Chapter 15

ADVANCES IN NMR TECHNIQUES FOR HYDROCARBON CHARACTERIZATION

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1. INTRODUCTION

It is clear from the amount of material in this book focused on various chromatographic techniques, that the analysis of complex hydrocarbon mixtures continues to be one of the biggest challenges facing analytical chemists in the pharmaceutical, biomedical, environmental, petroleum, polymer, and petrochemical arenas. Nuclear magnetic resonance (NMR) has long been recognised as the spectroscopic technique of choice for obtaining detailed structural, dynamic, and chemical information of organic compounds. However, the analysis of complex organic mixtures with traditional one-dimensional (1D) NMR techniques usually suffers from severe spectral overlap, making it virtually impossible to extract detailed compositional information. Many ingenious and elegant 1D, 2D, and multidimensional NMR spectral editing techniques have been developed that address various aspects of this resolution problem and are now routinely implemented on modern commercial spectrometers. Excellent texts describing both the theoretical aspects and the practical application of these techniques are available.1-5

NMR spectroscopy is a vibrant field and it is neither practical nor the intent of this chapter to capture all the recent advances in this multidisciplinary field. The intent of this chapter is to focus on some of the recent developments in NMR spectroscopy that have potential for improving our ability to analyse liquid phase or soluble hydrocarbons. Some of the improvements in NMR instrumentation that impact hydrocarbon characterisation include higher magnetic fields, improvements in probe technology, facile implementation of pulsed field gradients, and improved selectivity through coupling with separation techniques.
techniques (e.g. HPLC-NMR and coupling with capillary electroseparation techniques).

By design, this chapter will highlight certain techniques and examples the author thinks will be of interest to the reader. The choice of material presented, examples included, and references cited are by no means exhaustive. The goal of this chapter is to give the reader an appreciation for some of the recent advances in NMR techniques for hydrocarbon characterisation and to point them to areas of research rather than enumerate the vast amount of work in NMR technique development published in the past few years.

2. DISCUSSION

2.1 Availability of Higher Magnetic Field Strengths Provides Increased Sensitivity and Resolution

There have been continuous efforts to increase the field strengths ($B_0$) of NMR magnets ever since the first spectrometers were introduced. This is because NMR theory and experience have shown that the sensitivity increases in proportion to $B_0^{3/2}$ and chemical shift dispersion increases linearly with $B_0$. Thus, the information content and spectral interpretation are typically improved as the magnetic field strength is increased. The current state-of-the-art field strength is 18.8T (800 MHz for $^1$H) with the first 21.1T (900 MHz for $^1$H) delivered in 2001.

In the case of polyolefins it is well accepted that many important physical properties are related to the branching microstructure, the type of structural information readily determined from NMR analysis. High resolution $^{13}$C NMR has been used for many years in detailed structural studies of commercial polymers, and resonances for branches shorter than six carbons long have been successfully assigned. Rinaldi et al. recently described an interesting application of high magnetic fields (17.6T, 750 MHz for $^1$H) to improved spectral resolution in the $^{13}$C NMR of polyethylene where unique resonances from chain branches up to 10 carbons long were resolved. These higher magnetic field strengths are also finding important biomedical applications, such as in determining 3D structures of high molecular weight proteins.

Although the need for increased sensitivity and chemical shift dispersion have been the driving forces for increasing magnetic field strengths these newer ultra high field magnets are prohibitively expensive and are not yet widely available for routine use. This has lead to increased focus on national labs and centers of excellence to defray cost while maintaining capabilities. It is anticipated that the increased availability of these newer high field systems in the coming years will have far reaching influence on our ability to analyse complex