Available online at www.sciencedirect.com

ScienceDirect

Journal of Chromatography A, 1179 (2008) 33–40

JOURNAL OF CHROMATOGRAPHY A

www.elsevier.com/locate/chroma

High-performance liquid chromatography fractionation using a silver-modified column followed by two-dimensional comprehensive gas chromatography for detailed group-type characterization of oils and oil pollutions

Debin Mao[a,b], Hendrik Van De Weghe[a,*], Ludo Diels[a,b], Nicole De Brucker[a], Richard Lookman[a], Guido Vanermen[a]

[a] *Flemish Institute for Technological Research (VITO), Boeretang 200, B-2400 Mol, Belgium*
[b] *University of Antwerp, Department of Biology, Universiteitsplein 1, B-2610 Wilrijk, Belgium*

Available online 11 October 2007

Abstract

Successful remediation of oil-contaminated soils relies on a sound preceding characterization of the oil chemical composition and physicochemical properties. Comprehensive two-dimensional gas chromatography with flame ionization detection (GC × GC/FID) is known to be very suitable for the analysis of complex samples such as petroleum hydrocarbons. However, in spite of the high-separation power offered by GC × GC, it fails to completely separate certain hydrocarbon groups in petroleum hydrocarbon mixtures. This hampers a detailed chemical composition assessment which can lead to wrong conclusions on the behaviour of the oil in soil systems, e.g. biological degradability and water solubility. This paper describes a high-performance liquid chromatography (HPLC) system with a silver-modified column as a prefractionation step to GC × GC to improve chemical identification. With HPLC, the petroleum hydrocarbons were baseline separated into a saturated fraction (including alkanes and cycloalkanes) and an unsaturated fraction (including alkenes, aromatic hydrocarbons and heterocyclic components). Each fraction eluted in a small time window limiting the dilution caused by HPLC. The two fractions were collected and quantitatively analyzed with GC × GC/FID. Cold splitless injection of 4 μl was adopted to compensate the dilution caused by the prefractionation step. With oil-spiked soil samples, a good reproducibility was obtained (RSD = 3.5%; $n = 7$) and the recovery was satisfactory (87.7%).

Keywords: Oil; Soil contamination; HPLC; Silver; Comprehensive two-dimensional gas chromatography; Cycloalkanes; Alkenes

1. Introduction

Oil contamination in soils and groundwater is a worldwide environmental problem requiring risk assessment and often remedial actions. Remediation success strongly depends on the physicochemical and biological properties of the oil, i.e. the volatility, solubility, toxicity and (bio)degradability of the components. From an analytical point of view it is obvious that the quality of the risk assessment and the design of a successful remediation approach will profit from a precise characterization of the chemical composition, physicochemical and biological properties of the oil contamination.

Oil pollution in soils is usually characterized following the total petroleum hydrocarbon (TPH) protocol [1]. Because of the very complex chemical composition of oils, conventional gas chromatography (GC) cannot provide a satisfactory separation between the different hydrocarbon groups present. Thus, TPH results (which are GC-based) are not optimal for the assessment of oil pollutions. Van De Weghe et al. have demonstrated that GC × GC/FID is more suited because this technique can provide more detailed information on the chemical composition of petroleum hydrocarbon mixtures [2]. However, in spite of the high-separation power offered by GC × GC, it fails to give a clear separation between certain chemical groups, i.e. alkanes, cycloalkanes, alkenes and aromatics. Even when using various column combinations and optimal temperature programs, two or more of these hydrocarbon groups still overlap in the two-dimensional (2D) chromatogram [3–5]. This leads to incorrect

---

[*] Corresponding author. Tel.: +32 14 33 50 32; fax: +32 14 31 94 72.
E-mail address: hendrik.vandeweghe@vito.be (H. Van De Weghe).

0021-9673/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.chroma.2007.09.085

group-type assignments of individual compounds, which may in turn lead to inaccurate assessment of physicochemical properties of the oil pollutants studied.

Different attempts have been tried to solve this limitation of GC × GC. One method is to couple time-of-flight mass spectrometry (TOF-MS) to GC × GC. GC × GC/TOF-MS has proven to be very powerful for chemical identification purposes owing to its high-acquisition rate which is necessary for quantitative description of the very narrow peaks (typically 100–200 ms) eluting from the second column of the GC × GC. The potential of GC × GC/TOF-MS for group-type identification of oil samples was demonstrated by various authors [6–8]. Although GC × GC/TOF-MS shows to be very powerful in group-type identification of complex mixtures, the costly price limits its application in routine analysis. Furthermore, certain hydrocarbon groups such as cycloalkanes and alkenes have similar unique masses and similar eluting regions in the 2D chromatogram and are thus difficult to distinguish. Most importantly, as different compounds have unique relative response factors in MS, it makes GC × GC/TOF-MS very difficult to be used for quantitative analysis.

Another way of improving the GC × GC separation is to apply a fractionation step preceding GC × GC. Multiple prefractionation methods have been proposed. Frysinger et al. [9] examined the chemical composition of hydrocarbon unresolved complex mixtures (UCM) in petroleum contaminated marine sediments. An open-silica column together with a homemade silver-impregnated silica gel column was used to produce four fractions: alkanes and cycloalkanes, monoaromatics, alkylnaphthalenes, and polycyclic aromatic hydrocarbons (PAHs). Compared to the non-fractionated samples, the open-column approach provided a better resolution and improved peak identification. However, a complete separation of classes was not achieved since some hydrocarbon groups were distributed over more than one fraction. A similar fractionation method was also used recently by Reddy et al. [10]. Van De Weghe et al. reproduced the silica fractionation step used in the TPH method to separate aliphatic from aromatic compounds, but break-through of aromatic hydrocarbons in the aliphatic fraction was observed [2]. This break-through problem is mainly due to an insufficient separation power of the open-column fractionation (the particle sizes in open columns are usually much coarser than in HPLC columns). Another problem with open-column systems is that the break-through is unnoticed because no detection system is applied. Edam et al. [4] achieved similar results as Frysinger et al. [9] by using an amino-bonded silica HPLC column, based on the separation presented in the IP391 method [11]. The collected fractions were subsequently analyzed by GC × GC. Group-type separation was achieved for both cycloalkanes and aromatics. Unfortunately, this method is less suited for PAHs beyond di-aromatics due to their late elution and associated band broadening which causes a serious concentration dilution. Also the elution pattern of certain groups such as alkenes was not investigated in this method. The negligence of alkenes is mainly due to their low occurrence in common oil products. However, when characterizing oil-contaminated soils, oils of unknown composition are involved which may have a high-alkene content such as oil processing products or drilling fluids [10]. Recently, Vendeuvre et al. [5] employed an interesting method for the detailed analysis of heavy naphtha. In this method, a silver-based alkene trap was coupled to GC × GC. This hyphenation technique successfully provided a detailed analysis of hydrocarbons in the C8–C14 range. However, due to the operating temperature limitation of the alkene trap (250 °C), application of this technique is limited to gasoline range hydrocarbon samples (up to C14). Furthermore, isomerization of alkenes was observed which could be attributed to the high temperatures used for desorption. Also, the author pointed out that the limited capacity of the trap prevents analysis of oil samples with a high content of unsaturated compounds.

In this article, a HPLC system with a silver-modified column was chosen as a fractionation step preceding GC × GC to provide a complete separation between saturated compounds and unsaturated compounds. To our knowledge, this is the first time a silver-based HPLC column is used as a prefractionation step for GC × GC analysis. The method was evaluated for the analysis of a wide range of petroleum hydrocarbons (C8–C40, including heterocyclic components) and was applied to (spiked) polluted soils. A BPX50 (50% phenyl polysilphenylene-siloxane) column was used as the second-dimension column, because it is a medium-polar stationary phase that can tolerate high-operating temperatures making it appropriate for the analysis of high-boiling components up to C40 [2,12].

2. Experimental

2.1. Chemicals

Acetone and *n*-hexane (both chromatographic grade), anhydrous sodium sulphate, Celite545 (0.02–0.1 mm) and sulfuric acid (95–97%) were supplied by Merck (Darmstadt, Germany). Hexane (HPLC grade) used as mobile phase in HPLC separation was purchased from Acros Organics (Geel, Belgium). Chromatographic pure grade helium (for GC × GC/TOF and GC/MS) and hydrogen (for GC × GC/FID) were purchased from Air Products (Vilvoorde, Belgium). The *n*-alkenes from 1-nonene to 1-octadecene plus 4-nonene and 2-methyl-1-undecene were obtained from Sigma–Aldrich (Bornem, Belgium). Solution of *n*-alkanes (C10–C40) plus pristane and phytane in cyclohexane were purchased from Chiron (Trondheim, Norway). Solutions of even *n*-alkanes in hexane USL-250 (C8–C24) and USL-251 (C26–C40) were obtained from Promochem (Wesel, Germany). A solution of 16 US Environmental Protection Agency (EPA) PAHs in hexane was supplied by Supelco (Sigma–Aldrich, Bornem, Belgium). The following individual compounds were purchased as pure product or in solution: indane, anthracene, biphenyl, *p*-xylene, *o*-xylene, ethylbenzene, 3-ethyltoluene, diethylbenzene, 1,2,4-trimethylbenzene, 1,2,4-triethylbenzene, phenyloctane, phenyltridecane, butylcyclohexane, *cis*-decalin, cyclodecane, bicyclohexyl, 5α-cholestane, benzothiophene, 2-methylbenzothiophene, dibenzothiophene, carbazole, 9-methylcarbazole, dibenzofuran (Sigma–Aldrich); dodecane, octadecane, triacotane, quinoline (Fluka, Bornem, Belgium); 2-methylphenol, 2,3-dimethylphenol, 2,3,5-trimethylphenol