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Development of a selective solid phase extraction method for nitro musk compounds in environmental waters using a molecularly imprinted sorbent

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ABSTRACT

A powerful analytical method for the determination of the family of the nitro musk compounds at trace level in environmental waters—river, sea, and water from a treatment plant—is presented. The method is based on the use of molecularly imprinted silica (MIS) as sorbent for solid phase extraction (SPE) used for the clean-up and the concentration step of the target analytes previous to their determination by gas chromatography–mass spectrometry. The optimized extraction procedure allowed extraction recoveries between 61% and 87% using the MIS. The comparison with a non-imprinted silica (NIS) sorbent, for which extraction recoveries between 8% and 26% were obtained, showed the high selectivity of the MIS for the nitro musks. Moreover, high enrichment factors, ranging between 580 and 827, were achieved. The imprinted sorbent was compared to a conventional polymeric SPE sorbent for the extraction of the target compounds from environmental waters, showing high selectivity of the MIS and its clean-up potential. For the first time, the five nitro musk compounds were selectively extracted with an imprinted material.

1. Introduction

Musk compounds are valuable fragrance chemicals used in many consumer products such as cosmetics, detergents, herbicides, food additives or household products. Natural musk, a product from natural origin, is no longer used due to economical and ethical reasons. Nowadays synthetic musks, other compounds with totally different chemical structures but possessing musk-like odor properties, have replaced it [1]. Synthetic musks have been generally divided in three subgroups: nitro musks, polycyclic musks and macrocyclic musks. Polycyclic musks are the most used in Europe while nitro musks are the ones that dominate in North America [2,3].

The nitro musks group is basically formed by five compounds i.e., musk ambrette (MA), musk xylene (MX), musk moskene (MM), musk tibetene (MT) and musk ketone (MK), all of them possessing a nitro-aromatic moiety. Table 1 shows the chemical structure of these compounds and some of their relevant characteristics. Nitro musks are hazardous compounds as they are related with different types of dermatitis, carcinogenic effects and endocrine dysfunction [4–10]. They are also considered persistent pollutants as they present a strong bioaccumulation potential [11]. Moreover, nitro musks can indirectly reach the aquatic environment, in which they have been found at trace levels [12,13]. Therefore, it is important to develop new analytical methods that allow carrying out their determination on the ecosystems. To do so, due to the low concentration at which they are usually found, it is necessary to use suitable extraction techniques to concentrate the compounds and to remove interfering substances.

Nitro musks have been determined in different samples, such as cosmetic products [14,15], air [16], water and sediment [17–33], blood [34,35], fish [36,37], human adipose tissue [38] or human milk [39,40]. Different techniques for the extraction of nitro musks in environmental water samples have been reported in the literature. Liquid–liquid extraction (LLE) [18,19,26], liquid–liquid microextraction (LLME) [29,31], solid phase extraction (SPE) [20–22,24,25] and solid-phase microextraction (SPME) [17,23,27,30,32] have been used as clean-up and preconcentration techniques. The most commonly used analytical technique for their determination is by far gas chromatography (GC) either with electron capture (ECD), flame ionization (FID) or mass spectrometry (MS) detection.

SPE has been broadly used as a clean-up step. However, this technique presents some disadvantages as the co-extraction of interfering compounds with a similar polarity to the analytes, which interfere in the subsequent determination of the compounds of interest. An option to improve selectivity in SPE is the use of molecularly imprinted sorbents, which contain cavities

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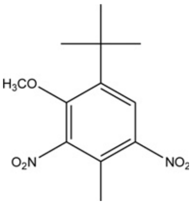
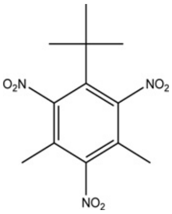
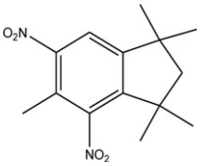
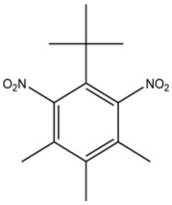
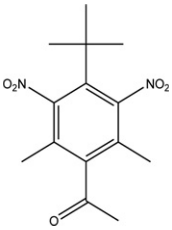
Table 1
Main characteristics of the target compounds.

Common name	CAS N°	Structure	Log Kow (25 °C)
Musk ambrette (MA)	83-66-9		4.039 ± 0.318
Musk xylene (MX)	81-15-2		4.369 ± 0.295
Musk moskene (MM)	116-66-5		4.839 ± 0.337
Musk tibetene (MT)	145-39-1		4.931 ± 0.295
Musk ketone (MK)	81-14-1		2.510 ± 0.472

designed for a target compound [41]. This provides a retention mechanism based on molecular recognition, in which great potential in selectivity has been largely demonstrated [42–45].

Molecular imprinted polymers (MIPs), synthesized by radical polymerization of organic monomers, are the most commonly used imprinted sorbents. However, it has been shown that the crucial interactions between the template and the monomer are difficult to achieve in the case of templates with a nitro group [46,47]. A strong retention by hydrogen bonds is unlikely and taking advantage of hydrophobic interactions by using the styrene as monomer is neither an option as nitro aromatic compounds inhibit the radical polymerization of the styrene. A different approach is the synthesis of imprinted sorbents by sol–gel polymerization that results in a hybrid material (inorganic–organic) known as molecularly imprinted silica (MIS). In this case, organically modified silica is used as a monomer that commonly forms polar or hydrophobic interactions with the template, and an alkoxysilane is used as cross-linking [46,47].

Unfortunately, as the template is usually not completely removed, residual leaking during the elution is common. This leads to a lack of accuracy in the determination, especially in trace analysis. The simplest and most common way of avoiding this problem is the use of a structural analog of the target compound as template, known as dummy molecule, in the synthesis of the material [41]. Residual leaking of the template is still present but is no more a problem as it elutes at a different retention time than the target compound in the subsequent chromatographic technique. This procedure is also a good option when the use of the target compound as template is not feasible due to its high price or that the conditions used in polymerization may cause degradation in undesired compounds.

The aim of this work was to find a molecularly imprinted material to be used as SPE sorbent for the simultaneous selective extraction of the five compounds from the nitro musk family in wastewater and surface water samples. A MIS synthesized using the same procedure as the one described by our group for nitro explosives using 2,4-dinitrotoluene (2,4-DNT) as template was used because of its structural analogy with the target nitro musks [47]. Then, an extraction procedure different from the procedure developed for nitroaromatic explosives but well adapted to the selective extraction of nitro musk was optimized and applied to their extraction from wastewater and surface water samples.

2. Experimental

2.1. Reagents, materials and samples

1-Tert-butyl-3-methyl-2,4-dinitroanisole (Musk Tibetene, MT) 99%, 1,1,3,3,5-pentamethyl-4,6-dinitroindane (Musk Moskene, MM) 99% and a cyclohexane solution of 100 mg mL^{-1} of 1-tert-butyl-3,5-dimethyl-2,4,6-trinitrobenzene (Musk Xylene, MX) 99.5%, purchased from LGS standards (Lancashire, United Kingdom) and 6-tert-butyl-3-methyl-2,4-dinitroanisole (Musk Ambrette, MA) 99% and 4-tert-butyl-2,6-dimethyl-3,5-dinitro-acetophenone (Musk Ketone, MK) 98% purchased from Dr. Ehrenstorfer (Augsburg, Germany) were used as standards. Hexachlorobenzene (HClB) 99% from Aldrich (Steinheim, Germany) was used as an internal standard.

HPLC grade methanol (MeOH) and acetonitrile were from Carlo Erba (Val de Reuil, France). Deionised water (resistivity ≥ 18 MΩ cm) obtained by means of a Milli-Q purification system (Millipore, Saint-Quentin en Yvelines, France) was used to prepare the working standard solutions.

To synthesize the MIS, 2,4-DNT from Sigma Aldrich (St. Quentin Fallavier, France) was used as a template, phenyltrimethoxysilane (PTMS) and tetraethoxysilane (TEOS), both from Sigma Aldrich, were used as monomer and cross-linker respectively. Lastly, a 32% commercial ammonia solution provided by Merck was used as solvent.

High purity helium (99.9995%) from Messer (Puteaux, France) was used as carrier gas in the GC–MS system

Oasis HLB cartridges (phase of N-vinylpyrrolidone and divinylbenzene) 60 mg sorbent, 3 mL cartridges from Waters were also used to compare the results of the MIS with a conventional cartridge.

Water samples were all collected from different sources: sea water from La Vila Joiosa (Alicante, Spain), river water from the Seine River (Paris, France) and effluent wastewater from a treatment plant (Valencia, Spain). All samples were stored in the dark at 4 °C and filtered through 0.45 μm nylon membrane filters before the analysis.

2.2. Analytical conditions

The GC–MS system used consisted of a trace GC gas chromatograph coupled to an ISQ mass spectrometry detector equipped with a triplus autosampler, all from Thermo Fisher Scientific (Austin, TX, USA). The chromatographic separations were made using a DB-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).

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 injection volume was 1 μL in splitless mode (splitless time: 1 min). The inlet, transfer line and ion source temperatures were set at 280 °C, 280 °C and 250 °C, respectively. The chromatograms were recorded in selected ion monitoring (SIM) mode at the following mass/charge (*m*/*z*) ratios: *m*/*z* 284 from minute 11.0 to 13.50 for HClB, *m*/*z* 253, 263 and 282 from minute 13.50 to 16.90 for MA, MX and MM, respectively, and *m*/*z* 251 and 279 from minute 16.90 to 21.0 for MT and MK, respectively. A full scan mode (m/z from 50 to 350) was simultaneously recorded from minute 5.0 to the end of the analysis time.

2.3. Evaluation of the imprinted sorbent

The MIS was synthesized according to the procedure previously described by some of the authors of this work for the extraction of nitroaromatic explosives [47]. In summary, it was synthesized using 2,4-DNT as template, PTMS as monomer and TEOS as crosslinking in a 1/4/30M ratio (template/monomer/cross-linker). A nonimprinted silica (NIS) sorbent synthesized simultaneously with the MIS without introduction of the template molecule was also used during the evaluation of the MIS to ensure the development of a selective extraction procedure.

The extraction procedure was optimized by studying the composition and the volume of the percolated and the washing fractions. The conditioning of both, MIS and NIS, consisted in the percolation of 5 mL of water. The optimized procedure consisted in the percolation of 200 mL of a water/MeOH (95/5, v/v) standard solution containing 500 ng L^{-1} of the five nitro musks followed by 1.3 mL of a MeOH/water mixture (60/40, v/v) as washing step. Finally, 1 mL of ACN was chosen for the elution step. In order to quantify the nitro musks only the elution fractions were analyzed by GC–MS. For this, these fractions were directly injected after the addition of the internal standard or evaporated to dryness under a nitrogen stream and dissolved in 200 μL of ACN containing the internal standard at 15 ng L^{-1}.

2.4. Application to environmental samples

Three water samples from different sources—sea water, river water and wastewater—were collected. All samples were stored in the dark at 4 °C and filtered through 0.45 μm nylon membrane filters before the analysis.

The optimized extraction procedure on MIS was applied for each one of them. For this, a conditioning step of 5 mL of water was carried out and it was followed by the percolation step of 200 mL of the water sample containing 5% of methanol and spiked with 100 ng of each nitro musk, a washing step of 1.3 mL of a MeOH/water mixture (60/40, v/v) and an elution step with 1 mL of ACN. After that, the elution fraction was evaporated to dryness and dissolved in 200 μL of ACN containing the internal standard at 15 ng L^{-1}.

To prove the potential of the imprinted sorbent to selectively extract the analytes, a similar method with a conventional sorbent was developed to compare the results in real samples. The conventional sorbent chosen was an Oasis HLB, (60 mg). The procedure consisted in a conditioning step with 2 mL of acetonitrile, 2 mL of methanol and 2 mL of water. The loading step consisted in the percolation of 200 mL of the water sample containing 5% of MeOH spiked with 100 ng of each nitro musk. Washing was accomplished with 1 mL of water/MeOH (80/20, v/v) mixture and compounds were finally eluted with 1 mL of acetonitrile. The elution fraction was evaporated to dryness and dissolved in 200 μL of ACN containing the internal standard at 15 ng L^{-1}.

3. Results and discussion

3.1. Selectivity of the imprinted sorbent

The aim of this study was to provide a selective sample pretreatment by using a MIS to analyze the nitro musks in water samples. The structure of these compounds is reported in Table 1. Indeed, the analysis of the nitro musks in these samples requires the clean-up of the matrix and a high preconcentration in order to detect trace level of these compounds. In these conditions, the use of a dummy molecule during the synthesis of the MIS was necessary to avoid the risk of residual template leaking from the polymer and causing erroneous results. Because of its structural analogy with the nitro musks, 2,4-DNT was used as a template and the synthesis of the MIS was achieved in the same conditions as for the MIS previously synthesized for nitro explosives [47].

First, the selective retention of the nitro musk compounds on the MIS synthesized with the 2,4-DNT as template was studied by the development of an optimized extraction procedure for these compounds. The optimization of the extraction procedure is generally performed by studying the extraction profiles that must be different when using the MIS and the NIS [41]. This comparison necessitates the quantification of the analytes in the percolation, washing and elution fractions. This approach cannot be applied in this study because the percolation and the washing fractions contain mainly water and aqueous samples cannot be injected on the GC-column. Moreover, it was not possible to evaporate the aqueous fractions without losing the nitro musks. So, only the elution fractions were injected for the quantification. Therefore, the comparison of both sorbents only consists in measuring the recovery yields in the elution fraction of the MIS/NIS that must be lower for the NIS than for the MIS.

The retention on both sorbents was then studied after the percolation of 200 mL of pure water sample spiked with nitro musks followed directly by the elution step. Five per cent of MeOH was added in the percolated water sample in order to ensure that the highly hydrophobic nitro musks did not adsorb to any of the surfaces on which they came in contact. In this case, extraction recoveries for MIS ranged between 75% and 100% for the MIS and between 55% and 70% for NIS. So, these results show the retention of the nitro musks on the MIS applying this condition of percolation, with a high volume of water, to obtain a high enrichment factor. Moreover, the higher retention on the MIS than on the NIS demonstrates the presence of cavities on the MIS allowing this slight selectivity, which could be probably increased by modifying the proportion of MeOH in the sample and in the washing solution. Thus, various water/MeOH mixtures containing the nitro musks were percolated through the MIS and the NIS and followed by the elution with ACN. The best results were obtained when the percolation was carried out with water/MeOH (40/60, v/v). Indeed, the extraction recoveries were about 80% and 92% on the MIS and about 28% and 63% on the NIS for all the compounds. This difference in recoveries confirms again the presence of cavities in the MIS that are able to retain more strongly the nitro musks than the NIS.

The volume of the washing fraction was optimized after the percolation of 200 mL of water/MeOH (95/5, v/v) solution spiked with the nitro musks, the effect of various volumes of the washing mixture (water/MeOH, 40/60, v/v) on the recoveries were studied, the elution being carried out with ACN. First, the extraction recoveries reported for the MIS in Fig. 1, for a washing fraction of 1 mL, are the same as those obtained without applying a washing solution while, recovery values for NIS did reduce to values between 34% and 54% (instead of 55% and 70%) depending on the nitro musks.

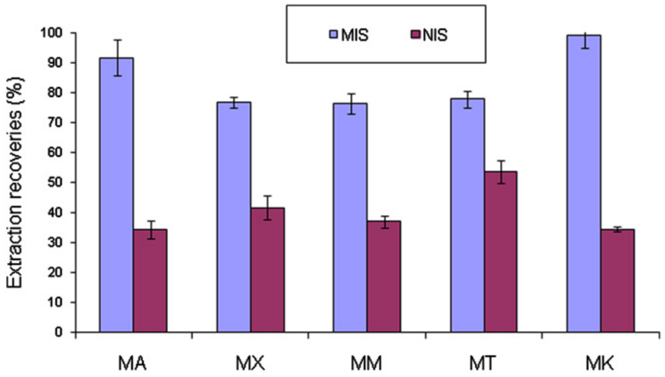


Fig. 1. Extraction recoveries obtained on MIS and NIS after the percolation of 200 mL of a water/MeOH (95/5, v/v) standard solution containing 500 ng L^{-1} of the five nitro musks and a washing step of 1 mL of a MeOH/water mixture (60/40, v/v) ($n=3$).

In order to reduce the non-specific interactions, higher volumes of washing solution were considered and the best results were obtained for the percolation of 1.3 mL of water/MeOH (40/60, v/v). Fig. 2 shows a chromatogram corresponding to the analysis of the eluate after the percolation of 200 mL of a 95/5 water/MeOH solution spiked with five target compounds at 50 ng L^{-1} and subjected to the described procedure.

The extraction recoveries obtained after the accomplishment of this procedure in triplicate are shown in Fig. 3. This optimized extraction procedure allowed extraction recoveries between 61% and 87% using the MIS while recoveries for the non-imprinted sorbent ranged between 8% and 26%. This process allowed the highest selectivity, when comparing MIS and NIS, with satisfying extraction recoveries using the MIS. Relative standard deviations lower than 6% for the MIS and for the NIS show the good repeatability of the extraction procedure.

Finally, the procedure with a washing step of 1.3 mL, was chosen for all the next experiments. This procedure allowed the selective extraction of the nitro musks using a MIS synthesized with the 2,4-DNT as a template with a high selectivity. So, the cavities are sufficiently large to accept the nitro musks but when applying specific conditions of extraction. The extraction procedure

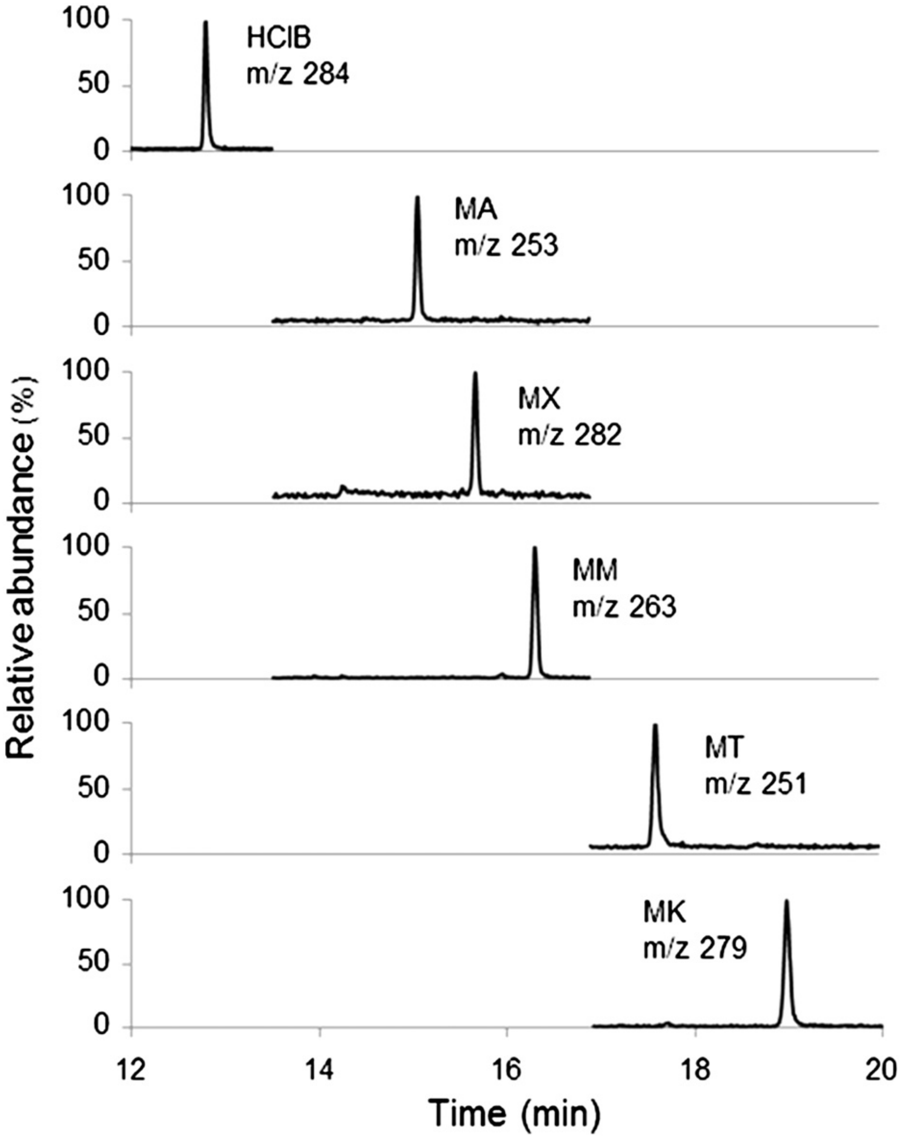


Fig. 2. A chromatogram obtained applying the proposed method to a water/MeOH (95/5, v/v) standard solution containing 50 ng L^{-1} of the five nitro musks.

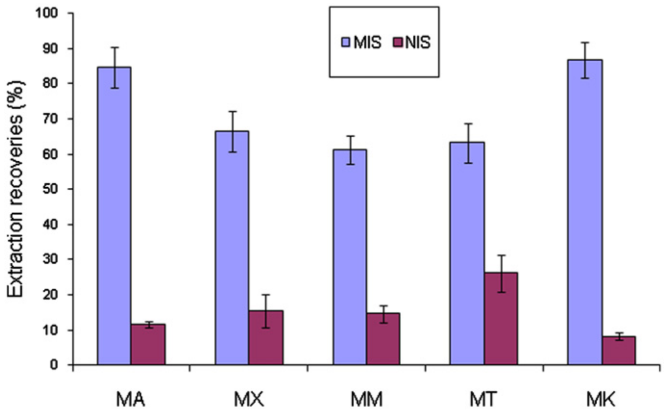


Fig. 3. Extraction recoveries obtained on MIS and NIS after the percolation of 200 mL of a water/MeOH (95/5, v/v) standard solution containing 500 ng L^{-1} of the five nitro musks and a washing step of 1.3 mL of a MeOH/water mixture (60/40, v/v) (n=3).

developed previously for the nitro explosives cannot be used for these compounds. Indeed, a washing step with a water/ACN mixture (75/25, v/v) used for the selective extraction of the nitro explosives led to the loss of the nitro musks before the elution fraction. Moreover, it was observed that the use of MeOH and water in the washing step gave rise to a lowest selectivity for the extraction of nitro explosives on the same MIS than an acetonitrile/water mixture thus highlighting again the necessity to adapt the nature and the volume of the solvent constituting the washing fraction to the nature of the studied compounds.

3.2. Evaluation of the analytical method

The enrichment factors for all the nitro musks were calculated with the optimized extraction procedure. After the extraction, and in order to lower the limits of detection, an evaporation step was performed. The 1 mL elution fraction was evaporated to dryness under a nitrogen stream and re-dissolved in 200 µL of ACN containing the internal standard at 15 ng L^{-1}. Before this, a test, evaporating to dryness in triplicate and redissolving to ensure no nitro musks were lost in the evaporation, was performed. Results showed that there was no loss of compounds during this step.

The enrichment factors achieved by the method were calculated taking into account the dilution of 5% with MeOH, the extraction recoveries of the SPE process and the evaporation step. These factors ranged between 580 and 827 depending on the nitro musk studied, thus showing the high enrichment of this procedure. The enrichment factors are reported in Table 2.

A calibration curve of the standards in ACN was constructed for each nitro musk in the range 8–20 ng mL^{-1}. Then, the instrumental limit of detection (IDL) and quantification (IQL) was calculated as 3 or 10 times the standard deviation of the residuals divided by the slope of the calibration curve. These results are presented in Table 2. The IDL and the IQL obtained range between 1.1 and 2.1 µg L^{-1} and between 3.6 and 7.0 µg L^{-1}, respectively.

The limits of detection (LOD) and quantification (LOQ) of the method were then estimated taking into account the IDL or IQL and the enrichment factors of each nitro musk. All these parameters are summarized in Table 2. The development of this procedure allowed a large decrease of the LOD and the LOQ of the method which ranged between 1.5 and 2.7 ng L^{-1} and between 4.7 and 8.4 ng L^{-1} respectively.

The proposed method provides good analytical features with LODs comparable to other methods that use very sensitive techniques, such as SPME [27,32] or LLME [29,31], and presents a high selectivity.

Table 2
Main parameters of the method.

Analyte	IDLs (µg L^{-1})	IQLs (µg L^{-1})	Enrichment factor	LOD (ng L^{-1})	LOQ (ng L^{-1})
MA	2.1	7.0	808	2.6	8.2
MX	1.7	5.6	637	2.7	8.4
MM	1.3	4.2	580	2.2	7.0
MT	1.1	3.6	599	1.8	5.8
MK	1.2	4.1	827	1.5	4.7

3.3. Evaluation of the repeatability of the synthesis

To confirm the potential of the MIS for the selective extraction of the nitro musks, a second synthesis was carried out at a different time, by another manipulator and evaluated applying the previously optimized procedure. Fig. 4 presents the comparison of the average extraction recoveries obtained after three extractions carried out on each MIS and each NIS. These results show again the high selectivity of each synthesized MIS. The repeatability of the extraction procedure on a given MIS and NIS was also observed with RSD values lower than 6%. Finally, recoveries obtained on MISs resulting from different syntheses are very close, thus confirming that the imprinted sorbents present similar performances. Additional syntheses will be required to confirm the real reproducibility of the MIS synthesis but these first results confirm the selectivity of the MIS for the nitro musks.

3.4. Evaluation of the capacity

The proposed method was applied to a 95/5 water/MeOH (v/v) standard mixture containing increasing amounts of the five nitro musk compounds. This test is usually used for the MIS capacity study, which is the maximum amount of nitro musk that can be selectively retained by the sorbent. Previous studies [47] already showed that this MIS presented a very high capacity that was not possible to reach due to the limit of solubility in water of the 2,4-DNT. The objective in this work was to verify that the extraction recoveries kept constant at the working range i.e. mass range between the limit of quantification to a higher concentration than that found in real samples in the bibliography for the nitro musks. Table 3 shows the curves and regression coefficient obtained. The linearity obtained for the calibration curves shows the possibility to quantify the nitro musks after the extraction on the MIS in the mass range tested. The slopes obtained for each curve, ranged between 0.61 and 0.89, confirm the average extraction recoveries ranged between 61% and 87% for the MIS. The selectivity of the extraction procedure is again demonstrated by the average extraction recoveries between 11% and 27% on NIS.

3.5. Application for real water samples

The selective extraction procedure on MIS was applied to three real samples of different sources: sea water, river water and effluent water from a treatment plant (see Section 2.1), in order to determine the five nitro musk compounds.

The water samples were first analyzed applying the optimized extraction procedure before the analysis by GC–MS. The results showed that all of the target compounds were below the limits of detection. Then, recovery studies were performed with the purpose to evaluate the matrix effect. So, the proposed method was applied to the above-mentioned real samples, previously spiked with 100 ng L^{-1} of the target compounds using the MIS.

In order to compare the results obtained using the MIS with an extraction using a conventional sorbent, an extraction procedure was developed using an Oasis HLB sorbent. The extraction recoveries

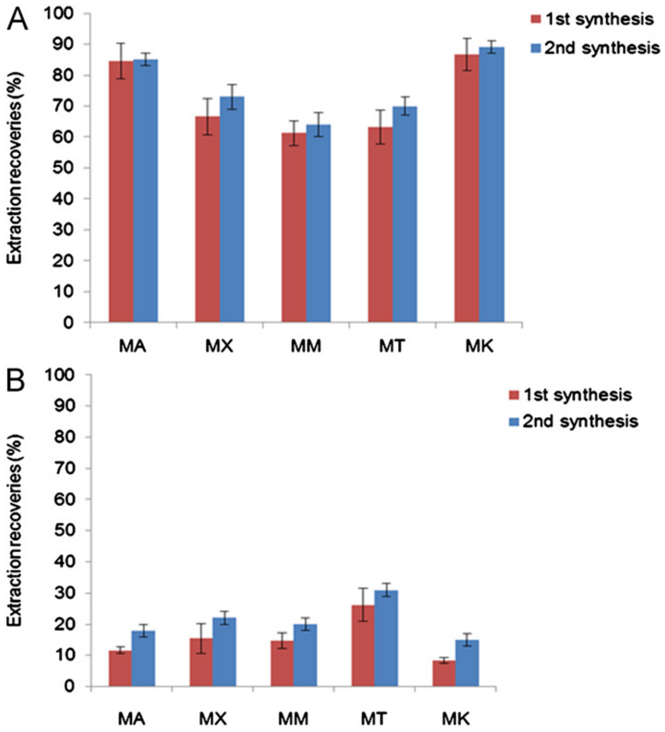


Fig. 4. Extraction recoveries obtained after the application of the optimized procedure to two different syntheses on (A) MIS and (B) NIS ($n=3$).

Table 3
Calibration curves and regression coefficient obtained after the percolation of 200 mL of a water/MeOH mixture (95/5, v/v) containing increasing amounts of the five nitro musks on the MIS and the NIS.

Analyte	MIS		NIS	
	Calibration curve	Regression coefficient	Calibration curve	Regression coefficient
MA	$y=0.8303x-0.0251$	1.0000	$y=0.1819x-1.9978$	0.9984
MX	$y=0.6124x+4{,}052$	0.9980	$y=0.2198x-1.5167$	0.9871
MM	$y=0.6414x-1.1348$	0.9997	$y=0.1915x-0.4496$	0.9986
MT	$y=0.6129x+2.7467$	0.9986	$y=0.2793x+0.3796$	0.9997
MK	$y=0.8881x-2.7873$	0.9995	$y=0.1104x-0.8206$	0.9907

This data is extracted from a calibration curve where the percolated amount (in ng) and the amount obtained (in ng) after the application of the method was plotted. Number of calibration points: 6 (4, 10, 50, 100, 300, and 800 ng).

obtained after applying, in triplicate, the percolation of a water/MeOH (95/5, v/v) standard solution containing 500 ng L^{-1} of the five nitro musks followed by a washing step with 1 mL of water/MeOH (80/20, v/v) and an elution with 1 mL of ACN, using Oasis HLB sorbents were 93 ± 4%, 75 ± 6%, 72 ± 5%, 69 ± 2% and 105 ± 9% for MA, MX, MM, MT and MK respectively. These extraction recoveries obtained for pure water with the Oasis HLB sorbent are very close to those obtained with the MIS.

Finally, recovery studies for the real samples using the Oasis HLB sorbent and the method developed were also carried out. The recoveries obtained are shown in Table 4 for the MIS and Oasis HLB. First, similar extraction recoveries are obtained using the MIS for the extraction of the nitro musks in pure water and in the real samples. However, the extraction recoveries obtained after the extraction of the nitro musks in the real samples using the Oasis HLB sorbent are very different from those obtained in pure water, especially in the case of sea water and wastewater, where most of the recoveries are lower than 50%. From these results it can be concluded that the imprinted sorbent does not present significant matrix effects while in the case of the conventional sorbent, there are matrix effects resulting in a large decrease of the extraction recoveries.

Table 4
Extraction recoveries (%) obtained in the analysis of three water samples ($n=3$) (spiking level 100 ng L^{-1}).

	Standard		River water		Sea water		Wastewater	
	MIS	OASIS	MIS	OASIS	MIS	OASIS	MIS	OASIS
MA	85 ± 6	93 ± 4	77 ± 4	76 ± 3	77 ± 5	40 ± 5	69 ± 3	47 ± 7
MX	67 ± 6	75 ± 6	68 ± 5	56 ± 2	63 ± 1	32 ± 2	59 ± 3	25 ± 1
MM	61 ± 4	72 ± 5	63 ± 1	55 ± 2	57 ± 3	30 ± 1	52 ± 1	27 ± 3
MT	63 ± 6	69 ± 2	64 ± 1	63 ± 3	57 ± 3	32 ± 1	55 ± 6	31 ± 3
MK	87 ± 5	105 ± 9	92 ± 2	116 ± 5	87 ± 2	76 ± 3	87 ± 3	92 ± 8

Finally, data show that in most of the cases the recovery values for real samples are better for the imprinted sorbent than for the conventional sorbent. So, the MIS presents a higher retention of the nitro musks than the Oasis HLB for real samples. Moreover, the extraction recoveries are similar for all the tested matrices using the MIS showing the repeatability of the procedure on complex samples.

As previously mentioned, these shows that molecularly imprinted sorbents, with a retention mechanism based on molecular recognition, enable a better clean-up of the sample than conventional sorbents, in which the co-extraction of interfering compounds can interfere in the subsequent determination.

4. Conclusions

A high sensitive analytical method, with great clean-up potential, is presented in this paper in order to determine the complete family of nitro musk compounds in environmental water samples. To the best of our knowledge this is the first time an imprinted sorbent is used to selectively extract the nitro musk compounds.

The selective extraction of the target compounds from real samples by the MIS easily succeeded. A high degree of selectivity was obtained allowing a good quantification of the nitro musks after the MIS extraction compared to a conventional sorbent.

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