Talanta 189 (2018) 543–549

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

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

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ARTICLE INFO

Keywords:
Nitrophenols
Soils
Waters
Stir bar sorptive extraction
Thermal desorption
Gas chromatography-mass spectrometry

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 $\mu g\ L^{-1}$ 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 $\mu g\ L^{-1}$ and 0.7–40 $ng\ g^{-1}$ ranges were obtained for waters and soils, respectively.

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

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https://doi.org/10.1016/j.talanta.2018.07.043
Received 11 May 2018; Received in revised form 9 July 2018; Accepted 11 July 2018

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] and 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 [12] or LC-UV [24,27,29,30].

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 °C 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 °C for 0.2 min. Next, a temperature ramp of 60 °C min^{-1} was programmed up to 280 °C, 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 °C 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 °C, increase to 240 °C at 12 °C s^{-1} and hold for 4 min.

The TDU unit was installed in a 6890 N 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 °C hold for 0.5 min, increase to 150 °C at 10 °C min^{-1} and maintain for 1 min; next, the temperature of 165 °C is reached at 5 °C min^{-1} and finally increased to 250 °C at 50 °C 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 °C, 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.

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	43,157 (35),82 (26)
2-NP	$C_6H_5NO_3$	139.1	1.61	8.65	43, 139 (46), 63 (35)
3-NP	$C_6H_5NO_3$	139.1	1.61	9.62	43, 63 (32), 139 (22)
4-NP	$C_6H_5NO_3$	139.1	1.61	9.95	43, 63 (32), 139 (28)
4-M-2-NP	$C_7H_7NO_3$	153.1	2.12	10.55	43, 153 (53), 77 (38)
5-M-2-NP	$C_7H_7NO_3$	153.1	2.12	10.72	43, 153 (81), 77 (42)
2-M-4-NP	$C_7H_7NO_3$	153.1	2.12	11.46	43, 153 (78), 77 (36)
4-HP	$C_{12}H_{18}O$	178.3	–	12.63	107, 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.