BROAD-LINE NUCLEAR MAGNETIC RESONANCE AS AN ANALYTICAL TECHNIQUE

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Nuclear magnetic resonance techniques offer a non-destructive method of analysis which can readily be adapted to continuous analysis of flowing samples. Very few papers, however, have been published on the use of the technique for quantitative analysis and these have been confined to hydrogen analysis [1, 2, 3]. This paper describes some applications of the technique to the field of quantitative analysis, using a magnet with a degree of homogeneity sufficient to provide simple spectra.

THE BASIC TECHNIQUE

If a nucleus of an isotope has a spin quantum number, its energy levels will be split when it is placed in a magnetic field, the amount of splitting being proportional to the field applied. As in all spectroscopic techniques it is possible to find a frequency at which energy can be absorbed in order to promote transitions between the levels, and in the N.M.R. technique, the field strengths of 1000–20,000 G that are used require frequencies in the range 1–60 Mc/s. Unfortunately the population of the levels is very nearly equal so that observation of the total energy absorbed, which is all that is possible in nuclear resonance, corresponds to that of the small majority (1 in 10^6) of nuclei in the lower state.

The method of excitation used was to place the sample in an R.F. coil between the poles of an electromagnet and irradiate it at an appropriate frequency; scanning either the field or the frequency to reveal the characteristic resonance absorption.

APPARATUS

The electromagnet was manufactured by Newport Instruments Ltd., England, and has shimmed pole-faces 10 cm in diameter. The magnet was operated with a 3 cm pole-gap (2.7 cm working gap) at 3.2 A giving a field strength of 7000 G. To reduce temperature fluctuations the coils were encased in felt-lined aluminium boxes.

The magnet has a homogeneity of 3 parts in 10^5 over a volume of 1.5 ml and the coil system was standardized at this volume. The magnetic field of the electromagnet is controlled by comparing the voltage drop across the coils with a fixed voltage; the difference between these is amplified and fed to the grids of forty CV345 valves in parallel. The comparison voltage can be supplied from three 85A2 neon stabilizers in series, which gives a current stability of 2–3 parts in 10^6 or the comparison voltage can be directly supplied from a resonance signal obtained from a second spectrometer in the magnet gap. A modulated and detected signal from resonance in this circuit has a characteristic error voltage form and this provides a convenient form of stabilizer directly related to the parameter to be controlled, i.e. the magnetic field. The auxiliary controlling spectrometer interacts with the main analyzing spectrometer when these work at the same frequency. The fluorine signal from a saturated solution of ammonium fluoride in hydrofluoric acid is therefore used when hydrogen analyses are carried out, and the hydrogen signal from water containing 0.1 M manganese sulphate is used when all other isotopes are being determined. A disadvantage of this technique is that the volume of field homogeneity where useful signals can be obtained by both spectrometers is limited with a small magnet, and has to be shared. This results in a loss of analytical sensitivity of about a factor two.

SPECTROMETER

The spectrometer used is of the marginal oscillator type in which the sample sits in the R.F. coil of the primary oscillating circuit. This spectrometer is sensitive to the changes in conductance that occur when resonance takes place. The signal is modulated at 280 c/s, by secondary coils wound on the magnet, and this modulated signal is amplified, filtered and finally converted to a d.c. signal of characteristic derivative form by a phase-sensitive detector. The signal is fed to a centre-zero Honeywell–Brown recorder, and facilities are available for recording this derivative signal or its first or second integral.

ANALYTICAL STUDIES

The area under the signal is proportional to the number of nuclei excited and for conditions of incipient saturation and spectra of the same line-shape the peak height is proportional to the number of nuclei present. This therefore can be used as a quantitative measurement of isotope concentration. It is relatively simple to establish these conditions for liquid samples and
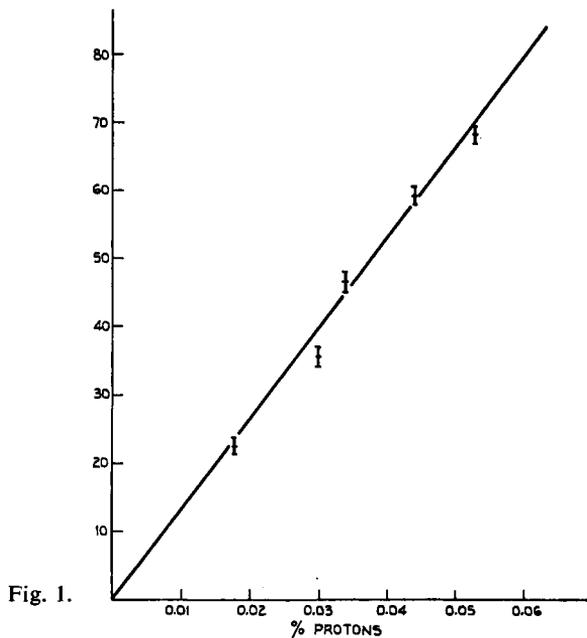
Fig. 1.

the apparatus once set up for a specific isotope can be used to analyze sample and standard with triplicate runs on each in about 30 minutes.

The samples are sealed in Pyrex or silica tubes selected for close internal coil fitting and constant wall thickness. Comparisons between known and unknown samples are made by replacing sample and standard in the coil. A calibrator facility exists for producing a known change in the absorption level of the system, but in general the use of this was not found to improve reproducibility of measurement.

ANALYTICAL RESULTS

Liquid systems

Hydrogen

Hydrogen is one of the most sensitive nuclei for the nuclear resonance technique, and its resonant frequency occurs at 30 Mc/s for a field strength of 7000 G. The hydrogen signal from a wide range of materials has been used for quantitative analytical determinations. Of particular interest are the determination of light water in D_2O, and of residual hydrogen in highly fluorinated or deuterated compounds.

Fig. 1 shows the relationship between peak height of the hydrogen signal and hydrogen content determined by the infra-red technique. It will be seen that there is a linear relationship and that concentrations as low as 0.03 per
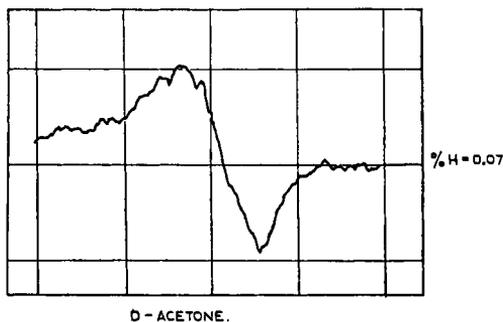
% H = 0.07

Fig. 2.

D - ACETONE.

cent hydrogen can be measured. Whereas at high concentration ranges 1 σ values of 1–3 per cent are generally available, at these lower ranges 1 σ value of 5 per cent was found.

The non-destructive determination of the residual hydrogen present in highly fluorinated or deuterated compounds is difficult by conventional means, but these analyses may be readily carried out by N.M.R. technique. 0.02 per cent hydrogen was detected in perfluorocyclomethylhexane, corresponding to one residual hydrogen atom for every 20 organic molecules. Fig. 2 shows 0.07 per cent hydrogen present in a sample of D-acetone.

Fluorine

The resonance frequency of a given isotope varies with its chemical grouping. This effect is the basis of high resolution N.M.R. spectroscopy. Such variations in the frequency of the hydrogen isotope are too small to be detected with the magnet used, but with ^{19}F, the effect is much greater and can be observed with magnets of lower homogeneity. Quantitative analysis therefore of fluorine-containing organic molecules should lead to the determination of both the total fluorine content and the fluorine present in different groups. Thus with dihydrodecafluorobenzene, where CF : CF_2 is 4 : 1, the integrated areas under the peaks were in the ratio 4.04 : 1, while the total fluorine content was measured to within 2 per cent accuracy.

Other nuclei

Other nuclei that have been examined in the liquid state include deuterium, [11]B, [7]Li, [23]Na and [27]Al. Of particular interest has been the use of [11]B to analyse boron trifluoride etherate complexes and the study of aluminium in nitrate solutions. Table I shows the results obtained from the boron compounds.

Fig. 3 shows a typical signal from a 3 *M* solution of aluminium nitrate. This signal occurs at 7.7 Mc/s in a field of 7000 G. The line-width from a

TABLE I. *Boron trifluoride etherate.*

[11]B as % of total B.

Known	Found
81.17	81
99.5	99
1.1	1.22

stoichiometric solution of aluminium nitrate is determined by the inhomogeneity of the field and the peak height is proportional to concentrations down to 20 mg aluminium.

Solid state analyses

In the liquid state the high degree of mobility of atoms and molecules averages out inter-molecular magnetic fields, so that the line-width observed is fixed, with our equipment, by the homogeneity of the magnetic field. In solid systems however, the possibilities of movement are more restricted and the resonance absorption from many solids have shapes characteristic of the arrangement of the nuclei in the lattice. In order to make accurate assessments therefore it is necessary to integrate the signal. Fig. 4 shows a typical signal from the hydrogen present in $CdSO_4 \cdot 8/3 \ H_2O$, where the solid structure is evident. The line widths associated with such solids are of the
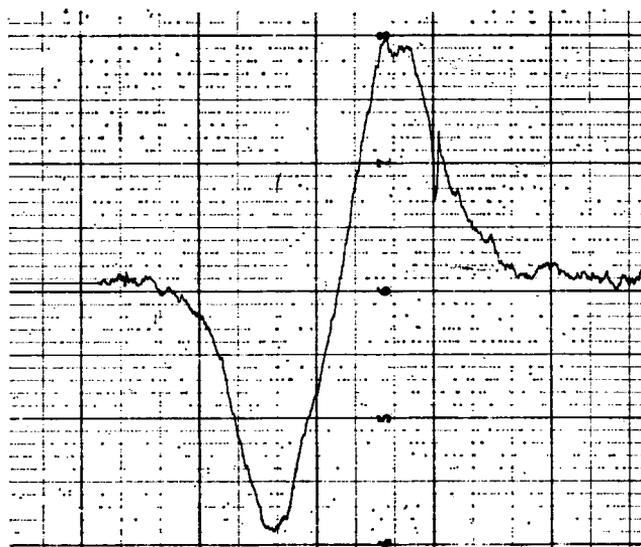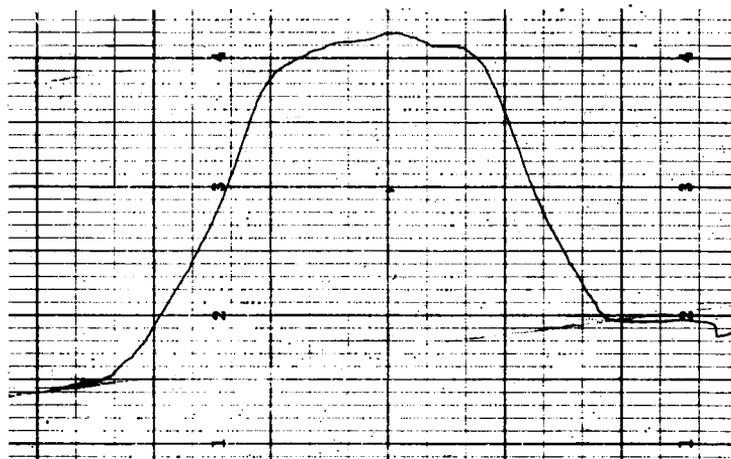

Fig. 3.—[27]Aluminium in 3 *M* nitrate solution.

Fig. 4.—Hydrogen in 3CdSO$_4$·8H$_2$O First integral.

order 1–10 G compared with the 0.1 G or less observable with liquids. The relaxation process associated with this inter-molecular interaction also affects the conditions under which the signal is best observed. Fortunately the effects of varying relaxation times between samples can be minimized by using low radio-frequency powers, and the studies of solids made were carried out under these conditions.

Examples of the determination of hydrogen in solids are the analysis of cerium hydride and zirconium hydroxide compounds, both of which were thought to be non-stoichiometric. 4 g samples of these materials were weighed and sealed and the cerium hydride signal was compared with that
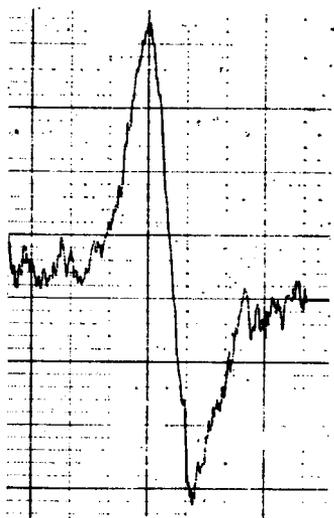

Fig. 5.—Residual water in TiO$_2$.

from a standard glucose sample. The hydrogen content was found to be 30 ± 2 cc H_2/g. Zirconium hydride was used as a standard for the zirconium hydroxide sample which was found to contain 0.48 per cent hydrogen.

Analysis of a sample of titanium oxide for hydrogen, revealed the presence of a line whose width was characteristic of the liquid state, i.e. 0.1 G (see Fig. 5). This was attributed to the presence of absorbed water in the sample. The sample was analyzed by comparing the peak height of the signal with that obtained from standards made by adding 10 mg portions of water to calcium fluoride and by comparing the peak area with that obtained from a sample of titanium hydride of known composition. From peak-height comparisons the hydrogen content was found to be 213 ± 7 μg hydrogen and from area comparison 223 ± 30 μg hydrogen.

REFERENCES

1. BERL, W. G. (Ed.), *Physical Methods in Chemical Analysis*, Vol. 3 (1956).
2. MITCHELL, A. M. and PHILLIPS, G., *Brit. J. Appl. Phys.* 7, 67 (1956).
3. SHAW, T. M. and ELSKEN, R. H., *J. Appl. phys.* 26, 313 (1955).