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Application of comprehensive two-dimensional gas chromatography for the assessment of oil contaminated soils

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Abstract

A crucial step in the remediation of oil contaminated soils is the characterization of the pollution. Information on the chemical composition is used to assess the toxicity (and thus the need for remediation) and to determine the most appropriate technology for treatment. Mostly these analyses are carried out in routine environmental laboratories using gas chromatography with flame ionization detection (GC/FID) based on a protocol developed by the Total Petroleum Hydrocarbon Criteria Working Group (TPHCWG). In the present study, an alternative method was developed using comprehensive two-dimensional gas chromatography (GCXGC) with FID. Sample preparation was limited to pressurized liquid extraction (PLE), and the analysis was carried out on a commercially available instrument with a conventional column combination (RTX-1/BPX50) and with standard chromatographic software. Compared to the TPH method, the group-types in the GCXGC analysis are chemically better defined and more specific information is obtained especially for the (toxicologically important) aromatic hydrocarbon fraction. Preliminary results indicate that higher recoveries and lower RSDs are obtained with GCXGC, probably because of the less complex sample preparation. Furthermore a data processing method was developed to generate TPH results from GCXGC data; the volatility distribution profiles compared very well with conventional TPH data. The possibility of extracting physicochemical properties directly from the GCXGC chromatogram was briefly explored, but software limitations hindered this promising application.

Keywords: Comprehensive two-dimensional gas chromatography; Petroleum hydrocarbons; Soil contamination; Remediation

1. Introduction

Numerous locations polluted with petroleum hydrocarbons are being investigated each year in the context of soil remediation projects. These projects involve different aspects, mainly dealing with risk assessment and remediation strategy, and require a characterization of the soil pollution in terms of chemical composition, toxicity and physicochemical properties (volatility, water solubility, degradability). From an analytical point of view it is clear that the quality of the risk assessment and the chances for a successful soil remediation will improve with the level of characterization.

Most analytical methods for oil characterization rely on gas chromatography (GC). Capillary GC offers a high separation power (peak capacity typically 100–500), and by using a non-polar (boiling point) column a volatility-based distribution is obtained. However, petrochemical mixtures such as mineral oil easily contain thousands of different compounds [1]. Capillary GC thus cannot resolve such mixtures up to the level of individual compounds, but yields oil fractions with predefined boiling point (or equivalent carbon, EC) ranges. Recent methods tried to refine the classification by incorporating a fractionation prior to GC analysis. A good example is the Total Petroleum Hydrocarbon (TPH) method [2]. With this method, the hydrocarbons are solvent extracted from soil or water samples; the extract is fractionated on a silica gel column into an aliphatic and an aromatic extract. Both extracts are analyzed by GC with flame ionization detection (FID). The GC is equipped with a non-polar capillary column and the chromatogram is divided into discrete EC boiling point ranges defined by the retention times of marker compounds (e.g. C10–C12 aliphatics). The concentration of each boiling point range is reported along with the total

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hydrocarbon concentration. Although TPH-based characterization methods yield very limited information on the chemical composition of the oil pollution, the results are used for risk assessment as toxicity-based limit values have been assigned to each of the EC fractions. However, considering that the chemical composition of an EC fraction is not constant but dependent on the type of petroleum product and on the influence of aging and weathering processes, a methodology based on the actual composition instead of boiling point fractions is expected to yield a more accurate risk assessment.

A powerful analytical tool for the separation of complex mixtures is comprehensive two-dimensional GC (GCXGC). This technique, introduced by Liu and Phillips [3], combines two GC columns with different separation mechanisms. The two columns are connected by a modulator, a device that traps, focuses and re-injects the peaks that elute from the first column into the second column. Each peak eluting from the first column (representing a number of overlapping peaks) is further separated on the second column. The second separation is fast, allowing the introduction of subsequent fractions from the first column without mutual interference. Several reviews have been presented in the literature, describing the principles, applications and developments of GCXGC [4–16]. One of the main advantages is the very high separation power making the technique ideal for unraveling the composition of complex mixtures [4]. An equally important feature is the generation of structured chromatograms: isomers appear as distinct groups in the chromatogram as a result of their similar interaction with the second dimension column phase [5]. The usefulness of GCXGC for the general characterization of complex petrochemical mixtures has already been described by different authors [1,17–22]. Applications of GCXGC/FID in the field of petrochemical environmental pollution include oil spill source identification [23], crude oil biomarker analysis [24], characterization of unresolved complex mixtures (UCM) in petroleum-contaminated sediments [25] and screening of polycyclic aromatic hydrocarbons (PAHs) in soil [26,27]. Recently Arey et al. [28] established a relationship between the GCXGC retention indices and the partitioning properties of diesel fuel hydrocarbons. As the authors stated, these findings are of great interest for environmental research and will allow modeling of weathering processes.

For chemical identification, GCXGC can be coupled to a mass spectrometer. GCXGC/quadrupole mass spectrometry (qMS) has been applied for the identification of organic compounds in petroleum products and petroleum-contaminated soil and sediment [29–31]. However, the peaks eluting from the second dimension column are very narrow (typically 100–200 ms) and only a time-of-flight MS (TOF-MS) can deliver the high acquisition rates necessary for quantitative description of the peaks without imposing limits to the mass scan range [32]. The potential of GCXGC/TOF-MS for group-type identification of oil samples was demonstrated by van Deursen et al. [33].

In the present study we evaluated GCXGC as a tool for oil characterization in connection with soil remediation. For this routine application TOF-MS was considered too expensive, and therefore a method was developed based on GCXGC/FID. It was expected that the highly structured chromatograms would make identification straightforward. Moreover, for quantification FID is preferred because of its wide linear range and simple calibration procedure, owing to the fact that the detector response of hydrocarbons is (almost) not influenced by the chemical nature of the compound.

For the first dimension separation a RTX-1 (100% dimethylpolysiloxane) was used because this phase separates on the basis of volatility, and the volatility distribution of an oil sample is an important quality in regard of characterization. The RTX-1 was combined with a BPX50 (50% phenyl(equiv.) polysilphenylene-siloxane) in the second dimension. It has been shown that the interaction of aromatic and naphthenic species with the phenyl group in the polysilphenylene-siloxane stationary phase results in useful group-type separation of complex oil fractions, including the separation of aliphatic from aromatic components [18]. An additional advantage of the BPX50 column is the high maximum operating temperature, making it appropriate for the analysis of high boiling components up to tetracontane. The GCXGC operating conditions were optimized for group-type separation of the (polycyclic) aromatic hydrocarbons, because from a toxicological viewpoint this fraction is the most relevant: besides being generally more toxic than aliphatic hydrocarbons, the aromatics are more easily dispersed because of the higher water solubility.

For the extraction of the soil samples, pressurized liquid extraction (PLE) was used. This technique suits routine analysis because of the fast extraction times and lower solvent consumption [34]. The GCXGC/FID method was applied to oil-polluted soil samples and the results were compared with the TPH method. Only the extractable petroleum hydrocarbons (from n-C8 to n-C40) were quantitatively analyzed. During the method development a fast scanning quadrupole mass spectrometer (Thermo Electron DSQ) was coupled to the GCXGC. With the qMS operated in scan mode (with limited mass range) an acquisition rate of 10–20 Hz was obtained, which resulted in approximately 2 data points/s dimension peak. The mass spectral data were used for confirmation of the compound class assignments.

2. Experimental

2.1. Chemicals

Acetone, *n*-hexane and dichloromethane (all chromatographic grade), anhydrous sodium sulphate, silica (0.063–0.200 mm) for column chromatography and Celite545 (0.02–0.1 mm) were supplied by Merck (Darmstadt, Germany). Chromatographic pure grade helium (for GC) and hydrogen gas (for GCXGC) were purchased from Air Products (Vilvoorde, Belgium). Solutions of even *n*-alkanes in *n*-hexane USL-250 (C8–C24) and USL-251 (C26–C40) were purchased from Promochem (Wesel, Germany). A solution of 16 US Environmental Protection Agency (EPA) PAHs in dichloromethane was supplied by Supelco (Sigma–Aldrich, Bornem, Belgium). The following individual compounds were purchased as pure product or in solution: ethylbenzene, xylenes, styrene, 2-ethyltoluene, 3-ethyltoluene, 4-ethyltoluene