A Powerful Method for Complex Mixture Analysis:

High Resolution Mass Spectrometry of Mineral Oils

The Innovators in Magnetic Sector Mass Spectrometry

AMD Intectra GmbH

Introduction

Crude oils are complex mixtures, containing a variety of compounds and compound groups. The analysis of biomarkers, like monoaromatic steranes, is important and essential for the investigation of crude oils. The analytical data can be successfully used for differentiation of oils, tracking the source of long-term spilled oils, or determining the conditions of generation of crude oils.

The distribution pattern of monoaromatic steranes is normally determined by recording the characteristic fragment ion $C_{19}H_{25}^+$ (m/z 253) with a GC-MS instrument. Unfortunately, the pilot ion $C_{18}H_{37}^+$, given by the saturated species, has the same nominal mass. With low resolution measurements of these mixtures it is impossible to distinguish between these two compound groups. It is necessary to separate the aromatic compounds before the GC run by fractionation, a very critical and time-consuming method. Therefore, see below:

Experimental

The analysis was performed using an AMD 402 double focusing mass spectrometer, coupled with a Hewlett Packard 5890 GC. All samples were injected splitless on a 30 m OPTIMA 5 MS fused silica capillary column. The instrument was equipped with an electron impact ionisation source.

The pilot ions $C_{18}H_{37}^+$ and $C_{19}H_{25}^+$ were recorded in the HR-SIM (high resolution selected ion monitoring) mode with the lock-mass-technique. The reference compound was PFTBA (perfluorotributylamine). The resolution was R=3000 (10% valley).

An extract of a mineral oil sample containing n-alkanes and monoaromatic steranes was investigated by the method described above [GC-HR-SIM-MS; figure 4 (b) and (c)], and in the low resolution full scan mode (GC-MS; figures 1,2,3).

This paper shows:
⇒ **a new, powerful method for analysing complex mixtures without any sample preparation steps.**
⇒ **the increase of selectivity by increasing the mass resolution.**
⇒ **the increase of sensitivity in the high resolution single ion monitoring acquisition mode (HR-SIM).**

Figure 1. Total ion current of the crude oil extract in the low resolution full scan mode. The gaschromatogram is dominated by the intensive n-alkane peaks.
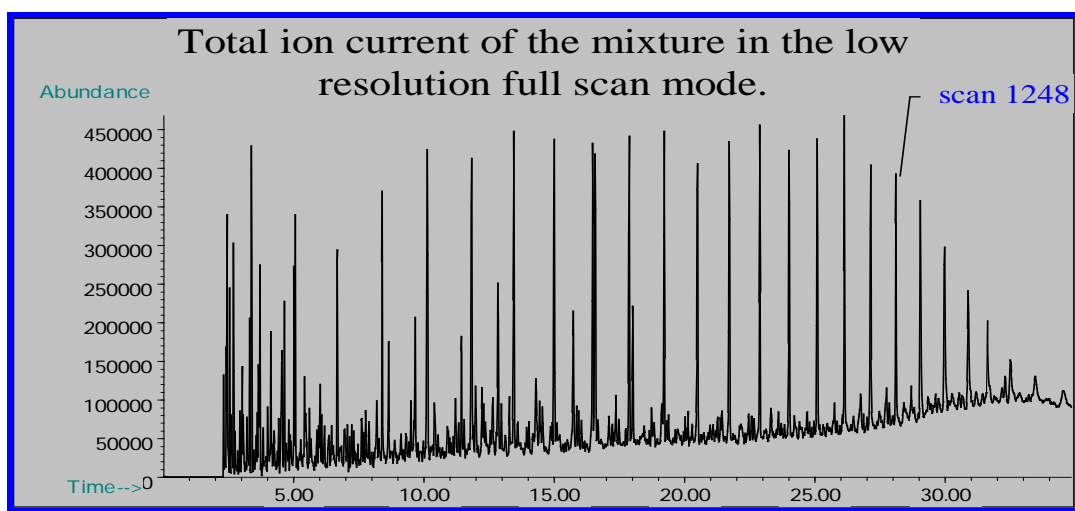
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Figure 2. Spectrum obtained from scan 1248 in fig. 1. M/z 253 is of very low intensity.
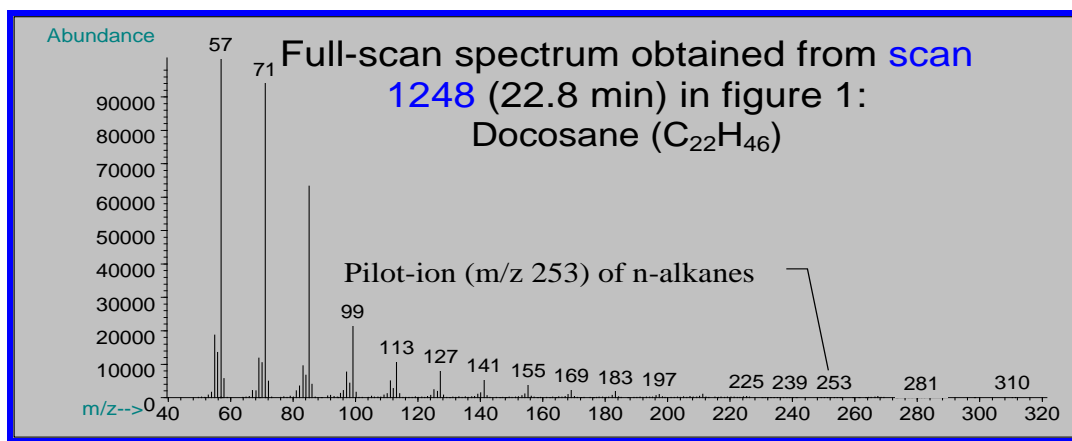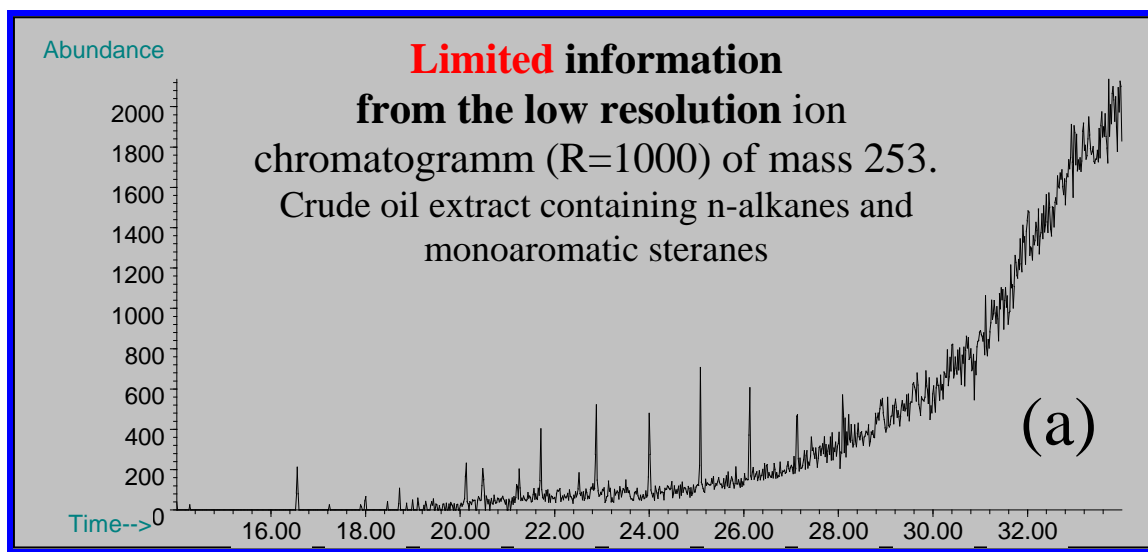

Figure 3. Ion chromatogram of the crude oil extract containing n-alkanes and monoaromatic steranes in the low resolution (R=1000) full scan mode. There is no information about both, because of poor separation of the pilot ions, and low signal to noise ratio.

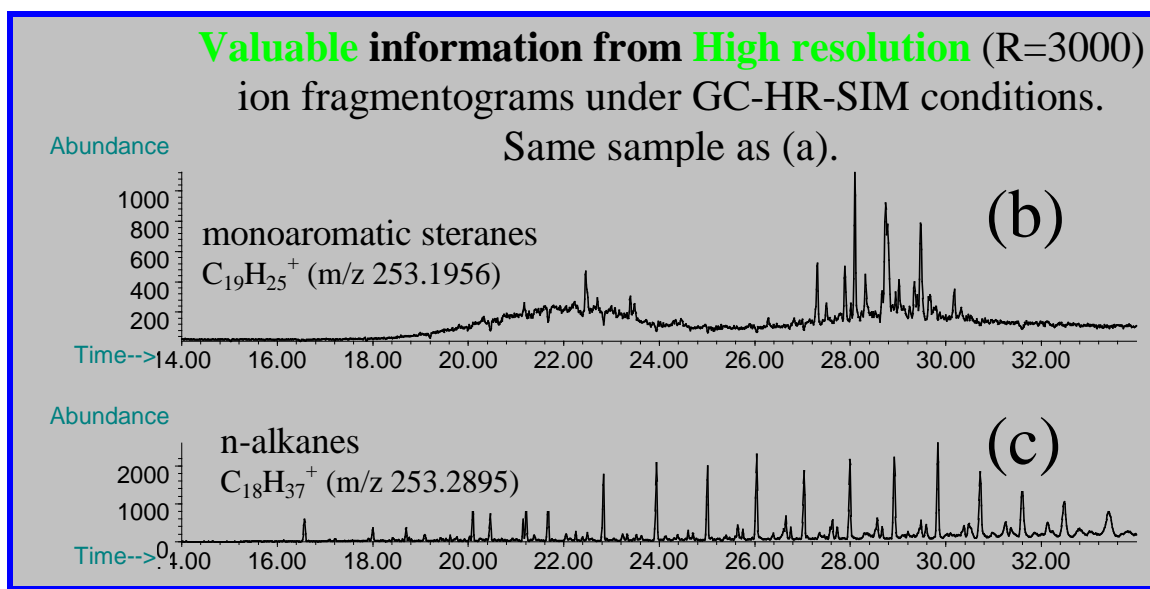The Innovators in Magnetic Sector Mass Spectrometry

Results

Investigating an extract of crude oil, containing n-alkanes and monoaromatic steranes in the low resolution full scan mode (R=1000), without previous fractionation, allows only the characterisation of the saturated species, for example making use of library search (figures 1 and 2). There is no information about the monoaromatic steranes, because of their very low concentration in the extract. Moreover the ion chromatogram in figure 3 (m/z 253) gives neither an information about the alkanes, nor about the aromatics, because the characteristic fragment m/z 253 is of low intensity in the spectra of both, alkanes and steranes. This shows the spectrum of scan no. 1248 in figure 2. Full scan spectra of monoaromatic steranes were not available, because of their very low concentration in the sample, and the poor selectivity in the low resolution mode.

Figure 4 shows two well-resolved graphs, one for the n-alkanes (b), and the second for the monoaromatic hydrocarbons (c). The distribution pattern of both analytes can be estimated without complicated sample preparation.

Figure 4. Ion fragmentogram of the same sample investigated in figure 3 (a). In the **high resolution** SIM-mode it is possible to get the **distribution patterns** of both compound groups **with high selectivity and sensitivity**.

Valuable information from **High resolution** (R=3000) ion fragmentograms under GC-HR-SIM conditions. Same sample as (a).

monoaromatic steranes $C_{19}H_{25}^+$ (m/z 253.1956) (b)

n-alkanes $C_{18}H_{37}^+$ (m/z 253.2895) (c)

Conclusions

High resolution GC-MS using the AMD high performance, low cost magnetic sector product line, provides a sensitive and high selective method for the analysis of complex mixtures, e.g. crude oils. No additional fractionation is needed before the GC run The monoaromatic steranes can be detected side by side with the higher concentrated n-alkanes. This is the supposition for easy quantitative measurements in the near future.

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