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Dispersive liquid–liquid microextraction followed by gas chromatography–mass spectrometry for the determination of nitro musks in surface water and wastewater samples

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ABSTRACT

A new, simple, fast and high sensitive analytical method based on dispersive liquid–liquid microextraction (DLLME) followed by gas chromatography–mass spectrometry (GC–MS) for the simultaneous determination of nitro musks in surface water and wastewater samples is presented. Different parameters, such as the nature and volume of both the extraction and disperser solvents and the ionic strength and pH of the aqueous donor phase, were optimized. Under the selected conditions (injection of a mixture of 1 mL of acetone as disperser solvent and 50 μL of chloroform as extraction solvent, no salt addition and no pH adjustment) the figures of merit of the proposed DLLME–GC–MS method were evaluated. High enrichment factors, ranging between 230 and 314 depending on the target analyte, were achieved, which redound to limits of detection in the ng L^{-1} range (i.e., 4–33 ng L^{-1}). The relative standard deviation (RSD) was below 5% for all the target analytes. Finally, the recoveries obtained for different water samples of diverse origin (sea, river, irrigation channel and water treatment plant) ranged between 87 and 116%, thus showing no matrix effects.

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1. Introduction

Musk compounds have been widely used as fragrance chemicals in many consumer products such as cosmetics, detergents, herbicides, food additives or household products [1,2]. Natural musk, obtained as a secretion produced by the testicles of the musk deer, was already used in ancient times but due to economical and ethical motives synthetic musks were developed and are the ones used at present. Synthetic musks have been generally divided in three subgroups: nitro musks, polycyclic musks and macrocyclic musks [3].

The nitro musk group is formed by five compounds, which structure is shown in Fig. 1. They are considered persistent pollutants due to their strong tendency to bioaccumulate [4] and many papers have been written about their health risks, showing they are related with different types of dermatitis, carcinogenic effects and endocrine dysfunction [2,5–10]. In fact, the use in cosmetic products of musk ambrette (MA), musk tibetene (MT) and musk moskene (MM) is banned in the European Union while the use of musk xylene (MX) and musk ketone (MK) is restricted [11]. Nevertheless, its use is permitted in North America [12]. Moreover, the removal of nitro musks in municipal sewage treatment plants is not quantitative (in fact, it has been estimated to be between 60 and 80% [13]) and in some cases they are transformed to amino derivatives [4,14], which may be even more dangerous than their parent compounds [15]. This highlights the need of better wastewater treatments. Thus, nitro musks indirectly reach the aquatic environment via wastewater treatments plants. Additionally, owing to their presence in cosmetic products, they can directly reach the aquatic environment from swimming activities in seas, rivers and lakes. Therefore, it is important to develop new analytical methods to evaluate its potential for bioaccumulation on aquatic ecosystems.

Some articles dealing with the determination of nitro musks in environmental and biological samples can be found in the literature [4,16]. They have been identified in very diverse samples, such as air [17], water and sediment [18–27], fish [12,28], blood [29,30], human adipose tissue [31] or human milk [32,33], thus showing their bioaccumulation potential. They have also been determined in cosmetic products [34,35]. As nitro musks are found at trace level in the environment, extraction techniques to clean up and concentrate are needed. The most commonly used are liquid–liquid extraction (LLE) [21,22,24], solid phase extraction (SPE) [19,26] and solid-phase microextraction (SPME) [20], and in a minor extent stir

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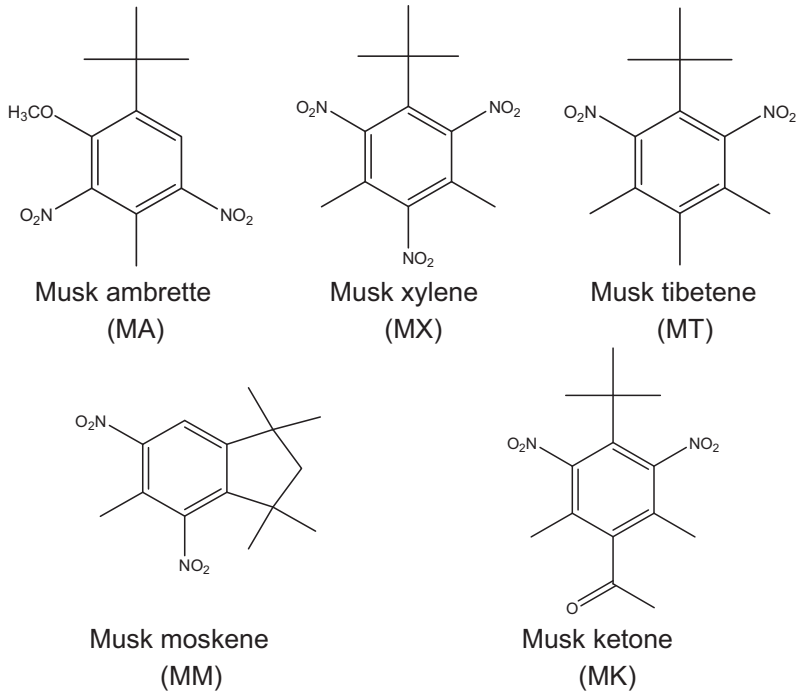

Fig. 1. Chemical structure of the target compounds.

bar sorptive extraction (SBSE) [27], followed by gas chromatography with electron capture (ECD), flame ionisation (FID) or mass spectrometry (MS) detection [4,16].

Recently, a very simple and rapid technique, called dispersive liquid–liquid microextraction (DLLME) was developed [36] in order to reduce the volume of solvent and time required in other extraction techniques while achieving high enrichment factors. The good results in terms of concentration levels are due to the fact that only a few μL of organic extracting solvent are used. On the other hand, the low extraction times are due to the fact that the equilibrium state is immediately achieved since the contact area between the extracting solvent and the sample solution is infinitely large. The principles of this extraction technique can be read elsewhere [36,37].

DLLME has been used to concentrate in environmental water samples different substances found in cosmetics, such as hydroxylated benzophenones [38], used as UV-filters, some phthalates [39], used as solvents in perfumery, and even polycyclic musks [39]. A further modification of DLLME based on the use of ultrasounds as emulsifying system was also used for the determination of some phthalates, besides of some nitro (MX, MK and MM) and polycyclic musks [40]. Nevertheless, as far as we know, the high potential for preconcentration of the DLLME has never been used before for the determination of the complete family of the nitro musk compounds.

In this sense, the aim of this paper is to develop a simple, fast and high sensitive analytical method to determine all the above mentioned nitro musks in wastewater and surface water samples, which could be useful for environmental surveillance purposes. This method is based on DLLME as extraction technique followed by GC–MS analysis.

2. Experimental

2.1. Reagents and samples

1-Tert-butyl-3-methyl-2,4-dinitroanisole (MT) 99%, 1,1,3,3,5-pentamethyl-4,6-dinitroindane (MM) 99% and a cyclohexane solution of 100 mg mL^{-1} of 1-tert-butyl-3,5-dimethyl-2,4,6-trinitrobenzene (MX) 99.5%, purchased from LGS standards (Lancashire, United Kingdom) and 6-tert-butyl-3-methyl-2,4-dinitroanisole (MA) 99% and 4-tert-butyl-2,6-dimethyl-3,5-dinitro-acetophenone (MK) 98% purchased from Dr. Ehrenstorfer (Augsburg, Germany) were used as standards. Deuterated benzophenone (benzophenone-d_{10} (BZ-d_{10})) 99% from Sigma–Aldrich (Miamisburg, OH, USA) was used as surrogate.

LC grade absolute ethanol (EtOH) from Scharlau (Barcelona, Spain), was used as solvent to prepare dilute solutions (1 and 10 μg mL^{-1}) of the standards. Deionised water (resistivity ≥ 18 MΩ cm) obtained by means of a Nanopure II water purification system from Barnstead (Boston, MA, USA) was used to prepare the working standard solutions.

Analytical reagent grade chloroform and dichloromethane, from Scharlau Chemie (Barcelona, Spain), were tested as extraction solvents. EtOH, ultrapure acetone and LC grade acetonitrile, all from Scharlau Chemie (Barcelona, Spain), were tested as disperser solvents.

Analytical reagent grade sodium chloride (NaCl) 99% from Scharlau Chemie (Barcelona, Spain) was used to adjust the ionic strength. Analytical reagent grade sodium hydroxide (NaOH) and phosphoric acid (H_3PO_4), also from Scharlau Chemie (Barcelona, Spain), and analytical reagent grade sodium dihydrogen phosphate monohydrate ($NaH_2PO_4{\cdot}H_2O$) from Panreac (Barcelona, Spain) were used to adjust the pH.

High purity helium (99.9999%) from Carburos Metalicos S.A. (Paterna, Spain) was used as carrier gas in the GC–MS system.

Water samples were all collected from different sources in the province of Valencia (Spain): sea water from the *Malvarrosa Beach* (Valencia), river water from the *Mijares River* (Montanejos), irrigation water from a local irrigation channel (La Eliana) and influent and effluent wastewater from a treatment plant (Gandia). All samples were stored in the dark at 4 °C and filtered through 0.45 μm nylon membrane filters before the analysis.

2.2. Apparatus

The GC–MS system consisted of a Focus GC gas chromatograph coupled to a DSQII mass spectrometry detector equipped with an AI3000 autosampler, all from Thermo Fisher Scientific (Austin, TX, USA).

The chromatographic separations were made using a HP-5MS Ultra Inert (95% dimethyl-5% diphenylpolysiloxane, 30 m length, 0.25 mm i.d., 0.25 μm film thickness) analytical fused-silica capillary column from Agilent Technologies (Palo Alto, CA, USA).

An EBA 21 centrifuge from Hettich (Tuttlingem, Germany) and a Micro-pH 2000 pHmeter from Crison (Alella, Spain) were also used.

2.3. Proposed method

2.3.1. DLLME procedure

5 mL of an aqueous standard solution containing the analytes in a concentration between 100 and 1000 ng L^{-1} or an environmental water sample (in triplicate) were transferred to a polyethylene 15 mL centrifuge tube, and 10 μL of a 2.5 μg mL^{-1} solution of BZ-d_{10} (as surrogate) in EtOH were added. Then, 1 mL of acetone previously mixed with 50 μL of chloroform was injected to this solution. After shaking with a vortex mixer (ca. 3 s), the tube was centrifuged for 5 min at 6000 rpm. Thus, separation of two phases occurred, and approximately 10 μL of the sedimented phase were collected with a 50 μL Hamilton 1705 RNR syringe (Bonaduz, Switzerland) and transferred into a 100 μL insert placed inside a 1.5 mL injection vial, which was then ready to be injected into the chromatographic system.

2.3.2. GC–MS analysis

1 μL of the aforementioned sedimented phase was injected into the GC system coupled to a mass spectrometry detector operated in positive electron ionisation mode at ionisation energy of 70 eV and with a multiplier voltage set at 1400 V. The inlet temperature was 280 °C and the injection was accomplished in splitless mode (splitless time: 1 min). The separation was run at a 1 mL min^{-1} helium constant flow rate. The oven temperature program was: from 60 °C (1 min) to 120 °C at 20 °C min^{-1}, then to 185 °C (0 min) at 10 °C min^{-1}, then to 195 °C (0 min) at 1 °C min^{-1} and finally to 280 °C (5 min) at 25 °C min^{-1}. The transfer line and ion source temperatures were set at 280 and 250 °C, respectively. The chromatograms were recorded in selected ion monitoring (SIM) mode at the following mass/charge (m/z) ratios: m/z 110 from 10.0 to 14.0 min for BZ-d_{10}, m/z 253, 263 and 282 from 14.0 to 16.6 min for MA, MX and MM, respectively, and m/z 251 and 279 from 16.6 to 20.0 min for MT and MK, respectively. A full scan mode (m/z from 40 to 300) was simultaneously recorded from 10.0 min to the end of the analysis time.

Fig. 2 shows a chromatogram of an aqueous standard solution containing the five target analytes at 500 ng L^{-1} (and BZ-d_{10} as surrogate at 5 ng mL^{-1}) subjected to the described DLLME–GC–MS procedure.

3. Results and discussion

The optimum DLLME parameters, such as the nature and volume of both the extraction and disperser solvent or the ionic strength and pH of the aqueous donor phase, need to be selected in order to achieve high enrichment factors (EF), defined as the ratio between the concentration of the compound in the organic sedimented phase and the initial concentration in the aqueous donor phase.

In DLLME, the extraction time is defined as the period between the injection of the binary mixture of disperser and extraction solvents and the centrifugation.

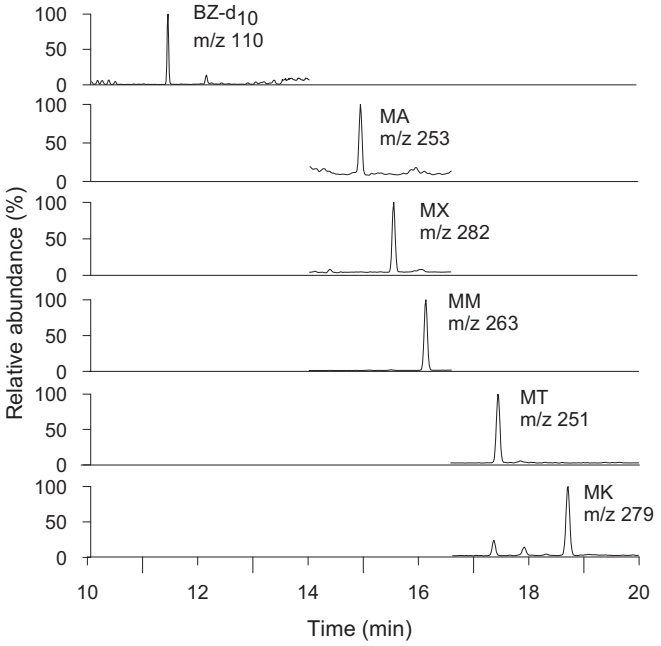

Fig. 2. A chromatogram obtained applying the proposed DLLME–GC–MS method to an aqueous standard solution containing the five target analytes at 500 ng L^{-1} and BZ-d_{10} as surrogate at 5 ng mL^{-1}.

In this work, the effect of extraction time has not been studied because, as stated in the literature, it does not affect the results in DLLME [36,37]. This is, in fact, one of the major advantages of DLLME and is due to the fact that the surface area between the extraction solvent and the aqueous phase is extremely large, reaching equilibrium state almost instantaneously.

Thus, to study the different parameters, the DLLME procedure was carried out to 5 mL of a standard aqueous solution of the five target analytes at 10 ng mL^{-1}. The peak area of each target analyte (A_i) was used as response function.

3.1. Selection of the extraction and disperser solvents

The selection of the extraction and disperser solvents is, probably, one of the most important parameters in DLLME. The selected extraction solvent has to be immiscible and have higher density than the aqueous donor phase so it can settle after centrifugation. It should also extract the compounds of interest and have a good behavior for the further analytical technique going to be used (in this case GC). Regarding the disperser solvent, it has to form the cloudy solution and has to be miscible both in the aqueous donor phase and the extraction solvent.

In this sense, dichloromethane (density 1.25 g mL^{-1}) and chloroform (density 1.48 g mL^{-1}) were studied as extraction solvents, and acetone, acetonitrile and ethanol as disperser solvents. Carbon tetrachloride is usually used as extraction solvent in DLLME [37,41] but its use is banned by the Montreal Protocol from 2010. Thus, 1 mL of each disperser solvent previously mixed with 50 μL of each extraction solvent were rapidly injected into 5 mL of the aqueous standard solution. Dichloromethane did not form cloudy solution in none of the three combinations tested. A cloudy solution was also not obtained when the chloroform–ethanol combination was tested. When comparing the other two options (chloroform as extraction solvent and acetone or acetonitrile as disperser solvent) similar results were obtained. The chloroform–acetone combination was chosen because of low toxicity and cost.

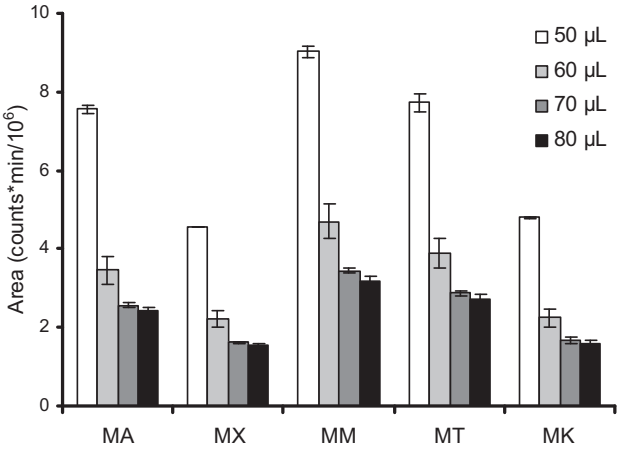

Fig. 3. Effect of the extraction solvent volume on the DLLME process. Extraction conditions: standard aqueous solution volume: 5 mL; disperser solvent volume: 1000 μL. Results are the average of 3 replicates, and the error bars show the standard deviation.

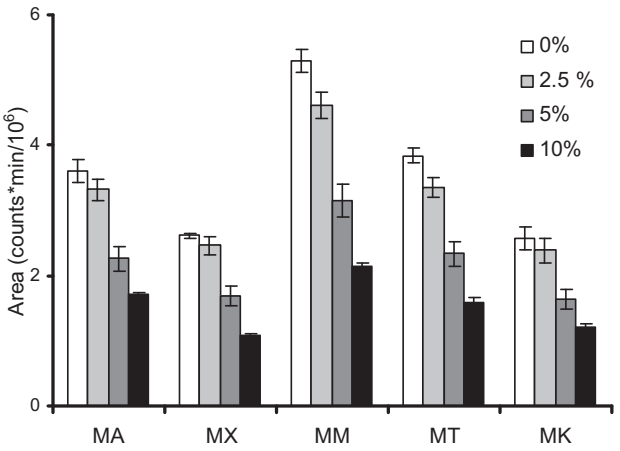

Fig. 5. Effect of the ionic strength of the donor phase on the DLLME process. Extraction conditions: standard aqueous solution volume 5 mL; extraction solvent volume: 50 μL; disperser solvent volume: 1000 μL. Results are the average of 3 replicates, and the error bars show the standard deviation.

3.2. Effect of the extraction solvent volume

In order to study the effect of the extraction solvent volume, different volumes of chloroform, ranging from 40 to 80 μL, were mixed with 1 mL of acetone and injected into 5 mL of the standard aqueous solution. 40 μL of chloroform was discarded because the obtained sedimented phase volume was not enough to handle and inject into the GC. According to the data (Fig. 3), the best results were obtained when the extraction solvent volume was 50 μL.

3.3. Effect of the disperser solvent volume

In this case, different volumes of acetone, ranging from 250 to 1000 μL, were tested while all other parameters were kept constant. Fig. 4 shows that the signal increases with the disperser solvent volume and tends to stabilize after 750 μL. Thus 1000 μL of disperser solvent was selected for further experiments.

3.4. Effect of the ionic strength of the aqueous donor phase

To study this effect, the DLLME procedure was performed to different aqueous standard solutions, all containing 10 ng mL^{-1} of the target compounds but different concentrations of NaCl (ranging from 0 to 10% (m/v)). It should be noted that the addition of salt could have different effects in the extraction procedure. On one hand, the increase of the ionic strength decreases the solubility of the extraction solvent in the aqueous phase, due to the salting out effect, and therefore, the volume of the sedimented phase increases. On the other hand, the salting out effect is expected to favour the extraction of the target compounds from the aqueous phase to the organic phase. In this case, Fig. 5 shows how the addition of salt reduces the signal obtained, due to the fact that the dilution caused by the higher volume is more important on the target compounds than the salting out effect. In fact, volume did increase considerably with the ionic strength, as volumes of 8 ± 2, 17 ± 2, 23 ± 4 and 42 ± 2 μL for 0, 2.5, 5 and 10% (m/v) of NaCl concentration in the aqueous donor phase, respectively, were collected. Therefore, in subsequent experiments, no salt was added to the donor phase.

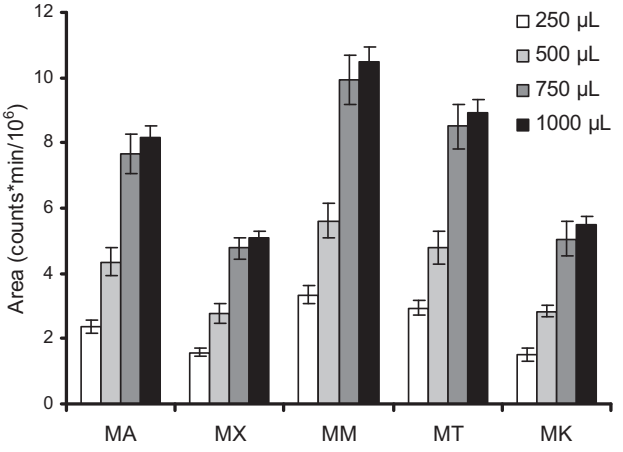

Fig. 4. Effect of the disperser solvent volume on the DLLME process. Extraction conditions: standard aqueous solution volume: 5 mL; extraction solvent volume: 50 μL. Results are the average of 3 replicates, and the error bars show the standard deviation.

3.5. Effect of the pH of the aqueous donor phase

The pH of the donor phase can considerably affect the extraction of compounds with potentially ionisable functional groups. In this case, the five target nitro musks do not present ionisable moieties, thus it is expected that pH does not affect the extraction. Nevertheless, it was studied using different aqueous standard solutions buffered at different pH values (ranging from 2 to 10) with 10^{-3} M phosphate buffer.

Results confirmed, as expected, that there was no difference in the extraction of the target compounds at the different pH values studied. Thus, in subsequent experiments the pH was not adjusted.

3.6. Use of surrogate

In order to reduce the variability of the measurements, especially caused by the handling of low volumes in the DLLME process, the use of deuterated benzophenone, i.e., benzophenone-d_{10} (BZ-d_{10}), as surrogate was considered. Thus, A_i/A_{sur} (where A_i is the peak area of the target analyte and A_{sur} that of the surrogate) was used as response function for quantification purposes.

BZ-d_{10} was selected for various reasons: (1) it is extractable in chloroform by the DLLME proposed method; (2) its volatility is suitable to be measured by GC; (3) as it is a deuterated compound, its possible presence in the environmental samples is nil, on the contrary of its non-deuterated homologous; and (4) it does not present ionisable functional groups in its structure, and thus, its extraction is not expected to be influenced by the pH.

Table 1
Main parameters of the proposed DLLME–GC–MS method.

Analyte	Slope[a] ($ng\,L^{-1})^{-1}$	Intercept[a]	Regression coefficient[a]	LOD[b] ($ng\,L^{-1}$)	LOQ ($ng\,L^{-1}$)[c]	Enrichment factor	RSD (%)[d]
MA	$(94 \pm 2) \times 10^{-5}$	0.12 ± 0.03	0.9992	33	109	289	3.2
MX	$(613 \pm 9) \times 10^{-6}$	0.11 ± 0.02	0.9993	19	63	263	3.5
MM	$(129 \pm 3) \times 10^{-5}$	0.22 ± 0.06	0.998	6	19	248	4.3
MT	$(107 \pm 2) \times 10^{-5}$	0.14 ± 0.05	0.998	4	14	230	3.1
MK	$(62 \pm 1) \times 10^{-5}$	0.04 ± 0.02	0.9991	7	24	314	1.4

[a] Working range: 100–1000 $ng\,L^{-1}$. Number of calibration points: 5.
[b] Limit of detection, calculated as 3 times the signal-to-noise ratio.
[c] Limit of quantification, calculated as 10 times the signal-to-noise ratio.
[d] Relative standard deviation (RSD) obtained in the analysis of five replicates of an aqueous standard solution containing 500 $ng\,L^{-1}$ of the target compounds.

Since the pH of the samples is not adjusted (see Section 3.5), it is mandatory to check that the extraction of BZ-d_{10} is not influenced by the pH of the samples. In this sense, different aqueous solutions buffered at different pH values (ranging from 2 to 10) containing 5 $ng\,mL^{-1}$ of BZ-d_{10} were prepared and analyzed according to the DLLME–GC–MS proposed method. As expected, results revealed that the extraction of BZ-d_{10} was not affected by the pH.

On the other hand, and as concluded before (see Section 3.4), the ionic strength is not adjusted in the samples. This could involve serious problems from the accuracy standpoint if sea water samples are analyzed, since their salt content can reach up to 3.5% (m/v) and could affect the extraction of the target compounds. However, when the influence of the ionic strength was studied on the extraction of BZ-d_{10}, results revealed that it was affected in the same way as analytes, owing to the increase in the sedimented phase volume. Thus, when A_i/A_{sur} was used as response function, the effect of the ionic strength was negligible.

3.7. Analytical figures of merit of the proposed DLLME–GC–MS method

Under optimized conditions different quality parameters were evaluated and are summarized in Table 1.

Calibration curve was constructed and linearity reached at least 20 $ng\,mL^{-1}$. The working range employed was set from 100 to 1000 $ng\,L^{-1}$. Table 1 shows the equations obtained for all the target compounds and its regression coefficient.

Table 1 also shows the limits of detection (LOD) and quantification (LOQ) calculated as 3 or 10 times the signal-to-noise ratio, respectively. These values are ranged in the $ng\,L^{-1}$ level. Nevertheless, analytical methods providing lower LOD can be found in the analytical literature, but they are based on more time-consuming extraction techniques, such as SPME and SBSE. In any case, the LOD obtained by the proposed method are suitable to determine these compounds at ultratrace levels in water.

The EF ranged between 230 and 314 depending on the analyte. As concentration is proportional to the signal obtained, the EF were calculated comparing the areas obtained when measuring the sedimented phase after applying the proposed DLLME–GC–MS method to a standard aqueous solution and a standard solution of the target analytes in chloroform.

The repeatability, expressed as relative standard deviation (RSD), was evaluated by applying the proposed DLLME–GC–MS method to five replicates of a standard aqueous solution containing 500 $ng\,L^{-1}$ of the target compounds and 5 $ng\,mL^{-1}$ of the surrogate and resulted below 5% in all cases.

3.8. Application of the proposed DLLME–GC–MS method to the analysis of environmental water samples

The target analytes were determined in different wastewater and surface water samples of different matrix composition (sea, river, irrigation channel and water treatment plant) (see Section 2.1). The results showed that all of them were below the limits of detection. Moreover, the full scan mode also showed that no amino-musks derivatives, which can be formed in the processes of the wastewater treatment plants [4], were detected in the analyzed samples.

Table 2
Recovery values obtained in the analysis of five water samples by using the proposed DLLME–GC–MS method.

Analyte	Recoveries (%)[a]				
	Sample 1[b]	Sample 2[c]	Sample 3[d]	Sample 4[e]	Sample 5[f]
MA	93 ± 4	95 ± 5	106 ± 4	98 ± 13	95 ± 14
MX	88 ± 6	105 ± 8	103 ± 6	107 ± 9	96 ± 10
MM	87 ± 5	95 ± 6	103 ± 6	109 ± 11	94 ± 11
MT	87 ± 6	93 ± 7	102 ± 6	105 ± 9	93 ± 10
MK	88 ± 6	92 ± 8	99 ± 8	107 ± 3	116 ± 5

[a] Spiking level: 500 $ng\,L^{-1}$.
[b] Sample 1: Sea water (Valencia).
[c] Sample 2: River water (Montanejos).
[d] Sample 3: Irrigation water (La Eliana).
[e] Sample 4: Wastewater treatment plant influent (Gandia).
[f] Sample 5: Wastewater treatment plant effluent (Gandia).

3.9. Recovery studies

In order to evaluate matrix effects, recovery studies were carried out. In this sense, the proposed DLLME–GC–MS method was applied to the five above-mentioned samples that had been previously spiked with the target analytes at 500 $ng\,L^{-1}$. The recoveries obtained (Table 2) ranged between 87 and 116%, depending on the analyte. These results demonstrate that these water matrices have no significant effect on the extraction process.

4. Conclusions

A simple, fast and high sensitive analytical method is presented in this paper in order to determine the complete family of nitro musk compounds in environmental water samples.

This method is based on DLLME as extraction technique prior to analysis by GC–MS and presents good analytical features, especially high enrichment factors that allow their determination in the decade $ng\,L^{-1}$ range. Although analytical methods providing lower LOD can be found in the analytical literature, these are based on more time-consuming extraction techniques, which make the proposed method a good alternative for treating a lot of samples, as environmental surveillance demands.

Finally, it should be emphasized that the present method is a good alternative to other methods as it consumes very low levels of solvents and is very fast.

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