Applications of Nuclear Magnetic Resonance Spectroscopy in the Fat and Oil Industry

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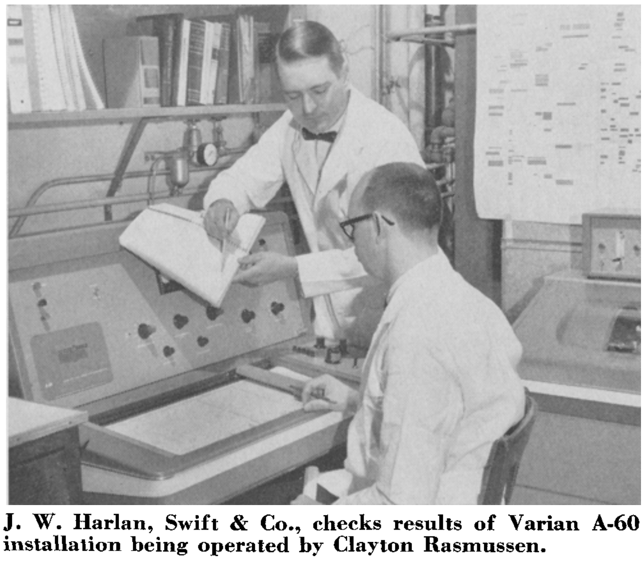
NUCLEAR Magnetic Resonance (NMR) is becoming an increasingly important analytical tool in the fat and oil industry, both in laboratory research and in product control. Low Resolution or Wide Line NMR has been used both in the laboratory to determine solid/fat ratios, polymorphism, premelting phenomena and phase relationships in triglycerides, and in the plant to determine and control moisture and oil content in the processing of cereal grains including corn and soybeans. High Resolution NMR has found applications in the laboratory as a method of studying the chemical structure and composition of oils and their derivatives.

Since the introduction of the Varian A-60 field-frequency stabilized high resolution NMR spectrometer late in 1961, commercial instruments have been available for both high resolution and wide line NMR spectroscopy which are reliable, simple to operate and priced within the reach of most laboratory budgets.

As a result, NMR spectroscopy has taken its place in the laboratory among the other new and powerful instrumental techniques for the analysis of fats and oils such as GLC, mass spectrometry, and IR, UV and X-ray spectroscopy which during the last decade have been brought from the physics laboratory into general use in the analytical and organic chemistry laboratory, largely through the efforts of physical chemists and electronic instrument specialists.

With this arsenal of new techniques (to which we should add thin layer, paper and column chromatography and radioactive tracer methods) at his command, the chemist today can undertake and accomplish investigations that would have been impossible or fantastically difficult ten years ago, and the fat and oil processor can establish and maintain the more rigid and meaningful product specifications demanded in today's market. However, with the rapid and simultaneous development of so many new techniques, it is difficult for the chemist who must address himself to problems other than those in these special areas of analytical instrumentation, to keep abreast of the progress in all of these fields.

It is hoped that this paper, by discussing some past and potential applications of NMR to fat and oil chemistry in the light of basic NMR theory, may make those chemists and food technologists who are not already expert in NMR spectroscopy more familiar with the possibilities and limitations inherent in this technique. Those already familiar with, or working in NMR spectroscopy, are referred to the comprehensive and excellent review article which appeared in the April issue of *Analytical Chemistry* and to the current issue of *Annual Review of Physical Chemistry* for a more complete and detailed coverage of recent developments in theory, instrumentation, and applications.



J. W. Harlan, Swift & Co., checks results of Varian A-60 installation being operated by Clayton Rasmussen.

Some Basic Principles and Definitions

It was postulated by Pauli in 1924, and confirmed experimentally by Dennison and Hund in 1927, that the nuclei of certain isotopes possess quantized spins and magnetic moments. When such nuclei are placed in a uniform magnetic field they may absorb electromagnetic radiation of a frequency given by the Larmor equation:

$$\nu_0 = \gamma H_0/2\pi$$

where ν_0 is the frequency in cycles per second
H_0 is the magnetic field strength in gauss
and γ is the gyromagnetic ratio (an intrinsic property of the nucleus under consideration).

If we consider the spinning nucleus to be equivalent to a tiny bar magnet, the absorption of a quantum of radiation of frequency ν_0 is accompanied by a reorientation or "flipping" of the nucleus in the external field, H_0, from a lower to higher energy level. This absorption of electromagnetic energy at the resonate frequency given by the Larmor equation is the signal observed in NMR spectroscopy.

In order to obtain useful absorption spectra, rather complex and sophisticated magnetic and electronic circuits are required. The basic circuitry requirements were established independently by Bloch at Stanford and Purcell at Harvard who built the first successful NMR spectrometers in 1946 and received the 1952 Nobel Prize in Physics for their achievements. Current NMR spectrometers using similar basic circuitry operate at magnet field strengths of 5–25 Kilogauss and employ radio frequency (RF) electrical circuits operating from 10–100 megacycles depending on the particular isotope to be studied.

Isotopes of a number of elements including carbon, oxygen, nitrogen and phosphorous give detectable resonant absorptions. However, the most easily detected isotope is the ordinary proton or hydrogen nucleus. Since the applications of NMR in the fat and oil industry almost always involve the study of the NMR spectra of protons as they exist in organic compounds or in water, we shall restrict our attention to NMR studies of protons, throughout the balance of this paper.

An important part of the NMR measurement conditions established by Bloch and Purcell is the technique of irradiating the sample with RF radiation of fixed power and frequency while increasing the magnet field strength continuously through that field strength where resonance absorption occurs. By plotting the absorption signal observed in the RF receiver vs. field strength during the sweep, an absorption peak is observed as the resonant condition is passed which may be readily distinguished from the static noise of the RF receiver circuit. In addition, if one "sweeps through" the resonant position in this manner, using an RF power level low enough that saturation of the signal does not occur, the total power absorbed during the sweep is proportional to the number of nuclei in the sample.

If all of the nuclei being observed in an experimental sample experienced exactly the same magnetic field strength, H_0, the absorption peak observed would be a single extremely narrow line at the frequency given by the Larmor equation. However, this is not the case. The effective mag-

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