Programmed temperature vaporizer based method for the sensitive determination of trihalomethanes and benzene, toluene, ethylbenzene and xylenes in soils

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ABSTRACT

A methodology based on the coupling of a headspace autosampler with a GC and a MS detector operating in SIM mode has been developed for the determination of volatile organic compounds (THMs and BTEX) in soils. The GC device used is equipped with a programmable temperature vaporizer (PTV) packed with Tenax-TA® to introduce the samples (the injection mode used was solvent vent), and a modular accelerated column heater (MACH™) to control column temperature. The proposed measurement procedure reduces the sample pretreatment step to a minimum. Combined use of solvent vent injection mode and mass spectrometry detection allows a highly sensitive method to be proposed, with limits of detection of the order of ng/kg for all the target compounds. Furthermore, the capillary column used allows rapid separations of compounds in less than 4.60 min, affording a very short total analysis cycle time of 9 min.

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1. Introduction

Volatile organic compounds (VOCs) are widespread in the different environmental matrices. The soil is one of the more sensitive and vulnerable receptors for this type of compounds. Additionally, pollution agents in the soil can be readily transferred to the atmosphere and underground waters [1]. Many such compounds and their degradation products are either known or suspected of being toxic and carcinogenic, such that they pose a severe risk to human health and ecosystems.

These factors underscore the need for normative instruments that will ensure the protection of soils, establish their use, and fix the concentration levels for each of the VOCs above which a soil should be considered polluted. Accordingly, the development of analytical methods able to determine trace concentrations of VOCs in soils in a rapid, simple and reliable way is paramount.

This type of analysis has usually been performed by extraction of VOCs from soil and quantification by gas chromatography (GC), followed by mass spectrometry (MS), flame ionization detection (FID) and, in the case of halogenated compounds, electron capture detection (ECD) [2]. The most critical step in the method is compound extraction. This is due to the diversity and complexity of the samples and to the low concentrations and high volatility of

the compounds. A broad variety of extraction procedures has been proposed [3–5].

Classical solvent extraction techniques such as Soxhlet extraction [6–8] and liquid–solid extraction [6,9] are usually time-consuming, multi-step procedures, require large volumes of organic solvents, and often require a lot of extract manipulation. Over the past few years, new technologies that use less solvent and are faster than classical procedures have been applied to the determination of VOCs in soils. Some examples are: supercritical fluid extraction (SFE) [10] and pressurised liquid extraction (PLE) [7], which have usually been applied in the determination of semi-volatile compounds in soils [11–15], or microwave-assisted extraction (MAE) [16,17] or ultrasonic solvent extraction. The advantage of these techniques is that they are not very matrix-dependent since they achieve almost complete extraction of the analytes. However, an important drawback is that they usually need additional cleaning and enrichment steps of the extracts obtained and are therefore carried out off-line [12]. Recently, a technique called Stir Bar Sorptive Extraction (SBSE) has been combined with these solvent extraction methods in the determination of semi-volatile compounds in soils [18–21]. The compounds are adsorbed and preconcentrated in the Stir Bar and then are analyzed by thermal desorption (TD)-GC. The technique has proved to avoid tedious clean-up and preconcentration steps, have higher throughput capacity and improve detection limits.

Headspace techniques have also been widely applied. Static headspace (HS) [22] and purge and trap (P&T) [23] are, together

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with vacuum distillation [24], the techniques proposed by the United States Environmental Protection Agency (USEPA) for this type of analysis [25]. Many articles have been published reporting the use of HS [6,26–30], P&T [31–33] and HS-solid-phase microextraction (SPME) [8,26,34]. These techniques have the advantages of being solvent-free; sample manipulation is minimum, and they are easy to automate in on-line procedures. The main drawback is that they are generally more matrix-dependent than those described above. Different strategies have been proposed to improve the efficiency of extraction, among which the addition of water or of an organic solvent is common. Some reports describe the use of a methanol extraction step prior to analysis by P&T [35,36]. Other authors propose the use of an internally cooled SPME device [37] or the multiple headspace-SPME technique [38].

Non-separative methods such as HS-MS [28,30] and purge and membrane (PAM)-MS [39] have also been proposed.

Within the VOCs considered in different protocols and legislative norms [1,2], trihalomethanes (THMs: chloroform, bromodichloromethane, bromodichloromethane and bromoform) and BTEX (benzene, toluene, ethylbenzene and xylenes) are common soil pollutants. The International Agency for Research on Cancer (IARC) has classified benzene [40] as being carcinogenic to humans (Group 1); ethylbenzene [41], chloroform [42] and bromodichloromethane have been considered possibly carcinogenic to humans (Group 2B), and toluene, xylenes, dibromochloromethane and bromoform [43] belong to Group 3, which encompasses compounds that are not classifiable as regards their carcinogenicity in humans.

The presence of trihalomethanes in the soil can be attributed to many human activities, to their use as coolants in refrigerators, and as propellants and cleaning solvents in industry [36]. They may also derive from irrigation with chlorinated water or leaking drinking water distribution and sewer pipes, since they are generated as subproducts in the water chlorination process [44]. Additionally, there are many studies, especially in the case of chloroform, that have confirmed the formation of these compounds in the soil due to natural processes [45–52]. McCulloch performed an estimation of the sources of chloroform present in the environment and concluded that 90% of chloroform emissions derived from natural sources, among which the processes that occur in the soil account for 37% [51].

BTEX are found in petroleum and its derivatives such as gasoline or fuel-oil. Spills during transport, leaking storage tanks or pipelines, and motor vehicle emissions are the main sources of contamination to soils and groundwater by these compounds [26].

Our research group has experience in the use of headspace sampling for the extraction of organic compounds from soils [28,53]. Recently, a methodology based in the use of a headspace autosampler followed by fast gas chromatography and mass spectrometry, using a programmable temperature vaporizer (PTV), has previously been applied satisfactorily to the determination of VOCs in different liquid matrices [54–56]. In the present work, we propose for the first time the use of such a methodological strategy for the determination of THMs and BTEX in soils. With this configuration it is possible to retain the advantages of the simple headspace instrumentation, achieving high sensitivity thanks to the preconcentration of the analytes in the PTV and rapid separation of the compounds via fast gas chromatography.

2. Experimental

2.1. Chemicals

The solvents used were purchased from the following sources: methanol was from Merck (Darmstadt, Germany); trihalomethanes

(chloroform, bromodichloromethane, dibromochloromethane and bromoform) were from Supelco (Bellefonte, PA, USA); toluene, ethylbenzene and m-xylene from Acros Organics (Geel, Belgium), and benzene from Sigma Aldrich (Sleinheim, Germany).

2.2. Standard solutions and samples

2.2.1. Water samples

The analytical conditions of the method were optimized by preparing standard solutions of the four THMs and BTEX in water. A mineral water (with the lowest content of some of these compounds) was used to prepare the standards, since in previous assays with distilled water and ultrapure water, trace concentrations of some of the compounds studied were detected. To perform the measurements, the samples were placed in 10 mL vials sealed with silicone septum caps. The vials were placed in the tray of the headspace autosampler and were analyzed under the conditions described in Section 2.3.

2.2.2. Soil samples
2.2.2.1. Spiked soils.
Soil matrices were used to determine the analytical characteristics of the method, study the effect of the addition of water and NaCl on the efficiency of compound extraction, and explore the possible existence of a matrix effect. Extreme examples of soil types were used: a soil with a high organic content, from a public garden, a clay soil (a Vertisol from Mexico) and commercial sand purchased from Scharlau (Barcelona, Spain).

In order to obtain VOC-free blank matrices of natural soils, the soil samples collected (garden soil and Vertisol) were air-dried on a heating plate at 90 °C for 48 h, with frequent turning. This procedure removed any organic traces or humidity from the soil. These blank soils were checked to be free of the target VOCs before spiking. Then, a portion of 20 g of soil was placed in a 100 mL vial and 2 mL of a BTEX and THMs solution in methanol was added (at a suitable concentration for each case). The vial was hermetically sealed and shaken vigorously for 15 min to achieve perfect homogenization of the compounds in the matrix. The samples were stored in a refrigerator (4 °C) for 15 days to allow the interaction between the compounds and the matrix to take place. Similar aging times have been reported in literature [16,17,29,9]. Soils spiked and aged for long periods of time resemble real samples more than those analyzed directly after spiking. These latter can be considered to approximate freshly contaminated soils [33,34,8] and the recoveries obtained are mainly an indication of instrumental determination recoveries [29].

2.2.2.2. CRM soils.
To validate the optimized method, three certified reference materials (CRMs) were analyzed. The CRM soils employed were: a loamy sandy soil (RTC-CRM633), a clay soil (RTC-CRM635) and a silty clay soil (RTC-CRM631). All of them were purchased from LGC Promochem (Barcelona, Spain).

2.3. HS-PTV-GC–MS instrumentation

The instrumental configuration used consists of four main parts. A schematic diagram of the apparatus is shown in Fig. 1. HS sampling was performed with a model 7694 headspace sampler from Agilent Technologies (Waldbronn, Germany). This sampler is equipped with a tray for 44 consecutive samples and an oven with positions for 6 sample vials. The sampling system consisted of a stainless steel needle, a 316-SS six-port valve with a 3 mL nickel loop (heated to 95 °C), and two solenoid valves (for pressurization and venting). The headspace sampler was coupled to a PTV injector through an inert transfer line heated to 100 °C. The carrier gas was helium N50 (99.995% pure; Air Liquide). A PTV inlet (CIS-4; Gerstel, Baltimore, MD, USA) with a liner packed with Tenax-TA® was used.