

Overview

In recent years new ionization techniques, including laser desorption, fast atom bombardment and plasma desorption, and new separation techniques, combined with mass spectrometry, including tandem mass spectrometry, liquid chromatography, and supercritical fluid chromatography, have become standard analytical mass spectrometric capabilities. This book describes recent developments in the applications of these new techniques, including some computer software innovations, to the complex problems associated with the fossil fuel industry. These techniques bring new mass spectrometric capabilities to the fossil fuel analytical laboratory to complement the standard capabilities already in use, like low- and high-resolution electron ionization, chemical ionization, and gas chromatography/mass spectrometry. This book describes the details for better understanding some of these novel techniques and the application of given techniques to the solution of specific problems. Therefore, this book will provide the practicing researcher with a better appreciation for the application of specific techniques in fossil fuels analysis. One good example is the increasing need to analyze higher molecular weight, nonvolatile polyfunctional materials (such as resids) without thermally degrading them. In time, these novel ionization and separation techniques will have a dramatic impact on the fossil fuels analytical chemist.

Background

Fast atom bombardment (FAB) involves directing a neutral atom beam (argon, in most cases) at a liquid matrix in which the sample is dissolved. The liquid matrix is typically glycerol due to its relatively low vapor pressure. The ions observed can result from pre-charged species or protonation of neutral molecules. FAB has been shown to give molecular weight information for a wide range of chemical classes. In addition to glycerol, a large array of matrices have been used including thioglycerol, dithiothreitol, dithioerythritol, lithium sulfolane, and dimethylsulfoxide to name a few of the most common solvents. Campana and Freas¹ have utilized both positive and negative FAB for the screening of additives in base oils and lubricants. While negative ion FAB provided less structural information it proved more useful as a means for profiling the various materials. An ionization technique closely related to FAB is organic secondary ion mass spectrometry (SIMS) in which an ion beam is used instead of the neutral atom beam of FAB. In SIMS either a liquid matrix or a dry sample can be used.

Another relatively new ionization technique for obtaining molecular weight information from nonvolatile and thermally labile compounds is laser desorption. In this technique the sample is ionized by photon irradiation. Both continuous wave (for example, carbon dioxide) and pulsed (for example, neodymium: yttrium aluminum garnet) lasers have been used. Data acquisition is an important parameter for laser desorption due to the time

¹ Campana, J. E. and Freas, R. B., *Transactions, American Society of Lubrication Engineers*, Vol. 29, No. 2, 1986, p. 235.

dependence of ion formation and subsequent collection. For example, Brown and Wilkins² have utilized a pulsed CO₂ laser coupled to a Fourier Transform Mass Spectrometer for laser desorption studies of synthetic porphyrins. The M⁺ ions were favored by high laser energy output whereas the cationized species were favored at low laser energy output.

The final novel ionization technique to be discussed in this brief review is plasma desorption ionization. Typically this technique utilizes ²⁵²Californium as the ionizing source, such that the nuclear event causes atom fission with one fragment starting a clock and the other penetrating the sample with subsequent ionization. The resulting ions are then mass analyzed with a time-of-flight mass spectrometer.

Tandem mass spectrometry (MS/MS) a relatively new separation technique for the direct analysis of complex mixtures, is comprised of two mass analyzers separated by a collision cell. Analogous to gas chromatography/mass spectrometry (GC/MS) which separates neutrals prior to ionization and mass analysis, MS/MS separates by mass-to-charge ratio with the first mass analyzer (after the mixture has been ionized), passing the separated ions into the collision cell where they undergo collision induced dissociation (CID). The resulting fragments are then mass analyzed with the second mass analyzer. In this manner the CID spectra of individual mass-to-charge ions (termed daughter spectra) can be obtained. The spectra can then be compared with authentic or interpreted a priori in a similar manner to GC/MS data. In addition to this mode of operation other scan modes are also amenable to MS/MS increasing the selectivity for specific compound types (for example, parent scans for characterizing a complex mixture for those components having a selected substructure or neutral loss scans for characterizing a complex mixture for those components having a specific functional group). A number of fuel-related studies in which tandem mass spectrometry was utilized have been reported. For example, Wood et al.³ have shown that the combination of a calcium/mixed amine reduction of an SRC II middle distilled fraction with MS/MS parent scans proved invaluable for characterizing this complex coal-derived liquid for sulfur-containing polynuclear aromatic hydrocarbons (PNAs). Reduction of the benzothiophene and dibenzothiophene-type molecules resulted in C-S bond scission with subsequent hydrogenation of the nonthiophenolic portion of the molecule. Using negative ion chemical ionization parent scans for the negative thiatropylium ion enabled characterization of the entire series of alkyl benzothiophenes and dibenzothiophenes.

Another novel mass spectrometric separation technique involves the coupling of liquid chromatography to the mass spectrometer. This technique enables nonvolatile thermally labile compounds to be successfully analyzed with a mass spectrometer. The major breakthrough enabling this successful coupling involved the interface—one of the most successful being a combination interface/ionization assembly called thermospray. In this interface the LC effluent is utilized as a medium for ion formation. However, solvents, salts, solvent flow rate, and interface temperature are all important parameters for successful ion formation using the thermospray interface.

The most recent separation technique combined with mass spectrometry is supercritical fluid chromatography. Supercritical fluid chromatography has been shown to have some enhanced separation potential which surpasses both gas chromatography and liquid chromatography. This technique utilizes the fact that the properties of the supercritical fluid (that is, low viscosity) result in the mobile phase having a character intermediate between

² Brown, R. S. and Wilkins, C. L., *Analytical Chemistry*, Vol. 58, 1986, p. 3196.

³ Wood, K. V., Cooks, R. G., Laugal, J. A., and Benkeser, R. A., *Analytical Chemistry*, Vol. 57, 1985, p. 692.

a gas and a liquid. While CO_2 is a common supercritical mobile phase the addition of other more polar solvents increases the separating capability.

Highlights

The papers in this book can be divided roughly into three general categories. The first few papers deal with some relatively new approaches to fossil fuel analysis using mass spectrometry. The majority of papers, comprising the middle section, apply novel techniques to specific problems. The last two papers deal with the impact computers have in coupling mass spectrometry with real world analyses.

The three relatively new approaches to fossil fuel analysis presented include supercritical fluid chromatography/mass spectrometry, GC/MS hydrocarbon type analysis and chemical ionization proton exchange analysis. Chess et al. detail the development of supercritical fluid chromatography (SFC)/mass spectrometry for fossil fuels analysis. Particular emphasis is placed on both the use of polar fluids and the interfaces available for doing SFC. Furthermore they show examples of chemical class separation using SFC/MS. They feel that the advancement of SFC/MS in fossil fuels analysis is limited, at present, by the number of active participants, but the potential for major contributions using SFC/MS is there. Gehran and Yost describe development of a method for using GC/MS to do hydrocarbon type analysis (HTA) of jet fuels. This method utilizes a short DB5 capillary column for sample introduction. The type analysis generated is based on the current ASTM D 2789 inverse calibration matrices. Particular emphasis was placed on investigating component discrimination in GC introduction as well as sensitivity and limits of detection. The GC/MS/HTA results were found to be both reproducible and relatively consistent with ASTM D 2789 results which represent the industry standard. Miller and Hawthorne describe the use of chemical ionization—proton exchange (CIPE) for the determination of the number of unsubstituted positions on an aromatic molecule. This information can be utilized to identify a number of isomeric aromatic species whose electron ionization mass spectra are indistinguishable. This method utilizes methanol- d_1 for the reagent gas. Upon ionization only the aromatic hydrocarbons undergo deuterium exchange. CIPE analysis was shown to be useful in identifying a considerable number of isomeric benzenes, indans, and tetralins in a coal-derived jet fuel after electron ionization had proven unsuccessful.

The middle section of papers in this book deals with the application of novel mass spectrometric techniques to specific problems. For example, Johnson and Yost have used tandem mass spectrometry to study the MS/MS characteristics of steranes. EI MS/MS was shown to be more sensitive and selective than using PCI MS/MS. The sterane distribution in different oils could be determined by utilizing a parent scan of m/z 217. However, only the most abundant steranes could be confirmed by EI MS/MS daughter spectra. Some sample cleanup was suggested as the most viable approach to low-level detection of steranes and to prevent instrument contamination. Harriman et al. have compared two different methods for increasing the sensitivity of biomarker analysis beyond conventional capillary column GC/MS using nominal mass resolution. The two different methods involve (1) increasing the resolving power to 2000 to 3000 or (2) monitoring fragments formed in the first field free region of a double focussing mass spectrometer. The second method was shown to provide adequate sensitivity using whole oils without sample cleanup in addition to providing results which are easier to interpret and less susceptible to interferences than the first method. Beato and Yost investigated the electron ionization and ammonia chemical ionization behavior of metalloporphyrins. The purpose of this study was to correlate the degree of fragmentation with the metal involved in the complex. Their results were correlated with the stability index, $S_1 = [100(PE)(V)]/R$, where PE is the Pauling electro-

negativity of the metal, V is the valence, and R the ionic radius. Metalloporphyrins with high stability indices gave intense doubly charged ions in EI and little fragmentation in CI. On the other hand, metalloporphyrins with low stability indices gave less abundant doubly charged ions in EI and fragmented to mono- and dipyrrolic fragments in CI. Gallegos reports the analysis of *n*-alkylbenzothiophenes by GC/MS. The close similarity between identified *n*-alkylbenzothiophenes and *n*-alkylbenzenes in an Arabian heavy Crude suggests the sulfur analog is formed from the latter. This reaction is postulated as occurring during maturation of the oil when *n*-alkylbenzenes come in contact with sulfur. Schmidt and Sprecher report the utilization of a low voltage high-resolution mass spectrometric direct insertion probe method for determining the heteroatomic composition, homologous series and carbon number distribution of coal-derived materials. Application of this method to a study investigating the removal of organosulfur compounds from coal extracts treated with molten caustic is described. Crawford et al. describe an on-line method to study the kinetics and chemistry of formation and evolution of ammonia during pyrolysis of oil shale. Isobutane chemical ionization was used because of its sensitivity and selectivity for ammonia overcoming possible interferences with water. Taghizadeh et al. investigated the combination of low voltage mass spectrometry with multivariate analysis for on-line process monitoring of coal-derived liquids. This method was applied to compositional changes which occur during hydrotreatment using fixed bed catalysts. As expected the major trend was the "hydrotreatment effect;" an increase in the percentage of hydroaromatics relative to aromatics in the product stream. Secondly, with increased time and temperature, more higher molecular weight components, primarily alkyl substituted aromatics, were detected.

The last two papers contain a significant component of computer programming expertise to facilitate the mass spectrometry data/identification interface. Aczel et al. describe development of an expert system for interpretation of the GC/MS spectra of fossil fuel distillates. This system uses interpretation rules generally carried out by a skilled professional, such as the deconvolution of peaks, sets acceptability limits for commercial data system identifications and identifies components not identified by commercial data systems. The need for such a system stems from the need to identify complex hydrocarbon mixtures. Results indicate identifications are correct 90 to 95% of the time and result in a considerable reduction in skilled interpretation time. In the final paper Grigsby describes the processing of high resolution mass spectral data using Kendrick masses. The computer programs used for this method enable elemental formulas to be assigned to ions in high resolution mass spectra and displayed in a rectangular array to facilitate identification. Results are presented for a selected fraction containing one-ring aromatic neutrals from a Venezuelan heavy petroleum.

The papers presented in this book provide the reader with an overview of and some insight into the types of ionization, separation and computer techniques which will become routine in the near future. The editors would like to acknowledge the efforts of the authors as well as the ASTM personnel who have made publication of this book possible.

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