IS LOW FIELD NMR NOW A "MUST HAVE" TECHNIQUE FOR THE MODERN PETRO INDUSTRY LABORATORY?

Nuclear Magnetic Resonance Spectroscopy (NMR) has been a major technique for the Petroleum and Petrochemical industries (1) for many years and instrumental advances in the area have largely centred around the development of higher magnetic field cryo-cooled superconducting magnets and associated control electronics in the search for increased sensitivity and spectral resolution.

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However, this increased performance comes at a significant cost penalty both in terms of high instrument capital cost and the annual revenue cost to run the instrument. In addition, high field instruments require significant laboratory space and a high degree of analyst expertise to extract the maximum performance from the instrument. Because of the continued drive to reduce costs the availability of high field instrumentation in many parts of the industry has decreased as installations become limited to large corporate research centres or have been outsourced. In addition, because of globalisation, many companies have set up modern regional technology centres to support emerging markets where it is difficult to justify the costs of high field NMR and as a result the routine application of the technique has declined.

However, in the last 10 years or so, significant progress has been made in the development of stable, cryogen free, rare earth permanent magnets which, when combined with modern miniaturised radio frequency electronics and chemometric data analysis and processing, have led to the development of bench top low field NMR instruments (2). In this article, we give a brief overview of the technology and identify some key potential laboratory based application areas in the petrochemical industry. Note in this article we will not be considering Low Field Downhole NMR applications which is a very specialised application area for NMR.

The main advantages claimed for Low Field NMR techniques are:- they are non-destructive, fast, low cost, requires minimal sample preparation, gives a bulk measurement of the whole sample and generally do not require the use of solvents.

Low Field proton NMR bench top instruments can be broadly split into 2 operating modes, those which operate in a time domain mode based on relaxometry and those operating in classical NMR Spectroscopy mode.

Low Field Time Domain Nuclear Magnetic Resonance (TDNMR) Relaxometry

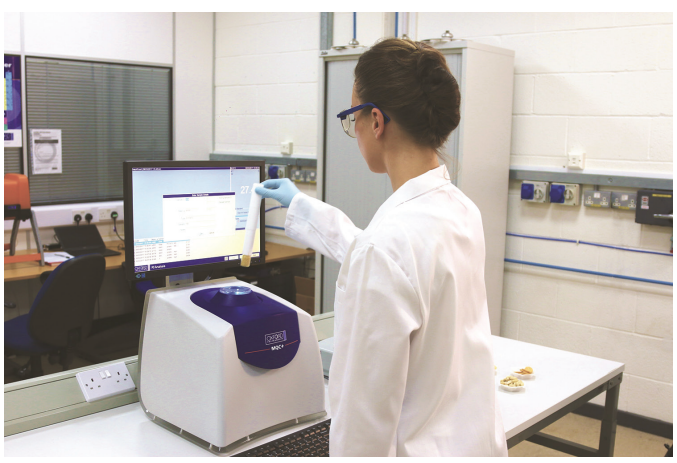
TDNMR measurements don't give detailed chemical composition information and are most commonly used for the measurement of physical properties such as bulk quantification, solid vs liquid content and sample morphology.

In a typical experiment the sample is placed in a tube inside sample holder where the hydrogen protons align with the fixed magnetic field within a few seconds. The sample is then exposed to a radio frequency (RF) pulse matching the 1H frequency which causes the nuclei to realign with the RF induced field. When the RF pulse is finished the nuclei relax and return to realign to their equilibrium state with the fixed magnetic field and emit energy. For proton NMR total emitted energy is proportional to the hydrogen content of the sample and the decay rate, often called the Free Induction Decay (FID), can be related to the hydrogen content and many of the physical properties of the sample. Relaxation times, T1 and T2, are time constants which can be determined from multi-pulse TDNMR experiments and are related to molecular mobility, viscosity, and paramagnetic nuclear interactions. These relaxation times and decay profiles can be used to determine water content in oil, or oil content in water, and can also be employed to study chemical and physical properties of petroleum materials such as molecular size, asphaltene content, wax content and hydrogen content of fuels and refinery process streams (1).

Commercial TDNMR instruments fall into 2 main types, those configured and pre-programmed for a single application, such as the Xigo Nanotools Acorn products, and the more sophisticated multipurpose instruments such as the Oxford Instruments MQC+ and the Bruker Minispec instruments which can perform a wide range of experiments using complex pulse sequences and advanced chemometric data analysis techniques

The Acorn range focusses on studying the particle liquid interface and offers instruments for nanoparticle size measurement in fluids, emulsion or foam droplet size and distribution, and a flow based

Oxford Instruments MQC+



system for studying the influence of additives on the particle-liquid interfaces of dispersions.

The more sophisticated instruments from Bruker and Oxford Instruments are capable of a wide range of standard methods such as the Hydrogen content of Middle Distillate Petroleum Products (ASTM D7171) and for the development of in house methods for a wide range of samples of interest in the petroleum and petrochemical industry. A recent publication described the application of TDNMR to quantify the Biodiesel content of Diesel fuels (3) and other applications include oil and water measurements in crude, oil in paraffin and wax, water and bitumen content of oil sands and the analysis of polymers and co-polymer mixtures.

Although these instruments are primarily aimed at the QA and QC markets they also offer a wide range of method development options such as sophisticated pulse sequence experiments which when combined with the comprehensive data analysis software and chemometric methods allow the rapid development of in-house methods.

Low Field NMR Spectroscopy (LFNMR)

In the last decade the development of Low Field NMR Spectroscopy instruments has accelerated due to a combination of permanent magnet and RF electronics developments from mobile phone technology, together with powerful data analysis software, to produce true bench top cryogen free systems. In this technique, a conventional NMR spectrum is generated through a Fourier Transform of the FID signal and although the target market for these instruments was originally to provide low cost spectrometers for educational establishments they are now gaining wide spread application in academia and industry as powerful additions to the analyst's tool box. Instruments offering a wide range of capabilities are available from a range of companies including the Oxford Instruments Pulsar, the Thermo picoSpin, the Nanalysis NMReady series and the Magritek Spinsolve series.

Although these instruments produce lower resolution spectra than their high field cousins the application of advanced data processing and chemometric analysis which has been so successful in the application of other low resolution spectroscopic techniques, such as Near Infra-Red (NIR) spectroscopy, is revolutionising the potential for applications of LFNMR in many industries.

Most of these instruments use conventional NMR tubes to introduce samples and can therefore handle a wide range of sample matrices but the Thermo picoSpin employs micro-coil technology to facilitate the use of a low volume capillary flow cell with a volume of only 40uL which makes it very useful where sample availability is limited. It can also be easily coupled to auto samplers for high throughput analysis of liquid samples as illustrated in their Application Note (AN52906) titled "Automation of the picoSpin 80 1H NMR benchtop spectrometer for high-throughput determination of the research octane number of fuel". However, the flow cell technology does limit it to liquid samples with a suitably low viscosity for sample injection.

All the manufacturers have listed Petroleum and Petrochemical applications in their marketing documentation but, at the moment, published applications are limited. However, the literature is full of many high field NMR applications in the industry which with the improved performance of modern LFNMR instruments and chemometric data analysis techniques could be adapted for application in laboratories globally where installing conventional high field NMR would not be contemplated.

In addition to proton NMR some of the manufacturers also offer Fluorine as a second nucleus and in the case of the Magritek Spinsolve 80 an optional upgrade to include a third nuclei like 7Li, 11B, 13C, 15N, 23Na, 29Si, 31P can be chosen. The Oxford Instruments Pulsar offers 13C, 23Na and 31P as options.

Application areas include QC/QA for finished products, reaction monitoring in research, process development and process control, and crude oil to finished product classification.

Some of the more sophisticated instruments also offer the capability to perform 2D homo- and heteronuclear sequences including COSY, J-resolved, TOCSY, DEPT and HMQC making these particularly powerful analytical tools for problem solving and troubleshooting issues in the field.

Summary and Conclusions

In recent years there has been significant development in Low Field NMR techniques and instrumentation which have revolutionised the potential for applying the technique across a wide application area. These bench top instruments offer new possibilities to introduce NMR into laboratories, such as refineries, petrochemical plants and blending facilities where the cost and space requirements for conventional high field NMR were previously considered prohibitive.

Acorns Xigo Nanotools

LFNMR techniques can be employed to replace existing techniques which may be costlier, time consuming and require the use of solvents and reagents, or where the improved compositional data provided by NMR adds new knowledge and improved product quality and control. They can also can be used to complement other commonly used techniques, such as FTIR, GC-MS and LC-MS, and be incorporated into multi technique spectral and compositional databases which can be employed in all areas of the petroleum and petrochemical industry from basic research through product development and manufacture to customer support in the field.

(1) A Review of Applications of NMR Spectroscopy in the Petroleum Industry, Chapter 16 in "Spectroscopic Analysis of Petroleum Products and Lubricants" © ASTM International, 2011

Dr. John C. Edwards Process NMR Associates, LLC, 87A Sand Pit Rd, Danbury, CT 06810, USA

(2) A Renaissance For NMRs, Big And Small, Marc S. Reisch, Chemical and Engineering News, Volume 93 Issue 37, pp. 19-21, Sept, 2015

(3) Determination of Biodiesel Content in Diesel Fuel by Time-Domain Nuclear Magnetic Resonance (TD-NMR) Spectroscopy Grazielli da Rocha et al, Energy Fuels, 2017, 31 (5), pp 5120–512

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