Determination of nitrophenols in environmental samples using stir bar sorptive extraction coupled to thermal desorption gas chromatography-mass spectrometry

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ABSTRACT

This paper presents a procedure for the determination of seven nitrophenols (NPs) in water and soil samples using stir bar sorptive extraction (SBSE) coupled to gas chromatography with mass spectrometry (GC-MS) by means of a thermal desorption unit (TDU). Microwave assisted extraction (MAE) is proposed to release the NPs from the soil matrices into an aqueous phase, prior to their acetylation. The different variables affecting the preconcentration efficiency of SBSE, during both the adsorption and the thermal desorption steps, are studied. As regards the analytical characteristics of the method, the accuracy was measured through recovery studies, recovery percentages in all cases being in the 79-120% range, as well as by analyzing a certified reference material. The precision was evaluated in terms of relative standard deviation, which provided values lower than 15% for both repeatability and reproducibility. The limits of detection were between 0.001 and 0.031 μg L^{-1} for water and 0.020-0.107 ng g^{-1} for soil samples. When environmental samples of different origins were analyzed, contents in the 0.01-1.0 μg L^{-1} and 0.7-40 ng g^{-1} ranges were obtained for waters and soils, respectively.

Keywords:

Nitrophenols

Soils

Waters

Stir bar sorptive extraction

Thermal desorption

Gas chromatography-mass spectrometry

1. Introduction

Nitrophenols (NPs) are organic compounds whose presence in the environment may have different potential sources. Their aromatic structures consist of a benzene ring with hydroxyl and nitro groups, including mono-, poly-, halo-, methyl- and amino-nitrophenols [1]. None of these compounds appears naturally in the environment, but are used in the manufacture of paints, adhesives, explosives, pesticides and pharmaceutical products [2]. Thus, NPs have been found in the environment in increasing quantities due to the wastes from different industrial, agricultural and medical activities, among others [1]. In agriculture they can be generated by the hydrolysis of some pesticides, in the form of alkyl- or cycloalkyl- NPs, such as dinoseb, 4,6-dinitro-o-cresol or parathion. NPs have been detected in air due to diesel engine emissions. However, the highest concentrations have been found in waters and soils, where microorganisms produce slow degradation processes [3]. Different methyl-NPs may also be found in the environment as degradation products of pesticides, or be generated in atmospheric pollution processes

NPs are toxic compounds, whose adverse effects in humans include irritation of the eyes, skin and respiratory tract. Exposure to them may occur as a result of contaminated air, through direct contact, or by the intake of water or contaminated food [1,3]. Pollution from NPs seems to be particularly serious close to explosive factories and military plants, while, the concentrations detected in crop fields treated with fungicides or areas near waste disposal plants are lower.

NPs have previously been analyzed in air and atmospheric particles [4–7], waters [8–30] and soils [3,18,27,31–35], applying different analytical techniques, including liquid chromatography (LC) with mass spectrometry (MS) [36] and diode array detection (DAD) [20,23,24,27–31], gas chromatography (GC) with detection by MS [3,11,13,16,18,19] and capillary electrophoresis (CE) coupled to MS [7].

Taking into account the low levels of NPs generally found in waters, as well as the need to include a cleaning step in the analytical procedure for some samples, solid phase extraction (SPE) [8,14,16,19] has also been applied. In recent years, classical preconcentration techniques have gradually been replaced by microextraction techniques, which are simpler, cleaner and faster than conventional techniques, requiring less consumption of organic solvents. The determination of NPs in water samples has been carried out using liquid phase microextraction (LPME) based on single-drop microextraction (SDME) [11], ultrasonic assisted emulsification microextraction (USAEME) [17], hollow fiber liquid phase microextraction (HF-LPME) [18], HF liquid-liquid-liquid microextraction (HF-LLLME) assisted by membranes [9], and dispersive liquid-liquid microextraction (DLLME) applied in conventional mode [21] and in-syringe (ISDLLME) [20]. The miniaturized extraction techniques in solid phase applied to the analysis of NPs in water are solid phase microextraction (SPME) [10,13,15,22,28], stir bar sorptive extraction (SBSE) [12,24,27,29,30] and stir cake sorptive extraction (SCSE) [23].

For soil analysis, it is necessary to include a previous extraction stage by Soxhlet extraction [33], QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe) [35], ultrasonic assisted extraction (UAE) [3,27,31,32,34] and

microwave assisted extraction (MAE) [18,33]. However, MAE is only applicable to thermally stable compounds, due to the increase of temperature during the process, and it is necessary the use polar solvents, such as water to absorb the microwave energy. The effectiveness of microwave energy for the extraction of organic contaminants from environmental samples has been demonstrated [37]. The isolation of NPs from soil matrices has been tackled using different extractant solvents, such as water [19], methanol [3], acidic methanol [28, 29], methanol containing triethylamine [30], and acidic acetonitrile [33]. The extract obtained from the soil sample is subjected to cleaning and/or preconcentration steps, such as LLE [31], SPE [32–34], SBSE using home-made synthesized coating [27] different LPME techniques such as HF-LPME [18] and DLLME [3].

In this paper, an analytical procedure based on SBSE coupled to GC-MS by means of a thermal desorption unit (TDU) is proposed for the determination of three NPs, three methyl-NPs and 4-fluoro-2-nitrophenol in water and soil samples. Considering the proven advantages of microwave energy for the extraction of organic compounds from different environmental samples [37], MAE is applied in the soil treatment. The novelty of the present work is the coupling for the first time of SBSE with GC-MS using thermal desorption for the determination of NPs, as previous studies based on SBSE have used liquid desorption [13] or LC-UV [25,27,29,30].

2. Materials and methods

2.1. Chemicals and reagents

2-Nitrophenol (2-NP, 98%), 3-nitrophenol (3-NP, 99%), 4-nitrophenol (4-NP), 5-methyl-2-nitrophenol (5-M-2-NP, 97%), 2-methyl-4-nitrophenol (2-M-4-NP, 97%), 4-fluoro-2-nitrophenol (4-F-2-NP, 99%) and 4-hexylphenol (HP, internal standard) were obtained from Sigma-Aldrich (St. Louis, MO, USA). Standard solutions of 1000 μg mL^{-1} were prepared in methanol, and stored at -18 °C in glass vials provided with stoppers with a PTFE/silicone septum. Microfiltered water obtained by a Milli-Q purification system (Millipore, Bedford, MA, USA) was used. The derivatizing agent employed was acetic anhydride (AA, Fluka, Buchs, Switzerland, >99%). To adjust the pH of the derivatization medium, dipotassium hydrogen phosphate (Fluka) was used. Other reagents were sodium chloride (Sigma) and methanol (Lab-Scan, Dublin, Ireland). As carrier gas in the chromatographic system, high purity helium, supplied by Air Liquide (Madrid, Spain), was used.

2.2. Instrumentation

Commercial stir bars (Twisters®) coated with a 0.5 mm-thick layer of polydimethylsiloxane (PDMS, 24 μL), obtained from Gerstel (Mulheim an der Ruhr, Germany), were conditioned prior to their first use in an empty TD tube at 275 ºC for 0.5 h with helium at a flow-rate of 50 mL min^{-1}. A magnetic stirrer (IKA RH KT/C, Supelco, Bellefonte, USA) working at 900 rpm was used in the SBSE extraction step.

The sample introduction system consisted of a thermal desorption unit (TDU-2) equipped with a multipurpose autosampler (MPS) and a programmed temperature vaporization (PTV) cooled injector system (CIS-4) provided by

Gerstel. The TDU was initially operated in solvent vent mode, maintaining a temperature of 50 ºC for 0.2 min. Next, a temperature ramp of 60 ºC min^{-1} was programmed up to 280 ºC, this temperature being held for 3 min. A helium vent flow of 50 mL min^{-1} was applied in the sample introduction system. The PTV-CIS, equipped with a liner packed with silanized glass wool (Gerstel), was cooled to 15 ºC by a Peltier unit while the analytes were desorbed from the stir bar in the TDU. The PTV-CIS temperature programme was as follows: start at 15 ºC, increase to 240 ºC at 12 ºC s^{-1} and hold for 4 min.

The TDU unit was installed in a 6890N gas chromatograph (Agilent, Waldbronn, Germany) coupled to a quadrupole mass selective spectrometer (Agilent 5973) equipped with an inert ion source. An HP-5MS (5% diphenyl–95% dimethylpolysiloxane, Agilent) capillary column (30 m × 0.25 mm I.D., 0.25 µm film thickness) was used with a constant helium flow-rate of 1 mL min^{-1}. The GC temperature programme was: start temperature of 80 ºC hold for 0.5 min, increase to 150 ºC at 10 ºC min^{-1} and maintain for 1 min; next, the temperature of 165 ºC is reached at 5 ºC min^{-1} and finally increased to 250 ºC at 50 ºC min^{-1}, and held for 1 min. The compounds were eluted with retention times of between 7.7 and 12.63 min for 4-F-2-NP and 4-HP, respectively. The total analysis time for a GC run was 14.2 min. The retention time and the monitored ions for each compound are shown in Table 1. The temperatures of the transfer line, ion source and quadrupole were 300, 230 and 150 ºC, respectively. The mass spectrometer was operated using electron-impact (EI) mode (70 eV). The electron multiplier voltage was set automatically. The compounds were quantified in the selected ion monitoring (SIM) mode in order to improve the limits of detection (Table 1). Identification was confirmed by injection of pure

standards and comparison of the retention time and scan mass-spectra for each compound.

A Perkin Elmer microwave digester model-3000 (Massachusetts, USA), with a maximum output of 1400 W provided by two 2455 MHz magnetrons, was used. PTFE microwave sample vessels of 100 mL capacity were used.

2.3. Samples and analytical procedures

Water samples: A total of eight freshwater samples (tap water, ornamental fountain, wastewater treatment plant prior to any secondary treatment, river water, irrigation water, snow and two leaching waters), obtained from south-eastern Spain, were analyzed. Insoluble particles were removed by filtration through 0.24 μm Nylon filters (Agilent). A 10 mL-aliquot of sample was placed in a 15-mL glass vial and 25 μL of a 1 μg mL^{-1} 4-HP solution, 0.3 g of K_2HPO_4 and 75 μL of AA were added. An SBSE stir bar was then incorporated and the mixture stirred at room temperature for 4 h until extraction equilibrium was reached. Finally, the stir bar was withdrawn with the help of a magnet and dried with paper before inserting into the desorption tube, where the analytes were thermally desorbed by applying the temperature programme indicated in the previous section.

Soil samples: Five soil samples were obtained from agricultural areas in south-eastern Spain. Soils were collected from the top 20 cm, air-dried overnight at room temperature, manually ground and sifted through a 2-mm sieve. Table 1S shows the characterization of the agricultural soils studied. All samples were stored in a cool and dry place until analysis. The MAE step was

carried out by adding 10 mL of ultrapure water and 50 µL of a 1 µg mL^{-1} 4-HP solution to 3 g of soil previously placed in a PTFE microwave digestion vessel. Once hermetically closed, the vessels were submitted to a programme consisting of a power increase from 0 to 200 W in 1 min and held for 15 min. A volume of 8.5 mL of the resulting solution was collected and made up to 10 mL with water in a calibrated flask. The derivatization reaction was carried out by adding 0.3 g of K_2HPO_4 and 75 µL of AA. Finally, the mixture was filtered through 0.24 µm Nylon filters and the SBSE stir bar was introduced in the glass vial and stirred for 4 h. The SBSE desorption step was applied as previously described for water analysis. Sample analysis was carried out in triplicate.

Matrix-matched calibration was applied for the analysis of soil samples. The preparation of these matrix-matched calibration specimens was carried out by adding volumes of 0, 5, 10, 25, 50, 75 and 100 µL of a 3 µg mL^{-1} solution of a standard mixture to 3 g of the soil sample.

A soil certified reference material, CRM143 (BNAs - Sandy Loam 1), obtained from Sigma-Aldrich, was used for method validation purposes, by submitting a 10 mg sample to analysis in triplicate by MAE and SBSE-TDU-GC-MS. Method validation was completed by means of recovery studies. For this, 3 g of soil were fortified at two concentration levels (8 and 33 ng g^{-1}). Aliquots of 10 mL of two water samples (irrigation and river waters) were also fortified at two concentration levels (0.5 and 2.5 ng mL^{-1}). The samples were homogenized and kept for 1 h to attain a homogeneous distribution of the analytes and to allow their interaction with the sample matrix. Each analysis was performed in duplicate.

3. Results and discussion

3.1. Treatment of soil samples

The application of external energy accelerates analyte transfer from solid to liquid phase, providing adequate recoveries in short times. MAE is here applied for extraction purposes. Taking into account the limited compatibility of organic solvents with PDMS stir bar coatings, preliminary experiments were carried out by submitting 3 g of a fortified soil at 40 ng g^{-1} level, to the microwave effects in the presence of 10 mL of aqueous extractant phase. Acid medium provided by 0.025 and 0.05 M hydrochloric acid, alkaline medium provided by 0.025 and 0.05 M sodium hydroxide, as well as pure water, were assayed as extractant phases. Even though no significant differences were observed between the extractants used, the highest sensitivity for most compounds was attained with water, which was therefore selected.

The soil mass was optimized with a fortified sample at 40 ng g^{-1} between 0.5 and 5 g. Above 3 g sample mass the matrix effect was severe and so this amount was selected.

3.2. Optimization of derivatization reaction

The benefits of reducing the acid character of the target compounds in terms of chromatographic behavior and extraction into extractant solvents of low polarity have been described previously. The determination of the analytes as acyl derivatives was considered in this work, taking into account the

demonstrated advantages of *in-situ* acetylation related to other derivatization reactions, such as high chemical reaction speed, high efficiency and the possibility of application in aqueous medium [3]. Thus, AA was selected to reduce the polarity of the analytes and therefore, improve the affinity of the analytes for non-polar coating extractant phases.

The AA volume and the K_2HPO_4 mass, derivatization parameters which have a related influence, were studied by means of a Taguchi design at 3 levels (9 experiments) using 10 mL aqueous solutions containing 20 ng mL^{-1} of each analyte. Derivatization reagent volume was studied at 75, 150 and 200 µL and K_2HPO_4 mass at 150, 300 and 500 mg. The best responses were obtained when 75 µL of AA and 300 mg of K_2HPO_4 were used.

3.3. Optimization of the SBSE adsorption step

Preliminary experiments were carried out using both a 10 mL-volume of a 20 ng mL^{-1} standard solution NPs and a soil extract, and similar trends were observed in both cases. The non-polar PDMS stir bar coating was selected due to its greater robustness compared with that provided by polar coatings such as ethylene glycol and polyacrylate, and its higher extraction efficiency for acetylated NPs.

The ionic strength was studied by adding sodium chloride concentrations of 0, 1, 2.5 and 5% (w/v). The presence of salt up to 2.5% (w/v) slightly affected the solubility of most of the analytes in the aqueous solution, while their partition coefficients to the PDMS phase were practically constant. For salt concentrations above this value, the extraction efficiency decreased probably as

a result of the increase in the medium viscosity, which makes the diffusion more difficult. Therefore, the addition of NaCl to the aqueous phase was discarded.

The most important parameter affecting SBSE is extraction time. Considering the direct relation of this variable with temperature, both parameters were studied using a Taguchi design at four levels (16 experiments). The time was studied at 0.5, 1, 2 and 4 h and the adsorption temperature at 25, 30, 40 and 50 ºC. No significant effect was observed for temperature, so extraction of the analytes at room temperature was adopted. However, the analytical signals increased over all the time range studied. When higher time values were assayed, the results obtained showed that the extraction equilibrium was reached at 4 h, and so this value was selected.

The presence of organic modifiers can avoid the retention of some analytes on the inner glass walls of the vials during the extraction step, and so has a positive effect on SBSE extraction efficiency [38]. Generally, this effect is higher for analytes with log $K_{o/w}$ values greater than 5, and negligible for compounds with log $K_{o/w}$<2.5, which has been attributed to an increase in their solubility in the sample solution. Considering that log $K_{o/w}$ for the underivatized NPs studied are in the 1.61-2.12 range, and that these values increase for the corresponding acyl derivatives, the influence of methanol percentage was studied from 0 to 5% (v/v). The results obtained showed that for most NPs, the presence of this solvent did not improve their extraction into the PDMS phase. Consequently, the addition of methanol was discarded.

3.4. Optimization of the SBSE desorption step

The effect of the different variables involved in the thermal desorption stage was studied using the Taguchi method (5 variables at 3 levels): TDU desorption temperature (220, 250, 280 °C), TDU desorption time (3, 5, 10 min), desorption flow-rate (50, 80, 120 mL min^{-1}), CIS final temperature (220, 240, 260 °C) and CIS time (2, 4, 6 min). The best results were obtained by applying a TDU desorption temperature of 280 °C maintained for 3 min (Fig. 1S, Supplementary material). A carrier gas is required to propel the analytes to the PTV injector while they are being thermally desorbed in the TDU. A helium gas flow-rate of 50 mL min^{-1} provided the highest sensitivity. Desorbed compounds were focused in the CIS before entering the chromatographic column. The retention efficiency of the analytes in the CIS depends on the temperature and the nature of the adsorption liner used to retain the analytes while being desorbed from the TDU. As expected, best responses were reached with low temperatures, which minimized the losses of the most volatile analytes. The Peltier unit only allowed cooling to temperatures slightly below 20 ºC, and so 15 ºC was selected. Different adsorbents such as silanized glass wool, PDMS and quartz wool were tested, the best results being found when liners containing silanized glass wool were used. As regards PTV maximum temperature, maximum sensitivity was attained at 240 ºC maintained for 4 min (Fig. 1S). Therefore, a PTV programme temperature increasing from 15 to 240 ºC (12 ºC s^{-1}), with a hold time of 4 min, was applied.

3.5. Analytical characteristics of the method

The optimized SBSE-TD-GC-MS method was validated for linearity, limits of detection (LODs), selectivity, recovery, precision and accuracy. For samples quantification, 4-hexylphenol (4-HP) was used as internal standard, minimizing the possible uncertainty associated with analyte losses or possible matrix effects. The 4-HP showed similar chromatographic and SBSE preconcentration behavior to that of the studied NPs. The absence of this compound in all the studied samples was previously checked.

Calibration curves were obtained using standard solutions prepared at six concentration levels ranging from 0.05 to 30 ng mL^{-1} (with the IS at 2.5 ng mL^{-1}) for water samples, and 0.5-100 ng g^{-1} (with the IS at 15 ng g^{-1}) for soil samples, by least-squares linear regression analysis of the peak area ratios with respect to IS *versus* analyte concentration.

The standard additions method was applied to five water (leaching water, tap water, irrigation water, river water and snow) and the five soil samples in order to check the possible chemical dependencies between the sample matrix and the compounds of interest. The comparison of the slopes obtained using aqueous standards and those obtained by standard additions to water samples using a t-test (at the 95% confidence level), provided “p” values higher than 0.05 in all cases. Therefore, quantification of the waters was carried out against aqueous standards. However, significant differences between the slopes obtained with aqueous standards and that provided by standard additions to soil samples were observed, the “p” values lower than 0.05 indicating the presence of a matrix effect. Therefore, the standard additions method was used to quantify the soil samples.

The sensitivity of the method was evaluated through the values of LODs, which were calculated on the basis of a signal-to-noise ratio of three. LODs for waters ranged from 0.001 to 0.031 μg L^{-1}, corresponding to 4-M-2-NP and 3-NP, respectively (Table 2). For soils, LOD values were between 0.020 and 0.107 ng g^{-1}, corresponding to 4-M-2-NP and 2-NP, respectively (Table 2). Note that LOD values provided for soil samples were calculated as the mean value for each compound in the different soils studied.

Table 3 shows a comparison of the proposed method with other previously published for the analysis of water samples using miniaturized preconcentration procedures based on microextraction into solid phase. It is noteworthy that the developed method provides the highest sensitivity. A comparison of different features of the proposed method with others found in the literature for soil analysis appear in Table 4. Newly, different advantages can be observed for the here developed method related to sample and organic solvents consumptions, as well as sensitivity.

To evaluate the precision of the method, the tap water sample and a soil fortified at 2.5 ng mL^{-1} and 16.7 ng g^{-1}, respectively, were submitted to 10 consecutive analyses, obtaining the average relative standard deviation (RSD). Thus, RSD values in the 6.1-10.7% and 6.9-11.4% ranges were obtained for water and soil, respectively, corresponding in both cases to 4-F-2-NP and 4-NP. For reproducibility (evaluated through 10 analyses carried out in different days) RSD between 8.9 and 12.9% for 4-F-2-NP and 2-NP, respectively, were obtained for waters; and between 9.4 and 14.5% for 4-F-2-NP and 5-M-2-NP, respectively, for soils.

The accuracy of the method was checked by analyzing a reference material (CRM) whose 2-NP and 4-NP contents were certified by the manufacturer. CRM143 (BNAs - Sandy Loam 1) was used, with a certified content of 2-NP (6860±618 ng g^{-1}) and 4-NP (6800±889 ng g^{-1}), for the validation of the developed method for use with soils. Considering the high certified contents, only 10 mg of CRM were used in order to obtain extracts within the linear range of the optimized method. The contents found were 7343±942 ng g^{-1} for 2-NP and 5782±867 ng g^{-1} for 4-NP. The application of a comparison t-test at the 95% confidence level showed “p” values of 0.29 and 0.82 for 2-NP and 4-NP, respectively. Therefore, there were no significant differences between the reported and measured contents. When 3 g of CRM were submitted to the MAE step and next, the aqueous extract had to be appropriately diluted before being submitted to the procedure due to the high NPs concentration, and similar results were obtained. For the rest of the NPs, recovery studies in two soil samples at two concentration levels (8 and 33 ng g^{-1}) were carried out. The recovery values obtained were in the 85-116 and 79-88% ranges for 8 and 33 ng g^{-1}, respectively.

For water samples, the accuracy test was only performed using recovery studies with a water fortified at two concentration levels. The recovery values obtained were in the 80-120 and 89-120% ranges for 0.5 and 2.5 ng mL^{-1}, respectively.

The selectivity of the method was corroborated by the absence of interfering compounds eluting at the retention times of the analytes.

3.6. Analysis of samples

The optimized SBSE-TD-GC-MS method was applied to the analysis of eight freshwater samples in triplicate. Water samples collected from an ornamental fountain, tap water and snow did not contain the NPs under study, at least above their corresponding LODs. The results obtained for the rest of the waters are shown in Table 5. Neither 4-F-2-NP nor 2-M-4-NP was detected in any of the samples, while 4-M-2-NP and 5-M-2-NP were found in several samples. The contents found are in accordance with those previously reported by other authors [11,13-15,18,19,22,23,28,29]. The results found in the analysis of the soil samples are also shown in Table 5. Since these compounds may appear in the environment as degradation products of certain pesticides, it is not surprising that they were detected in the agricultural soils studied. 2-NP and 4-NP were detected in all the samples, while 3-NP was only found in one soil sample. Note the agreement between the found contents and other previously reported [3,18,27,31].

Figure 1 shows the chromatograms obtained for a water and a soil fortified at concentration levels of 10 ng mL^{-1} and 33 ng g^{-1}, respectively, using SIM mode. The NPs were identified by comparing the retention time with a 1% tolerance, identifying the target and qualifier ions, as well as the abundance relationships between the different qualifier ions in the mass spectra, considering 20% of variability, between samples and standard solutions.

4. Conclusion

SBSE is shown to be a good choice for the preconcentration of NPs from water and soil samples, complying with the principles of green analytical

chemistry as no organic solvents are used. The coupling with GC-MS carried out by thermal desorption permitted maximum transfer efficiency.

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Legend for the figure

Fig. 1. Elution profile obtained with the optimized SBSE-TD-GC-MS procedure under SIM mode for a fortified water at 10 ng mL^{-1} **(A)** and a fortified soil at 33 ng g^{-1} **(B)** for each analyte.

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Table 1

Characteristics of the NPs and the procedure.

Compound	Molecular formula	Molecular weight	log $K_{o/w}$	t_R, min	Monitorized ions[a] *(m/z)*
4-F-2-NP	$C_6H_4FNO_3$	157.1	1.75	7.70	<u>43</u>,157 (35),82 (26)
2-NP	$C_6H_5NO_3$	139.1	1.61	8.65	<u>43</u>, 139 (46), 63 (35)
3-NP	$C_6H_5NO_3$	139.1	1.61	9.62	<u>43</u>, 63 (32), 139 (22)
4-NP	$C_6H_5NO_3$	139.1	1.61	9.95	<u>43</u>, 63 (32), 139 (28)
4-M-2-NP	$C_7H_7NO_3$	153.1	2.12	10.55	<u>43</u>, 153 (53), 77 (38)
5-M-2-NP	$C_7H_7NO_3$	153.1	2.12	10.72	<u>43</u>, 153 (81), 77 (42)
2-M-4-NP	$C_7H_7NO_3$	153.1	2.12	11.46	<u>43</u>, 153 (78), 77 (36)
4-HP	$C_{12}H_{18}O$	178.3	-	12.63	<u>107</u>, 178

[a] Underlined values correspond to the target ion and values into brackets represent the abundance in percentage of each secondary ion respect the target ion.

Table 2

Analytical characteristics of the proposed SBSE-TD-GC-MS method

	Waters			Soils		
Compound	LOD[a] (μg L^{-1})	RSD[b] (%)	RSD[c] (%)	LOD[a] (ng g^{-1})	RSD[b] (%)	RSD[c] (%)
4-F-2-NP	0.026	6.1	8.9	0.095	6.9	9.4
2-NP	0.026	9.5	12.9	0.107	8.8	10.5
3-NP	0.031	9.1	11.0	0.098	9.3	11.7
4-NP	0.013	10.7	10.0	0.080	11.4	14.2
4-M-2-NP	0.001	7.3	12.2	0.020	7.6	14.4
5-M-2-NP	0.002	8.8	10.8	0.034	9.0	14.5
2-M-4-NP	0.012	9.8	12.2	0.070	9.9	13.7

[a] Calculated for a signal-to-noise ratio of 3. [b] Intraday (n=10). [c] Interday (n=10).

Table 3

Comparison with other methods proposed for NPs analysis in water samples using preconcentration steps based on microextraction on solid phase.

Sample volume (mL)	Preconcentration methodology			Detection system	LOD (μg L^{-1})	Ref.
	Name	Time (min)	Organic solvent consumption (mL)			
3.5	SPME-LD	32	Not given	LC-UV-ED	UV: 0.4–4.1 ED: 0.03–15	[10]
20	SPME-LD	80	0.4	LC-DAD	0.075–0.27	[22]
4	SPME-LD	33	About 0.05	LC-UV	0.25–0.67	[28]
2	SPME-TD	45	0	GC-MS	0.2–99.3	[13, 15]
100	SCSE-LD	180	3	LC-DAD	0.097–0.28	[23]
10	SBSE-LD	75	0.05	LC-UV	0.08–0.17	[24]
50	SBSE-LD	240	3	LC-DAD	0.87–1.5	[29, 30]
10	SBSE-LD	55	0.1	LC-UV	0.14–1.18	[27]
15	SBSE-LD	270	0.2	GC-MS	0.044	[12]
10	SBSE-TD	240	0	GC-MS	0.001–0.031	This work

ED, electrochemical detector; TD, thermal desorption; LD, liquid desorption.

Table 4

Comparison with other methods proposed for NPs analysis in soil samples.

Sample mass (g)	Extraction step: mode and time	Preconcentration step: mode, organic solvent consumption and time	Detection system	LOD (ng g^{-1})	Ref.
20-25	UAE, 30 min	LLE, 150 mL	LC-DAD	0.3	[31]
5	UAE, 30 min	SPE, 7 mL	GC-FID	200-1000	[32]
10	Soxhlet, 12 h	SPE, 17 mL	LC-APCI-MS	0.05-0.3	[33]
5	UAE, 30 min	On-line SPE, Not given	LC-UV	4	[34]
10	SLE, 60 min	QuEChERS, 0 mL, 7 min aprox.	GC-QqQ-MS/MS	1-50	[35]
1	MAE, 5 min	HF-LPME, 25 μL, 40 min	GC-MS	2-4	[18]
1	UAE, 20 s	DLLME-LVI, 300 μL, 2 min	GC-MS	0.4-0.8	[3]
0.5	UAE, 30 min	SBSE, 1.1 mL aprox., 55 min	LC-UV	14-118	[27]
3	MAE, 16 min	SBSE, 0 mL, 4 h	GC-MS	0.02-0.107	This work

APCI, atmospheric pressure chemical ionization; DAD, diode array detection; FID, flame ionization detection; LVI, large volume injection; QqQ, triple quadrupole; SLE, solid liquid extraction.

Table 5

Contents[a] found for NPs in waters (μg L^{-1}) and soils (ng g^{-1}).

Sample	4-F-2-NP	2-NP	3-NP	4-NP	4-M-2-NP	5-M-2-NP	2-M-4-NP
Leaching water 1	ND	0.23±0.03	0.10±0.01	ND	0.27±0.02	0.99±0.08	ND
Leaching water 2	ND	0.20±0.02	ND	ND	0.03±0.003	0.03±0.003	ND
Irrigation water	ND	ND	ND	0.17±0.01	0.22±0.02	0.02±0.003	ND
River water	ND	ND	ND	ND	0.04±0.005	0.04±0.004	ND
Wastewater	ND	ND	ND	ND	0.01±0.001	0.04±0.002	ND
Soil 1	1.0±0.1	40±2	ND	18±1	ND	ND	ND
Soil 2	1.3±0.1	3.1±0.3	ND	1.7±0.1	5.8±0.8	0.7±0.04	ND
Soil 3	ND	40±4	ND	7.2±1.1	16±1	4.7±0.4	17±2
Soil 4	ND	1.7±0.2	ND	20±1	3.8±0.1	1.6±0.3	8±1
Soil 5	ND	5.4±0.3	7.8±1.1	14±1	6.1±0.3	4.3±0.9	2.1±0.2

[a] Mean value ± standard deviation (n=3).

ND means not detected.

Figures

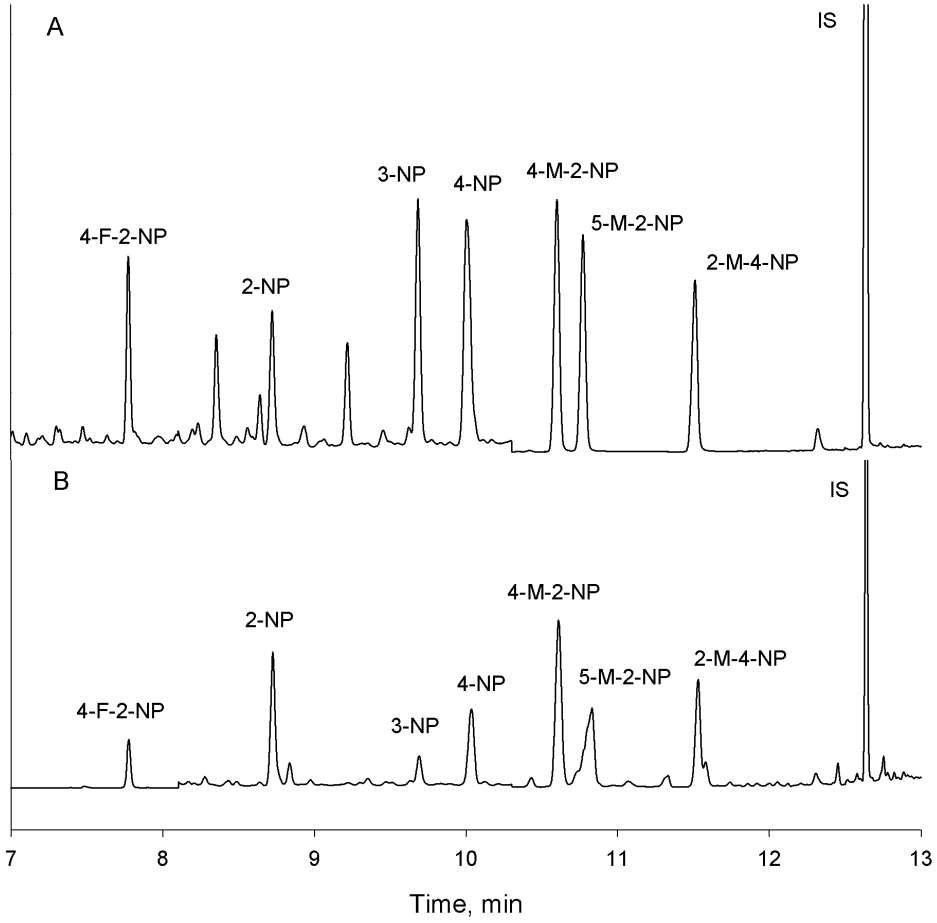

Figure 1.

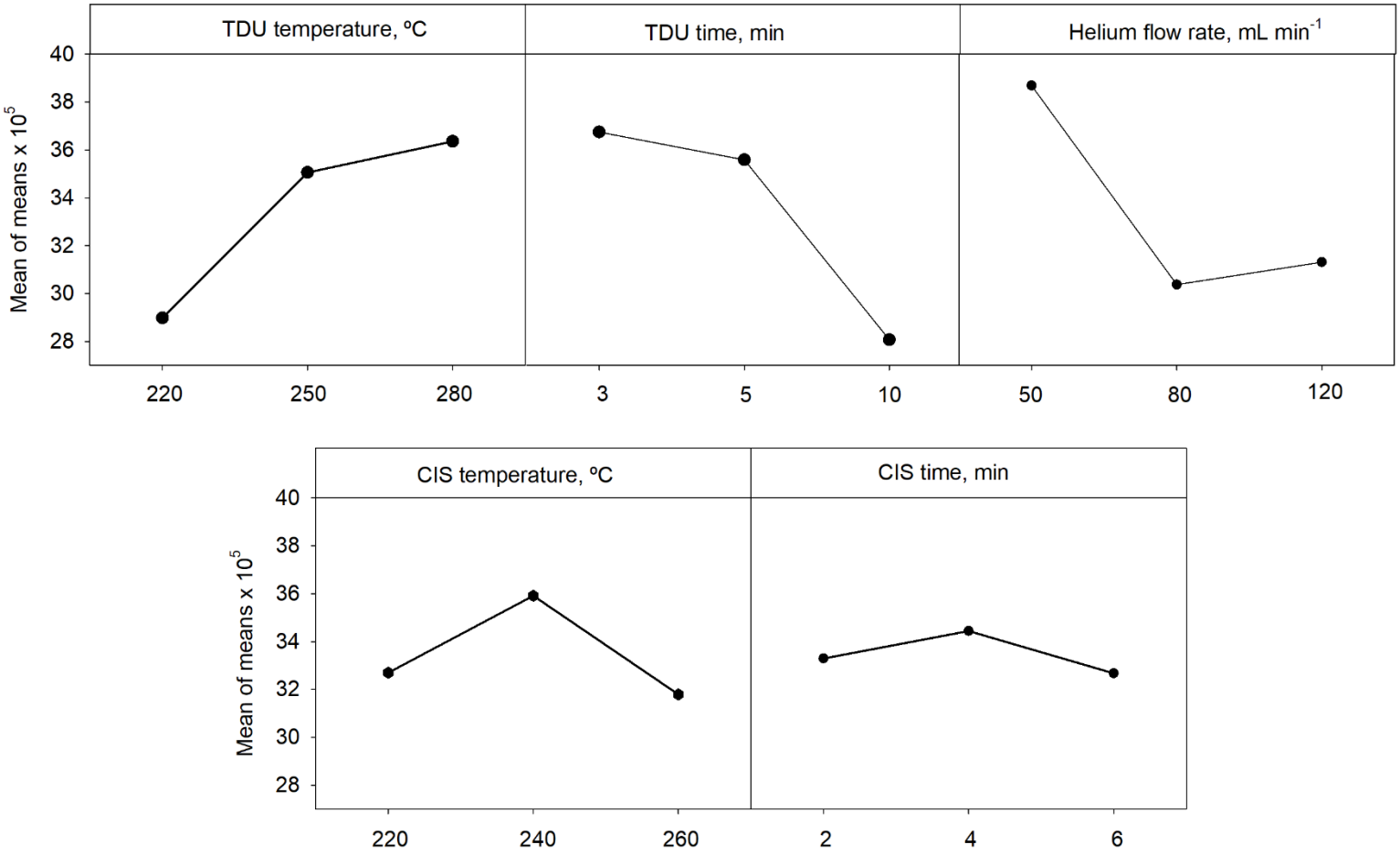
TDU temperature, ºC
TDU time, min
Helium flow rate, mL min-1
Mean of means x 10^5
40
38
36
34
32
30
28
220
250
280
3
5
10
50
80
120
CIS temperature, ºC
CIS time, min
Mean of means x 10^5
40
38
36
34
32
30
28
220
240
260
2
4
6

Figure 1S