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Continuous flow configuration for total hydrocarbons index determination in soils by evaporative light scattering detection

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Abstract

A continuous flow configuration is proposed for the estimation of the hydrocarbon index in soils using for the first time evaporative light scattering detection (ELSD). The method is based on a membrane-enrichment of the hydrocarbons of interest (C_{10}–C_{40}), which are previously extracted from the soil matrix with a water:hexane mixture using a household microwave oven. The organic supernatant is cleaned-up through silica, evaporated and redissolved in a sodium dodecyl sulphate aqueous solution which is introduced in the loop of an injection valve. The sample, carried by an aqueous stream, passes through a continuous filtration unit fitted with a 1 μm pore size PTFE membrane, where the hydrocarbons are retained while the potential coextracted compounds are wasted. Quantitative elution of the C_{10}–C_{40} fraction is accomplished by passing an acetone stream through the filter which drives the analytes to the ELSD system for analytical measurement. The detection limit was 1.8 $\mu g\,ml^{-1}$, the linear range 5–25 $\mu g\,ml^{-1}$ and the precision 4.3 %. The recoveries were between 93 and 97%. The proposed method was also evaluated by attenuated total reflexion-Fourier transform (ATR-FT-IR) analysis of the extracts.

Keywords: Hydrocarbon index; Soil; Membrane; Flow configuration; Evaporative light scattering detection

1. Introduction

The presence of oil and grease in matrices of environmental concern, such as water and soil, can be attributed to different human activities, as a consequence of accidental leakages or continuous release after agricultural, industrial and even domestic activities [1,2]. Taking into account the large variety of compounds that can be present depending on the nature and source of contamination, reference values usually refer to a global (total hydrocarbons index) rather than an individual value for each hydrocarbon [3]. Indeed, maximum tolerated levels in environmental matrices have been established by international legislation as a global concentration of hydrocarbons. The Spanish legislation has set the maximum concentration of hydrocarbons in soil at 50 $\mu g\,g^{-1}$ [4].

The developed methodologies for hydrocarbons determination in environmental samples involve different and well-defined general steps: isolation of the analytes from the sample matrix, purification of the extracts removing potential interferences, preconcentration in order to reach the appropriate detection limits, and finally, detection by different instrumental techniques. No doubt, the simplest described procedures are devoted to water samples [5], being liquid–liquid (LLE) or solid-phase extraction (SPE), the usual approaches. Traditional methodologies for the extraction of aliphatic hydrocarbons from a soil matrix involve several manipulative steps and are prone to analyte losses. Reference methods for hydrocarbon index determination in soil use Soxhlet extraction, using large volumes of organic solvent mixtures and requiring ca. 2–25 h per extraction. As an alternative, microwave-assisted extraction (MAE) has been proposed, which requires lower solvent volumes and less time for the extraction providing similar recoveries to Soxhlet extraction [6]. MAE has been applied for the quantitative extraction of polycyclic aromatic hydrocarbons (PAHs) [6–10] and aliphatic hydrocarbons [6,10,11] in sediments and soils. The extracts obtained in the extraction process can be further purificated and preconcentrated using different processes, including solvent evaporation and SPE.

Gravimetry [12], infrared spectroscopy (IR) [13–16] or gas chromatography (GC) [1,2,11,17–20] have been used for the

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determination of the total hydrocarbon content in environmental matrices. GC is considered the reference instrumental technique [21–23], replacing IR determination [24,25] as it requires a previous extraction of the samples with chlorofluorocarbons (CFCs), which deplete the ozone layer. This total index is calculated after a full sample treatment, and chromatographic separation of the analytes for further summing of the corresponding peak area. Evaporative light scattering detection (ELSD) is a good alternative for the determination of total indexes, because it can provide a global signal in a reliable, simple, fast and non-expensive way [26]. The joint use of a continuous flow configuration (for automated sample treatment) and ELSD has been used in previous studies to determine global indexes in both biological [27–29] and environmental [30,31] matrices with satisfactory results.

In the present article, a new alternative for hydrocarbon index determination in soil samples is proposed. Soils are extracted using a household microwave oven using a water–hexane mixture. After a solvent-changeover step, the extracts are introduced into a flow manifold on-line coupled to the ELSD system. A continuous filtration unit allows the isolation and enrichment of the target analytes; the whole hydrocarbon fraction is eluted by means of acetone and carried to the detector. The calibration of the instrumental response was achieved by using the recommended standards of the official methods which assess the traceability of the results obtained.

2. Experimental

2.1. Reagents and standards

All reagents were of analytical grade or better. HPLC gradient grade acetone (Sigma Aldrich, Madrid, Spain), sodium dodecyl sulfate (SDS) (Merck, Darmstadt, Germany), *n*-hexane (Panreac, Barcelona, Spain) and silica (40 μm particle size) (Varian Ibérica, Madrid, Spain) were used for method development. All the aqueous solutions were prepared in Milli-Q water (Millipore, Madrid, Spain). PTFE membranes (1 μm pore size, 175 μm thickness and 25 mm diameter), purchased also from Millipore, were placed in a commercial filter obtained from Scharlab (Barcelona, Spain).

Mineral oil standards type A and type B, which consist of mixtures of hydrocarbons in the diesel oil and lubricating oil range, respectively, were purchased from Fluka (Buchs, Switzerland). These environmental standards are used for hydrocarbon index determination according to EN ISO 9377-2 to provide a mixture of hydrocarbons within the range C_{10} and C_{40}. Besides, individual aliphatic hydrocarbons, namely, C_{10}, C_{23}, C_{30}, and C_{40} supplied by Sigma–Aldrich (Madrid, Spain) were also used. Stock standard solutions of 1/1 (v/v) diesel oil/lubricating oil and the individual *n*-alkanes were prepared in HPLC gradient acetone at a concentration of $1\ \mathrm{g\,l^{-1}}$ and stored at 4 °C in the dark. Working solutions at the microgram per milliliter level were prepared in $2.5\ \mathrm{g\,l^{-1}}$ SDS aqueous solution by appropriate dilution of the stocks (acetone was previously removed under a nitrogen stream).

2.2. Apparatus

The flow system consists of a Hewlett-Packard 1050 high-pressure quaternary gradient pump for solvents (water and acetone) delivery; a high pressure injection valve (Rheodyne 7725, Cotati, CA) fitted with a 1 ml PTFE sample loop (filled by means of a glass syringe) and a DDL 31 ELSD system (Europe, Cergy-Pontoise, France) for analytes determination. The detector settings were kept constant in all experiments using an evaporation temperature of 50 °C, an air-pressure of 1.5 bar and a photomultiplier gain of 700 V. PTFE tubing of 0.5 mm I.D. for coils, and standard connectors were also employed. The flow system was connected to the ELSD system by means of a 50 cm × 0.1 mm I.D. poly ether ether ketone (PEEK) tubing. For analytes retention, a commercial filter was fitted with a PTFE membrane. The diameter of the membrane was adapted to that of the filtration unit. Signals were acquired using HPChem Station software (Agilent Technologies) interfaced via an HP 35900C A/D converter. Peak area was used as analytical signal.

The extraction system comprised a household microwave oven equipped with a magnetron of 2450 MHz with a nominal maximum power of 800 W as marketed. The extraction time was set at 5 min and the oven power at 425 W. A Vortex agitator (Heidolph, Mérida, Spain) and an ultrasonic bath (Selecta, Barcelona, Spain) were also employed.

To corroborate the peak assignment with the ELSD system and the composition of the extracts from the continuous flow configuration, a Bruker Tensor37 Fourier transform infrared (FT-IR) spectrometer, equipped with a diamond attenuated total reflection (ATR) cell with a circular surface of 3 mm diameter and three internal reflections was employed. A liquid nitrogen-cooled mercury-cadmium-telluride (MCT) detector was used for spectra acquisition between 4000 and $700\ \mathrm{cm^{-1}}$ at a $4\ \mathrm{cm^{-1}}$ resolution with 128 co-added scans each. Data collection and processing was made using OPUS software (Bruker, Ettligen, Germany). A spectrum of the dry ATR surface was used as background.

2.3. Sample preparation

Uncontaminated soils (blank samples) were collected at different depths (from 0 to 15 cm). These samples were air-dried at room temperature for 1 week, ground and sieved to a size smaller than 0.5 mm. Blank soils were spiked 1 month before analysis in order to simulate weathering and allow analyte–matrix interactions to occur on an extent similar to actual contaminated soils of similar properties. For this purpose, 1 ml of acetone containing the required volume of the stock standard solution of 1/1 (v/v) diesel oil/lubricating oil was added to aliquots of 0.1–1 g of soil. Then, each slurry obtained was air-dried for 10 h in the dark at room temperature so that the complete evaporation of the solvent occured. During this step, the aliquots of soil were homogenized for uniform distribution of the hydrocarbons and protected from draughts by shaking every 30 min at the beginning and 1 h at the end. The samples thus prepared were stored in amber glass bottles at 4 °C before extractions.