Analytical Advances for Hydrocarbon Research

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This review of Analytical Advances for Hydrocarbon Research, edited by C.S. Hsu is based on material presented at the 220th American Chemical Society Symposium held in Washington DC, August 2000.

Fossil fuels and crude oils in particular are complex mixtures of hydrocarbons and heteroatomic compounds covering a wide range of molecular weights, polarities, melting points, boiling points and other physical properties. Detailed characterization of these complex mixtures is essential for all areas of exploration, production and refining. Since the earliest discovery of crude oil, methods have been continually developed and improved for this purpose. In the early days, the techniques available were very facile compared to the complex tools available today. Properties such as gravity, color, optical activity were used to differentiate or characterize products. Various distillation techniques were used to provide an indication of the fractions present in the oils and their boiling point distributions.

Significant breakthroughs started to occur in the mid-1900s with the development of techniques such as gas chromatography (GC) and mass spectrometry (MS). By the early 1970s, hyphenated techniques such as GC-MS started to become commercially available and a quantum leap was made in our ability to characterize complex mixtures on a molecular level.

This book, in my opinion, is very timely since it provides a compilation of 18 chapters dedicated to many of the latest developments in analytical techniques widely used in areas of the petroleum industry concerned with exploration, production, refining, and, more recently, environmental concerns. The chapters in the book cover virtually all of the techniques being used today in these areas. However, I was a little disappointed that coverage on supercritical fluid chromatography (SFC) and high temperature gas chromatography was not adequately provided. Both topics are relatively important in many areas of hydrocarbon characterization.

One of the appealing aspects of this volume is that it covers such a wide range of techniques, many of which are often not described in detail in the mainstream literature. The techniques may be described in specialist journals but here they are all together in one readily accessible reference volume. For example, Chapter 1 describes methods to characterize and estimate thermodynamic and physical properties of hydrocarbon and petroleum products through the use of properties such as boiling points, viscosity, refractive index and others. A chapter such as this is extremely useful for reference purposes for those of us who may encounter these properties on an irregular basis but occasionally need more information on such properties. Chapter 2 is valuable for the same reason. We all make use of elemental analyses, but most of us, at least those working with the organic fractions tend to think of C,H,N,O and S when we think of elemental analyses. In this chapter we are provided a summary of methods and developments to determine a wide range of elements in both crude oils and refined products, both new and used. It also provides a brief but useful explanation of techniques such as ICP/MS and XRF which again is useful for non-experts in the field.

Chapter 3 focuses on N and S containing compounds and their detection by GC with a brief description of the various N and S specific detectors available and advances made in these areas, such as the nitrogen chemiluminescence detector (NCD). Chapter 4 is the first of many chapters concerned with mass spectrometric techniques in hydrocarbon characterization. Chapter 5 provides an excellent overview on thin-layer chromatography (TLC)—again, a tool we all use routinely but one which most of us pay little attention to when it comes to new developments. Geochemists and other analytical chemists would be well-advised to look into the section on the use of berberine-impregnated plates for the detection of saturate hydrocarbons. A useful summary of ASTM standard methods utilizing GC, SFC, LC (liquid chromatography) and TLC for characterizing various low boiling fractions is given in Chapter 6. As with the other chapters in this book, having all of this information in one place is very useful for those of us who need the information occasionally but do not want to spend a lot of time searching widely-dispersed sources of information.

The importance of retention indices in identifying compounds in complex mixtures such as crude oils and other liquid fuels is described in Chapter 7. Retention indices are also provided for over 150 compounds for use in conjunction with GC and GCMS data as an aid in identifying these compounds. Simulated distillation GC is described and a standard method introduced for this purpose. In view of the ever-increasing environmental concerns related to S containing compounds in refined products, Chapter 8 provides a useful summary of the
latest developments of methods available for the determination of S containing compounds in fossil fuels.

Chapters 9 and 10, which was written by Exxon geochemists, provide a good overview of both biomarker applications to exploration problems and molecular and isotopic characterization of light hydrocarbons and application to petroleum exploration problems. In addition to discussing the use of GCMS in these areas, both chapters devote sections to the utilization of isotopic compositions of individual compounds in a variety of applications through the use of GC combined with isotope ratio mass spectrometry (GCIRMS). GCIRMS has been available for carbon determination for almost a decade and applications continue to advance almost exponentially. More recently a GCIRMS system which permits determination of H and C has become commercially available permitting one to obtain both carbon and hydrogen isotopic composition of individual compounds. It has now become an extremely useful tool for characterization of lighter products and gases that do not contain the traditional biomarkers widely used for exploration purposes.

Although LCMS has been around for many years in one form or another, for many years it has never achieved the same level of use as GCMS in fossil fuel related studies, primarily due to the fact that you cannot get the same chromatographic resolution with LC as you can with GC and for many applications in hydrocarbon research maximum resolution is critical. However, LCMS does have a number of applications and in Chapter 11, Hsu provides a summary of LCMS developments over the years and describes advances in a number of current applications of this approach. High-resolution MS methods are described in Chapter 12, primarily dealing with the use of high-resolution MS methods for characterization of crude oil components without chromatographic separation. Perhaps more importantly it describes how this approach is also used to detect contaminants in refined products, the presence of which could of course have detrimental effect following the use of the contaminated product.

Characterization of NSO compounds and the heavy ends of crude oils are described in Chapters 13 and 14 respectively. Again these are both extremely important areas of research and will become even more important in years to come as the oil available for refining becomes heavier and more polar in nature and with somewhat different characteristics than the oil used as feedstock in most refineries today. The discussion of API-MS for characterization of polar compounds is particularly useful for non-experts in this area.

New NMR applications for use in characterization of hydrocarbons are described in Chapter 15 and particularly interesting here is the description of the concept of chromatography in an NMR tube and its application in the characterization of hydrocarbon mixtures. However, while this is a very interesting approach and clearly permits identification of a certain number of techniques, one wonders how long it will take to develop this technique to provide the same degree of separation obtained with GCMS.

Applications of matrix desorption/ionization (MALDI) techniques to the characterization of heavy hydrocarbons and polymers are described in Chapters 16 and 17. Fourier transform ion cyclotron resonance MS applied to analysis of hydrocarbons and metalloporphyrins is also discussed in Chapter 17. Particularly useful are the descriptions of the sample preparation techniques necessary in order to successfully complete these analyses. Finally, Chapter 18 provides a useful overview of X-ray absorption spectroscopy to the characterization of heavy hydrocarbon matrices, polymers/rubbers, and hydrocarbon synthesis catalysts, all areas of direct relevance to hydrocarbon research.

This book is strongly recommended to people working in all areas of hydrocarbon characterization in exploration and exploitation, particularly those directly or indirectly involved in any of the analytical aspects of this work. The breadth of techniques and applications covered in this book make it a valuable reference work for such people. The chapters are not exhaustive reviews of the topics, nor were they meant to be, but they provide sufficient references for the interested reader to readily delve further into published literature for more information if necessary. The authors of all the chapters are experts in their fields and provide valuable insights into their particular areas of expertise. As one may expect there are large numbers of chapters dealing with some aspect or other of mass spectrometry. However this is not surprising as one considers the extremely important role MS has played in the characterization of hydrocarbon mixtures for many decades. Furthermore, varied applications of MS are covered, along with applications specific or unique for a particular MS technique. All of the chapters are well written, with high-quality diagrams, and as mentioned above, good literature coverage while at the same time not being extensive reviews. I particularly liked the fact that several chapters contained a section on future challenges and developments and was a little disappointed that not all chapters actually contained a similar section. My one criticism of the book would be that the index leaves a lot to be desired. For example, when I looked for “supercritical fluid chromatography” or “SFC” there was no entry on it in the index. There is a citation for “SFCNMR” and “SFCSFC” but for example the whole section on “SFC” on pages 134–137 did not merit a mention in the index. This is but one example and there are many others. This is a pity since many people will buy and use this as a reference work and will want to find specific topics quickly and not want to spend a lot of time digging through an incomplete index. But all in all, the arrival of a book like *Analytical Advances for Hydrocarbon Research* is timely and will serve as a useful guide for many years to come.