Awards

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Translated from French by Dr. Raymond Milward

INDUSTRIAL ANALYSIS
THE NMR ANALYZER MOVES UP TO PROCESS

- In 1999, FOXBORO introduced the first on-line Nuclear Magnetic Resonance (NMR) analyzer for petroleum refineries. We have thus presented it to you in our review. The benefits and potential of this analytical technique merit that one stops here a little longer. This article compares the advantages and disadvantages of NMR with near infrared spectroscopy (NIR). It addresses itself particularly to refinery applications.

The heart of the analyzer is heavy. 250Kg is the weight of the box that contains the magnet and outer shielding to protect the surrounding environment against stray magnetic fields. Until now, the need for such a "carapace" has held back the development of industrial applications of Nuclear Magnetic Resonance (NMR). In the past, the instruments were generally confined to rooms, at the entry of which a placard advises to take off one's watch and to empty pockets of all keys or magnetically coded credit cards. Persons carrying pacemakers were advised to not approach too close to the magnet.

To bring this so-called "high resolution" NMR to an idustrial site, it was now necessary to create a protective enclosure for all other factory equipment and personnel. Hence the 250Kg of magnet and shielding. In the inverse sense, the analyzer finds itself at the mercy of vibrations or thermal shocks.

So packaged, NMR has everything to become one of the most powerful methods of industrial analysis. The NMR spectra associated with the magnetic properties of protons permit the identification of the different molecules of which the sample is composed. The intensity contains quantitative information, directly proportional to concentrations. NMR now becomes a competitive technology to infrared optical spectrometry, and more particularly to the near infrared (NIR) beween 700 and 3000 nm, which utilizes molecular optical absorption properties.

NIR has had the advantage of being the first to be deployed at production sites. Already, in numerous petroleum refineries, on-line near infrared (NIR) analyzers continuously monitor the composition of fluids at different process points, (distillation, cracker, gasoline blender...) *BP Chemicals*, Lavera, France have developed an NIR system for the control of different refinery processes. The annual savings recovered for each site has been estimated at one million dollars.

In aiming its NMR analyzer at petrochemical applications, *Foxboro* knows the economic benefits. In addition, the American supplier has chosen a sole commercial strategy for the marketing of their package in the area of production control systems: emphasis of the Return On Investment. It has now taken account. Not less than 19 possible NMR measurement points have been counted in a refining process. And the payback lies between 0.20 and 0.55 dollars per barrel of crude oil.

Multicomponent analysis

NMR and NIR have in common to be spectroscopic methods (optical for the infrared, electronic for NMR), and to be able to analyze in a few seconds, many decades of components. A measurement cycle with an average of several spectra (to improve signal/noise ratio) takes around one to two minutes. Regarding the detection sensitivity, it is normally in the region of several hundreds of ppm (it is generally better for NMR but is still inferior to that obtained by chromatographic separation analysis).

The two techniques make use of chemometric analysis, which provide the tools for choice for quality control or prodution control. Using mathematical regression methods, which break down a complex multicomponent spectrum into a sum of primary spectra, chemometrics delivers a global picture of a sample, which could then be validated in real time in comparison to a reference sample. In petroleum chemistry, NIR and NMR alloow the validation of octane numbers (RON, MON) of gasoline, which are the result of a known mixture of scores of components.

Out of the experience already gained with optical methods in the industrial domain, the attributes of spectrometric techniques are known: a very high signal/noise ratio, optical paths according to the nature of the sample (depending on the sample viscosity or opacity) to give good sample statistics. Measurements are insensitive to pressure or to a moving fluid, which allow an in-situ measurement, either directly in the process or in a sampling loop. To note again, is the maintenance of equipment that is becoming progressively easier. Finally, optical multiplexing permits one analyzer to be connected to several measurement points.

Medium Resolution NMR

On the other hand, new on the scene, NMR has to one more regain the confidence of industry. It has several strong points to make for it.

The first lies in the **direct relation between the measured signal and total proton concentration** (in contrast to optical measurements, where a specific extinction co-efficient for each molecule has to be taken into account). As well as the infrared brings information over several physical properties, such as boiling point, NMR is incontestably richer concerning the characterization of physical and physico-chemical properties of the product. The frequency shift being related to the chemical environment of the protons permits the determination of viscosity, density, cloud point, melting point, etc.

Another advantage is the **superior resolution of chemical information** contained in the signals. Unlike NIR, where there is a heavy overlapping of spectral signals, the NMR spectra of protons related to functional groups of aromatics, aliphatics and olefins are well separated. A polynuclear aromatic can be easily distinguished from a mononuclear aromatic. Similarly, fuels for diesel engines are clearly recognizable by the ratio of CH_2 and CH_3 peaks (directly related to the aliphatic chain length). The concentration of aromatics and the chain length of aliphatics relate to the fuel physical properties, e.g. cetane index. The chemical information is so well resolved in the NMR spectra, that the first known method of measuring the cetane index of fuels by NMR was effected without resorting to chemometrics (the ratios of integrated areas of the spectrum were compared, with a reproducibility conforming largely with the ASTM reference method).

This resolution facilitates access to the chemical information necessary to characterize a process fluid. It unravels simplicity in the measurement model (in the case of NIR the bands can overlap and require deconvolution before commencing correlation manipulations). This accessibility of information should permit the attainment of industrial models capable of extrapolation, or the detection of out-of-range values.

The realization of calibrations and the chemometric model is equally simplified due to **the insensibility of NMR to temperature variation variations, or chemical composition of the product.** The measured frequency, characteristic of the molecule, remains conctant, in contrast to the infrared, for which these influential parameters induce changes in response (shift). Therefore, in an NMR analysis of oils, it suffices to make ten calibrations for the ten parameters that one wishes to study. The infrared method could require fifty-odd, because it would be necessary to make calibrations in different temperature ranges. Thus one loses time both at set-up and during operation.

Another advantage of NMR - water does not disturb the measurement of other components. It appears in the form of a distinct non-interfering peak. If necessary, the spectral range can be adjusted to exclude the H_2O peak, or conversely the peak can be measured **to follow the water content** in the product. In NIR, the presence of water interferes over a large part of the spectrum, and it is often difficult to correlate of varying humidity.

NMR also has its own limitations. As we have already seen, risks of magnetic disturbances associated with the magnet, require the use of shielding. Also, the sample has to pass through the center of the magnet. This requires the use of shielding. Also, the sample has to pass through the center of the magnet. This requires a sample loop and measurement cell in the form of a standard tube, several mm in diameter with regulated flow, or static fluid (stopped-flow). In the case of a change of process fluid, NIR cells require cleaning and re-adjustment. But NMR is much more suitable than optical analyzers for the measurement of opaque, viscous or optically 'dirty' samples (for example, crude oil).

The absence of moving components in the sample path (outside of the valves used to control the passage of process fluid through the analyzer) gives the instrumentation a certain robustness.

Technical details extracted from article of Raymond Milward (Foxboro Great Britain Ltd.)

Figure Captions

Foxboro has counted 19 possible NMR measurement sites in a refinery, for gasoline, reformates, naphtha streams, distillates, crude oils, etc. With analysis of chemical composition (aromatics, olefins, saturated chains...), determination of octane numbers, cetane index, or physical properties like API gravity, viscosity, cloud point, NMR is rich in information.

NMR SPECTROSCOPY - MEASUREMENT PRINCIPLE
Nuclear Spin

NMR is related to the magnetic properties of atomic nuclei. An atom in which the spin (which characterises the magnetic moment) is non-zero has a magnetic dipole. This nuclear spin is the aggregate of the spins carried by each proton and each neutron. In addition, the spins can only exist in two states of opposing energy values. All the nuclei formed by an even number of protons and an even number of neutrons are now of zero nuclear spin and can not be measured by NMR. This is the case with carbon (isotope 12) or oxygen (isotope 16) which are nuclei of capital importance for organic chemists. Happily, the nucleus of hydrogen present in all organic materiael, is constituted of a singe proton of non-zero spin. it represents by its simplicity, an exemplary model. In the absence of other magnetic influences, the spins orient randomly in space. On the other hand, when they are subjected to a unidirectional external magnetic field, they align either with the field or against the field, according to their spin energy states. Nuclei with low energy align with the field, and those of higher energy in the opposite sense, their energy gap increasing with field intensity. At ambient temperatures the difference in population between nuclei in the lower and excited energy states is only a few parts per million, and it is on this minute population difference that NMR is based. If the nuclei are now subjected to an appropriate high-frequency (RF) magnetic field, there will be a resonant absorption of RF power corresponding to excitation from the lower to higher excited states. The power absorbed is directly proportional to the total proton concentration of the sample, and can be readily measured.

NMR and Chemical Structure

The majority of current NMR analyzers operate in a pulsed mode, whereby the sample is irradiated by short, low power (~W) pulses of precise duration (5 to 15 us). These are sufficient to deflect the magnetic moment 90 degrees from the external magnetic field direction. When the pulse is switched off, the excited spins re-radiate an electromagnetic signal or free induction decay (FID) during the time that they become relaxed and re-align with the external magnetic field. The FID is detected by the same coil producing the excitation, and has the form of an oscillatory exponential delay, which is a composite of all the relaxing spin signals. The FID amplitude is sampled and digitized at regular time intervals (ms time domain), and converted into an NMR frequency spectrum using a Fast Fourier Transform (FFT) algorithm, similar to those commonly employed in FTIR spectroscopy.

The location and amplitudes of spectral lines in NMR are a precise indication of molecular structure, as hydrogen atoms located in different parts of a molecule will appear as unique signals at frequencies indicative of their molecular environment. The frequency axis of NMR spectra is usually expressed in terms of the shift as a percentage of the RF excitation frequency, in parts per million (ppm). In additon, NMR spectra can be influenced by interactions with neighboring nuclei, leading to further complex splitting patterns. Together, these details provide a wealth of information and chemical structure of the sample.

Quantitative Aspects of NMR

If the frequency domain of gives information on the chemical and molecular structure, the inttensity of an NMR spectrum contains quantitative information form the total number of nuclei. During the excitation pulse, nuclei absorb the RH energy, exciting spins to the higher energy state. After the RF pulse, the relaxing nuclei radiate RF energy at specific frequencies depending on their chemcial and molecular environment. The amplitude of the FID signal isproportional to the toaltal number of excited nuclei. Unlike any other spectroscopy, this energy absorption remains quantitative and linear across the whole NMR spectral range (the absorption of RF energy depends only on the number of nuclei present). It is not enhanced or attenuated by specific molecular environments or chemical functionality.

The Foxboro NMR Spectrometer

THE CEL

The measurement is made in 4 stages; 1st stage: the pipeline sample fills the cell. The flow is stopped. 2nd stage: the magnet creates the magnetic field that induces the orientation of the hydrogen nuclei in the field direction. 3rd stage: a pulse of 57 MHz radio frequency waves changes the orientation of the molecules (to 90 degrees). 4th stage: The RF power is cut. The molecules return to thier original orientation, at the same time emitting a radio frequency signal, in which the frequencies are characteristic of the chemicial environments of the hydrogen atoms, and which the signal amplitude is directly proportional to their concentration.

THE ANALYZER

The sampling system for the fluid flow operates as a by-pass of the process stream. Sample tubes of up to 13 mm diameter are available. Samples are usually measured in a 'sopped-flow' mode, using valves at the entrance and exit (return of sample to process stream). **The high field permanent magnet** corresponds with a frequency of 57 MHz. There are no special restrictions regarding its siting, and it presents no security problems for installation. It is sensitive to heat, and requires a temperature-controlled environment. To assure maximum magnetic field homogeneity, a pre-programmed and automated compensation system has been incorporated. A **computer** controls all spectrometer functions and data acquisition of FID signals. In order to enhance the signal/noise ratio, a number of seuential FID traces or (preferably) the NMR spectra can be c-added and averaged. The computer uses a (fast) Fourier transform algorithm to calculate the NMR spectra from FID traces, complete with phase error correction. The computed NMR spectra are then normalized for the purpose of **chemometric analysis**. This is carried out using the partial-least-squares (PLS) regression algorithm. Once calibrations have been established, 'real-time' concentration readings from process streams are automatically available.

An **Ethernet** (co-axial cable) system assures communication between the NMR analyzer and remote computer and control system.

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