

Overview

This publication contains selected papers given at a Symposium on the Mass Spectrometric Characterization of Shale Oils that was jointly sponsored by the American Society for Mass Spectrometry (ASMS) and ASTM Committee E-14 on Mass Spectrometry. The symposium was held at the Thirtieth Annual Conference of ASMS, 6–11 June 1982, Honolulu, HI.

The symposium was organized to provide mass spectrometry practitioners with information on state-of-the-art methodology for the characterization of shale oils. This information should be also useful for chemists and engineers that are involved in developing processes for the use of shale oils or, in general, any type of synthetic fuel (synfuel).

Characterization of complex synfuel or petroleum mixtures or both that are designated for ultimate use by industry and the public at large has several important objectives. First, such characterization is essential for the fundamental understanding of the chemistry involved in generating a particular material, for example, obtaining liquid synfuels from coal or oil shale. Second, in-depth characterization is required to monitor the efficiency of upgrading processes that convert raw synfuels into commercially useful end products. Such processes will be required in most cases and might involve several steps, each with a different function and therefore presenting different analytical challenges. Thirdly, potential impact on the environment of the end products must also be assessed. The main point is that determination of the chemical composition of complex fossil fuels is a prime requirement for developing a viable and economical process.

The above considerations apply well to the production and upgrading of shale oils. Shale oils are very complex mixtures and so are the processes designed to deal with their production and upgrading. This complexity makes in-depth analysis of shale oils a significant challenge that, in general, can be solved only by using a multiple technique analytical approach.

The complexity of shale oils is well illustrated by a simple list of major components that are likely to be present in typical samples. These include normal and isoparaffins, cycloparaffins, linear and cyclic olefins, one to four plus ring aromatics, aromatic olefins, aromatic thiophenes and furans, phenols, ketones, both aliphatic and aromatic nitrogen compounds, components with more than one heteroatom per molecule, and so forth for a total of 150 to 200 compound types (homologous series). Each compound type consists of at least 20 to 50 carbon number homologs and a much larger number of individual isomers.

Analytical techniques developed to cope with this complex system include extensive separations into saturates, olefins, several aromatic subfractions, acids, bases, neutral polars, and subsequent instrumental analysis of the separated fractions. The most suitable instrumental techniques are those that can provide the user with either molecular type information, such as mass spectrometry and related hybrid techniques, or with fundamental, but average basis structural characterization such as nuclear magnetic resonance or infrared spectrometry. Actually, these techniques are in most cases complementary.

The symposium papers included in this publication deal mainly with mass spectrometric techniques. All or any of these must constitute an integral part of any characterization of shale oils and related products. In selecting the subjects, emphasis was placed on frontier-type applications that illustrate the maximum capabilities of the mass spectrometric techniques used, rather than focusing on a cookbook-type recommendation for a standard methodology. We trust that the reader will be able to develop the approach and analytical mix best suited to his or her particular application.

The first paper in the book, by E. J. Gallegos of Chevron Research, illustrates the application of gas chromatography/mass spectrometry (GC/MS) to the analysis of a light distillate from Paraho shale oil, a shale oil naphtha (or gasoline) boiling approximately from 66 to 260°C (150 to 500°F). GC/MS combines the separation capabilities of a gas chromatograph with the identification capabilities of a mass spectrometer and a computerized library search. It is thus particularly well suited for the detailed analysis of very complex mixtures that contain relatively light boiling components. In the study discussed, the author identified 235 individual components, including paraffins, cycloparaffins, olefins, alkylbenzenes, indans, tetralins, naphthalenes, phenols, ketones, as well as sulfur and nitrogen compounds. A detailed quantitative list of these is given together with advanced qualitative isometric mass/intensity/retention time MAP displays of some of the major components.

The second article in the book deals with the characterization of the most complex fractions of shale oils—the acid and base fractions. Techniques used in this work, by Gil Greenwood of Phillips Petroleum Company, included high resolution mass spectrometry and field ionization mass spectrometry. High resolution mass spectrometry is particularly well suited to the analysis of these fractions that are too heavy for detailed GC/MS characterization and contain large numbers of oxygen and nitrogen compounds that can be separated only by this technique. This work also illustrates the integration of data from several analytical tools such as separations, MS, and infrared. The research described revealed striking differences between the compositions of acids and bases from eastern and western U.S. shale oils.

The third paper in the book also deals with the characterization of the elusive and difficult nitrogen compounds. This work by Heppner et al, from the Western Research Institute in Laramie, compares data obtained with high resolution mass spectrometry and potentiometric titration in a novel and interesting

approach. Good agreement between these very different techniques is shown for the chemically stable fractions; the comparison also points out areas in which the mass spectrometric characterization could be improved. In addition, the paper shows that high resolution mass spectrometry can be used to identify those compounds that cause polymerization and sediment forming.

The next paper in the series is also a contribution from the Western Research Institute; this laboratory, formerly operating under the aegis of the Bureau of Mines and the Department of Energy, has been the location for most of the pioneering research on shale oils in the United States. The contribution, by Guffey and Barbour, deals with the GC/MS analysis of yet another difficult class of shale oil components, low molecular weight sulfur compounds that are present in gases from oil shale retorts. These compounds, in ppm ranges, include H_2S , alkylmercaptans, and others. Advantage is taken of the excellent identification capabilities of the GC/MS for these materials.

The fifth paper in the publication, by Scheppele et al from the U.S. Department of Energy, Bartlesville, introduces another analytical approach, field ionization mass spectrometry (FIMS). This technique is particularly useful for the analysis of saturates. It generates mainly molecular ions rather than fragmenting these relatively unstable components, as for example, electron impact ionization does. FIMS thus can give detailed information on both the carbon number and compound type distribution of complex saturate mixtures. The paper gives calibration values for a large number of pure compounds and compares FIMS data on type distribution to other MS analyses. Good agreement is shown for the lighter boiling point fractions, less for the heavier ones, indicating a need for further research in this area.

Another novel approach to the characterization of heavy fossil fuel materials is pyrolysis/MS. This approach allows the user to look at molecular breakdown products from components that might be not volatile, and therefore, not analyzable under conventional MS conditions. One can thus examine the primordial organic material in shale kerogen, distinguish chemically different kerogen types, and gain an insight into the kerogen origins. This exciting area is the subject of the sixth paper in the publication, contributed by Meuzelaar et al, from the University of Utah. In addition to the physical part of this approach, the paper also discusses the complex and innovative statistical treatment the authors use to take maximum advantage of the high information yield available from pyrolysis/MS.

The next paper in the book evaluates the suitability of a triple quadrupole MS/MS for on-line gas analysis of trace sulfur compounds generated during oil shale processing. It is by Wong et al, from the Lawrence Livermore National Laboratory and the University of Florida. This highly selective, sensitive, and specific technique is capable of detecting and quantitating several alkylmercaptans and alkyl-sulfides at 1 to 10 ppm and even lower concentration levels in a few seconds time.

The final article of the publication is a review by Seifert et al, of Chevron Oil

Field Research on the GC/MS characterization of biological markers, such as steroids and terpenoids. These compounds are present in crude source shales and can be used to gather information on the source, maturation, migration, and degradation of crude oils, as well as on the origins of oil shale. The review provides the reader with a fundamental understanding of this arcane but extremely important subject.

The information presented in this publication covers a truly wide gamut of the analytical methods used in the analysis of shale oils and, less extensively, oil shales, including high and low resolution MS, GC/MS, FIMS, MS/MS, pyroprobe/MS, covering both on-line and off-line applications, and associated techniques such as separations and complex mathematical data handling tools.

Additional mass spectrometric techniques, such as field desorption MS, fast atom bombardment, and so forth, not included in this book, could also play an important role in the characterization of shale oils. A "complete" characterization would certainly require the use of integrated analytical technology that would at minimum include extensive separations, several mass spectrometric techniques, nuclear magnetic resonance (NMR), infrared, elemental analyses, and other associated methods, plus extensive, computerized mathematical manipulations. Such an effort lies yet in the future. We believe that the pioneering research discussed in this publication constitutes an important and fundamental step towards accomplishing not only that goal, but the much broader one of characterizing very complex mixtures of fossil fuels and other natural products.

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