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Analytical Methods

A novel ultrasound-assisted back extraction reverse micelles method coupled with gas chromatography–flame ionization detection for determination of aldehydes in heated edibles oils

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ABSTRACT

A novel ultrasound-assisted back extraction reverse micelles coupled with gas chromatography–flame ionization detection has been developed for the extraction and determination of some short chain aldehydes in different heated edible oil samples. After the homogenization of the oil samples with Triton X-100, 200 μL of methanol was added to facilitate the phase separation. The aqueous micelle phase has been separated by centrifugation, then it was treated with a mixture of H_2O: $CHCl_3$ and ultrasonic vibration, were used to effectively back-extraction of the analytes into the chloroform phase. The sedimented organic phase was obtained after centrifugation, withdrawn into the microsyringe and directly injected into the GC–FID system. The calibration graphs were linear in the range 0.05–20 mg L^{-1}. The limits of detection were in the range of 0.02–0.15 mg L^{-1}. This procedure was successfully applied for determination of propanal, butanal, hexanal and heptanal in real heated oil samples.
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1. Introduction

Frying is one of the most commonly used means for preparing foods, that may be considered as a rapid combination of drying and cooking. During deep-frying, fats and oils are repeatedly used at elevated temperatures (between 160 and 240 °C, with an optimal value of 180 °C) in the presence of atmospheric oxygen and receive maximum oxidative and thermal abuse (Cvengros & Cvengrosova, 2004; Katragadda, Fullana, Sidhu, & Carbonell-Barrachina, 2010).

Edible vegetable oils during storage, food processing and/or culinary treatments can suffer from degradation (Guillén & Uriarte, 2012a, 2012b). Different causes for edible oils degradation include both oxidation and thermal degradation, can occur when the oil is submitted to high temperature (Guillén & Uriarte, 2009, 2010, 2012a, 2012b; Totani et al., 2008; Zárate, Goicochea, Echeverría, & Guillén, 2009). Aldehydes, ketones, alcohols, dienes and acids, commonly formed during edible oil degradation, create unpleasant flavor, reduce the shelf-life of edible oils, and may further cause health problems (Guillén & Uriarte, 2012a, 2012b). Aldehydes are major products of this degradation and due to their capacity to induce toxicological effects (e.g., their reactivity with amino groups of proteins), (Fullana, Carbonell-Barrachina, & Sidhu, 2004) medium and short chain aldehydes were intensively studied by food chemists. These compounds are responsible for the unpleasant rancid off-flavor of deteriorated fats, oils and fat containing foods (Basheer, Pavagadhi, Yu, Balasubramanian, & Lee, 2010). Many sample preparation methods such as solid-phase extraction (SPE), solid phase microextraction (SPME) and headspace solid phase microextraction (HS-SPME) (Cancho, Ventura, & Galceran, 2001; Das, Jain, & Patel, 2004; Ji et al., 2012; Kardani, Daneshfar, & Sahrai, 2011; Pileni, 1993; Zhu, Feng, & Schelly, 1992) have been reported for the pretreatment of aldehydes in different samples. However, in addition to time consuming, tedious and dependent on large volumes of samples, SPE may cause environmental pollution by using and discarding abundant organic solvents.

Although, SPME needs considerably less volume of solvent compared to SPE method, but it is relatively expensive. Therefore, investigation for a simple, fast and more efficient method for extraction and quantification of aldehydes in oil samples is a challenge for chemist.

Reversed micellar extraction is an attractive separation method for large-scale operation because the process could be carried out using the existing liquid–liquid extraction system in the chemical and biochemical industries (Lee, Hong, Lee, & Kuboi, 2004). Reverse micelles, formed by surfactants in a non-polar organic solvent mixed with water, are nanometer sized aggregates of surfactant molecules in non-polar solvents which are

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thermodynamically stable and optically transparent (Garcia-Prieto, Lunar, Rubio, & Perez-Bendito, 2008). These inverted aggregates are drawn together by hydrogen bonding in the presence of minimal amounts of water and provide water-cores in the organic phase that carry water-soluble compounds (Bu et al., 2012; Yang, Xiaoyan, & Yan, 2008). Reverse micelles have been applied to large-scale separations of proteins and other biomolecules (Chen, Su, & Chiang, 2006; Goto, 2006; Lee, Kim, Sung, & Lee, 2004b; Yang et al., 2008) and consists of forward and backward extraction steps. Forward extraction step involves the solubilization of target molecules into reverse micelles from an oil sample, then solubilized molecules will be subsequently stripped from reverse micelles into a fresh aqueous solution during backward extraction. The reverse micelle can be formed both in the presence and in the absence of organic modifiers (Kilikian, Bastazi, Minami, Gonçalves, & Junior, 2000). In the absence of an organic modifier, the aggregates are very small but addition of an organic modifier causes the partial dissolution of the micellar aggregates, which makes the micelle–micelle interactions easier and leads to the formation of larger surfactant aggregates (Wilson & Poole, 2009; Abel, Sterpone, Bandyopadhyay, & March, 2004). There are some advantages in using the reverse micelle solvent extraction system, such as large-scale sample loading, simple operation and continuous preparation. Thus, the reverse micelle solvent system is very attractive, and it can be widely used in separation and enrichment systems. The aim of the present work is the development of a simple, rapid, sensitive, and inexpensive ultrasound-assisted back extraction reverse micelles method with Triton X-100 and gas chromatography for direct determination of some of the low-molecular weight saturated aliphatic aldehydes. These aldehydes include propanal (propionaldehyde), butanal (butyraldehyde), hexanal and heptanal emitted from extended heating of edible oil were chosen because of their possible contributions to carcinogenicity (Zhu, Feng, & Schelly, 2003).

2. Experimental

2.1. Reagents and standards

Propanal, butanal, hexanal, heptanal, SDS (sodium dodecyl sulfate), CTAB (cetyl trimethylammonium bromide), chloroform, dichloromethane, ethanol, acetone, acetonitrile and n-hexane were supplied form Merck (Darmstadt, Germany). Triton X-100 (Isooctyl phenoxy polyethoxy ethanol) and Triton X-114 (octyl phenol poly ethylene glycol ether) were purchased from Aldrich (USA). Soybean, sunflower and olive oils were purchased from local markets and stored in 4 °C in the dark before analysis. A stock solution of 1000 mg L^{-1} of propanal, butanal, hexanal and heptanal was prepared by dissolving 0.1 g of the aldehydes in ethanol and diluting to 100 mL in a volumetric flask.

2.2. Apparatus

Experiments were carried-out using a gas chromatograph (7890A Agilent, Little Falls, DE, USA) equipped with a flame ionization detector (GC–FID) and a DB-1MS fused silica capillary column (30 m × 0.25 mm I.D., 0.25 μm film thickness). Helium was used as the carrier gas at a flow rate of 1 mL min^{-1}. After injection of samples, the oven temperature was programmed as follows: initial temperature 45 °C (held for 1 min), ramped at 30 °C min^{-1} to 80 °C, then ramped at 40 °C min^{-1} to 270 °C (held for 5 min). Injector and detector temperatures were set at 280 and 300 °C, respectively.

2.3. Oil sample

The oils subjects of this study were sunflower (liquid at room temperature; saturated fatty acids 14%, monounsaturated fatty acids 22%, and polyunsaturated fatty acids 50%), soybean (liquid at room temperature; 72% of monounsaturated fatty acids) and olive oils (liquid at room temperature; saturated fatty acids 10%, polyunsaturated fatty acids 75% and monounsaturated fatty acids 10%). The oils were of edible quality and purchased from a local supermarket and stored in the dark before analysis.

2.4. Heating conditions

250 mL of oil sample was heated at 250 °C for periods of 5 h. The temperature was adjusted by calibrated thermometer. Although these oils are not usually submitted to such high temperatures it has been selected as a model system in which the evolution of selected aldehydes under these conditions may be clearly observed. Throughout the heating process cover flask was open. At the end of heating the hot plate was turned off and the oil reach to the ambient temperature, then oil samples refrigerated until their study in order to avoid or hinder the continuation of the degradation process.

2.5. Extraction procedure

The reverse micelle extraction system is schematically shown in Fig. 1. A reversed micellar extraction cycle is basically composed of two steps: forward and back extraction. Therefore reverse micellar extraction was performed at the optimized conditions after forward and backward steps. The forward extraction process was performed as follows: 5.0 mL of oil sample containing analytes was poured into a screw-capped centrifuge tube and 1.0 mL of n-hexane was added to decrease viscosity. 0.6 mg of Triton X-100 was added to the oil sample and gently mixed for a few minutes until a homogeneous phase was formed. Then 200 μL of methanol (as organic modifier) was added and the content was mixed thoroughly for 10 min using magnetic stirrer and phase separation achieved by centrifugation at 8000 rpm for 5 min. The surfactant-rich phase became viscose and was settled at the bottom of the screw-capped centrifuge tube. The sedimented organic phase consists of reverse micellar phase enriched with extracted analytes completely transferred to another screw-capped centrifuge tube using a 1.0 mL HPLC syringe (F-LC, SGE, Australia). Back extraction was carried out by mixing the surfactant-rich phase, from forward extraction, with 1 mL of water and 0.3 mL of chloroform. The mixture was sonicated in an ultrasound water bath (Bandelin Sonorex, RK103H, 140/560W, 35 kHz, Germany) for 40 min to ensure maximum back extraction of analytes and then centrifuged for 3 min at 8000 rpm. Two distinct layers were formed, the upper was surfactant-rich phase, and the lower phase was organic solvent-rich (chloroform), the analytes were remained in the chloroform phase. The chloroform phase was removed using a micro-syringe (F-LC, SGE, Australia) and injected into the GC–FID.

3. Results and discussion

In this study the effects of several important parameters influencing the aldehydes extraction efficiencies including surfactant (type and concentration), non-solvent (type and volume), type and volume of organic solvent, volume of water and sonication time were investigated. In order to obtain accurate and repeatable results and to prevent deterioration the column and the injector, the interferences of Triton X-100 rich phase must be eliminated before injection into the GC, because major cause of column deterioration is contamination. However, ultrasonic-assisted back extraction was selected as a suitable procedure for coupling reverse micelle extraction to GC–FID instrument.

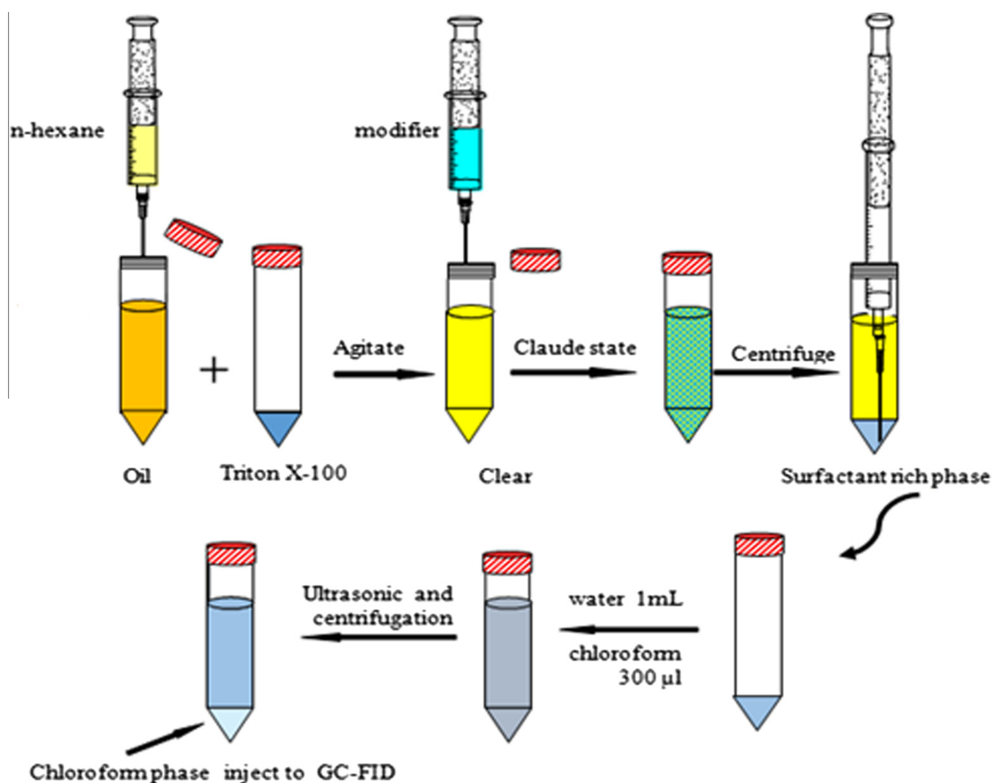

Fig. 1. Schematic illustration of reverse micelle device.

3.1. Effect of water-immiscible organic solvents

The choice of organic solvent is a fundamental step in the optimization of the reverse micelle extraction methods. Some properties need to be considered in this choice including: water-immiscibility to prevent the organic phase dissolution in the aqueous (donor) phase; high solubility for target analytes and compatibility with the analyte detection device used (Kardani et al., 2011). In order to obtain high extraction efficiency and selection of water-immiscible organic solvents, two solvents (chloroform and dichloromethane) were tested. The results showed that the responses of analytes in chloroform were higher than in dichloromethane. Therefore, chloroform was selected as the back-extracting organic solvent for further studies. The effect of the volume of chloroform was investigated in the range of 100–500 µL. From the results of Fig. 2a, it can be seen that an increase in the volume of chloroform up to 300 µL increased the recoveries of analytes and then decreased slightly. However, at higher volumes of chloroform due to the increase in sedimented phase volume and dilution of the analytes, recoveries of the analytes were decreased. Therefore, 300 µL was found to be optimum for the following experiments.

3.2. Effect of volume of water

Reverse micelles of various surfactants can solubilize different amounts of water, for a ternary water/oil/surfactant system, the initial size of the reverse micelles is linearly related to the water content (Hebbar, Hemavathi, Sumana, & Raghavarao, 2011). As the water content increases for a constant surfactant concentration, the reverse micelle size increases. The smallest reverse micelles have nearly all the water interacting directly with the interface while the largest have only a small fraction of the water interacting with the interface. Reverse micelles extraction is based on charge-charge interaction hydrophobicity, and the size of the target molecules relative to the micelle droplets size (Bhowal, Priyanka, & Rastogi, 2014; Marhuenda-Egea, Velazquez, Cadenas, & Cadenas, 2002). Thus volume of the water is one of the important factors to be considered in the proposed method. The effect of volume of water was investigated at a range of 300–1200 µL using 300 µL chloroform. From the results of Fig. 2b, it can be seen that up to 1000 µL volumes of water, slurry formation was observed. After 1000 µL, no increase was observed with additional water volume. Therefore, 1000 µL water found to be optimum for the further experiments.

3.3. Effect of sonication time

Sonication time was found to be key parameter for controlling reverse micelle back extraction. Ultrasonication is used to improve the extraction of target molecules from reverse micelle phase to organic phase, enhancement in mass transfer arises from creation of very high effective temperatures which increase the solubility, diffusivity, and pressures that favor penetration and transport (Luque-Garcia & Luque de Castro, 2003). The influence of ultrasonic extraction time on the extraction performance was examined over the time range between 10 and 50 min. It was observed that the analytical responses increased as the time increased and reaching a maximum at 40 min. The maximal effect of ultrasound was observed at 40 min (Table 1). Reverse micelle extraction is an equilibrium extraction procedure, in this work an equilibrium time of 40 min was sufficient to obtain the good extraction efficiency. Therefore, 40 min was chosen as the ultrasound-assisted back-extraction working time for further studies.

3.4. Effect of surfactant and its concentration

A choice of surfactant is one of the most important parameters for obtaining an effective extraction of the analytes in reverse

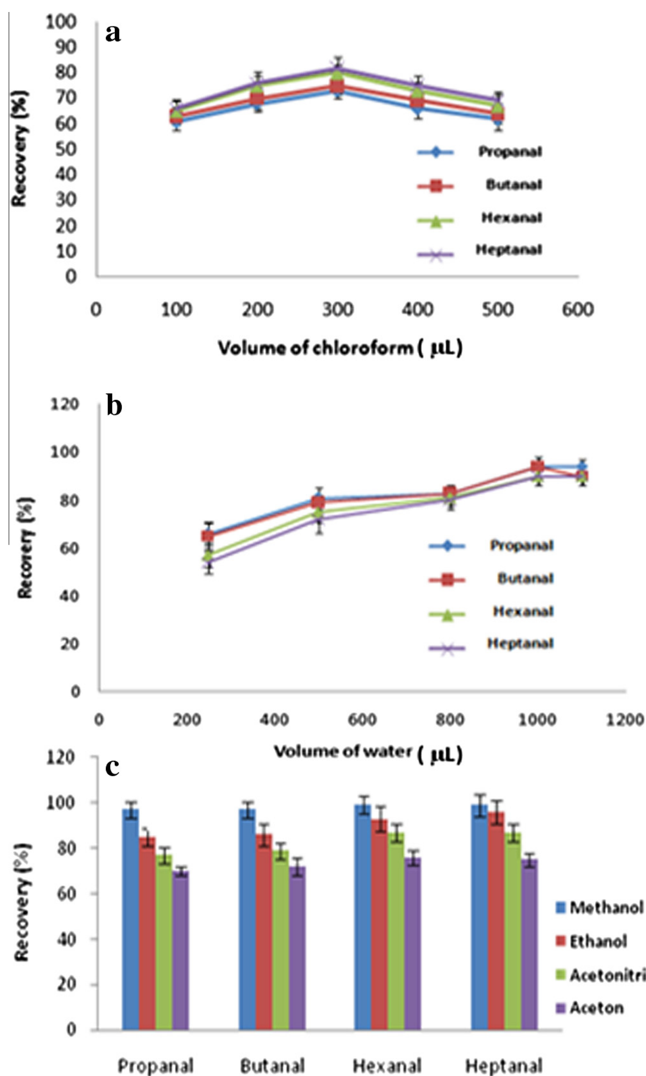

Fig. 2. (a) Effect of volume of chloroform. Condition: 10 mg L^{-1} of each analyte, Triton X-100 (10%), 200 μL of methanol, volume of water 1000 μL, forward extraction time 5 min; back-extraction time 40 min. (b) Effect of volume of water. Condition: the same as (a) and 300 μL of chloroform. (c) Effect of different organic modifiers. Condition: the same as (a) 12% (w/v) Triton X-100; 300 μL of chloroform.

micelle extraction. Both the type and the concentration of the surfactant are critically important factors in extraction using the reverse micelle solvent system. There are three types of surfactants often used in this kind of separations: anionic, cationic and nonionic surfactants. Type and concentration of surfactant has to meet certain requirements, the surfactant should be miscible with the oil sample, as well as with the organic modifier and it should have a good chromatographic behavior. In addition, the solubility of the target compounds in the surfactant should be higher than oil sample (in forward extraction step) (Sikalos & Paleologos, 2005; Xie, Paau, Li, Xiao, & Choi, 2010). Based on these considerations, four type surfactant including SDS (anionic surfactant), CTAB (cationic surfactant), Triton X-100 and Triton X-114 (nonionic surfactants) were tested. The results showed that nonionic surfactants had the best extraction efficiencies. The results demonstrated that 12% Triton X-100 provided the higher extraction efficiencies for all analytes (Table 1), this may be attributed to the strength of interaction between the target molecules and the nonionic surfactant so the nonionic surfactants are favorable for aldehydes stabilization in micelles droplets. At lower concentrations of Triton

Table 1
Effect of sonication time and Triton X-100 concentration on mean recoveries, and relative standard deviations (RSD) obtained for determination of 4 aldehydes in heated oil samples.

	Mean recoveries ((RSD) $n = 3$)[a]			
Parameter	Propanal (%)	Butanal (%)	Hexanal (%)	Heptanal (%)
Sonication time[b] (min)				
20	88.1 (5.2)	86.4 (4.8)	92.5 (3.5)	91.2 (4.6)
30	90.3 (5.0)	90.1 (3.8)	95.5 (4.0)	92.7 (4.5)
40	95.7 (3.8)	97.0 (4.0)	99.1 (3.7)	99.0 (3.7)
50	96.0 (3.4)	98.3 (4.3)	98.9 (4.1)	97.9 (4.5)
Conc. of Triton X-100[c] %(w/v)				
3	81.8 (3.8)	83.3 (3.5)	84.6 (2.5)	87.2 (2.5)
6	90.4 (3.5)	90.9 (3.3)	95.3 (3.0)	93.5 (3.0)
9	95.3 (3.2)	93.2 (4.2)	96.8 (2.8)	96.4 (2.8)
12	97.4 (3.8)	97.0 (4.0)	99.3 (2.7)	98.9 (2.7)
15	89.7 (3.9)	92.0 (3.2)	95.0 (3.0)	95.8 (3.0)
20	86.0 (3.2)	83.6 (4.5)	90.1 (3.7)	89.0 (3.7)
Conc. of Triton X-114[c] %(w/v)				
6	86.1 (3.1)	85.7 (3.5)	90.0 (3.1)	86.3 (2.9)
9	89.7 (2.8)	90.2 (3.6)	93.1 (2.7)	91.8 (3.0)
12	89.0 (3.3)	90.6 (2.8)	87.7 (2.9)	89.0 (3.2)
15	84.1 (3.2)	90.3 (3.3)	92.0 (3.6)	83.1 (2.8)
20	80.7 (3.0)	(3.1) 84.8	84.6 (2.8)	84.7 (3.1)

Condition: 10 mg L^{-1} of each analyte; 200 μL of methanol; forward extraction time 5 min; back extraction time 40 min; volume of chloroform 300 μL; 200 μL of methanol; volume of water 1000 μL.
[a] Number of replicate.
[b] Triton X-100 (10%).
[c] Sonication time = 40 min.

X-100, incomplete partitioning of the analytes into the surfactant micelles takes place (Sikalos & Paleologos, 2005) and results in a decrease in the extraction efficiency. Higher concentrations of Triton X-100, makes it difficult for the backward transfer of aldehydes into the organic phase and the phase separation of the surfactant and oil phases is not formed well. Thus, 12% (w/v) of Triton X-100 was used in the following experiments.

3.5. Effect of organic modifier

Another main factor to be considered in the development of reverse micelle extraction is the choice of organic modifier. Organic modifier is a substance added to a solvent to improve its properties (e.g. by increasing the solubility of an extractant can change interfacial parameters). In the reverse micelle back extraction of aldehydes from oil samples, the solvent used as modifier should be miscible with the surfactant and immiscible with the oil sample (Ruiz-Angel, Garcia-Alvarez-Coque, & Berthod, 2009). Because Triton X-100 is oil-miscible, the addition of such organic modifiers generally causes a phase formation between the Triton X-100 and oil phases. Four polar protic and aprotic solvents, ethanol, methanol, acetonitrile, and acetone were compared in the extraction of propanal, butanal, hexanal and heptanal. The results of extraction recoveries for the tested solvents were shown in Fig. 2c. As it can be seen, methanol provided better extraction efficiencies than other non-solvents. The effect of volume of organic modifier on the mean extraction recoveries were investigated in the range of 100–400 μL. The results showed that mean recoveries increased with increasing volume up to 200 μL. At lower volumes of methanol, the complete phase separation was not formed well, resulting in a decrease in the extraction efficiencies. However, a further increase in the volume of methanol followed by a decrease in recoveries of analytes extractions. This may be because of more dilution of extracts. Therefore, 200 μl was found to be optimum for following experiments.

Table 2
Figures of merit of the proposed method for determination of 4 aldehydes in different heated oil samples.

Oil sample	Compound	r^2	LR (mg L^{-1})	MDL (mg L^{-1})	LLOQ (mg L^{-1})	Intra-day RSD[a]%	Inter-day RSD[a]%
Soybean	Propanal	0.994	0.1–20	0.08	0.25	3.3	3.1
	Butanal	0.993	0.1–20	0.07	0.23	3.0	3.1
	Hexanal	0.995	0.05–20	0.05	0.16	2.7	2.4
	Heptanal	0.995	0.05–20	0.05	0.16	2.0	2.5
Sunflower	Propanal	0.994	0.1–20	0.04	0.13	3.4	3.8
	Butanal	0.993	0.1–20	0.03	0.1	3.2	3.5
	Hexanal	0.994	0.05–20	0.03	0.1	3.8	3.3
	Heptanal	0.994	0.05–20	0.02	0.08	3.6	4.0
Olive	Propanal	0.995	0.1–20	0.15	0.5	4.0	3.8
	Butanal	0.996	0.1–20	0.15	0.5	4.2	3.5
	Hexanal	0.996	0.05–20	0.09	0.3	3.8	3.7
	Heptanal	0.996	0.05–20	0.08	0.26	4.0	3.3

LR: linear range; MDL: method detection limit, calculated as three times the standard deviation of ten replicated runs of oil samples spiked with low concentration of analytes; LLOQ: lower limit of quantification.
[a] The concentration of aldehydes is 0.5 mg L^{-1}, $n = 5$.

Table 3
Recovery of added aldehyde standards to the heated soybean, sunflower and olive oil.

Compound	Added (mg L^{-1})	Soybean Recovery (RSD)[a] (%)	Sunflower Recovery (RSD)[a] (%)	Olive Recovery (RSD)[a] (%)
	0.0	n.d	n.d	n.d
Propanal	0.5	93.0 (3.7)	95.4 (3.0)	93.0 (3.6)
	5	94.3 (3.3)	96.3 (3.8)	95.8 (3.5)
	15	95.5 (4.2)	95.5 (4.2)	94.3 (3.8)
	0	n.d	n.d	n.d
Butanal	0.5	95.5 (4.0)	95.5 (4.0)	95.5 (4.0)
	5	96.2 (3.4)	95.3 (4.3)	97.4 (4.6)
	15	95.4 (4.4)	96.5 (4.5)	96.5 (4.2)
	0	1.86 (mg L^{-1})[b]	1.96 (mg L^{-1})[b]	1.40 (mg L^{-1})[b]
Hexanal	0.5	98.3 (2.4)	98.3 (2.4)	98.3 (2.4)
	5	99.0 (4.7)	101.0 (4.5)	102.2 (5.6)
	15	99.3 (4.4)	100.5 (4.7)	100.1 (4.6)
	0	1.86 (mg L^{-1})[b]	2.10 (mg L^{-1})[b]	1.43 (mg L^{-1})[b]
Heptanal	0.5	99.5 (3.0)	99.5 (3.0)	99.5 (3.0)
	5	98.4 (5.6)	99.7 (4.4)	103.4 (4.6)
	15	98.2 (4.7)	100.1 (5.3)	101.2 (4.8)

n.d. = not detected.
[a] $n = 5$.
[b] Found concentration of aldehydes in heated oils.

3.6. Method validation

The method under optimum conditions was satisfactorily validated with respect to accuracy, linearity, precision, sensitivity and limits of detection. The calibration plots were found to be linear in the range of 0.05–20 mg L^{-1}, with a coefficient of determination (r^2) of 0.994. For each concentration level, 5 replicate extractions were performed. The Method detection limits for, propanal, butanal, hexanal and heptanal (MDL, S/N = 3) were between 0.05 and 0.08 mg L^{-1} in soybean oil, between 0.02 and 0.04 mg L^{-1} in sunflower oil and 0.08–0.15 in olive oil. The lower limit of quantification (LLOQ) values were calculated as ten times the standard deviation of ten replicate runs of soybean and sunflower and olive oil samples spiked with low concentration of analytes. The LLOQ values were in the range of 0.26–0.5 mg L^{-1}. The coefficient of determinations (r^2), MDLs, and LLOQs of analytes are presented in Table 2.

The inter-day and intra-day precisions of the proposed method were calculated by analyzing replicate ($n = 5$) vegetable oil sample spiked with 0.5 mg L^{-1} of analyte (Table 2). As it can be observed the relative standard deviations (RSDs) calculated for the measured concentrations are lower than 4.2%. In order to determine the accuracy and the extraction recovery of the proposed method, the standard addition tests was performed. In which, the standard solutions of target compounds were prepared with different concentration levels. Three standard solutions of different concentration levels (0.5, 5 and 15 mg L^{-1}) were added to known volume of oil samples. The resultant samples were extracted with the proposed method and analyzed. Five replicate extractions were performed for each concentration level, and the ratio of measured and added amounts was used to calculate the extraction recovery. The results are summarized in Table 3. The results show that the mean recoveries of analytes, measured at three concentration levels, varied from 93% to 103% with relative standard deviations (RSDs) less than 5.6%. However, As can be observed, from the proposed volatiles only hexanal and heptanal were found in heated vegetable oils, while the rest of volatiles have not been detected. These aldehydes either not remained at applied temperature and vaporize, easily into the atmosphere due to their volatility or if remained, degrade very rapidly and are not present in the oils in sufficient concentrations to be detected. Table 4 compares the characteristic data for the proposed method with those of other reported techniques such as SPE, SPME, Headspace solid-phase microextraction, Polymer monolith microextraction, and Tenax TA trap coupled to a UV-ion mobility spectrometer. Compared to reported methods that some of them needs more preparation steps

Table 4
Comparison proposed method with other sample preparation methods for the determination of aldehydes.

Extraction method (detection technique)	Analyte (sample type)	RSD (%)	Linear range	LOD	References
Magnetic SPE[a] (HPLC-UV)	Hexanal Heptanal (human urine)	Less than 9.6%	6–5000 9–5000 (nmol/L)	1.7 2.5 (nmol/L)	Liu, Yuan, and Feng (2015)
SPME[b] GC–ECD[c] (derivatization)	Propanal Butanal Hexanal Heptanal (water)	4.7–12.1	0.1–8.9 2.0–15.3 0.5–18.0 0.4–16.9 ($\mu g\ L^{-1}$)	0.15 0.05 0.05 0.07 ($\mu g\ L^{-1}$)	Cancho et al. (2001)
PMME[d] (HPLC)	Hexanal Heptanal (urine-serum)	Less than 6.8%	2.5×10^{-2}–2.5 (μmol/L)	2.4 3.6 (nmol L^{-1})	Zhang, Huang, Lin, and Feng (2007)
Tenax TA trap UV-ion mobility spectrometer	2-Butenal, pentanal, 2-hexenal (olive oil)	Less than 10%	0.05–10 0.8–2 0 0.09–20 (mg kg^{-1})	0.3 (mg kg^{-1})	Garrido-Delgado, Mercader-Trejoa, Arcea, and Valcarcel (2011)
HS-SPME[e] GC-FID[f]	C_1–C_{10} aldehydes (fish meat)	4.2–7.5	1–1000 ($\mu g\ L^{-1}$)	1.0–5.0 ($\mu g\ L^{-1}$)	Wang, O'Reilly, and Pawliszyn (2005)
USABE[g] reverse micelles method GC–FID	Propanal, butanal, hexanal Heptanal (edible oils)	2.0–5.6	50–2000 ($\mu g\ L^{-1}$)	20.0–80.0 ($\mu g\ L^{-1}$)	This work

[a] Solid phase extraction.
[b] Solid-phase microextraction.
[c] GC–electron capture detection.
[d] Polymer monolith microextraction.
[e] Headspace solid-phase microextraction.
[f] GC–flame ionization detection.
[g] Ultrasound-assisted back extraction.

before determination, our results suggested that the ultrasound-assisted back-extraction coupled with gas chromatography–flame ionization detection methods provided a reliable and effective solution to direct extraction and determine low concentrations of mentioned aldehydes in heated vegetable oil samples. It is clearly noticed that the represented method gives comparable analytical results and can afford good sensitivity and quantification extraction efficiency, wide linear range, good limit of detections with advantages of better reproducibility relative to the other techniques.

The proposed method does not require extensive knowledge of chemical processing and reactions, but only needs a suitable selection of some aimed sequestering solvent that are commercially available, and may be of low cost. Applications of this method is only based on the preparation of some solvent solutions without going into deep synthetic routes as reported by using modified sorbents or nano sorbents. Due to the simplicity of this method, it can be manually handled and operated by undergraduate students.

4. Conclusions

A fast, simple, and sensitive reverse micelles back extraction method coupled with gas chromatography–flame ionization detection was developed and optimized for direct determination of propanal, butanal, hexanal and heptanal in soybean, sunflower and olive oils. In this method sample preparation time as well as the consumption of the toxic organic solvent were minimized without affecting the sensitivity of the method. The results from validation indicate the proposed method can be successfully applied for the determination of propanal, butanal, hexanal and heptanal in heated vegetable oil samples.

Compliance with ethics requirements

All authors of this manuscript declare that they have no conflict of interest.

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References

Abel, S., Sterpone, F., Bandyopadhyay, S., & March, M. (2004). Molecular modeling and simulations of AOT-water reverse micelles in isooctane structural and dynamic properties. *The Journal of Physical Chemistry, 108*, 19458–19466.
Basheer, C., Pavagadhi, S., Yu, H., Balasubramanian, R., & Lee, H. K. (2010). Determination of aldehydes in rainwater using micro-solid-phase extraction and high-performance liquid chromatography. *Journal of Chromatography A, 1217*, 6366–6372.
Bhowal, S., Priyanka, B. S., & Rastogi, N. K. (2014). Mixed reverse micelles facilitated downstream processing of lipase involving water-oil-water liquid emulsion membrane. *Biotechnology Progress*. http://dx.doi.org/10.1002/btpr.1941.
Bu, G., Liu, H., Chen, F., Liu, K., Yang, Y., & Gao, Y. (2012). Effects of different factors on the forward extraction of soy protein in reverse micelle systems. *African Journal of Biotechnology, 11*, 7247–7257.
Cancho, B., Ventura, F., & Galceran, M. T. (2001). Determination of aldehydes in drinking water using pentafluorobenzylhydroxylamine derivatization and solid-phase microextraction. *Journal of Chromatography A, 943*, 1–13.
Chen, Y. L., Su, C. K., & Chiang, B. H. (2006). Optimization of reversed micellar extraction of chitosanases produced by Bacillus cereus. *Process Biochemistry, 41*, 752–758.
Cvengros, J., & Cvengrosova, Z. (2004). Used frying oils and fats and their utilization in the production of methyl esters of higher fatty acids. *Biomass and Bioenergy, 27*, 173–181.
Das, K., Jain, B., & Patel, H. S. (2004). Nile Blue in Triton-X 100/benzene hexane reverse micelles: A fluorescence spectroscopic study. *Spectrochimica Acta Part A, 60*, 2059–2064.

Fullana, A., Carbonell-Barrachina, A. A., & Sidhu, S. (2004). Comparison of volatile aldehydes present in the cooking fumes of extra virgin olive, olive, and canola oils. *Journal of Agricultural and Food Chemistry, 52*, 5207–5214.

Garcia-Prieto, A., Lunar, M. L., Rubio, S., & Perez-Bendito, D. (2008). Determination of urinary bisphenol A by coacervative microextraction and liquid chromatography-fluorescence detection. *Analytica Chimica Acta, 630*, 19–27.

Garrido-Delgado, R., Mercader-Trejoa, F., Arcea, L., & Valcarcel, M. (2011). Enhancing sensitivity and selectivity in the determination of aldehydes in olive oil by use of a Tenax TA trap coupled to a UV-ion mobility spectrometer. *Journal of Chromatography A, 1218*, 7543–7549.

Goto, M. (2006). Recent advances in protein extraction and chiral separation of biomolecules. *Tsinghua Science and Technology, 11*, 194–201.

Guillén, M. D., & Uriarte, P. S. (2009). Contribution to further understanding of the evolution of sunflower oil submitted to frying temperature in a domestic fryer. study by 1H nuclear magnetic resonance. *Journal of Agricultural and Food Chemistry, 57*, 7790–7799.

Guillén, M. D., & Uriarte, P. S. (2010). Formation of toxic alkylbenzenes in edible oils submitted to frying temperature Influence of oil composition in main components and heating time. *Food Research International, 43*, 2161–2170.

Guillén, M. D., & Uriarte, P. S. (2012). Aldehydes contained in edible oils of a very different nature after prolonged heating at frying temperature: Presence of toxic oxygenated α, β unsaturated aldehydes. *Food Chemistry, 131*, 915–926.

Guillén, M. D., & Uriarte, P. S. (2012). Simultaneous control of the evolution of the percentage in weight of polar compounds, iodine value, acyl groups proportions and aldehydes concentrations in sunflower oil submitted to frying temperature in an industrial fryer. *Food Control, 24*, 50–56.

Hebbar, H. U., Hemavathi, A. B., Sumana, B., & Raghavarao, K. S. M. S. (2011). Reverse micellar extraction of bromelain from pineapple (Ananascomosus L. Merryl) waste: Scale-up, reverse micelles characterization and mass transfer studies. *Separation Science and Technology, 46*, 1656–1664.

Ji, J., Liu, H., Chen, J., Zeng, J., Huang, J., Gao, L., et al. (2012). ZnO nanorod coating for solid phase microextraction and its applications for the analysis of aldehydes in instant noodle samples. *Journal of Chromatography A, 1246*, 22–27.

Kardani, F., Daneshfar, A., & Sahrai, R. (2011). Determination of β-sitosterol and cholesterol in oils after reverse micelles with Triton X-100 coupled with ultrasound-assisted back-extraction by a water/chloroform binary system prior to gas chromatography with flame ionization detection. *Analytica Chimica Acta, 701*, 232–237.

Katragadda, H. R., Fullana, A., Sidhu, S., & Carbonell-Barrachina, A. A. (2010). Emissions of volatile aldehydes from heated cooking oils. *Food Chemistry, 120*, 59–65.

Kilikian, B. V., Bastazin, M. R., Minami, N. M., Gonçalves, E. M. R., & Junior, A. P. (2000). Liquid-liquid extraction by reversed micelles in biotechnological processes. *Brazilian Journal of Chemical Engineering, 17*, 21–38.

Lee, B. K., Hong, D. P., Lee, S. S., & Kuboi, R. (2004a). Analysis of protein back-extraction processes in alcohol- and carboxylic acid-mediated AOT reverse micellar systems based on structural changes of proteins and reverse micelles. *Biochemical Engineering Journal, 22*, 71–75.

Lee, S. S., Kim, B. G., Sung, N. C., & Lee, J. (2004b). Back-extraction processes of C.C. lipase with mediated AOT reverse micellar system. *Bulletin of the Korean Chemical Society, 25*, 873–877.

Liu, J. F., Yuan, B. F., & Feng, Y. Q. (2015). Determination of hexanal and heptanal in human urine using magnetic solid phase extraction coupled with in-situ derivatization by high performance liquid chromatography. *Talanta, 136*, 54–59.

Luque-Garcia, J. L., & Luque de Castro, M. D. (2003). Ultrasound: A powerful tool for leaching. *Trends in Analytical Chemistry, 22*, 41–47.

Marhuenda-Egea, F. C., Velazquez, S. P., Cadenas, C., & Cadenas, E. (2002). Mechanism of adaptation of an atypical alkaline p-nitrophenyl phosphatase from the archaeon Halobacterium salinarum at low-water environments. *Archaea, 1*, 105–111.

Pileni, M. P. (1993). Reverse micelles as microreactors. *The Journal of Physical Chemistry, 97*, 6961–6973.

Ruiz-Angel, M. J., Garcia-Alvarez-Coque, M. C., & Berthod, A. (2009). New insights and recent developments in micellar liquid chromatography. *Separation & Purification Reviews, 38*, 45–96.

Sikalos, T. I., & Paleologos, E. K. (2005). Cloud point extraction coupled with microwave or ultrasonic assisted back extraction as a preconcentration step prior to gas chromatography. *Analytical Chemistry, 77*(8), 2544–2549.

Totani, N., Burenjargal, M., Yawata, M., Ojiri, Y., Arise, I., & Nishi-ku, K. (2008). Chemical properties and cytotoxicity of thermally oxidized oil. *Journal of Oleo Science, 57*, 153–160.

Wang, Q., O'Reilly, J., & Pawliszyn, J. (2005). Determination of low-molecular mass aldehydes by automated headspace solid-phase microextraction with in-fibre derivatization. *Journal of Chromatography A, 1071*, 147–154.

Wilson, I. D., & Poole, C. (2009). *Handbook of methods and instrumentation in separation science* (1st ed.). Academic Press.

Xie, S., Paau, M. C., Li, C. F., Xiao, D., & Choi, M. M. F. (2010). Separation and preconcentration of persistent organic pollutants by cloud point extraction. *Journal of Chromatography A, 1217*, 2306–2317.

Yang, L., Xiaoyan, D., & Yan, S. (2008). New development of reverse micelles and applications in protein separation and refolding. *Chinese Journal of Chemical Engineering, 16*, 949–995.

Zárate, J., Goicochea, E., Echeverría, P. E., & Guillén, M. D. (2009). A study of the toxic effect of oxidized sunflower oil containing 4-hydroperoxy-2-nonenal and 4-hydroxy-2-nonenal on cortical TrkA receptor expression in rats. *Nutritional Neuroscience, 12*, 249–259.

Zhang, H. J., Huang, J. F., Lin, B., & Feng, Y. Q. (2007). Polymer monolith microextraction with in situ derivatization and its application to high-performance liquid chromatography determination of hexanal and heptanal in plasma. *Journal of Chromatography A, 1160*, 114–119.

Zhu, D. M., Feng, K. I., & Schelly, Z. A. (1992). Reverse micelles of Triton X-100 in cyclohexane: Effects of temperature, water content, and salinity on the aggregation behavior. *The Journal of Physical Chemistry, 96*, 2382–2385.

Zhu, X., Wang, K., Zhu, J., & Koga, M. (2003). Analysis of cooking oil fumes by ultraviolet spectrometry and gas chromatography–mass spectrometry. *Journal of Agricultural and Food Chemistry, 49*, 4790–4794.

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