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Application of Nuclear Double Resonance Technique for Detection of Pesticides in Water at Low Concentrations

R. Osredkar* and P. K. Kadaba

Department of Electrical Engineering, University of Kentucky, Lexington, KY 40506

Nuclear Double Resonance (NDR) was first conceived by HARTMANN & HAHN (1962) and later on developed as an ultrasensitive technique by SLUSHER & HAHN (1968) for detecting nuclear quadrupole interactions of rare isotopes such as D^2, O^{17}, S^{33}, Ca^{43}, etc., in suitable compuonds which can provide a strong resonance from an abundant nuclear species. The NDR technique is capable of high sensitivity combined with good resolution and is particularly suited for the detection of quadrupole resonance of light elements such an N^{14} which is of interest in the study of the structure of biologically important molecules. It has been reported that NDR technique could become for the study of solid-state structure, the widely used analytical tool that NMR has already become for liquids (EDMONDS 1977). In this investigation the NDR technique has been applied for the detection of organochlorine and carbamate pesticides in low concentration in water. Since the measurements are done below ice temperatures, heat-labile compounds can be detected without conversion to more suitable derivatives as would be necessary in gas chromatography technique. Fats and oils in sample extracts do not seem to interfere with the measurements.

Principle of the method

The double resonance method uses the 'strong' NMR signal of an abundant (A) spin system to detect the 'weak' nuclear resonance of the spin species (B). The method is based on the fact that the effect of a r.f. perturbation of the B system can be via A-B coupling transferred to the A system, integrated and detected as a change in the NMR signal of the A spins. The time sequence diagram shown in Figure 1 illustrates in detail the principle involved in detecting the zero field quadrupole resonance of the B spins. First the abundant A nuclei which are protons in this investigation are polarized in a high d.c. magnetic field H_o for a time of the order of the spin-lattice relaxation time T_1^o. At point a, the sample is removed from the high magnetic field to a region of zero external magnetic field. This demagnetization is performed in a time short compared to the spin-lattice relaxation time (a to b in Figure 1). In the demagnetized state, the A nuclear order or entropy remains essentially constant. In the high field H_o the A nuclei, that is protons, are preferentially aligned along the external H_o field. After the adiabatic demagnetization, they are preferentially aligned along the local nuclear dipole fields, h_L. This ordering of A nuclei along their local fields will decay because of spin lattice

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*Permanent address: Institut 'Jozef Stefan.' Jamova 39, 61001 Ljublignana, Yugoslavia

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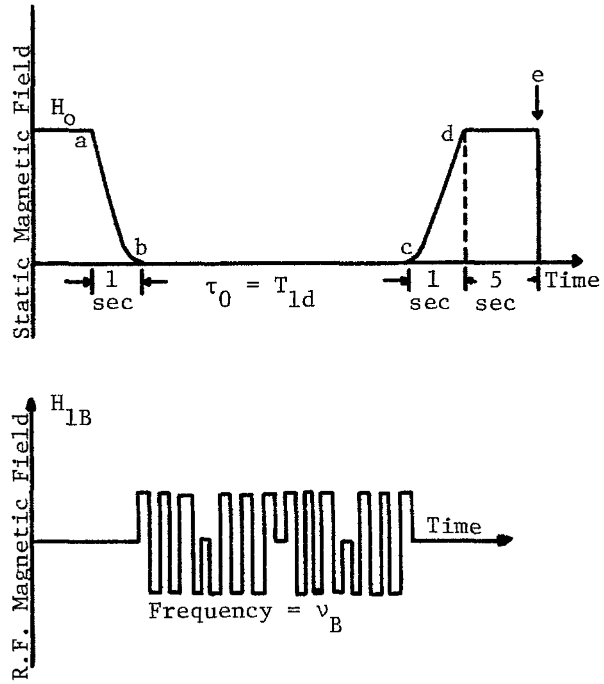

Fig. 1. Time sequence for detecting low concentration B-spin zero field quadrupole resonance

interactions in a time of the order of the dipolar relaxation time T_{1d} typically 10 to 100 seconds. The B nuclei which are chlorine in this investigation have negligible effect on the relaxation unless they are irradiated with an r.f. magnetic field H_{1B} at their quadrupole resonance frequency ν_Q. The irradiated B nuclei can now disorder the A nuclei via the A-B cross relaxation process. This disordering of the A nuclei by the B nuclei is continuously maintained by shifting periodically the phase of the r.f. field H_{1B} for a time interval τ_0 of the order of the dipolar relaxation time, T_{1d}. An alternative way is to frequency modulate the r.f. field H_{1B}. In this way high sensitivity for detection of the B nuclei can be achieved. At point c, the sample is adiabatically remagnetized by the former polarizing d.c. field, H_0. The remaining order of the A nuclei is measured by applying a 90° pulse at time point e, shown in Figure 1, and observing the resulting free induction decay. The double resonance effect due to the quadrupolar B nuclei is the difference inthe intensity of the two free induction decay signals measured at point e, one without the r.f. irradiation of the B nucleus and the other with the r.f. field H_{1B} applied. Figure 2 shows the block diagram of the nuclear double resonance spectrometer developed in this study.*

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*Details of design and construction of the developed instrument are given in research report number 116, Water Resources Research Institute, University of Kentucky, Lexington KY; Dept. of the Interior Contract No. 14-34-0001-6018,7037,7038.

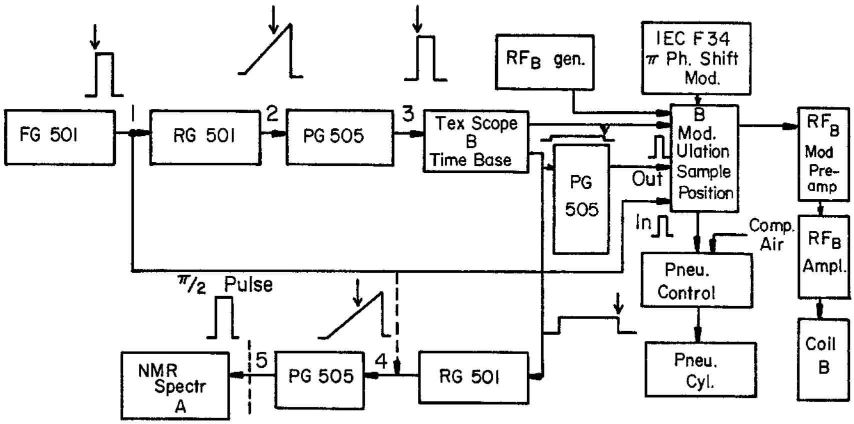

Fig. 2. Block diagram of the Nuclear Double Resonance (NDR) Spectrometer

Detection sensitivity considerations

A practical limit on τ_0, the time interval for shifting periodically the phase of the r.f. field H_{1B}, is the dipolar spin-lattice relaxation time, T_{1d}. If the signal-to-noise ratio of the A nuclei is good enough to see a one percent change in the effective relaxation time, the minimum detectable concentration of B nuclei is:

$$\frac{N_B}{N_A}_{\min} \simeq \frac{T_{AB}{}^1}{100T_{1d}}$$

where $T_{AB}{}^1$ is the time required for a B nucleus to achieve mutual spin flips with neighboring A nuclei. Typical values are in the range: $T_{AB}{}^1 \simeq 50$ to 500 u secs. and $T_{1d} \simeq 10$ to 100 seconds. So that $N_B/N_{A\,\min} \simeq 5 \times 10^{-9} - 5 \times 10^{-7}$. At the higher sensitivity in a sample of pesticide dissolved in a compatible solvent such as acetone or bromoform, this leads to about 500 ng of a typical pesticide as the theoretical limit of amount necessary for detection. This is a theoretical upper limit of sensitivity of 0.5ppb. So under optimum conditions with good signal averaging techniques, it should be possible to detect about 2ppb of a typical compound.

Sample preparation, extraction and concentration

Since the pesticides are hydrophobic compounds, in order to mix a known amount of pesticide in a known amount of water the mixture was stirred for ten minutes with a magnetic stirrer, the method suggested by LYONS & SALMAN (1972). The extraction and concentration procedures used were similar to that reported by THOMPSON et al. (1979), except bromoform was used as the solvent in case of chlorinated pesticides and chloroform in case of non-chlorinated carbamate pesticides. These solvents were chosen because they are insoluble in water. Starting with one liter of water spiked with a known amount of pesticide, the sample was extracted by adding 10 ml of either $CHBr_3$ or $CHCl_3$ and shaking vigorously and then allowing sufficient time for complete phase separation. This procedure was repeated four times. The extracted samples were concentrated in a Kuderna-Danigh (K-D) evaporator in a nitrogen atmosphere.

RESULTS AND CONCLUSIONS

For a typical pesticide, namely carbanolate, the following spectroscopic data necessary in the detection procedure have been obtained: The pure quadrupole resonance frequencies ν_Q for ^{35}Cl and ^{37}Cl are respectively 35.115 MHz and 27.675 MHz. The quadrupolar relaxation times T_{1Q} and T_{2Q} are respectively 29 ms and 212 μs. The proton spin-lattice relaxation time T_1 is 22 seconds and the dipolar relaxation time T_{1d} is 18 seconds. Short quadrupolar T_1 is helpful in obtaining a large effect on the proton in the double resonance experiment. This is given by the relation:

$$\frac{1}{T_{1p}\ (\text{effective})} \doteq \frac{1}{T_{1p}} + \frac{1}{T_{1Q}}$$

If T_{1Q} is short, we can neglect $1/T_{1p}$. This condition seems to obtain in the present study. Figures 3 and 4 show respectively the fourier transform representation of the chlorine signal of carbanolate in concentrations of 1ppm and 100ppb. The signals were observed at a temperature of -20°C. The data was time averaged and then fourier transformed using fast fourier transform routine available with DEC computers.

Table 1 gives the minimum detectable concentrations of the pesticides tested with the spectrometer.

Table 1: Minimum Detectable Concentrations of Pesticides Tested

Compound:	Carbanolate	Barban	CIPC	Atrazine	Simazine
Concentration: (ppb)	20	20	20	100	100

The sensitivity of the technique in its present form is less than that of electron capture gas chromatography, but as indicated earlier, has an advantage over the latter technique in detecting hear-labile compounds since measurements are done below room temperature. Most carbamate pesticides cannot be analyzed directly by gas chromatography unless conversion to more suitable derivatives is carried out, because they are themally unstable. In the present method, clean-up and separation procedures need not be elaborate in some cases. For example, fats and oils in sample extracts do not interfere with the measurements. Application to the analysis of organochlorine and triazine pesticides in waste water (industrial effluents) is possible with this technique provided the concentration of these compounds is between 10 to 100 microgram per liter. The instrument in its present form cannot be used as a routine analytical tool. Further improvement in sensitivity is possible by using liquid nitrogen-cooled ferrite-cored electromagnet, increasing the polarizing field and going to a two-magnet system.

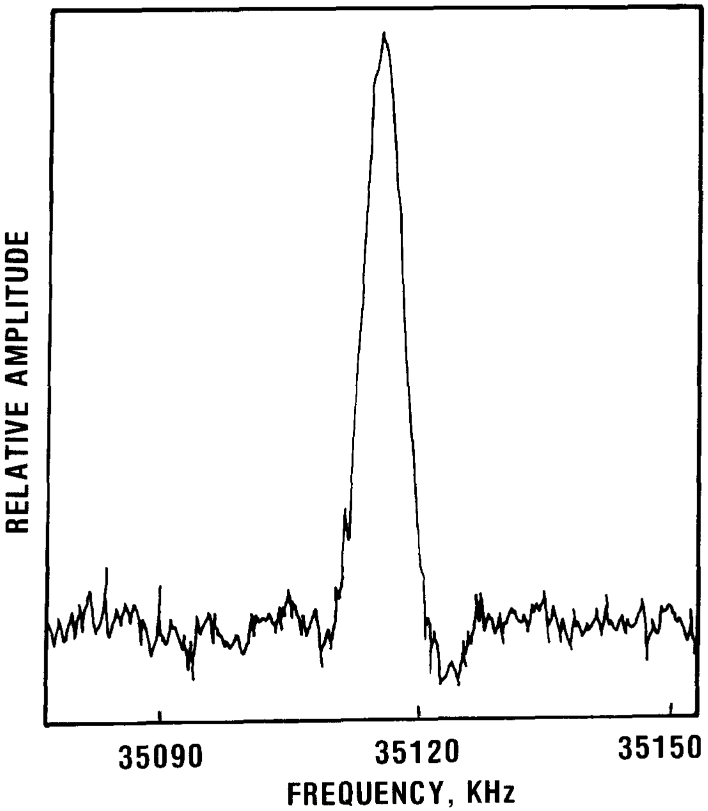

Fig. 3. Fourier transform of chlorine signal of carbanolate after signal averaging (concentration 1 ppm)

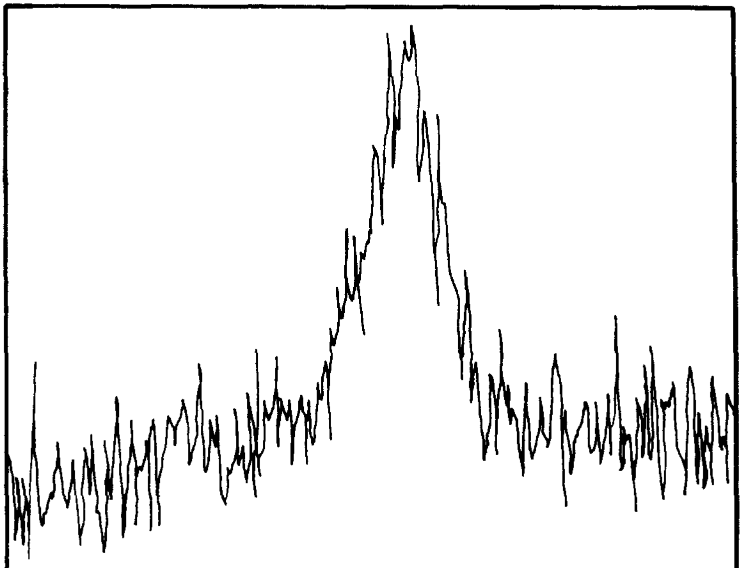

Fig. 4. Fourier transform of chlorine signal of carbanolate after signal averaging (concentration 100 ppb)

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REFERENCES

HARTMANN, S., and E. L. HAHN: Phys. Rev. 128, 2042 (1962).

SLUSHER, R. E., AND E. L. HAHN: Phys. Rev. 166, 332 (1968).

EDMONDS, D. T.: Physics Reports (Section C of Physics Letters), 29, 233 (1977).

LYONS, E. T. and H. A. SALMAN: "Development of Analytical Procedures for Determining Chlorinated Hydrocarbon Residues in Waters and Sediments from Storage Reservoirs," REC-ERC-72-15, PB 210839 (1972).

THOMPSON, J. F., S. J. REID, and E. J. KANTOR: Arch. Environm. Contam. Toxicol. 6, 143 (1977).