

RAPID ANALYSIS USING DIRECT SAMPLING MASS SPECTROMETRY*

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INTRODUCTION

Mass spectrometry instrumentation has undergone substantial changes recently due to the advent of trapped ion techniques such as Fourier transform ion cyclotron resonance mass spectrometry¹ (commonly referred to as FTMS) and rf quadrupole mass spectrometers². The introduction of these highly versatile instruments have opened up exciting new applications of mass spectrometry to environmental measurements, biomolecule characterization, molecular dosimetry, materials science, and others. We have been investigating the use of quadrupole ion traps for the rapid, sensitive detection of compounds in a variety of matrices, including water, soil, air, oils, food, and physiological media. In these studies, methods for the direct introduction of the analyte into the quadrupole ion trap have been developed which require little or no sample preparation steps, resulting in analysis times of about 3 minutes and detection limits commonly in the low picogram range. In this paper, applications of this new analytical approach to the characterization of fossil-derived fuels will be described.

EXPERIMENTAL

A Finnigan ion trap mass spectrometer (ITMS) was used in these studies and was specially modified with an electropolished vacuum chamber and two 330 L/sec turbomolecular pumps to increase pumping speed and reduce background signals. Samples are placed in a 40 mL glass vial and closed with a teflon-lined septum screw cap fitted with two lengths of 1/16 inch tubing. One length of tubing extends to near the bottom of the vial and is used to introduce a flow of helium purge gas. The other length of tubing extends just beneath the vial cap and is used to transport the purged materials into the ITMS. The oil samples were diluted in methylene chloride/methanol and a few microliters of the resulting solution was spiked into distilled water. Water was used as the chemical ionization reagent.

For the gas chromatographic studies, a Hewlett-Packard 5990 GC was employed with a flame ionization detector. An aliquot of each oil sample diluted in methylene chloride was injected onto a 40 meter, DB-5 capillary column programmed to hold at 50 °C for 10 minutes, and then ramp to 280 °C at 5 °C/minute. Each chromatographic run took approximately 100 minutes.

For the combined gas chromatography/mass spectrometry studies, a Hewlett-Packard 5985 GC/MS was used. An aliquot of each oil sample in methylene chloride was injected onto a 30 meter, DB-5 capillary column programmed to hold at 50 °C for 5 minutes and then ramp to 280 °C at 20 °C/minute. Methanol was used as a chemical ionization (CI) reagent and was introduced through the direct insertion probe. A mass spectrum was taken every 3 seconds during the chromatographic run, with the entire GC run taking approximately 30 minutes.

Crude oil samples were obtained from the National Institute for Petroleum and Energy Research, Bartlesville, OK.

RESULTS AND DISCUSSION

A gas chromatograph equipped with a flame ionization detector was initially used to profile the twelve crude oil samples. Figure 1 shows chromatographic profiles of two oils, 90SPR53 (Iraq) and 75047 (Iran), and illustrates the hydrocarbon patterns observed for most of the oil samples. As expected, these oils consist mainly of aliphatic hydrocarbons (paraffins), with other minor components present. The chromatograms from

all of the samples were qualitatively quite similar and differed primarily in the abundance of the paraffins. Small differences in the minor components were observed in some cases, although the ability to differentiate the oils based only on this information was very difficult. In addition, the chromatographic analysis required 100 minutes.

In order to selectively examine the non-paraffin components of these oil samples, methanol chemical ionization GC/MS was used. Methanol chemical ionization permitted selective protonation of the alkyl aromatic hydrocarbons, alkenes, and heteroatom-containing hydrocarbons present in the samples, while eliminating ionization of the more abundant paraffins. The resulting mass spectra for these oils consisted primarily of alkyl aromatics, C_2 - to C_7 -benzenes and C_0 - to C_4 -naphthalenes, as shown in Figures 2 and 3, respectively. Selected ion chromatograms of the alkyl benzenes and alkyl naphthalenes revealed differences in the relative and absolute abundances of these components in the various oil samples, but the ion signal levels were quite low in most cases and may be difficult to reproducibly quantitate. In these GC/MS studies, because the alkyl aromatics were selectively detected and only classes of compounds were quantitated, less chromatographic resolution was required than in the GC FID studies and a faster column program was employed. However, the GC/MS analysis still required approximately 30 minutes.

Previous research in our laboratory has demonstrated the capability of purging volatile samples from an aqueous matrix directly into an ion trap mass spectrometer without chromatographic separation². This method, called direct sampling ion trap mass spectrometry (DS ITMS) has been used as a rapid, sensitive means of differentiating a series of fuels, including gasoline, diesel, and jet fuels. The volatile components from the oil are then purged from the solution with helium directly into the transfer line of the ITMS (no chromatographic separation is used). The effluent entering the ITMS is ionized using water chemical ionization (the water purged from the sample is used as the chemical ionization reagent). This method allows selective ionization of alkyl aromatics and heteroatom-containing hydrocarbons but not the paraffins. Using this approach, all the volatile components from the oils could be characterized with the total analysis requiring approximately 3 minutes, as compared to 30-100 minutes for the chromatographic analysis. In addition, the remarkable sensitivity and versatility of the ITMS provided detailed information on trace levels of compounds that are characteristic of each oil.

This same DS ITMS approach was adapted to differentiate the crude oil samples. Figure 4 illustrates the total ion purge profile and extracted ion profiles for C_2 -benzenes (m/z 107) and C_3 -benzenes (m/z 121) for oil 90SPR53. The entire experiment required approximately three minutes. Figure 5 represents the mass spectrum obtained approximately 2 minutes into the purge and reveals the ions observed from this sample. Ions at m/z 83, 85, and 96 originate from the solvent and are present in the blank. The ions with m/z 93, 107, 121, 135, and 149 arise from C_1 - to C_5 -alkyl benzenes present in the oil sample.

Table 1 is the resulting compilation of relative ion abundances for the alkyl aromatics from the 12 crude oils studied thus far by ITMS. Because the signal from C_2 -benzenes at m/z 107 was usually the most abundant, all other ion abundances were normalized to its intensity. The samples were run in duplicate (some were acquired in triplicate), and the precision of the measurements are also included in Table 1. From these data, it may be seen that differentiation of many crude oils is possible using these ion ratios. Note that oils 74023 and 69080 yield similar ion abundance ratios and that they are from the same oil field, but sampled in different years, 1974 and 1969, respectively. In some cases, however, even though the relative ion ratios are similar, the absolute abundances of the alkyl aromatics vary considerably. This is shown in the bar graph in Figure 6, where absolute abundances of the ion with m/z 107 is illustrated. In the case of 90SPR53 and 75047, where the ion abundance ratios in Table 1 prohibit clear distinction of the crude oils, the differences in the absolute abundances of m/z 107 permit their differentiation. In order to quantitatively compare absolute ion abundances, an internal standard (possibly deuterated xylene) should be added to the oil samples prior to analysis to provide a standard ion for comparison.

These low molecular weight alkyl aromatics may not be the best components for the identification process, however, because "weathering" of the oils could lead to losses from volatilization, changing the relative and absolute abundances of the monitored ions. Thermal desorption ITMS, another type of DS ITMS technique developed in our laboratory, could be used to examine the less volatile, higher molecular weight constituents

of the oils (e.g., naphthalenes, phenanthrenes, etc.), which should be less susceptible to "weathering". The thermal desorption method employs rapid heating of a small aliquot of the neat sample to analyze compounds with lower volatilities by ITMS.

CONCLUSIONS

In this study, the potential of DS ITMS for the rapid differentiation of crude oils was examined. Twelve Middle Eastern crude oils were analyzed by GC FID, GC/MS, and DS ITMS. The GC FID chromatograms, which required approximately 100 minutes each to acquire, were qualitatively quite similar, making differentiation of various oils difficult. GC/MS using methanol chemical ionization provided selective ionization of alkyl aromatics and heteroatom-containing hydrocarbons in the presence of aliphatic compounds. However, this technique requires approximately 30 minutes per analysis and generated ion signal levels which were quite low and were difficult to reproducibly quantitate. Some differences in the alkyl aromatic hydrocarbons ratios of the different oils were observed, however. Direct sampling ITMS, using water chemical ionization, of oil samples provided a rapid, sensitive method of examining the abundances of volatile components in the samples. Examination of the ion ratios of the alkyl aromatics provided differentiation for most of the oil samples. Further differentiation could be obtained by comparing absolute ion abundances. Addition of an internal standard, such as a deuterated xylene, would allow the absolute ion abundances to be determined more accurately. The DS ITMS technique required a total analysis time of only three minutes compared with 30 to 100 minutes for chromatography-based techniques.

REFERENCES

- ¹M. V. Buchanan and M. B. Comisarow, in "Fourier Transform Mass Spectrometry", American Chemical Society, ed. M. V. Buchanan, American Chemical Society, Washington, 1987, pp. 1-20.
- ²R. G. Cooks and R. E. Kaiser, Jr., *Acc. of Chem. Res.*, **23**, 213 (1990).
- ³M. B. Wise, M. V. Buchanan, and M. R. Guerin, "Rapid Determination of Target Compounds in Environmental Samples Using Direct Sampling Ion Trap Mass Spectrometry," Proceedings, 38th ASMS Conference on Mass Spectrometry and Allied Topics, June 3-8, 1990, Tucson, AZ, pp. 619-620.

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Oil Sample ID ^a	121 107	135 107	149 107	93 107
90SPR53 ^a	0.90 ± .02	0.49 ± .03	0.09 ± .01	0.58 ± .02
75047 ^b	0.89 ± .02	0.51 ± .02	0.15 ± .01	0.68 ± .05
70007 ^c	0.91 ± .03	0.51 ± .02	0.11 ± .006	0.62 ± .05
67066 ^d	0.91 ± .03	0.61 ± .01	0.15 ± .004	0.71 ± .05
70070 ^d	0.85 ± .002	0.50 ± .01	0.09 ± .01	0.75 ± .003
69068 ^e	0.87 ± .02	0.52 ± .01	0.12 ± .02	0.66 ± .04
72022 ^e	1.23 ± .02	0.85 ± .02	0.23 ± .02	0.73 ± .001
74023 ^{b**}	0.82 ± .02	0.47 ± .02	0.11 ± .001	0.68 ± .03
69080 ^{b**}	0.80 ± .01	0.45 ± .03	0.10 ± .002	0.73 ± .01
69085 ^b	0.76 ± .01	0.35 ± .01	0.07 ± .004	0.74 ± .02
69086 ^b	0.72 ± .01	0.40 ± .02	0.11 ± .03	0.87 ± .10
70113 ^b	0.83 ± .001	0.42 ± .02	0.10 ± .02	0.68 ± .02

Country of Origin: ^aIraq, ^bIran, ^cUnited Arab Emirates, ^dSaudi Arabia, ^eKuwait

^aIdentities assigned by National Institute for Petroleum and Energy Research, Bartlesville, OK.

^{**}Oil from same field, but one sampled in 1974 and other in 1969.

Figure 1. Gas Chromatographic Profiles of Two Crudes. Total Analysis Time 100 Minutes.

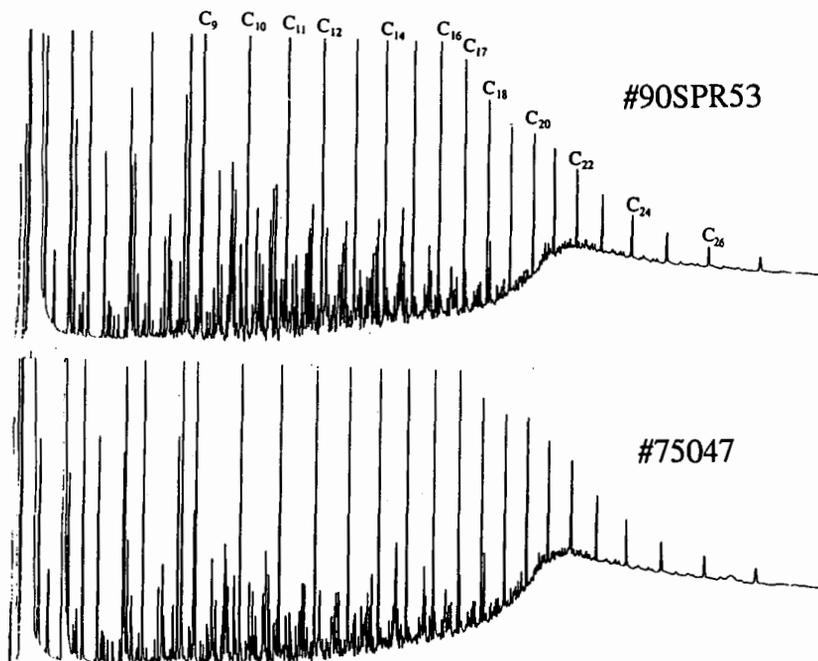


Figure 2. Extracted Ion Chromatograms for C₂-C₇ Alkyl Benzenes from Oil #90SPR53 Obtained by Methanol CI GC/MS.

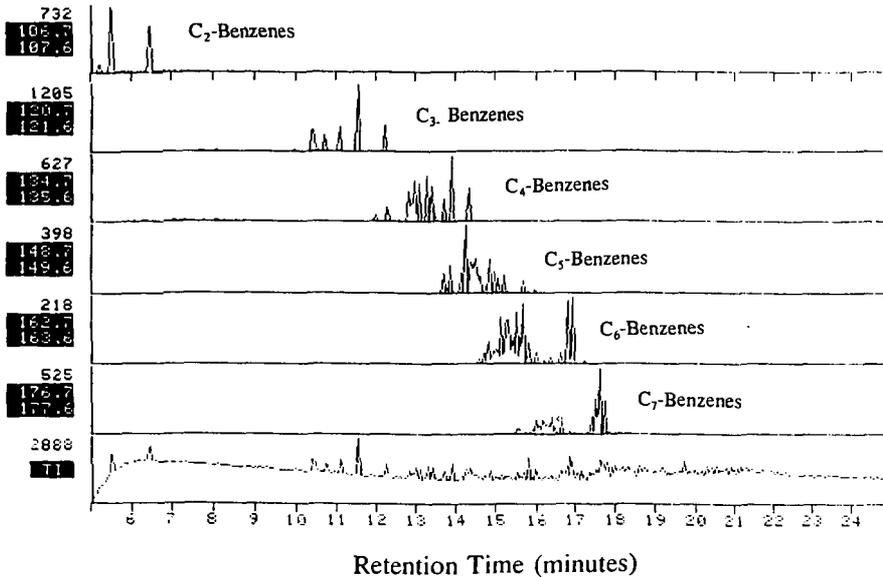


Figure 3. Extracted Ion Chromatograms for C₀-C₄ Alkyl Naphthalenes from Oil #90SPR53 Obtained by Methanol CI GC/MS.

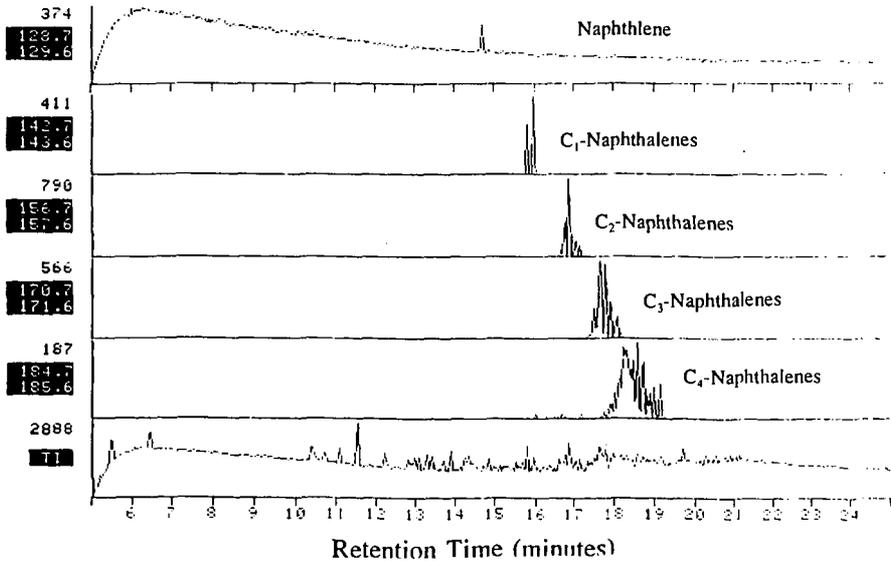


Figure 4. DS ITMS Purge Profile for Oil 90SPR531, Water CI.

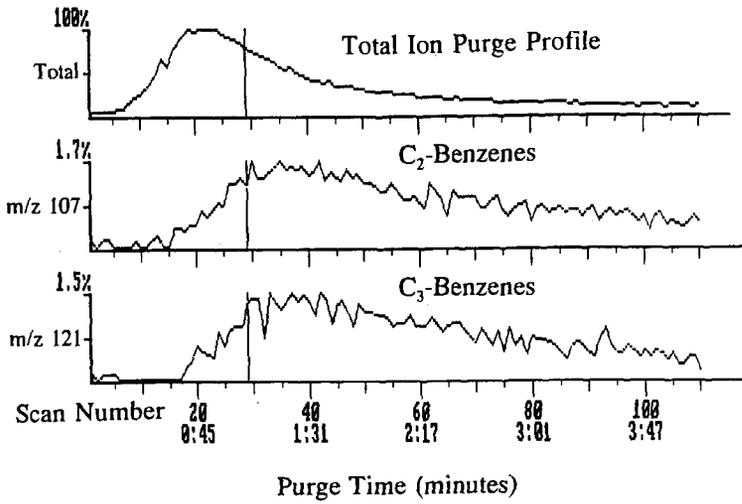


Figure 5. Water CI Mass Spectrum Taken 2 Minutes Into Purge Shown Above.

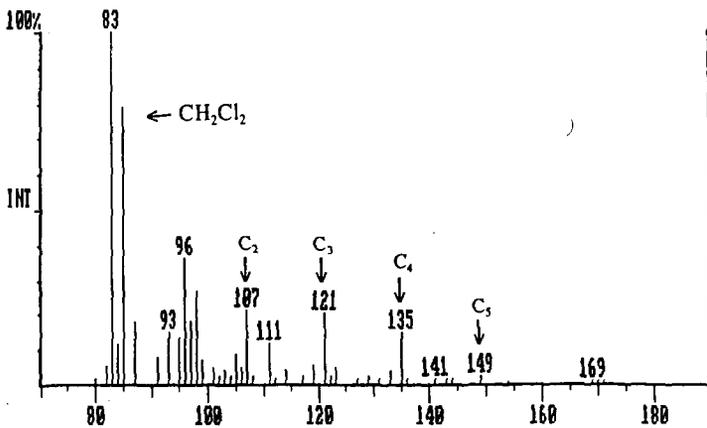


Figure 6. Absolute Abundance m/z 107. Direct Purge ITMS.

