Journal of Chromatography A, 1217 (2010) 550–557

Contents lists available at ScienceDirect

Journal of Chromatography A

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

Characterization of military fog oil by comprehensive two-dimensional gas chromatography

Anja Kohl[a], Jack Cochran[b], Donald M. Cropek[a,*]

[a] U.S. Army Corps of Engineers, Construction Engineering Research Laboratory, 2902 Newmark Drive, Champaign, IL 61822, USA
[b] Restek Corporation, 110 Benner Circle, Bellefonte, PA 16823, USA

ARTICLE INFO

Article history:
Received 14 September 2009
Received in revised form 3 November 2009
Accepted 17 November 2009
Available online 20 November 2009

Keywords:
GC×GC-FID
GC×GC-TOFMS
Military fog oil
Inverse column set
Shape selective column
Silica gel fractionation

ABSTRACT

The most commonly used military fog oil is characterized by comprehensive two-dimensional gas chromatography (GC×GC) coupled to either Flame Ionization Detection (FID) or Time-of-Flight Mass Spectrometric Detection (TOFMS) to advance the knowledge regarding the complete chemical makeup of this complex matrix. Two different GC×GC column sets were investigated, one employing a non-polar column combined with a shape selective column and the other an inverse column set (medium-polar/non-polar). The inverse set maximizes the use of the two-dimensional separation space and segregates aliphatic from aromatic fractions. The shape selective column best separates individual polycyclic aromatic hydrocarbons (PAHs) from the bulk oil. The results reveal that fog oil (FO) is composed mainly of aliphatic compounds ranging from C_{10} to C_{30}, where naphthenes comprise the major fraction. Although many different species of aromatics are present, they constitute only a minor fraction in this oil, and no conjugated PAHs are found. The composition of chemically similar aliphatic constituents limits the analytical power of silica gel fractionation and GC–MS analysis to characterize FO. Among the aliphatic compounds identified are alkanes, cyclohexanes, hexahydroindanes, decalins, adamantanes, and bicyclohexane. The aromatic fraction is composed of alkylbenzene compounds, indanes, tetrahydronaphthalenes, partially hydrogenated PAHs, biphenyls, dibenzofurans and dibenzothiophenes. This work represents the best characterization of military fog oil to date. As the characterization process shows, information on such complex samples can only be parsed using a combination of sample preprocessing steps, multiple detection schemes, and an intelligent selection of column chemistries.

Published by Elsevier B.V.

1. Introduction

Maintenance of appropriate states of readiness and alertness for the military requires extensive training maneuvers, which take place on U.S. installations under outdoor field conditions. Training events frequently require the release of smokes and obscurants to generate specific conditions. Fog oil (FO) is an obscurant used to create visually limiting, disruptive, and confusing conditions for soldier field training and maneuvering. It is a middle distillate petroleum oil consisting of innumerable organic constituents [1,2]. FO is vaporized by injecting the oil onto a hot metal manifold (boiling point = 300–600 °C) contained within a mobile smoke generator mounted on a military vehicle [3]. The vapors condense into micron-sized droplets upon release to form a dense white fog that is ejected over a wide training area [4].

Although toxicity experiments on aquatic organisms showed that this FO is of very low toxicity [5,6], knowledge of its composition is important to allow predictions of potential effects on the environment, and further research toward complete analytical characterization is a commendable goal. It is recognized, however, that oils are among the most complex and variable mixtures to characterize fully due to the vast number of chemical constituents (some estimates exceed 1,000,000 per oil type [7]), the associated array of physicochemical properties for each individual component, and even batch to batch irregularities in bulk oil composition [8].

FO begins as a petroleum distillate made up of a highly complex blend of aliphatic, olefinic, and naphthenic compounds, with only minor aromatic content. According to the current manufacturing requirements established in 1986, the distillate is then treated to eliminate potentially carcinogenic aromatic constituents to the greatest extent possible [9]. The distillate is subjected to a solvent refinement process designed to remove PAH and sulfur and nitrogen compounds followed by hydrotreatment for catalytic reduction of carbon–carbon double bonds, including aromatic rings [10]. Oils produced according to these new specifications are generally referred to as "new" fog oils and these are currently utilized during all military training sessions. Old fog oils that did not undergo

* Corresponding author. Tel.: +1 217 373 6737; fax: +1 217 373 7222.
E-mail address: Donald.M.Cropek@usace.army.mil (D.M. Cropek).

0021-9673/$ – see front matter Published by Elsevier B.V.
doi:10.1016/j.chroma.2009.11.054

this refinement process most certainly contain a higher fraction of unsaturated compounds.

Previously, Katz et al. [2] analyzed old FO from three different sources using liquid and gas chromatography fractionation, and gas chromatography/mass spectrometry. They found that old FO were composed of approximately equal fractions of aliphatic compounds from C_{14} to C_{22} and one to four ringed aromatic compounds. Brubaker et al. [10] analyzed military fog oils using gas chromatography/mass spectrometry. Due to its complex nature, only long chain aliphatic hydrocarbons and hexahydroindanes were tentatively identified as constituent chemical classes as well as two specific branched alkanes and one C_{14}-alkylcyclohexane.

With the advent of two-dimensional gas chromatography (GC×GC), a powerful technique is now available to better parse complex mixtures. Blomberg and Schoenmakers demonstrated its applicability for the characterization of petrochemical mixtures [11]. A unique feature of the resultant chromatogram is to place chemically related compounds into well-structured bands. The resulting pattern allows broad classification of the sample by identifying individual components within these bands. This strategy, among others, has been widely applied to the characterization of petroleum products, hydrocarbon solvents, kerosenes and crude oils, all highly complex samples [7,12–14]. Among the identified chemical classes in these petroleum products were alkanes, naphthenes (including alkylcyclohexanes, hexahydroindanes and decalins), monoaromatics, indanes, tetrahydronaphthalenes, fluorenes, two to 4-ring aromatics and associated alkyl-substituted species, biphenyls, and benzo- and dibenzothiophenes. But even the identification of chemical classes remains challenging since chemical standards for oil component analysis are frequently unavailable. In many demanding applications, therefore, the unmatched ability of GC×GC to isolate target classes is coupled with mass spectrometry, making it a three-dimensional technique with attendant identification capability. Frysinger and Gaines demonstrated that pure mass spectra can be obtained of even minor components [12] and were able to identify biomarkers such as steranes and hopanes in crude oils [15]. Principals of GC×GC as well as application reviews have been extensively described in the literature [16–18] and are therefore omitted here.

While most applications utilize a conventional column set consisting of a non-polar primary column and a more polar secondary column, the inverse configuration has proved valuable in the analysis of petroleum hydrocarbons, crude oil, and bitumen [19,20]. Vendeuvre et al. [21] give a detailed comparison of both sets for the analysis of middle distillates and provide explanations for the observed elution order on the inverse set. Other research has employed columns possessing different separation properties, e.g., a shape selective column [22] and an ionic liquid column [23], based on the application and expected outcome.

In this work, we employed GC×GC-FID and GC×GC-TOFMS with two different column combinations to characterize the chemical composition of the most commonly used military FO. The benefits of higher order dimensional separations/detection techniques over traditional GC–MS are also illustrated as well as the effects of FO fractionation via silica gel.

2. Experimental

2.1. Analytes and oil samples

Military FO was graciously provided by an active training installation and was used as received. All chromatographic analyses were performed with a solution of 1:10 FO in n-hexane.

Several standards were used in this study to elucidate elution patterns within the two-dimensional separation plane. A standard mixture of n-alkanes from C9 to C36 (Restek, Bellefonte, PA, Cat. No. 31459) and from C10 to C40 (Restek, Bellefonte, PA, Cat. No. 31678) were used to note the position of each linear paraffin within FO. Two other pre-mixed standards, one containing the highly branched hydrocarbon biomarkers, pristine and phytane (Restek, Cat. No. 31240), and one containing PAHs from naphthalene to dibenzo[ghi]perylene (Restek, Bellefonte, PA, Cat. No. 31458) provided retention data for comparative purposes. Standard solutions of individual compounds were also prepared as needed. Long chain alkenes with one terminal double bond and cyclohexanes with linear alkyl side chains delineated the location of these olefinic and naphthenic classes. These include octylcyclohexane, dodecylcyclohexane, heptadecylcyclohexane, nonadecylcyclohexane, 1-eicosene and 1-docosene (all from ChemSampCo, Dallas, TX) and 1-hexadecene, 1-octadecene, and 1-nonadecene (all from Fluka Chemical, Milwaukee, WI). Decahydronaphthalene (Kodak, Rochester, NY) was used to pinpoint the location of bicyclic species. BTEX standards were prepared from benzene (99.9%), toluene (99.8%), ethylbenzene (99.8%), and o-xylene (97%) (all from Sigma–Aldrich, St. Louis, MO) and p-xylene (99%, Fluka). Other aromatic standards employed were cumene (99.9%), tert-butyltoluene (96%), undecylbenzene (99%) (all from Acros, N.J.), and biphenyl (99.5%, Aldrich). All standards were used without additional purification and prepared in n-hexane (Fluka, puriss. >99.0%).

2.2. Silica gel fractionation

Standard pre-fractionation techniques with silica gel and $AgNO_3$ impregnated silica gel [22,24] were performed in an attempt to simplify the FO sample. The silica gel (100–200 mesh, Sigma–Aldrich) was dried over night at 150 °C prior to use and the $AgNO_3$ coated silica gel (~10 wt.%, Sigma–Aldrich) was first rinsed with methanol to remove contaminations and then dried over night at 120 °C. The procedure given in Ref. [22] was followed using either 20 μL of FO or 200 μL of a mixed solution of all standards defined in Section 2.1. The silica gel was extracted sequentially in 3 steps with 6 mL of each of the following solvents: n-hexane to obtain fraction F1, n-hexane with 10% dichloromethane to obtain F2, and n-hexane with 50% dichloromethane for F3. The $AgNO_3$ impregnated silica gel was extracted sequentially to obtain the following 5 fractions using 6 mL of the following solvents: n-hexane for F4, n-hexane containing 25% dichloromethane for F5, n-hexane containing 50% dichloromethane for F6, 100% dichloromethane for F7, dichloromethane with 10% acetone for F8. All fractions were reduced to 1 mL under nitrogen using a Zymark TurboVap II (Caliper Life Sciences, Hopkinton, MA) and analyzed by GC×GC-FID.

2.3. GC–MS analysis

GC–MS analysis was performed on an Agilent 6890N gas chromatograph, equipped with a split/splitless injector and an Agilent 7683 autosampler, in tandem with an Agilent 5973 mass spectrometer. The samples were run on a 30 m × 0.25 mm × 0.25 μm Phenomenex ZB-5 HT Inferno column. 1 μL of sample was injected at 300 °C into a gooseneck liner at a split flow of 20 mL/min. The column flow was held constant at 1 mL/min. The GC oven temperature at injection was held at 40 °C for 1 min. It was then ramped at 6 °C/min to 280 °C and then at 25 °C/min to 300 °C. It was held at 300 °C for 5 min to allow elution of all components. The mass spectrometer was run in scan mode from m/z 35 to 400 for a full analysis and from m/z 100 to 400 to eliminate most of the hydrocarbon fragmentation and focus on distinctive parent mass peaks of compounds such as PAH, biphenyls, dibenzofurans, and dibenzothiophenes.

Table 1
Column dimensions.

Column set I		
Primary column	Rxi-17	15 m × 0.25 mm × 0.25 μm
Secondary column FID	Rxi-1MS	1.0 m × 0.15 mm × 0.15 μm
Secondary column TOF	Rxi-1MS	1.5 m × 0.15 mm × 0.15 μm
Column set II		
Primary column	Rxi-5Sil MS	15 m × 0.25 mm × 0.25 μm
Secondary column FID	RSSC	1.5 m × 0.18 mm × 0.10 μm
Secondary column TOF	RSSC	1.7 m × 0.18 mm × 0.10 μm

2.4. GC×GC-FID analysis

A GC×GC-FID system from LECO (St. Joseph, MI) consisting of an Agilent 6890N gas chromatograph, dual-stage thermal modulator and a secondary oven for second column temperature control was used. The GC is equipped with a split/splitless injector and an Agilent 7683 autosampler. The benefit of this system is that the secondary oven and the modulator can be heated independently from the primary oven. This allows tuning the temperatures individually to best improve the resolution. The software used was LECO ChromaTOF for FID. 1 μL of sample was injected into a cyclosplitter liner at 300 °C at a split ratio of 1:20. The FID temperature was set to 325 °C. The columns used and oven temperature programs are listed below in Section 2.6 and in Table 1. The distance between the exit of the secondary oven and the FID was bridged with a deactivated transfer line of 0.3 m × 0.18 mm to avoid peak broadening in the cooler primary oven. Blank runs of n-hexane were performed between samples to verify the absence of contaminants in the system and to ensure that no compounds carry over from one run to the next.

2.5. GC×GC-TOFMS analysis

The GC×GC-TOFMS system used was a LECO Pegasus 4D consisting of an Agilent 6890 gas chromatograph equipped with a split/splitless injector, dual-stage thermal modulator and secondary oven connected to a Time-Of-Flight Mass Spectrometer. Again, 1 μL of sample was injected into a cyclosplitter liner at 300 °C at a split ratio of 1:20. The mass spectrometer was run in scan mode from *m*/*z* 35 to 550. The columns used and oven temperature programs are listed below in Section 2.6. The secondary column was fed directly into the mass spectrometer.

Data analysis was performed using LECO ChromaTOF for Pegasus with automated peak find and spectral deconvolution. The signal-to-noise ratio for the peak find processing was set to 500. Peak identification was performed with a NIST mass spectral library search using a required minimum similarity of 700 out of 1000.

2.6. Column sets for two-dimensional separations

Column set I consisted of a medium-polar Rxi-17 (50% diphenyl, 50% dimethyl polysiloxane, Restek) as the primary column and a non-polar Rxi-1MS (100% dimethyl polysiloxane, Restek) as the secondary column. In column set II, the primary column was an Rxi-5Sil MS (5% phenyl, 95% dimethyl polysiloxane, Restek) and the second dimension used an experimental shape selective column from Restek, referred to in this work as RSSC. This column was designed for better separation of monoaromatic isomers and was predicted to produce a novel separation pattern for complex oils. All column dimensions are given in Table 1. In order to counter the velocity increase caused by the MS vacuum, a longer secondary column was chosen for TOFMS detection than for FID detection, to make the chromatograms comparable.

The conditions for both FID and TOFMS analysis were chosen so that the column capacities were best exploited and the "Murphy" criterion, which requires at least three modulations per peak, was met [25]. Since the peak width in the first dimension is approximately 15 s, we limited the modulation time to 5 s to assure the three modulations per peak required for reproducible results. The oven was programmed to hold at 40 °C for 0.2 min, then ramped to 300 °C at a rate of 10 °C/min. The temperature was then held constant at elevated temperature for 5 min to assure elution of all compounds. The temperature offset between secondary and primary oven was 5 °C for column set I and 15 °C for column set II. The flow was held constant at 1.4 mL/min by pressure programming for FID analysis with both column sets. For the TOFMS analysis, the flow rates were adjusted to make the chromatograms visually comparable to the FID analysis, with 1.0 mL/min chosen using column set I and 1.5 mL/min using column set II.

3. Results and discussion

3.1. GC–MS results

GC–MS analysis of FO yielded an unresolved chromatogram with no distinct baseline separated peaks (chromatogram not shown). Few peaks were visible on top of the unresolved complex mixture (UCM). Their mass spectra showed the typical fragmentation pattern of aliphatic compounds but no single peak could be unambiguously identified due to coelution with other components. In an attempt to resolve and identify individual components, characteristic mass peaks of known oil constituents were extracted. Table 2 lists the chemical classes with their unique masses. The extraction of *m*/*z* 105, for example, resolved some peaks at the beginning of the UCM and the mass spectra of these peaks yielded good library matches with C_2- to C_4-benzenes.

Other typical oil constituents such as biphenyls and dibenzothiophenes [15,22], however, could not be isolated from the UCM using selected mass extraction. Extraction of the mass peaks listed in Table 2 from the UCM pulled out several individual peaks but all still displayed the common fragmentation patterns of aliphatic compounds despite careful baseline subtraction which made library identification impossible. Clearly, one-dimensional GC–MS with ion extraction cannot completely resolve individual components and provides almost no qualitative information on compound classes with a sample of this complexity. Since GC–MS did not deliver sufficient information to characterize this oil, we investigated using the capacity of GC×GC to isolate classes of FO compounds.

3.2. GC×GC with column set I

Although not shown here, preliminary investigations using other combinations of non-polar, polar and shape selective columns were performed. The column sets described in Section 2.6 were selected for further study since they made most use of the two-dimensional separation space for FO analysis. The choice was

Table 2
Characteristic mass peaks for hydrocarbon classes.

Compound class	*m*/*z*
Adamantanes	136, 149, 163
Benzene substitutes	105, 133
Indanes, tetrahydronaphthalenes	104, 117, 131, 145
Biphenyls	154, 168, 182, 196
Dibenzofurans	168, 182, 196
Dibenzothiophenes	184, 198, 212, 226
Hopanes	191

Table 3
Identification table for the numbered peaks in Figs. 2 and 3.

Peak	Name	Peak	Name
1	Pristane	20	Adamantane
2	Phytane	21	Methylnaphthalene
3	n-decane	22	C_2-adamantane
4	n-undecane	23	Methylnaphthalene
5	n-dodecane	24	C_2-adamantane
6	n-tridecane	25	C_2-decalin
7	n-tetradecane	26	C_2-decalin
8	n-pentadecane	27	C_3-adamantane
9	n-hexadecane	28	Bicyclohexane
10	n-heptadecane	29	Indane
11	n-octadecane	30	Tetrahydronaphthalene
12	Butylcyclohexane	31	C_5-benzene
13	Pentylcyclohexane	32	Dimethylindanes
14	Hexylcyclohexane	33	Biphenyl
15	Hexahydroindane	34	Methylbiphenyls
16	trans-decalin	35	Dibenzofuran
17	cis-decalin	36	Methyldibenzofurans
18	Methyladamantane	37	Methyldibenzothiophenes
19	Methyladamantane	38	Dimethyldibenzothiophenes

also limited to columns of high temperature stability due to the high boiling points of the late eluting oil components.

Identification of compounds and constituent classes was performed by comparing elution times with chemical standards on GC×GC-FID, mass spectrometric data obtained using the GC×GC-TOFMS system, and logical deduction from patterns on the two-dimensional plane.

Since the vacuum in the MS analyzer has a profound effect on gas velocity in the secondary column, secondary column length and flow rate must be adjusted properly to acquire comparable chromatograms on both instruments. For column set I, the secondary column length for the TOFMS analysis was increased by 50% compared to the FID analysis and the flow rate was reduced by 0.4 mL/min to 1.0 mL/min. The result is shown in Fig. 1 with the FID chromatogram on the left (Fig. 1a) and the TOFMS chromatogram on the right (Fig. 1b) both acquired at a temperature ramp rate of 10 °C/min. The *x*-axis represents the first dimension separation on a medium-polar Rxi-17, the *y*-axis is the second dimension separation on a non-polar Rxi-1MS. The colors denote the peak intensity from baseline (blue) to maximum peak intensity (red) with intermediate intensities represented by shades of green and yellow. The intensity scale is user selected for optimal clarity. The offsets are user selectable to minimize or eliminate peak wrap around. When comparing the peak patterns formed in the FID chromatogram with those in the TOFMS chromatogram, it is evident that the bands of resolved peaks are visually similar enough to allow transfer of information from one plot to the other. Although the TOFMS data appears to better occupy the 2nd dimensional separation space than the FID data, a TOFMS peak is frequently broader than its associated FID counterpart. Thus, the resolution of the two methods is approximately the same. Although the majority of oil components are not completely separated and the plot is dominated by the UCM, the numerous bands typical of GC×GC are clearly visible, enabling substantial progress toward a better characterization of FO through identification of individual peaks and elution patterns.

Unlike a conventional column set, column set I splits the UCM into two lobes; the larger, more intense upper lobe and a smaller, yet well defined lower feature. Peaks within the three marked rectangular regions in Fig. 1 are further discussed in the sections below.

3.2.1. Aliphatic compounds

Fig. 2a shows the chromatographic region marked with a yellow rectangle extracted from Fig. 1b. Numbered peaks are identified in Table 3.

As noted by others including Tran et al. [20] and Vendeuvre et al. [21] on an inverse column set, the highly branched alkanes elute at the highest 2nd dimension retention time (^2t_R). This includes the two biomarkers pristane and phytane (peaks 1 and 2) which are identified using both standard solution retention times and mass spectra. The linear alkanes from C_{10} to C_{18} (peaks 3–11) elute as discrete peaks just underneath the branched alkane band. The circled peaks 12–14 below the alkanes are naphthenes displaying a distinctive *m*/*z* 83 fragment, suggesting that these are cyclohexanes with one alkyl chain from C_4 to C_6, respectively. Peak 15 at the bottom of Fig. 2a is identified by its mass spectrum as hexahydroindane.

The diagonal bands that form below the cyclohexanes are composed of decahydronaphthalenes (decalins) and adamantanes. Adamantanes are biomarkers found in crude oils and were used by Chen et al. [26] and Grice et al. [27] to indicate the extent of biodegradation. The simplest decalin and adamantane contain 10 carbon atoms each, but since adamantane is a 3-ring structure it has two fewer hydrogen atoms. The mass spectra from the TOFMS analysis reveal that decalins elute in the same band as adamantanes possessing an additional methyl group. For example, cis-decalin (peak 17) and methyladamantane (peak 18) coelute. They are shown in Fig. 2a in the red oval containing decalins and methyladamantanes. The green band denotes C_1-decalins and C_2-adamantanes (peaks 21–24) and the yellow band contains the C_2-decalins and C_3-adamantanes (peaks 25–27). In order to better visualize the adamantanes, the inset within Fig. 2a displays the dotted region with the unique masses (136, 149 and 163) extracted. The inset also shows the mass spectrum obtained for adamantane (peak 20, top) compared to the library spectrum (bottom) to illustrate the excellent match. GC×GC structured peak pattern is neatly observed here as diagonal bands for adamantane, to methyladamantanes, to C_2- and finally, C_3-adamantanes. This pattern suggests that higher order decalins and adamantanes likely exist as this banding continues into the UCM. Peak 28 can be identified by its mass spectrum as bicyclohexane, an aliphatic structure possessing 12 carbon atoms. Substituted bicyclohexanes, if present, are quickly obscured by the UCM. At longer elution times in the first dimension (^1t_R) beyond bicyclohexane, the peaks become more difficult to isolate and identify due to the numerous possible and overlapping isomers of these chemical classes.

Although the presence of alkenes was not expected due to the hydrotreatment, the elution behavior of this chemical class was elucidated using standards in order to verify the effectiveness of the oil treatment. The linear alkenes with one terminal double bond are found to elute between the cyclohexanes and the decalins. However, since the mass spectra of cyclohexanes with branched side chains are very similar to those of alkenes, the presence or absence of this compound class in FO cannot be determined with certainty.

To investigate further the elution patterns of different aliphatic structures, the molecular mass peaks of compounds following the general formulae C_nH_{2n+2}, C_nH_{2n}, C_nH_{2n-2}, and C_nH_{2n-4}, where $C_nH_{2n+2} = 170$ are studied. Fig. 2b shows an example of compounds with 12 carbon atoms extracted from the TOFMS chromatogram of Fig. 1b. A trend is clearly observable in which the molecular mass increases by two with increasing ^2t_R. Three bands are visible each comprising peaks of molecular masses *m*/*z* 164, 166 and 168 as denoted by the ovals. Above the *m*/*z* = 168 oval, n-dodecane (peak 5) is resolved, its retention characteristics match the standard, and it displays its molecular peak of *m*/*z* 170. Other branched alkanes of identical mass do not display this molecular mass peak but are observed to elute above n-dodecane as seen in Fig. 2a. Mass spectrometric data reveals that most of the peaks displayed within the marked ovals are those already identified as cyclohexanes (marked by CH), dimethyldecalins, bicyclohexane and dimethyladamantanes (marked by A). From this perspective, it becomes apparent that, for instance, the C_2-adamantanes elute in a band at lower ^2t_R

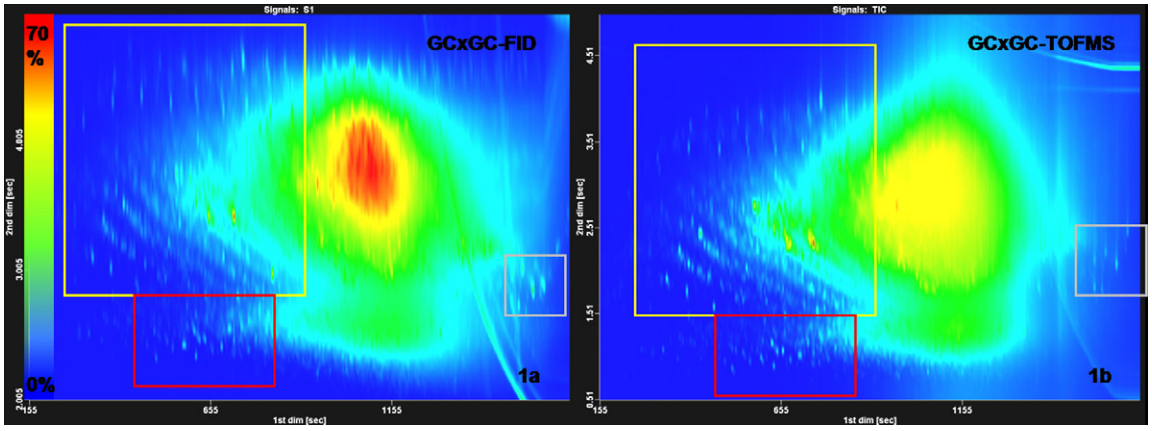

Fig. 1. Color contour plots of the two-dimensional separations on column set I (Rxi-17 x Rxi-1MS) with FID detection (1a) and TOFMS detection (1b). The similarity of the peak patterns is evident. The boxes represent regions of interest for further discussion below.

than the C_2-decalins. Since hexahydroindane was observed (peak 15, Fig. 2a), it is possible that some of the unidentified peaks within the *m*/*z* 166 oval are alkyl-substituted hexahydroindanes. Despite the good separation of compounds of different masses, identification is still difficult due to the large number of possible isomers for a given formula. All the above-mentioned formulae are not only met by cyclic structures, but also by unsaturated compounds and combinations of both. Moreover, many of the branched alkenes do

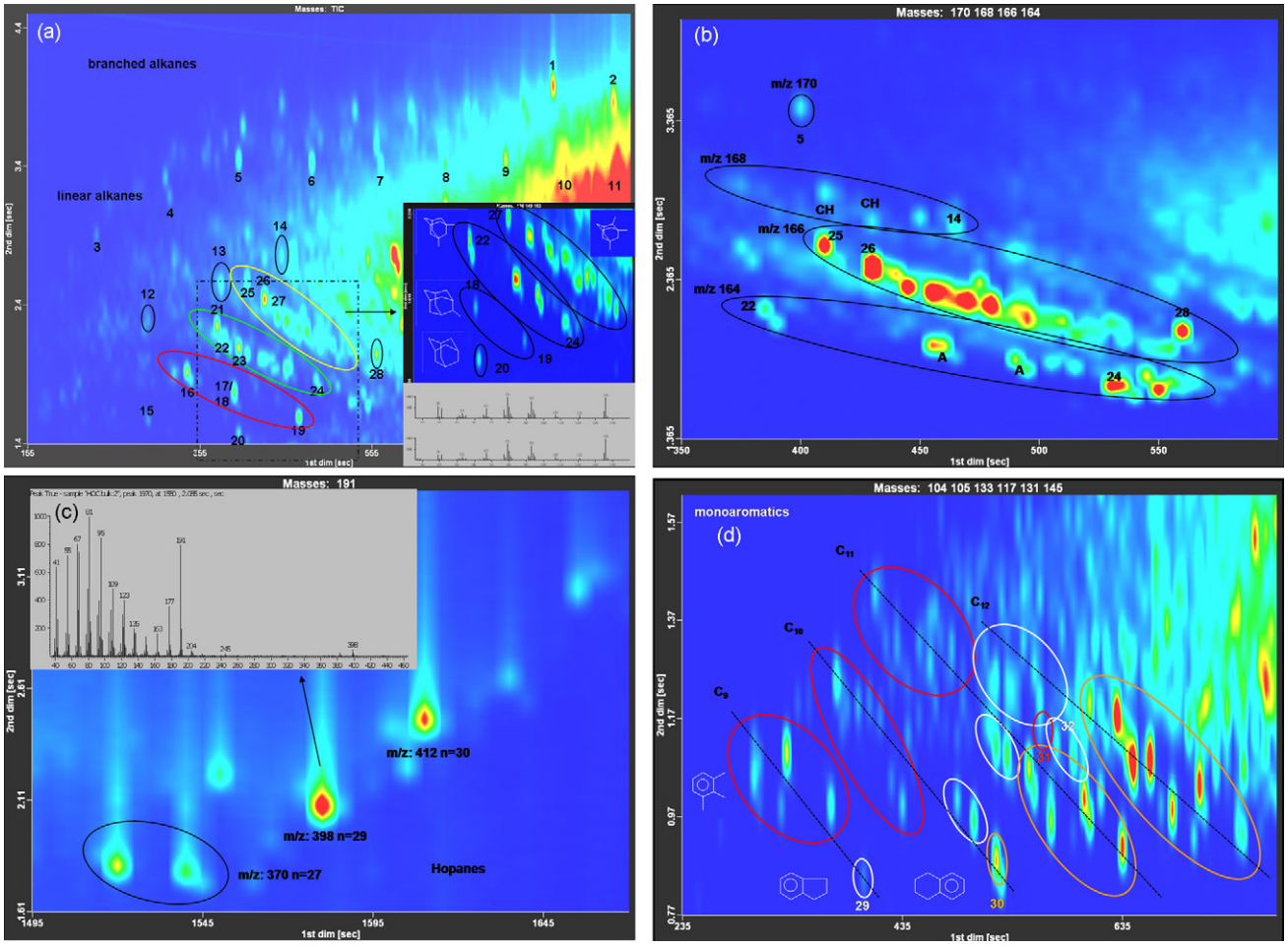

Fig. 2. (a) Extracted region of GC×GC-FID chromatogram using column set I. Identification of numbered compounds is given in Table 3. The inset shows the corresponding region of a TOFMS analysis with typical adamantane masses extracted. The mass spectra at the bottom of the inset show the peak fragmentation pattern of peak 20 (top) and the library spectrum for adamantane (bottom). Peaks within the ovals are described in the text. (b) Extracted region of GC×GC-TOFMS chromatogram showing the C_{12} aliphatic compounds. The molecular mass peaks (*m*/*z* 170, 168, 166, 164) are displayed. The ovals include peaks that share the same molecular mass. CH denotes a cyclohexane; A denotes a dimethyladamantane. Numbered peaks are identified in Table 3. (c) Extracted region of peaks that display the *m*/*z* fragment 191 typical of hopanes. The molecular mass peaks and corresponding number of carbon atoms are given. The inset shows the mass fragmentation pattern for the most abundant hopane. (d) Extracted region of GC×GC-TOFMS chromatogram indicating monoaromatic compounds. Alkylbenzenes are marked by red ovals, indanes by white ovals, and tetrahydronaphthalenes by orange ovals. Similar carbon numbers are shown with dotted lines. Numbered peaks are identified in Table 3.

not display a molecular mass peak and with the lack of unique masses, identifying them within such a complex matrix becomes impossible.

3.2.2. Hopanes

Hopanes are important biomarkers in mineral oils derived from prokaryotes that allow assessment of oil maturity. They are pentacyclic triterpenoids and share a unique mass of m/z 191 [15]. This mass peak is found in the group of compounds on the right side of the UCM marked with a gray rectangle in Fig. 1. The extracted ion chromatogram is shown in Fig. 2c. Although none of the peaks yield a high quality match with a library entry, their mass spectra are very similar to those published in the literature [28,29] for hopanes. The molecular mass peaks suggest the presence of the parent C_{30} hopane as well as one C_{29} and two C_{27} hopane compounds with degraded side chains. As an example, the mass spectrum for the peak with the highest abundance (marked with an arrow) is shown in the inset of Fig. 2c. In agreement with the literature [28], the characteristic 191, 177, 163 and 123 m/z fragments are observed as well as the molecular mass peak of 398 m/z.

3.2.3. Aromatic compounds

As can be seen in Fig. 1, column set I displays an interesting two-lobe structure on the two-dimensional plane with the upper lobe comprising about 90–95% of the constituents presumably of aliphatic nature, as all compounds identified so far are aliphatic and elute within this lobe of the chromatogram. On the other hand, all aromatic standards employed in this work elute within the lower lobe. Fig. 2d represents an expanded view of the red rectangle in Fig. 1. The unique masses of monoaromatics, e.g., alkylbenzenes, indanes and tetrahydronaphthalenes (see Table 2) are extracted. Bands become visible for these different aromatic classes. Alkylbenzenes are marked by red ovals, indanes by white ovals and tetrahydronaphthalenes by orange ovals. The bands of all three classes of monoaromatics with a given number of total carbon atoms form distinct lines shown as the dotted black lines. The trend for each C_n line is alkylbenzene first at the top of the line, to the indanes, and finally to the tetrahydronaphthalenes. However, with increasing alkyl content, the possible isomers become so numerous that the three groups begin to overlap. On the C_{11} line, for example, a C_5-benzene (peak 31) elutes close to two isomers of dimethylindane (peak 32) which, in turn, overlap with the tetrahydronaphthalenes. Although it is beyond the scope of this paper to identify all individual isomers of hydrocarbons, the position of peak 31 at the right end of the C_5-benzene band is indicative of a higher boiling point and suggests that it is pentamethylbenzene since aromatics with numerous methyl substitutions have higher boiling points than their respective isomers [10]. For isomers of more than 12 carbon atoms, coelution and similarity of mass spectra make unambiguous identification of individual peaks impossible. Yet it is likely that the components at higher ^1t_R within the UCM possess one of these three base molecular structures with more or longer aliphatic side chains.

Although not shown here, the presence of other aromatic classes is confirmed by extracting their unique masses and agrees with the results from column set II (see below). These include not only well-known oil constituents such as biphenyls, fluorenes and dimethyldibenzothiophenes, but also dibenzofurans and numerous species of partially hydrogenated 3-ring PAHs, for instance, dihydro-, tetrahydro-, hexahydro- and octahydroanthracenes and phenanthrenes. The presence of these compounds raises the possibility that the hydrogenation step of the refinement process aimed at removing the aromatic content, lends to the complexity of this oil by creating compounds with varying degrees of hydrogenation. Rosal et al., for instance, demonstrated that the catalytic hydrogenation of anthracene leads to intermediate products such as 9,10-dihydroanthracene and 1,2,3,4-tetrahydroanthracene [30]. It does not, however, explain the occurrence of minute amounts of dibenzofurans in this oil.

All these compounds elute at a low ^2t_R within the lower lobe which strengthens the conclusion that the upper lobe is comprised of primarily aliphatic compounds while the lower lobe indicates aromatic ring containing compounds. The spatial separation resulting from this column set thus provides a quick test whether a sample contains aromatic constituents.

3.3. Silica gel fractionation

One microlitre of each fraction described in Section 2.2 was injected onto the GC×GC-FID. Fraction composition was confirmed by analysis of the mixed standard fractions. In agreement with the literature [22,24], all aliphatic and monoaromatic standards appeared in F1, separated from PAHs and biphenyl, which eluted in both F2 and F3 on silica gel. On $AgNO_3$ impregnated silica gel, the saturated aliphatics were contained in F4, while the alkenes, all the PAHs and biphenyl were present in F5, which again is in agreement with the literature, although several of the 5-ring PAHs also eluted in F6. Cumene and undecylbenzene, however, eluted in F4. No standards appeared in F7 or F8.

Analysis of the FO silica gel fractions showed that almost all eluted in the aliphatic/monoaromatic fraction F1. This resulted in the two-lobe structure similar to Fig. 1a. The F2 fraction containing conjugated aromatic ring structure compounds and biphenyls is observed only as the lower lobe. Rough peak area estimates indicate that FO contains only about 5% in the higher aromatic fraction, with the majority of oil components aliphatic or monoaromatic in nature.

The $AgNO_3$ impregnated silica gel fractionation provided supporting information. Nearly all FO components eluted in the saturated aliphatic fraction F4 which again appeared as a two-lobe chromatogram. Only a small portion of FO is contained in F5 and all was present within the lower lobe. This suggests the lack of unsaturated aliphatic compounds in FO as these would appear within the upper lobe. This is not surprising given the hydrotreatment processing during manufacture of FO which appears to satisfactorily remove olefinic content but does not completely eliminate the aromatic content. Again, no FO components appear in F6, F7, or F8. The silica gel fractionations therefore reinforce the results from column set I and its ability to act as a quick method to roughly quantify aliphatic versus aromatic content of oils.

3.4. GC×GC with column set II

While column set I performs well for separation of the aromatic fraction from the purely aliphatic subset, it does not sufficiently resolve the aromatic subset for identification of individual constituents. The RSSC contains a phenyl methyl siloxane type stationary phase that separates m- and p-xylene (data not shown) and was therefore expected to have promise in resolving PAHs. In addition, since its thermal stability is high enough for FO analysis, the RSSC was employed as the second dimension column. A non-polar phase column was selected in the first dimension to ensure orthogonality to the RSSC separation properties. The separation power for aromatic compounds is clearly illustrated in Fig. 3a. FO is spiked with PAHs and analyzed by GC×GC-FID to show the relative positions of these compounds simultaneously. The x-axis represents the separation based on volatility and the y-axis illustrates separation based on shape. All PAHs are highly retained on the shape selective phase and elute well away from the bulk of the FO components. The retention is so strong that the 5-ring PAHs wrap around to coelute with the UCM and are therefore not observed here. Analysis of the PAH elution region of an

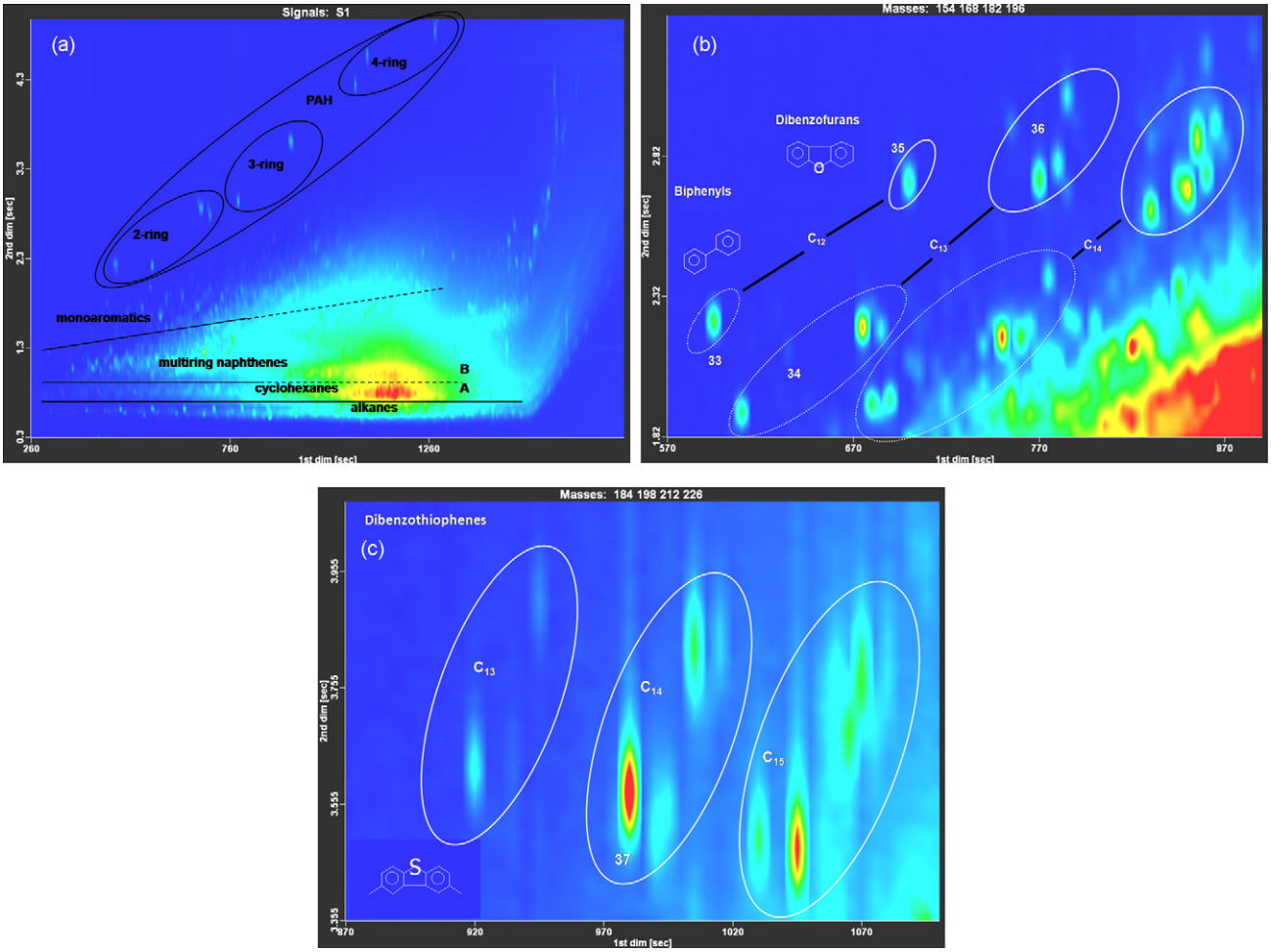

Fig. 3. (a) Color contour plot of the two-dimensional chromatogram using column set II (Rxi-5 SilMS × RSSC) with FID detection. PAH were spiked into the FO to show their placement on the two-dimensional plane. Solid lines indicate the known demarcation of chemical classes while the dashed lines are the estimated continuation of the peak elution patterns. (b) Extracted region of GC×GC-TOFMS chromatogram displaying biphenyls (dotted ovals) and dibenzofurans (solid ovals). The extracted masses are given at the top and the carbon numbers are identified. Numbered peaks are identified in Table 3. (c) Extracted region of GC×GC-TOFMS chromatogram showing dibenzothiophenes with similar carbon numbers circled and the extracted masses given at the top. Numbered peaks are identified in Table 3.

unspiked FO sample verifies that these species are not present in the oil.

The elution order on this column set is similar to that obtained with a conventional column set (non-polar/polar) with the branched and linear alkanes eluting at a low ^2t_R with increasing retention in the 2nd dimension with increasing cyclic and aromatic content. The separation space for column set II provides complementary information to that using column set I. One advantage over the inverse set is that the alkanes elute as a horizontal band at the bottom of the plane but separate from the UCM, thus allowing better determination of the carbon number range. The linear alkanes in this oil are found to range from C_{10} to C_{30}. In addition, of all investigated column combinations, only column set II provides any kind of band pattern within the most abundant part of the UCM as seen in Fig. 3a. The band marked with an A appears to be a continuation of the cyclohexane region through the UCM while band B falls within the expected elution region for more complex naphthenic components such as decalins, bicyclohexanes and adamantanes. This pattern formation suggests two possible conclusions: individual cyclohexanes are the most abundant single compounds within FO but the multiple ring naphthenes are the most populated structural class.

For identification of the aromatic oil components, this column set was used with TOFMS detection. Fig. 3b shows the extracted ion chromatogram for biphenyls and dibenzofurans. Both classes are separated from each other and other oil components up to a total carbon atom number of 14. The dibenzofurans are more strongly retained in the 2nd dimension and elute in a band just above the biphenyls. Isomers of both classes with a given number of carbon atoms elute within one diagonal band. However, isomers with more than 15 carbon atoms are obscured by the UCM.

The dibenzothiophenes are retained even stronger on this column and elute above the UCM. Fig. 3c depicts the identified isomers with 13–15 carbon atoms. They are present in small amounts and only become visible when extracting their unique masses and magnification of the separation region. A very small peak is observed at the retention time for the base molecule (dibenzothiophene) but its abundance is too low for mass spectral identification.

4. Conclusion

Military fog oil is a very complex hydrocarbon mixture mainly composed of a multitude of different aliphatic components and a minor fraction of aromatic constituents, making complete analysis and characterization a challenging task. This work coupled GC×GC with a mass spectrometer, combined this with the use of complementary column sets, analysis of standards, and pattern analysis, to make continued significant progress toward major component identification and chemical class categorization of FO. Use of GC×GC with the inverse polarity column set establishes a

fast and simple method to visualize the total aromatic content in a highly complex sample. This technique can be utilized to examine the efficiency of the refinement process on FO as well as studying weathering effects on oils and providing a quick fingerprint for petroleum products.

The use of an experimental shape selective column in the second dimension provided an informative band pattern within the most convoluted part of the chromatogram allowing estimates of the relative amounts of each aliphatic class. Moreover, it proved valuable for the characterization and identification of individual PAHs, as the retention behavior is dramatically altered over aliphatic and monoaromatic compounds. Minor components with aromatic character such as the dibenzothiophenes, can be identified by using the unique selectivity to separate them from the UCM followed by mass extraction.

The combined analyses described here conclude that FO is a complex mixture comprising 90–95% paraffins, isoparaffins, and naphthenes with carbon numbers from C_{10} to C_{30} with mono and multiring naphthenes dominating. Monoaromatic species make up the remaining 5–10%. Polyaromatic ring structures such as biphenyl, furans, and thiophenes are present in much smaller quantities but there is no evidence for the presence of conjugated polycyclic aromatic hydrocarbons. The FO refinement process likely increases the composition complexity by making multiply hydrogenated compounds from a single parent PAH compound. For further characterization of this fog oil, additional work is underway to verify the presence or absence of other chemical classes, using functional group derivatization or heart cutting followed by NMR.

Acknowledgements

The authors wish to acknowledge LECO Corporation for the use of the GC×GC-TOFMS instrument and are grateful for the loan of the RSSC column from Frank Dorman and Mike Wittrig of Restek Corporation. Funding for this project from the U.S. Army Strategic Environmental Research and Development Program is greatly appreciated. This research was supported, in part, by an appointment to the Student Research Participation Program at the U.S. Army Engineer Research and Development Center, Construction Engineering Research Laboratory, administered by the Oak Ridge Institute for Science and Education through an interagency agreement between the U.S. Department of Energy and ERDC-CERL.

References

[1] L.L. Getz, K.A. Reinbold, D.J. Tazik, T.J. Hayden, D.M. Cassels, USACERL Technical Report 96/38, Champaign, IL, 1996.
[2] S. Katz, A. Snelson, R. Butler, R. Farlow, R. Welker, S. Mainer, AD-A093 205, IIT Research Institute, Chicago, IL, 1980.
[3] K. von Stackleberg, C. Amos, T. Smith, D. Cropek, B. MacAllister, ERDC/CERL Technical Report 04/29, Champaign, IL, 2004.
[4] National Research Council (NRC), Toxicity of Military Smokes and Obscurants, vol. 1, National Academy Press, Washington, DC, 1997.
[5] D.M. Cropek, J.C. Esarey, C.L. Conner, J.M. Goran, T. Smith, D.J. Soucek, Ecotoxicology 17 (2008) 515.
[6] T.M. Poston, D.R. Bean, B.F. Kalkwarf, B.L. Thomas, M.L. Clark, Environ. Toxicol. Chem. 7 (1988) 753.
[7] J. Beens, J. Blomberg, P.J. Schoenmakers, J. High Resolut. Chromatogr. 23 (2000) 182.
[8] M.M. Singer, D. Aurand, G.E. Bragin, J.R. Clark, G.M. Coelho, M.L. Sowby, R.S. Tjeerdema, Mar. Pollut. Bull. 40 (2000) 1007.
[9] C.J. Driver, M.W. Ligotke, J.L. Downs, B.L. Tiller, T.M. Poston, E.B. Moore, D.A. Cataldo, AD-A271 244, Pacific Northwest Laboratory, Richland, WA, 1993.
[10] K. Brubaker, D. Rosenblatt, C. Snyder, ANL/ESD/TM-38, Argonne National Laboratory, Argonne, IL, 1992.
[11] J. Blomberg, P.J. Schoenmakers, J. High Resolut. Chromatogr. 20 (1997) 539.
[12] G. Frysinger, R.B. Gaines, J. High Resolut. Chromatogr. 22 (1999) 251.
[13] R. Gaines, G. Frysinger, M.S. Hendrick-Smith, J.D. Stuart, Environ. Sci. Technol. 33 (1999) 2106.
[14] M. van Deursen, J. Beens, J. Reijenga, P. Lipman, C. Cramers, J. Blomberg, J. High Resolut. Chromatogr. 23 (2000) 507.
[15] G. Frysinger, R.B. Gaines, J. Sep. Sci. 24 (2001) 87.
[16] T. Gorecki, J. Harynuk, O. Panic, J. Sep. Sci. 27 (2004) 359.
[17] C. von Mühlen, C.A. Zini, E.B. Caramao, P.J. Marriott, J. Chromatogr. A 1105 (2006) 39.
[18] R.C.Y. Ong, P.J. Marriott, J. Chromatogr. Sci. 40 (2002) 276.
[19] S.K. Seeley, S.V. Bandurski, R.G. Brown, J.D. McCurry, J.V. Seeley, J. Chromatogr. Sci. 45 (2007) 657.
[20] T.C. Tran, G.A. Logan, E. Grosjean, J. Harynuk, D. Ryan, P. Marriott, Org. Geochem. 37 (2006) 1190.
[21] C. Vendeuvre, R. Ruiz-Guerrero, F. Bertoncini, L. Duval, D. Thiebaut, M.C. Hennion, J. Chromatogr. A 1086 (2005) 21.
[22] G.S. Frysinger, R.B. Gaines, L. Xu, C.M. Reddy, Environ. Sci. Technol. 37 (2003) 1653.
[23] J.V. Seeley, S.K. Seeley, E.K. Libby, Z.S. Breitbach, D.W. Armstrong, Anal. Bioanal. Chem. 390 (2008) 323.
[24] C.M. Reddy, R.K. Nelson, S.P. Sylva, L. Xu, E.E. Peacock, B. Raghurama, O.C. Mullins, J. Chromatogr. A 1148 (2007) 100.
[25] R.E. Murphy, M.R. Schure, J.P. Foley, Anal. Chem. 70 (1998) 1585.
[26] J. Chen, J. Fu, G. Sheng, D. Liu, J. Zhang, Org. Geochem. 25 (3/4) (1996) 179.
[27] K. Grice, R. Alexander, R.I. Kagi, Org. Geochem. 31 (2000) 67.
[28] J.M. Moldowan, F.J. Fago, R.M.K. Carlson, D.C. Young, G. Van Duyne, J. Clardy, M. Schoell, C.T. Pillinger, D.S. Watt, Geochim. Cosmochim. Acta 55 (1991) 3333.
[29] J. Rullkötter, P. Philip, Nature 292 (1981) 616.
[30] R. Rosal, F.V. Diez, H. Sastre, Ind. Eng. Chem. Res. 31 (1992) 1007.