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Group-type characterisation of mineral oil samples by two-dimensional comprehensive normal-phase liquid chromatography–gas chromatography with time-of-flight mass spectrometric detection

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Abstract

Normal-phase liquid chromatography (NPLC) and capillary gas chromatography (GC) are complementary techniques, which makes them ideally suited for hyphenated and comprehensive coupling. In this work, an LC and a GC equipped with a time-of-flight mass spectrometer were on-line and comprehensively coupled (LC × GC–ToF MS) for the analysis of mineral oil samples. Classes of compounds present in the oil like paraffins, mono-aromatic and multi-aromatic compounds were separated by normal-phase LC, with a subsequent boiling-point separation within each class by means of GC. Sub-groups present in each class of compounds were distinguished by selecting their unique masses.

Keywords: Comprehensive two-dimensional chromatography; Comprehensive LC × GC; LC × GC–ToF MS; Mineral oil; Diesel

1. Introduction

Mineral oil analysis is one of the earliest application areas of chromatography. In the past half century, many methods have been developed to analyse mineral oils and a multitude of products. Gas chromatography, either with flame ionisation detection (GC–FID) or with selective detection devices such as mass spectrometry (GC–MS), nowadays is the most widely used technique for this purpose [1]. In recent years, a new technique became available for the characterisation of mineral oils: comprehensive two-dimensional gas chromatography (GC × GC), which was first reported in 1991 by Phillips and Liu [2]. This technique offers a very high resolving power and an unsurpassed peak capacity. To quote an example, Venkatramani and Phillips [3] counted more than 10,000 compounds in a kerosene sample, which was later confirmed by Blomberg et al. [4] and Beens et al. [5]. Nevertheless, baseline separation of each individual compound present in an oil sample is still absolutely impossible. Moreover, knowing the concentrations of more than 10,000 compounds in an oil sample probably is of little use. The true benefits of GC × GC in mineral oil analysis reside in its potential for the qualification of a limited number of specific compounds, such as, e.g. biomarkers or desulphurisation indicators, and in its improved potential for group-type separation. In situations were 'group-type selectivity' is desired, liquid chromatography (LC) coupled to ultra-violet (UV) detection currently is the method of choice [6]. The LC separation provides a polarity-based selectivity. In its simplest form, LC in the normal-phase mode (NPLC) separates a mineral oil into three main groups of compounds of increasing polarity: (i) aliphatic hydrocarbons, (ii) aromatic species and (iii) polar compounds, with some further fine structure within these groups. Information on the boiling-point distribution within a group can be obtained by using GC. The hyphen-

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ation of LC with GC (LC–GC) as a tool for obtaining combined polarity/boiling-point information was first described by Grob [7].

In a recent series of feasibility studies we showed the benefits of comprehensively coupled LC × GC and LC × GC–ToF MS for the analysis of edible oils and fats [8,9]. In LC × GC, narrow fractions of the polarity-based LC chromatogram are transferred to the GC for a separation by boiling point, which affects a far higher resolution than the use of either LC or GC as a stand-alone method. We also demonstrated the possibility of full automation of LC × GC and LC × GC–ToF MS [10]. Although very different at a first glance, mineral oils and edible oils are, at least from the analytical perspective, remarkably similar. Both oil types consist of a large number of (groups of) compounds. The benefits of LC × GC as found in edible oil analysis should, hence, also apply to mineral oils.

In the current contribution, we will describe the application of automated comprehensive NPLC × GC–ToF MS in mineral oil analysis. A diesel oil sample is pre-separated using NPLC in the first dimension. Narrow time slices of the LC separation are on-line and automatically transferred to the GC column. Identification of peaks or groups of peaks is performed by automated peak finding in the total-ion-current (TIC) chromatograms and by deconvolution of the ToF MS data followed by library searching.

2. Experimental

2.1. Instrumentation and conditions

The LC system was a Waters Alliance 2695 HLPC system (Waters, Milford, MA, USA). GC separations were performed on an Agilent Model 6890 GC equipped with an OPTIC 3 injector (ATAS GL, Veldhoven, The Netherlands). Detection was performed by time-of-flight mass spectrometry using a Pegasus III ToF MS (Leco, St. Joseph, MI, USA) in the positive ion EI mode. Helium was used as the carrier gas. The interface between the LC and the GC was described previously [10]. It consists of a 100 μl syringe, with two side entrances/exits in the upper part of the barrel, installed in a FOCUS injection robot (ATAS GL). The LC column was a 250 mm × 4.6 mm i.d. Microsorb 100-5 amino column (Varian, Middelburg, The Netherlands). The GC column was a 30 m × 0.25 mm i.d. × 0.25 μm VF-5 ms capillary column (Varian).

The LC separation was performed isocratically with hexane at a flow rate of 0.8 ml/min [6]. The hexane was dried prior to use, using Molsieve 5 Å. The LC × GC system was operated in the stop-flow mode. After transfer of an LC fraction to the GC, the flow was stopped until the GC separation of the fraction was finished. The LC slice width was 6 s, which corresponds to a fraction volume of 80 μl. Transfer to the GC was performed using the OPTIC 3 injector in the hot split mode at an injector temperature of 280 °C and with a split ratio of 1:150. The GC oven started at 50 °C. After a 1 min initial hold it was programmed at 30 °C/min to 325 °C where it was held for 5 min. The GC column flow was 1 ml/min. The ToF MS was operated at an acquisition rate of 20 spectra/s in the range of *m/z* 50–450.

2.2. Sample and chemicals

A diesel oil was obtained from Shell Global Solutions International (Shell Research and Technology Centre, Amsterdam, The Netherlands). A 30% (v/v) solution was prepared in hexane. From this solution, 30 μl were injected onto the LC column. Hexane for organic residue analysis was purchased from J.T. Baker (Deventer, The Netherlands).

3. Results and discussion

NPLC and GC are complementary techniques, which makes them good candidates for comprehensive coupling. In NPLC retention is largely based on the polarity of the analytes. Homologues tend to elute as one band with little or no separation on the basis of size. GC, on the other hand, separates mainly on the basis of boiling point or, within a homologous series, size. In mineral oil analysis, an LC peak will often contain compounds that cover a wide range of boiling points. Elution of these compounds in GC requires a temperature-programmed run covering a wide temperature range; this will result in relatively long GC cycle times. Automated comprehensive LC × GC has therefore to be performed in the stop-flow mode. To minimize the total analysis time of one LC × GC run, only fractions that contain compounds of interest should be transferred to the GC. For this reason, in the present study the LC effluent of the first 3 min was sent to waste. Next, fractions of 0.1 min (80 μl) were transferred to the GC–ToF MS system for the second-dimension separation. Fig. 1 shows the TIC NPLC × GC–ToF MS colour plot of such an analysis. The diesel oil is seen to be separated into three main groups in the LC step. The first group, with a retention time range of 3.3–4.4 min, contains the saturated

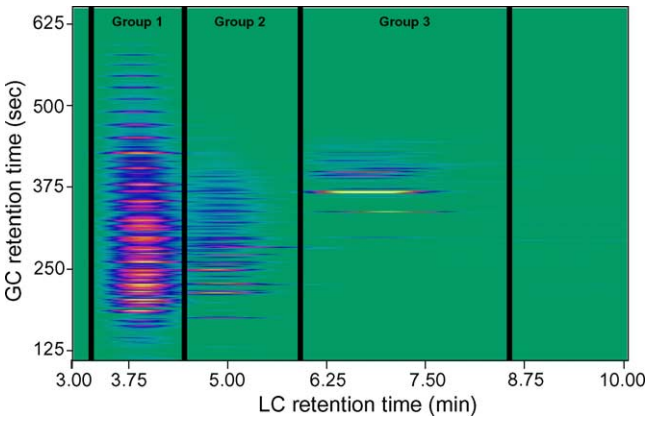

Fig. 1. LC × GC–ToF MS total-ion-current colour plot of a diesel oil analysis.

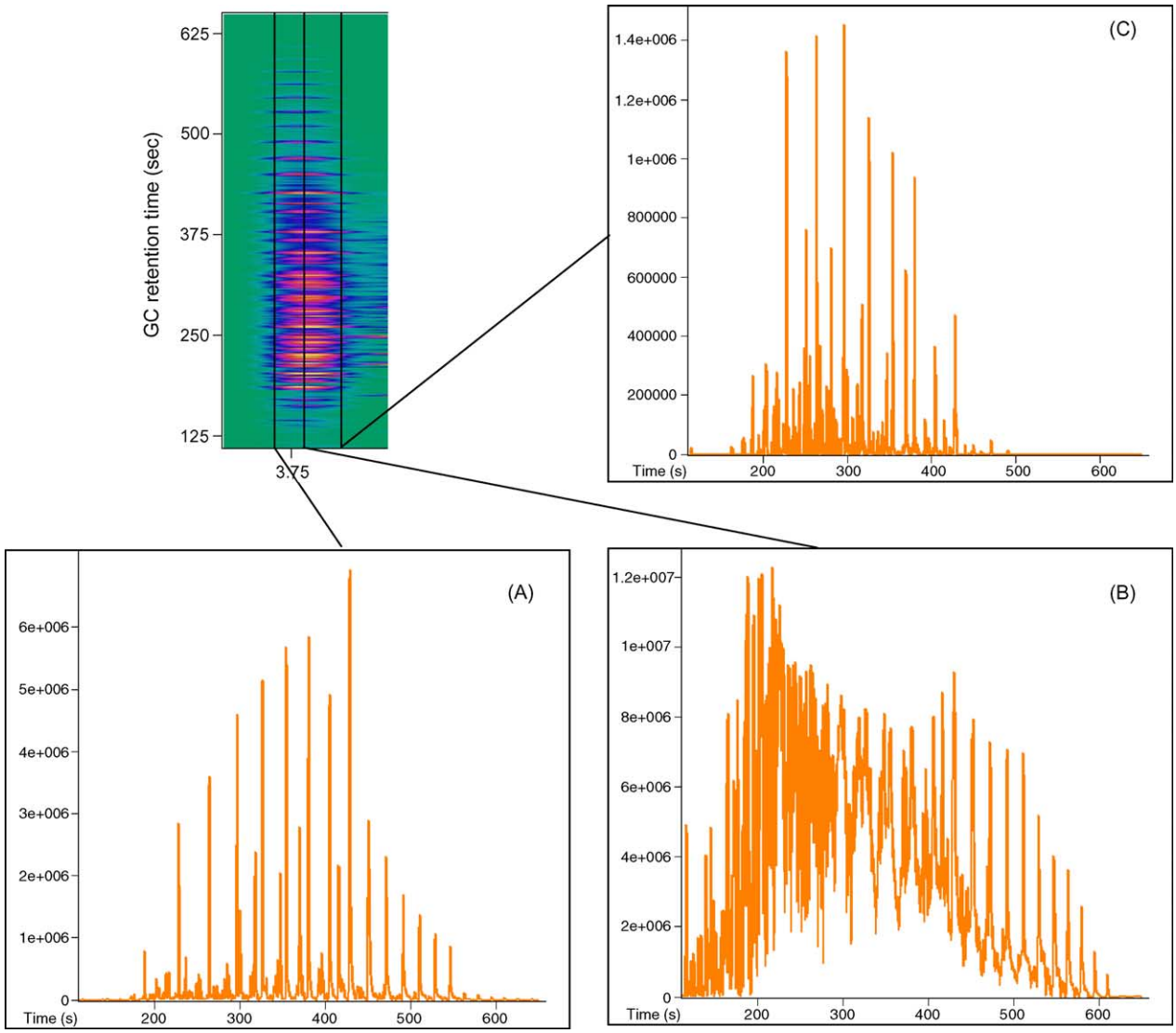

Fig. 2. GC–ToF MS total-ion-current chromatograms recorded across the NPLC group 1 band at retention times of (A) 3.6 min, (B) 3.9 min, and (C) 4.3 min.

analytes. The second group, ranging from 4.4 to 5.6 min, contains the mono-aromatic compounds. The di-aromatic compounds, finally, elute in the third group (5.9–7.8 min).

When comparing the present colour plot with that of a GC × GC analysis of a similar sample [11], it is evident that the group separation in the case of NPLC × GC analysis is much better than for the GC × GC analysis. In the latter instance the groups show much more overlap. On the other hand, GC × GC is far superior when looking at the total peak capacity in the comprehensive operation (also see ref. [12]): the separation within one group is generally much better. An example of the poorer separation within a group in LC × GC is shown in Fig. 2, which shows GC chromatograms recorded at the start, in the centre and at the end of the first LC band. The high complexity of the diesel oil is clearly reflected in the crowded nature of each of these chromatograms – especially the centre one, which contains a huge number of unresolved peaks. It is interesting to compare the GC chromatograms recorded across the first LC band. Fig. 2A seems to indicate that the *n*-alkanes elute slightly earlier from the LC column than the other saturates, although the selectivity of the LC column is clearly insufficient to separate this band into the various sub-classes of the saturates. The chromatogram of Fig. 2B is overloaded with a multitude of peaks which can, again, be assigned to various groups of saturates. The chromatogram of Fig. 2C is much less crowded and contains peaks of several branched and ring alkanes. Identifying these overlapping peaks on the basis of their mass spectra – a topic to be discussed in some detail below – is, of course, a challenging task. To achieve this, we used the deconvolution algorithm of the LECO ChromaTOF data acquisition software, as previously described in detail by Dallüge et al. [13]. A prerequisite is that the data are not skewed, as is the case with ToF MS data. In most instances, deconvolution of the MS data enables the reconstruction of the pure spectra of two or more co-eluting compounds. From the results for the

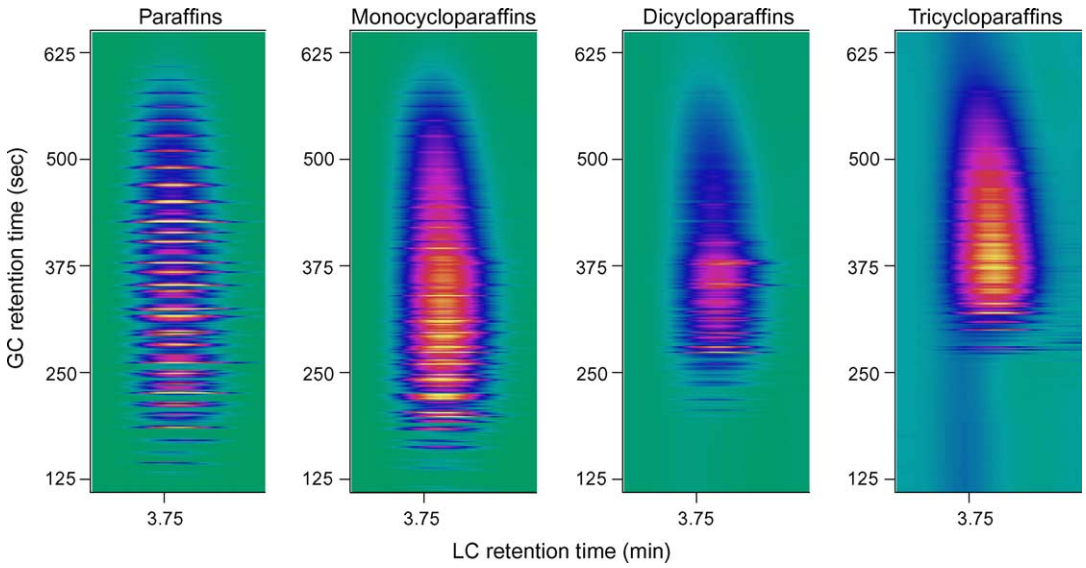

Fig. 3. Mass chromatograms of NPLC group 1, with mass selections as given in Table 1.

most complex LC fraction it is evident that highly selective MS-based detection has to be added to the system as a third dimension, to obtain a satisfactory separation at the sub-class level.

3.1. Mass spectrometric characterisation

Characteristic mass fragments for the various hydrocarbon types in middle distillates can be found in ASTM method D 2425 [14]. Relevant information for the various compound groups of interest in this study is given in Table 1. As an example, Fig. 3 shows the unravelling of the composition of NPLC group 1 of Fig. 1, as achieved by using this selective MS approach. The names of the various compound classes are given above each LC × GC plane. By using the same approach, NPLC groups 2 and 3 are unravelled into alkylbenzenes, indanes plus tetralines and indenes, and naphthalenes, acenaphthenes and acenaphthylenes, respectively (data not shown).

Besides the use in target analysis, it is evident from Fig. 3 that MS is an indispensable tool to distinguish compound groups, because the mass traces show considerable overlap. This aspect, already apparent from Fig. 2, is illustrated in more detail in Fig. 4 which shows the 372–388 s part of the GC analysis of the NPLC fraction eluting at 4.3 min and displays the selective mass traces of the four sub-classes

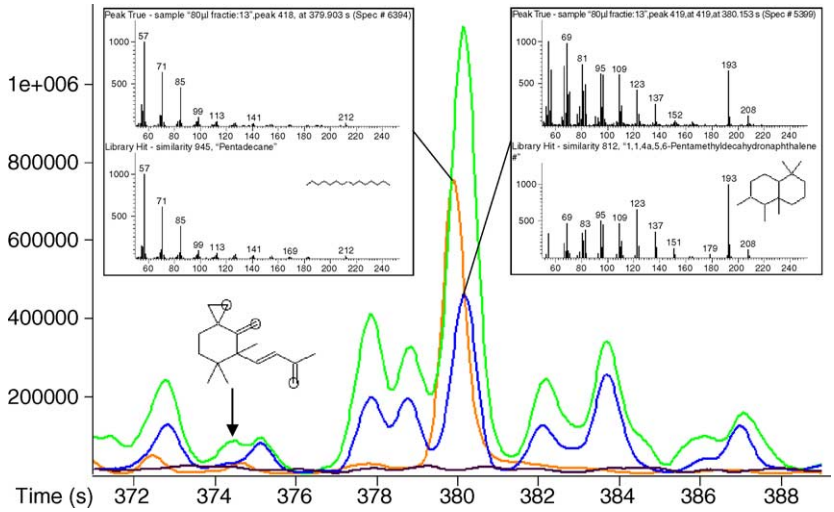

Fig. 4. Three hundred and seventy-two to three hundred eighty-eight seconds part of GC–ToF MS analysis of NPLC fraction eluting at 4.3 min. Orange, paraffins; green, monocycloparaffins; blue, dicycloparaffins; black, tricycloparaffins. Left-hand-side insert, deconvoluted mass spectrum (top) and library spectrum (bottom) of pentadecane. Right-hand-side insert, deconvoluted mass spectrum (top) and library spectrum (bottom) of pentamethyldecahydronaphthalene.

Table 1
Characteristic mass fragments for middle distillates

Compound class	Mass fragments (m/z)[a]
Group 1	
Paraffins	71 + 85
Monocycloparaffins	67 + 68 + 69 +81 + 82 + 83 + 96 + 97
Dicycloparaffins	123/124 + 137/138 + · · · + 249/250
Tricycloparaffins	149/150 + 163/164 + · · · + 247/248
Group 2	
Alkylbenzenes	91/92 + 105/106 + · · · + 175/176
Indanes and tetralines	103/104 + 117/118 + · · · + 187/188
Indenes	115/116 + 129/130 + · · · + 185/186
Group 3	
Naphthalenes	141/142 + 155/156 + · · · + 239/240
Acenaphthenes	153/154 + 167/168 + · · · + 251/252
Acenaphtylenes	151/152 + 167/168 + · · · + 249/250

[a]Paired data represent $M - 1/M$; increases are in steps of 14 mass units ($-CH_2-$).

of interest. To take an example, at a GC retention time of 380 s, three prominent peaks show up. Upon deconvolution and subsequent NIST-library searching, the paraffin peak was tentatively identified as pentadecane with a similarity match factor of 945 on a scale of 1–1000; the experimental and library mass spectra are displayed in the left-hand-side insert of Fig. 4. Similarly, the dicycloparaffin peak was identified as pentamethyldecahydronaphthalene (similarity, 812; mass spectra in right-hand-side insert of Fig. 4).

Another interesting observation regarding Fig. 4 is that the traces representing the di- and tri-cycloparaffins essentially have the same profile. This can be explained by comparing the masses selected in the ASTM method and those observed in the deconvoluted mass spectrum of pentamethyldecahydronaphthalene. Next to the masses suggested for the dicycloparaffins, e.g. m/z 193 and 208, the spectrum also contains the masses m/z 69, 81 and 97, which also are characteristic fragment ions for the monocycloparaffins. These masses appear when a dicycloparaffin is reduced to a monoparaffin fragment in the ion source of the mass spectrometer. No such phenomenon is observed for the tricycloparaffins. The masses selected for this class of compounds do not interfere with those for the other cycloparaffins and, indeed, the ion traces for these analytes have a completely different profile. By using the observation regarding the mono- and dicycloparaffins the other way round, the monocycloparaffins can be distinguished. In those positions where the mass traces of the monocycloparaffins display a peak, but the mass traces for the dicycloparaffins do *not*, peaks can be attributed to monocycloparaffins. In Fig. 4, this is the case for the peak at 374.3 s, marked by an arrow and the compound structure.

4. Conclusions

Due to its polarity-based separation selectivity, NPLC is very suitable for the group-type separation of complex samples, but the separation within one group is very poor. GC, on the other hand, which has a temperature-based separation selectivity is well suited for the on boiling-point/molecular-size separation of homologues. Comprehensive coupling of LC and GC combines the strong points of both techniques, making LC × GC an interesting approach for the characterisation of complex samples such as diesel. The addition of ToF MS to the system is highly desirable to further unravel the composition of a sample and to identify individual compounds or compound classes.

Group separations are much better in LC × GC than in GC × GC. On the other hand, the latter technique is superior as regards the separation within a specific group. It, therefore, lies at hand to go one step further and set up a comprehensive LC × GC × GC system, with ToF MS detection, and study the additional analytical benefits then created.

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