10 min. At shorter time the emulsion state was not well broken and the complete phase separation was not achieved, thereby, the extraction recovery decreased. Also long centrifuging time resulted in the heat generation which led to the increasing of the solubility of nitrobenzene and VFAs in aqueous phase and loss of sensitivity. Therefore, 10 min was adopted for further use.

3.9. Analytical performance of the purposed method

The presented method was validated for linearity, detection limit, accuracy and precision. The results were presented in Table 1. Calibration curves were obtained by least-squares linear regression analysis of the peak area versus concentration of each analyte concentration levels (n=10) between 0.02 – 25.0 μg mL^{-1}. The limit of detections (based on signal to noise ratio of 3) ranged from 0.01 to 0.05 μg mL^{-1} for investigated VFAs. The precision of the proposed USAEME–GC-FID method expressed as relative standard deviation of five replicate spiked at 2 μg mL^{-1} of each target analyte was found to be in the range of 5.4 – 6.4 %. The enrichment factor (EF), was calculated as the ratio between the analyte concentration in the sedimented organic phase after extraction (C_{sed}) and the initial concentration of analyte in the aqueous solution (C_0). The C_{sed} was obtained from the calibration graph (1–30 μg L^{-1}) of the standard solution of each VFA in nitrobenzene solutions. Quantitative results of purposed method are summarized in Table 1.

3.10. Real sample analysis

To test the applicability of the proposed method in real wastewater samples, it was applied to the determination of VFAs compounds in agricultural wastewater samples. All water samples were collected in amber glass bottles. The bottles were rinsed several times with the water samples and then, filled until overflow to prevent loss of volatile compounds to headspace. The water samples stored at the temperature of 4˚C until their analysis. These samples were filtered through 0.45 μm pore size cellulose acetate filter before analysis. No VFA compounds found in the real samples. Therefore, water samples spiked with VFAs compounds at a concentration of 2μg mL^{-1} were used for investigation of matrix effects. Fig.1 shows the chromatogram obtained for the spiked and non-spiked agricultural waste water sample at optimum working conditions. Table 2 shows the results of relative recovery for determination of the instigated VFA compounds in spiked water samples. Acceptable recoveries demonstrated that the matrices of waste water samples had no effects on the performance of the presented method.

Table 1. Analytical parameters for determination of VFAs by USAE-ME-GCFID

Analyte	LR[a] (μgmL^{-1})	Linearity (R^2)	LOD[b] (μgmL^{-1})	RSD(%)[c]	Enrichment factor (C_{sed}/C_0) [d]
Propionic acid	0.1- 25.0	0.9965	0.04	6.4	530
Butyric acid	0.1- 20.0	0.9982	0.05	5.4	410
Valeric acid	0.02- 20.0	0.9960	0.01	5.8	650
Iso-valeric acid	0.05- 15.0	0.9982	0.01	6.2	705

[a] Linear range

[b] Limit of detection ($3S_b$)

c Relative standard deviation ((2 μgmL^{-1},n =5)

[d] C_0: Analyte concentration in the sedimented organic phase after extraction; C_{sed}: Initial concentration of analyte in the aqueous solution

Table 2. Analysis of spiked real water samples with volatile fatty acids

Sample	Analyte	Added (μgmL^{-1})	Found[a] (μgmL^{-1})	Recovery (%)	Added (μgmL^{-1})	Found[a] (μgmL^{-1})	Recovery (%)
Tap Water	Propionic acid	2.0	1.94± 0.30	97	10.0	10.10± 0.30	101.0
	Butyric acid	2.0	1.90± 0.35	95.0	10.0	9.40± 0.65	94.0
	Valeric acid	2.0	2.10± 0.30	105.0	10.0	9.80± 0.30	98.0
	Iso-valeric acid	2.0	1.90± 0.30	95.0	10.0	9.80± 0.40	98.0
Agricultural Wastewater	Propionic acid	2.0	1.86± 0.35	93.0	10.0	9.10± 0.40	91.0
	Butyric acid	2.0	1.82± 0.30	91.0	10.0	9.24± 0.65	92.4
	Valeric acid	2.0	1.90± 0.25	95.0	10.0	10.6± 0.30	106.0
	Iso-valeric acid	2.0	2.14± 0.20	107.0	10.0	10.8± 0.40	108.0

[a] Mean ± Standard deviation of five replicate determinations (n = 5)

Table 3. Comparison of diverse sample preparation methods coupled with gas chromatography for determination of VFAs

Method	Linear Range (ng mL^{-1})	LOD[a] (ng mL^{-1})	Reference
SPME-GC/MS[b]	0.0-5.0	0.003-0.015	[33]
SDME-GC-FID[c]	0.13-120	0.02-0.07	[34]
LPME-GC-FID[d]	0.08-80	0.02-0.08	[35
P&T-GC-FID[e]	0.23-1.2	--	[36]
USAEME-GC-FID[f]	0.02-25.0	0.01-0.05	This Work

[a] Limit of detection

[b] Solid-phase microextraction-Gas chromatography-Mass spectrometry

[c] Single-drop microextraction-Gas chromatography-Flame ionization detector

[d] Liquid-phase microextraction-Gas chromatography-Flame ionization detector

[e] Purge-and-Trap-Gas chromatography-Flame ionization detector

[f] Ultrasound-assisted emulsification microextraction-Gas chromatography-Flame ionization detector

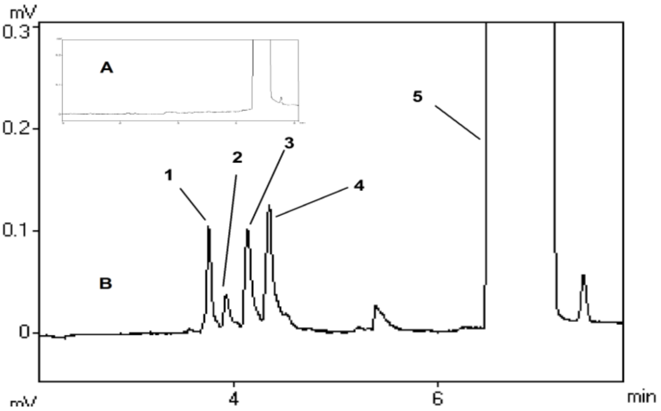

Figure 1. Gas chromatograms obtained after USAE-ME procedure for (A) agricultural wastewater and (B) spiked sample with 2 µg mL-1 of (1) Propionic acid, (2) Butyric acid, (3) Valeric acid, (4) Iso-valeric, (5) Nitrobenzene as a solvent.

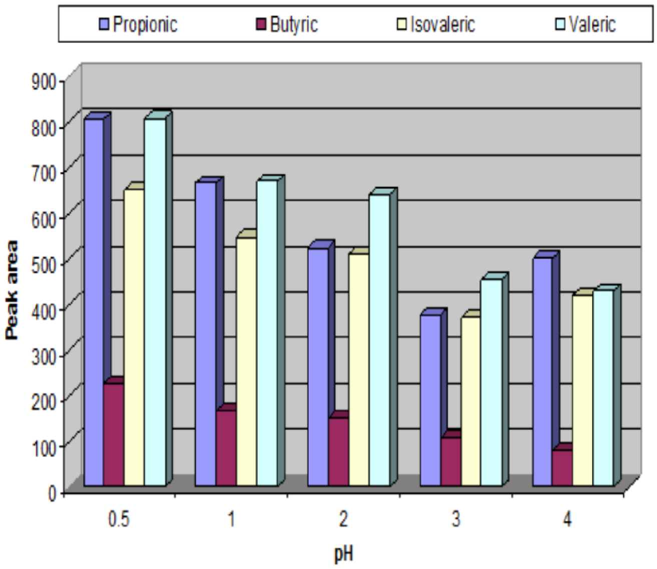

Figure 2. Effect of pH on the peak area. Extraction conditions: Concentration of each analyte, 2 µg mL^{-1} ; Extracting solvent Volume: 20 µL; Sample volume, 5 mL; sonication time 1 min; Equilibrium time, 1 min; Centrifuging time, 10 min at 3600 rpm, NaCl 4% (m/v).

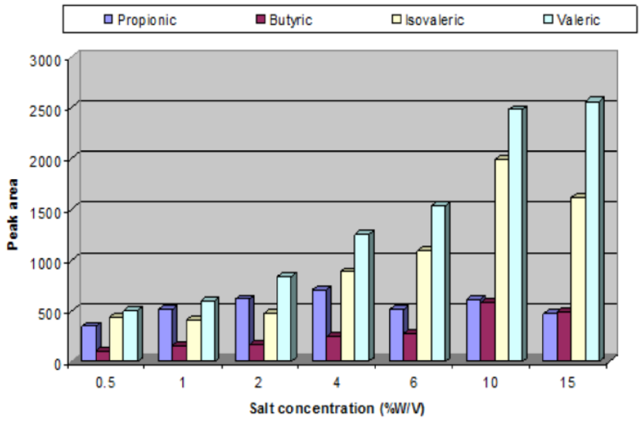

Figure 3. Effect of salt addition on the peak area. Extraction conditions: Concentration of each analyte, 2 µg mL^{-1} ; Extracting solvent Volume: 20 µL; Sample volume, 5 mL; sonication time 1 min; Equilibrium time, 1 min; Centrifuging time, 10 min at 3600 rpm, pH= 0.5.

4. Conclusion

In the present work USAEME was combined with GC–FID for the determination volatile fatty acids in wastewater samples. Determination of the VFAs compounds (propionic, butyric, valeric and iso-valeric acid) by the proposed method was possible at trace amounts (µg mL^{-1} level) with good accuracy and reproducibility. The proposed method had many advantages including simplicity of the extraction, minimum organic solvent consumption, excellent enrichment in a short period of extraction time, low cost, high accuracy, good repeatability and reproducibility for determination of VFAs compounds. A compression of the analytical features achieved by the proposed method and other sample preparation methods coupled with gas chromatographic techniques for determination of VFAs is presented in Table 3. The presented method has distinct advantages in terms of low detection limit, wide linear range and simplicity of instrumentation. The good spiked recoveries of VFAs compounds in water samples showed that the method was sufficiently applicable to determine VFAs compounds in real samples.

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