

Application of Ultrasound-Assisted Emulsification Microextraction Based on Applying Low Density Organic Solvents to the Extraction and Determination of Mononitrotoluenes in Water Samples

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In this study, simple and efficient ultrasound-assisted emulsification microextraction (USAEME) based on applying low density organic solvents combined with gas chromatography-flame ionization detector (GC-FID) was developed for the preconcentration and determination of mononitrotoluenes (MNTs) in water samples. In this method, the fine droplets of toluene were formed and dispersed in the sample with the help of ultrasonic waves which accelerated the formation of the fine cloudy solution without using disperser solvents. Several factors influencing the extraction efficiency such as the nature and volume of organic solvent, extraction temperature, ionic strength and centrifugation time were investigated and optimized. Using optimum extraction conditions, dynamic linear ranges of 0.5-500 $\mu\text{g L}^{-1}$, and limit of detections (LOD) of 0.3 $\mu\text{g L}^{-1}$ were obtained for o-nitrotoluene, m-nitrotoluene and p-nitrotoluene. Finally, the method was successfully applied to the extraction and determination of MNTs in the water samples in the range of micrograms per liter with relative standard deviations (RSD) < 12%.

Keywords: ultrasound-assisted emulsification microextraction, mononitrotoluenes, water samples, gas chromatography

Introduction

Isomers of mononitrotoluenes (MNTs) are widely presented in the aquatic environmental due to their vast spread of uses in several industrial and chemical manufacturing applications. In toluene nitration, three isomers are produced in a ratio of about 58.8%, o-nitrotoluene, 36.8% p-nitrotoluene, and 4.4% m-nitrotoluene. MNTs are used in the synthesis of intermediates for production of dyes, rubber chemicals, drugs, resin modifiers, optical brighteners, suntan lotions, and photographic developing agents.¹ Nitrotoluenes are highly toxic compounds in low concentrations. Moreover, the aromatic amines formed by biodegradation are suspected to be carcinogenic. The tolerance limits of m-nitrotoluene, o-nitrotoluene and p-nitrotoluene in water samples are below of 2 microgram per liter ($\mu\text{g L}^{-1}$). Consequently, there is increasing interest in

the determination of concentrations of MNTs at low levels in various matrices.^{2,3} The most common ways to extract MNTs are liquid-liquid extraction (LLE),⁴ solid-phase extraction (SPE),² solid-phase microextraction,⁵ single drop microextraction (SDME)⁶ and headspace solvent microextraction (HSME).⁷ LLE needs large amounts of toxic solvents and is a time-consuming procedure. SPE is also time-consuming method in which a solvent evaporation step is required in order to pre-concentrate the analytes before final analysis.⁸ SPME has been developed to extract MNT.⁵ However, it is expensive, and the fiber used is fragile and has limited life time. Further, sample carry-over in this method can be problematic.⁹ SDME has been developed as a solvent-reduction sample preparation procedure, and since small amount of solvent is used, there is minimal exposure to toxic organic solvent. However, it is a time-consuming method in which equilibrium could not be attained after a long time.¹⁰ Recently, Rezaee *et al.*,¹¹ have introduced a more effective solvent microextraction

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technique with high extraction recovery termed dispersive liquid-liquid microextraction (DLLME). In DLLME, the appropriate mixture of extraction solvent and disperser solvent is rapidly injected by syringe into aqueous samples containing analytes. Thereby, cloudy solution forms. In fact, the cloudy state results from the formation of fine droplets of extraction solvent dispersed in the sample solution. This cloudy solution is centrifuged and the fine droplets are sedimented at the bottom of conical test tube. The determination of analytes in the sedimented phase can be performed by instrumental analysis. However, consumption of disperser solvent in DLLME have lead to some disadvantages such as decreasing of partition coefficients of analyte into the extracting solvent and increasing of the cost, as well as, environmental pollution, plus the variety of solvents that can be used in this method is limited.¹²⁻¹⁵ Ultrasound-assisted emulsification microextraction (USAEME) procedure combines micro-extraction system and ultrasonic radiation in one step. In the USAEME technique, the application of ultrasonic radiation facilitates the emulsification phenomenon and accelerates the mass-transfer process between two immiscible phases. This leads to an increment in the extraction efficiency in a minimum amount of time.¹⁶ In fact, this preconcentration technique has been developed by Regueiro *et al.*,¹⁷ who successfully applied it to determine synthetic musk fragrances, phthalate esters and lindane in aqueous samples. Saleh *et al.*¹⁸ applied low-density organic solvent using home-designed centrifuge glass vials for determination of polycyclic aromatic hydrocarbons (PAHs) in water samples and Sobhi *et al.*¹⁹ applied DLLME for the determination of MNT in water samples.

This work evaluates the suitability of USAEME for the extraction and determination of MNTs in water samples. The factor affecting the microextraction efficiency was investigated in detail and the optimal conditions were then established. The results indicated that the method could be successfully applied to determine MNTs in different water samples.

Experimental

Chemicals and reagents

The studied MNTs including o-MNT, m-MNT and p-MNT were purchased from Merck (Germany). The stock standard solutions (500 mg L⁻¹) were prepared in methanol. All of the standard solutions were kept in the refrigerator at 4 °C. Working solutions of standards at suitable concentration were prepared every day from the stock solution. Toluene, 1-octanol, 1-undecanol, 1-dodecanol

and NaCl were obtained from Merck. The water used was purified on a Youngling ultra pure water purification system Aqua Max™ from Ultra (Dongan-gu, Korea).

Apparatus

A 40 kHz and 0.138 kW ultrasonic water bath with temperature control (Tecno-Gaz SpA, Parma, Italy) was applied to emulsify the organic solvent. 125 µL Hamilton syringes (Bonaduz, Switzerland) were used to inject the organic solvent into the samples. Twenty milliliters home-designed centrifuge glass vials were used for extraction and collection procedure (Figure 1). A 10.0 µL of a Hamilton gas-tight syringe was applied for the collection of floated organic solvent and injection into the gas chromatograph (GC). A GC (Agilent GC-7890, Santa Clara, USA) equipped with a split/splitless injector system and flame ionization detector was used for separation and determination of target analytes. Ultra pure helium gas (99.999%, Air products, Millennium Gate, UK) was passed through a molecular sieve and oxygen trap (Crs, Louisville, USA) and was used as carrier gas with a flow rate of 2 mL min⁻¹. The injection port was held at 250 °C and operated in the splitless mode for 1 min and then split valve was opened and split ratio of 1:5 was applied. Separation was carried out on a DB5, 25 m × 0.32 mm i.d. and 0.25 µm film thickness from J&W Scientific capillary column. The oven temperature was kept at 100 °C for 1 min and then increased to 140 °C at the rate of 10 °C min⁻¹ and then increased to 250 °C at the rate of 40 °C min⁻¹, and was held for 3 min. The flame ionization detector (FID) temperature was maintained at 270 °C. Hydrogen was generated by hydrogen generator (OPGU-2200S, Shimadzu) for FID at a flow rate of 40 mL min⁻¹. The flow of air (99.999%, Air products) for FID was 400 mL min⁻¹.

USAEME procedure

Sample was placed in a home-designed centrifuge glass vial (length: 11 cm and diameter: 1.5 cm) (Figure 1a). Then, 14.0 µL of toluene was injected into solution and sample was sonicated for 30 s at 25 °C in an ultrasonic bath (Figure 1b). As a result, oil-in-water emulsions of toluene in water were formed. After centrifuging at 3500 rpm for 5 min, the organic solvent droplet was floated on the surface of the aqueous solution due to low density below water. After separation of the two phases, a few microliters of doubly distilled water were added into the vial through the glass tube fixed on the side of the vial (length: 3 cm and diameter: 0.5 cm) (Figure 1c). The floated organic solvent was risen into the capillary tube attached to the top of the

vial and collected by a gas-tight syringe (Figure 1d). Two microliters of collected organic solvent was injected into GC-FID instrument.

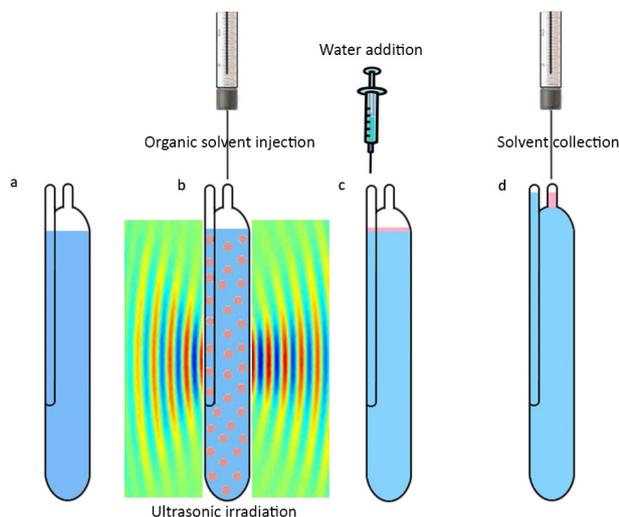


Figure 1. Schematic representation of the proposed method (a) sample solution in the home-designed emulsification glass vial without salt addition; (b) simultaneous injection and dispersion of 14.0 µL toluene into sample; (c) addition of a few µL of doubly distilled water into the vial and (d) collection of toluene transferred into the capillary tube at the top of the vial (about 6 µL).

Results and Discussion

In the proposed method, an ultrasound-assisted emulsification microextraction (USAEME) based on applying low density organic solvents as a new sample preparation technique was used for the extraction of MNTs from water samples. The influences of various parameters such as the kind and the volume of the extraction solvent, ionic strength, extraction temperature and centrifugation time on the extraction efficiency were studied and then the optimum conditions were selected.

Selection of extraction solvent

The selection of a suitable extraction solvent is critical for the USAEME process. In the USAEME, the extraction solvent should have following characteristics: (i) lower density than that of water, (ii) low solubility in water, (iii) the ability to extract interest analytes. Based on these requirements, four organic solvent candidates, including toluene, 1-octanol, 1-undecanol and 1-dodecanol were investigated. The results (Table 1) revealed that the extraction recovery obtained for the analytes using toluene were higher than those with the other solvents. Therefore, toluene was selected as the extraction solvent for the study.

Table 1. Extraction efficiency (%) of different extraction solvents evaluated for the extraction of the target analytes^a

Compound	Extraction efficiency / %			
	1-Octanol	1-Undecanol	Toluene	1-Dodecanol
o-MNT	44	22	68	27
m-MNT	38	18	66	24
p-MNT	34	11	64	19

^aExtraction conditions: extraction solvent volumes: 20.0 µL (1-octanol), 10.0 µL (1-undecanol), 14.0 µL (toluene), 12.0 µL (1-dodecanol); concentration of analytes: 100 µg L⁻¹.

Effect of centrifugation time

Centrifugation is essential to separate extraction solvent from aqueous solution in USAEME, because centrifugation time may affect the volume of floated phase. The effect of the centrifugation time on the extraction efficiency was examined from 2 to 20 min at 3500 rpm. Theoretically, a longer centrifuging time would result in more organic drops and higher enrichment factors of the target compounds because a fast separation of solvent extraction from the aqueous solutions would be difficult. Extraction solvent drops were very small when the centrifuging time was too short, and excessing centrifuging time resulted in heat generation, dissolving of part of the extraction solvent and losing sensitivity. Therefore, it is necessary to find suitable centrifuging time. In the presented work, at higher centrifugation times (> 15 min), the volume of collected solvent was decreased. Therefore, considering the extraction efficiency, 10 min was selected as the optimum centrifuging time.

Effect of volume of extraction solvent

The effect of the volume of the extracting solvent on the proposed method of MNTs was also investigated at five levels in the range of 12-50 µL. Volumes smaller than 10 µL were dissolved in aqueous bulk. The minimum collectable volume of organic solvent in the designed system was 2 µL (12 µL of emulsified toluene). Preconcentration factor (PF) was calculated using the equation 1:

$$PF = \frac{C_{\text{collected}}}{C_{\text{initial}}} \quad (1)$$

In the equation 1, $C_{\text{collected}}$ are the concentrations of the analytes in the collected organic phase and C_{initial} the initial concentrations of the analytes in the sample solution. Figure 2 shows the preconcentration factor of the analytes *versus* different volumes of toluene. As shown in Figure 2,

the concentration of the analytes in the organic phase decreased by increasing of the volume of the organic phase due to the dilution effect. Results showed that maximum preconcentration factor was achieved by using 12 μL of toluene for the extraction procedure. But, due to the difficulty of the collection of 2 μL of the floated toluene that produced poorer precision, the volume of 14 μL was chosen as the optimum volume of the organic solvent.

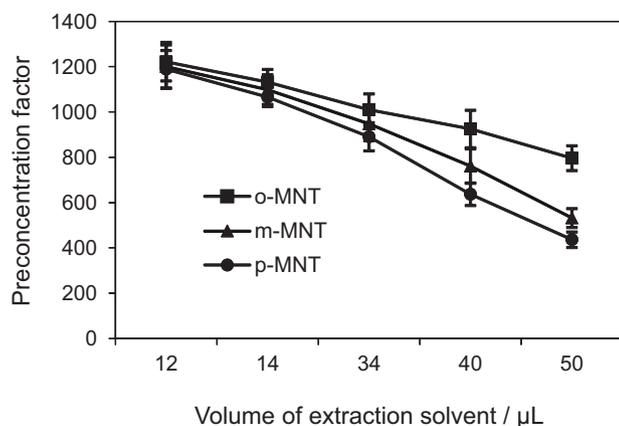


Figure 2. Effect of extracting solvent volume on the preconcentration factor. Conditions: sample solution: 10 mL of $100 \mu\text{g L}^{-1}$ of the analytes; solution temperature: $25 \pm 3 \text{ }^\circ\text{C}$; dispersion time: 30 s; centrifugation time: 10 min.

Salt addition

The influence of ionic strength was evaluated at 0-8% (m/v) of NaCl levels while other parameters were kept constant. The experimental results showed that salt addition had no significant effect on the extraction efficiency of the analytes. This is possibly because of two opposite effects of addition of salt. One is to increase the volume of the collected organic phase and decrease the dispersion efficiency, which reduces the extraction efficiency; another is the salting-out effect, which increases the extraction efficiency. It is mentioned that by increasing the salt concentration, the volume of the collected organic phase increases, because of the decrease of solubility of the extraction solvent in the presence of salt. Therefore, all the following experiments were carried out without adding salt.

Effect of emulsification-extraction temperature

Temperature affects organic solvent solubility in water as well as the emulsification phenomenon. Thus, this affects the mass-transfer process and the extraction efficiency. To determine the influence of the extraction temperature, extraction producers were done in different temperatures such as 20, 25, 35, 40 and 50 $^\circ\text{C}$. The results are shown

in Figure 3. It was observed that the highest extraction efficiency was obtained at the range of 20-25 $^\circ\text{C}$, but in higher temperature (35-50 $^\circ\text{C}$), extraction recoveries decrease. This event is possible because of the decrease in distribution coefficient (K_D) in higher temperature. Hence, 25 $^\circ\text{C}$ was used for further experiments.

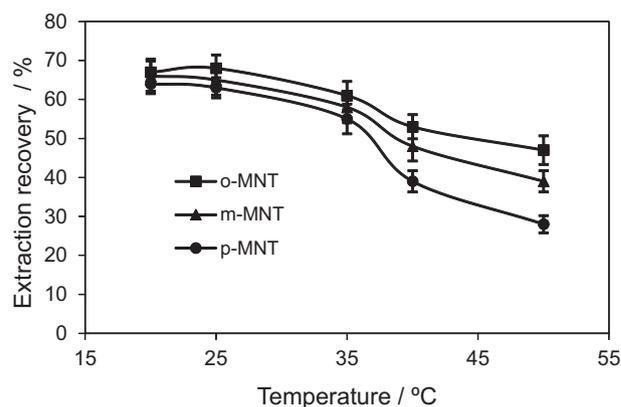


Figure 3. Effect of extraction temperature on the extraction efficiency. Conditions: sample solution: 10 mL of $100 \mu\text{g L}^{-1}$ of the analytes; volume of organic phase: 14.0 μL ; dispersion time: 30 s; centrifugation time: 10 min.

Influence of extraction time and ultrasound time

The extraction time is defined as the interval time started after dispersion and ended just before centrifugation. The results show that extraction time has no significant effect on the extraction efficiency of the analytes. It was revealed that the contact surface between extracting solvent and aqueous sample was infinitely larger and equilibrium state was achieved during a few second. Therefore, in further experiments the centrifugation was carried out just after dispersion process. The effect of ultrasound time on the extraction efficiency was examined in the range of 0-180 s. The results (Figure 4) show that in the less than 30 s, extraction efficiency is low, because of the ultrasound

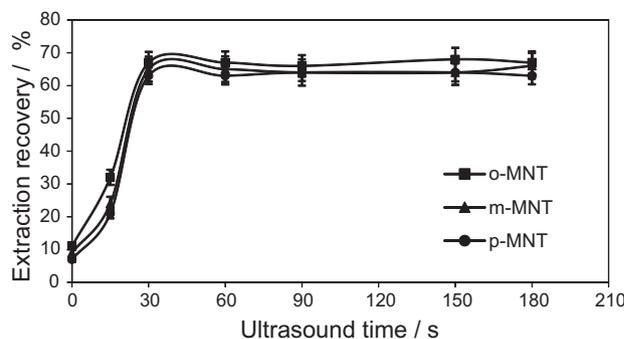


Figure 4. Effect of ultrasound time on the extraction efficiency. Conditions: sample solution: 10 mL of $100 \mu\text{g L}^{-1}$ of the analytes; volume of organic phase: 14.0 μL ; solution temperature: $25 \pm 3 \text{ }^\circ\text{C}$; dispersion time: 0, 15, 30, 60, 90, 150 and 180 s; centrifugation time: 10 min.

Table 2. Quantitative results of USAEME and GC-FID method for MNTs compounds

Analyte	Linear range / ($\mu\text{g L}^{-1}$)	LOD / ($\mu\text{g L}^{-1}$) ^a	LOQ / ($\mu\text{g L}^{-1}$) ^b	PF ^c	ER / % ^d	R ^{2e}
o-MNT	0.5-500	0.3	1.0	1132	68	0.9983
m-MNT	0.5-500	0.3	1.0	1099	66	0.9978
p-MNT	0.5-500	0.3	1.0	1066	64	0.9972

^aLOD: limit of detection for S/N = 3; ^bLOQ: limit of quantification for S/N = 10; ^cpreconcentration factor at the concentration analytes of 100 $\mu\text{g L}^{-1}$; ^dextraction recovery; ^ecoefficient of determination.

time is not enough for dispersion phenomenon and after 30 s the extraction efficiency do not changed significantly, because of equilibrium state was achieved a few second. Therefore, 30 s was selected as the optimum value for further experiments.

Method performance

Analytical performance

To evaluate the practical applicability of the USAEME method, analytical quality parameters (i.e., linearity, repeatability, limit of detection (LOD) and limit of quantification (LOQ)) were investigated. The performance of the method under the optimum conditions is shown in Table 2. The linear dynamic ranges were from 0.5 to 500 $\mu\text{g L}^{-1}$ for o-MNT, p-MNT and m-MNT in water samples. Good LODs (0.3 $\mu\text{g L}^{-1}$) were obtained, based on S/N = 3 and also, LOQs 1.0 $\mu\text{g L}^{-1}$ were obtained, based on S/N = 10. The preconcentration factors (PF) were in the ranges of 1066 to 1132 in water samples. The relative standard deviation (RSD%) for extraction and determination of the analytes were obtained at three different concentration levels and the results was shown in Table 3.

Table 4 compares proposed method with other extraction methods for the determination of the target analytes in water samples. The comparison of extraction time of the proposed method with solid-phase microextraction (SPME)⁵ and single drop microextraction (SDME)⁶ for the extraction of the target analytes indicates that this novel method has a very short equilibrium time comparing to the mentioned methods and the extraction time needed

Table 3. Relative standard deviation for MNTs compounds at three different concentration levels by using the proposed method

Analyte	Relative standard deviation (RSD%), n = 4		
	5.0 $\mu\text{g L}^{-1}$	10.0 $\mu\text{g L}^{-1}$	100 $\mu\text{g L}^{-1}$
o-MNT	8.6	7.2	5.1
m-MNT	10.1	9.1	6.3
p-MNT	7.3	6.6	4.7

for the proposed method is a few seconds. Quantitative results of proposed method are better than SPME and SDME without using sensitive detector such as mass spectrometer (MS). Quantitative results of the proposed method are comparable with homogeneous liquid-liquid extraction (HLLLE)²⁰ method and better than of dispersive liquid-liquid microextraction (DLLME) method.¹⁹ The RSD of the proposed method are better than of DLLME and HLLLE methods. Also, consumption of disperser and homogeneous solvents in DLLME and HLLLE have lead to some disadvantages such as decreasing of partition coefficients of the analytes into the extracting solvent and increasing of the cost as well as environmental pollution, plus the variety of solvents that can be used in this method is limited. Finally, it can be concluded that, the broad linear dynamic range combined with the low detection limit suggests a high potential for monitoring MNTs in water samples by applying the USAEME-GC-FID method.

Analysis of real samples

In order to test the applicability of the proposed method, four different water samples (tap, well, river and sea water)

Table 4. Comparison of the proposed method with other extraction methods for the determination of MNTs compounds in water samples

Method	RSD / %	Dynamic linear range / ($\mu\text{g L}^{-1}$)	Limit of detection / ($\mu\text{g L}^{-1}$)	Extraction time / min	Reference
DLLME-GC-FID	< 9.4	1.0-1000	0.5	< 3	19
SPME-GC-MS	< 3.6	20-1000	0.03	15	5
SDME-GC-MS	< 11.3	20-1000	0.08-0.11	15	6
HLLLE-GC-FID	< 13.2	0.5-500	0.09-0.10	< 3	20
USAEME-GC-FID	< 6.5	0.5-500	0.3	A few seconds	This work

Table 5. Determination of MNTs compounds in tap, well, river and sea water and relative recovery of MNTs compounds in them

Sample	Concentration of o, m and p-MNTs / ($\mu\text{g L}^{-1}$) \pm SD, n = 3			Added o, m and p-MNTs / ($\mu\text{g L}^{-1}$)			Found o, m and p-MNTs / ($\mu\text{g L}^{-1}$) \pm SD, n = 3			Relative recovery / %		
	o	m	p	o	m	p	o	m	p	o	m	p
Tap water ^a				2.0	2.0	2.0	1.91 \pm 0.1	1.90 \pm 0.2	1.88 \pm 0.1	95.5	95	94
	nd ^e	nd ^e	nd ^e	5.0	5.0	5.0	4.9 \pm 0.4	4.8 \pm 0.4	4.8 \pm 0.3	98	96	96
				10.0	10.0	10.0	9.9 \pm 0.7	9.7 \pm 0.8	9.8 \pm 0.7	99	97	98
Well water ^b				2.0	2.0	2.0	1.85 \pm 0.2	1.75 \pm 0.2	1.80 \pm 0.2	92.5	87.5	90
	nd ^e	nd ^e	nd ^e	5.0	5.0	5.0	4.7 \pm 0.3	4.5 \pm 0.4	4.6 \pm 0.3	94	90	92
				10.0	10.0	10.0	9.5 \pm 0.6	9.3 \pm 0.8	9.4 \pm 0.5	95	93	94
River water ^c				2.0	2.0	2.0	1.84 \pm 0.2	1.70 \pm 0.2	1.75 \pm 0.2	92	85	87.5
	nd ^e	nd ^e	nd ^e	5.0	5.0	5.0	4.7 \pm 0.3	4.4 \pm 0.4	4.5 \pm 0.4	94	88	90
				10.0	10.0	10.0	9.5 \pm 0.7	9.0 \pm 0.8	9.2 \pm 0.7	95	90	92
Sea water ^d				2.0	2.0	2.0	1.75 \pm 0.2	1.65 \pm 0.2	1.67 \pm 0.2	87.5	82.5	83.5
	n.d ^e	n.d ^e	n.d ^e	5.0	5.0	5.0	4.5 \pm 0.4	4.3 \pm 0.5	4.4 \pm 0.5	90	86	88
				10.0	10.0	10.0	9.2 \pm 0.7	9.0 \pm 1.0	9.1 \pm 0.9	92	90	91

^aWater was taken from Tonekabon Branch, Islamic Azad University (Tonekabon, Iran); ^bwater was collected from well in Tonekabon (Tonekabon, Iran); ^csample was collected from Langrud River (Gilan, Iran); ^dsample was collected from the Caspian Sea (Sari, Iran); ^enot detected.

were extracted and analyzed. The results are recorded in Table 5. All the water samples were spiked with MNTs standard solution at three different concentration levels (2.0, 5.0 and 10.0 $\mu\text{g L}^{-1}$ concentration levels) to assess the matrix effects. The obtained relative recoveries were between 82.5 and 99% (Table 5). The results show that matrix has negligible effect on USAEME of MNTs. Figure S1 shows GC-FID chromatograms of river water prior (Figure S1a) and after (Figure S1b) spiking with MNTs at 2.0 $\mu\text{g L}^{-1}$ level.

Conclusions

In the present study, USAEME combined with GC-FID was applied to determine MNTs at trace levels concentrations in water samples. The present USAEME technique reduced sample extraction time and organic solvent consumption. Under the optimized conditions, good recovery, linearity and reproducibility were obtained. The proposed method was simple, rapid and cheap and possessed great potential in the analysis of MNTs in real water samples and can be used to monitor MNTs in real water samples.

Supplementary Information

Supplementary data (USAEME-GC-FID chromatogram of MNTs) are available free of charge at <http://jbcs.sbgq.org.br> as PDF file.

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