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# Method of Measurement of Long Spin-Lattice Relaxation Times in Liquids

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*Résumé.* — Une méthode simple de mesure des temps longs de relaxation spin-milieu est décrite. La méthode a été appliquée, par les auteurs, à la mesure des temps $T_1$ dans l'intervalle 0,5 — 100 sec, les erreurs des résultats obtenus sont de 3% environ.

In the few last years the question of nuclear spin-lattice relaxation time $T_1$ of liquids became important in spite of its significance as a means for investigation of the structure of liquids. In this situation the problem of the method of precision measurements of $T_1$ is very actual.

*Description of the method.*

The following method was worked out. The measurement of spin-lattice relaxation time of liquid sample consists of two separate procedures: the measurement of the completely desaturated nuclear magnetization $M_\infty$ and the measurement of the momentary values of the vector M during the time of its growth from zero after a complete saturation.

The nuclear magnetic resonance device is arranged in such a way that it is possible to change alternatively the frequency of the current in the modulating coils. This can be done by means of a single switch. The used magnetic field modulations are $\omega_m = 2\pi\ 50\ \text{sec}^{-1}$, $H_m' = 2$ gauss and $\omega_m = 2\pi\ .\ 0{,}3\ \text{sec}^{-1}$, $H_m = 6$ gauss. This last type of modulation is made by means of an electrolytic potentiometer [1] moved by an electric motor. When the motor is not running it is possible to set the rotating electrode of the potentiometer in the desired position.

The output of the nuclear resonance detecting apparatus is recorded on a photographic paper tape by means of a mirror oscillograph.

The course of the magnetic field modulation is shown on figure 1. The central value of the magnetic field is exactly the resonance one $H_0$. At first the rotating electrode of the electrolytic modulator is set in one of its extreme position (e.g. the lower one) and the higher frequency modu-

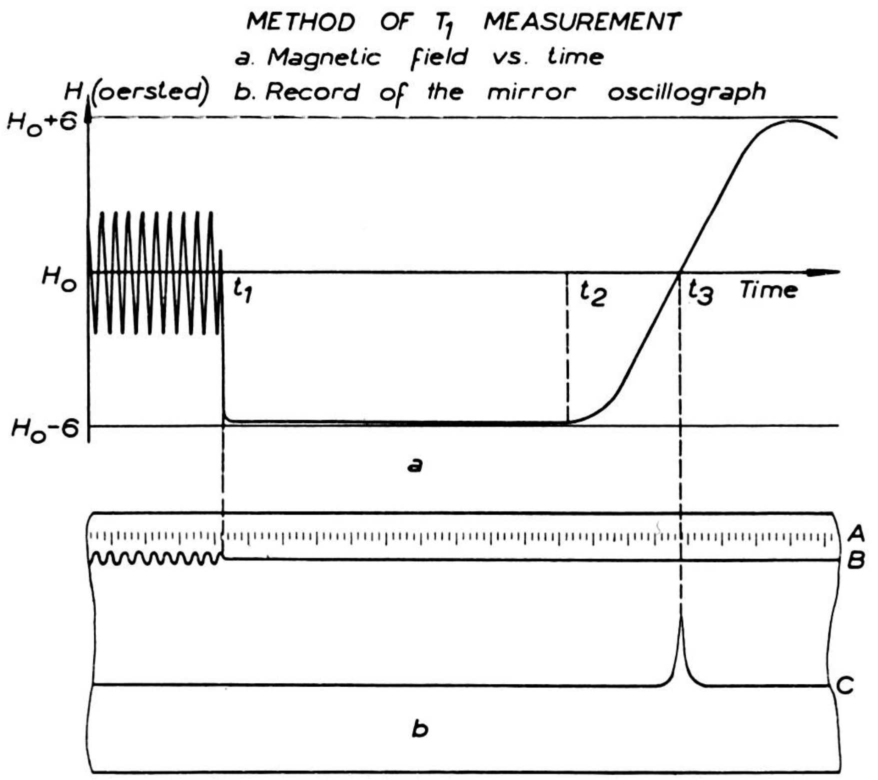


Fig. 1.

Method of $T_1$ measurement,
*a* — magnetic field vs. time, *b* — record of the mirror oscillograph.

lation current is switched on. If the proper value of the radio frequency magnetic field $H_1$ is used the sample is completely saturated after a few seconds. The authors used $H_1 = 0{,}25$ gauss for the relaxation time range over 0,7 — 100 sec. When the lines do not disappear completely in spite of the phase memory, about 5% (in amplitude) of about 30 c.p.s. modulation was added to the 50 c.p.s. modulation for destruction of this memory.

After the sample is completely saturated by means of the 50 c.p.s. modulation the switch is turned to the second position and the modulation coils are conected with the electrolytic potentiometer. In this moment ($t_1$ on figure 1) the magnetic field intensity jumps to the lower extreme value because of the initial position of the rotating electrode. Since this time the sample is very far away from the resonance conditions and the growth of the nuclear magnetization goes without external perturbation. The next passage through the resonance value (moment $t_3$) can be made by setting in motion the electrolytic modulator in a suitable chosen moment $t_2$.

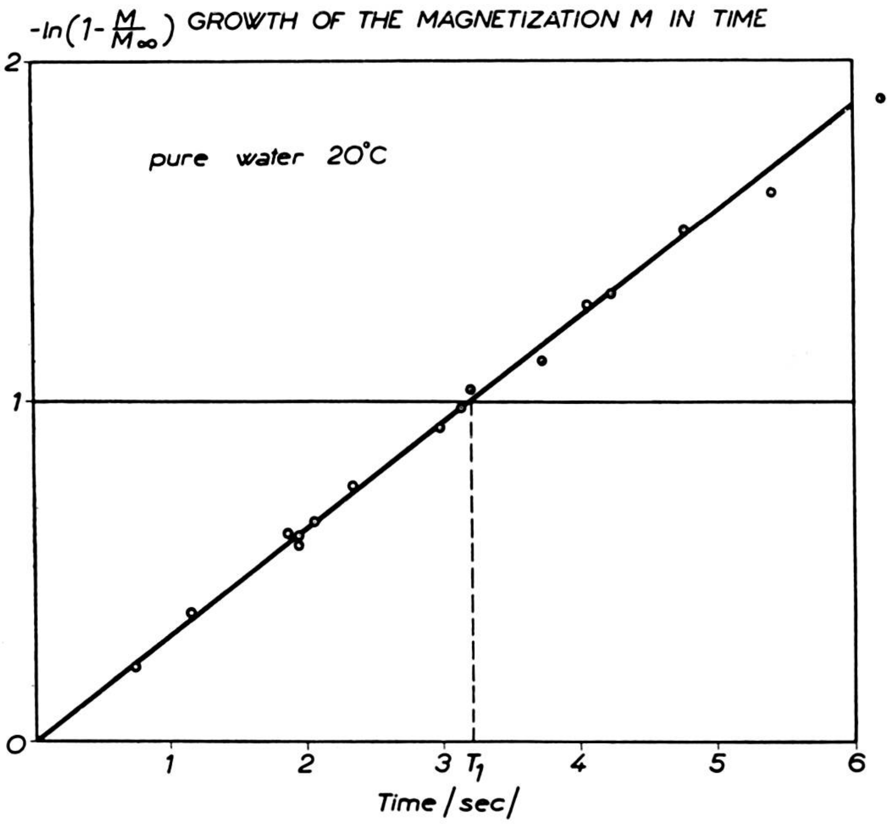


Fig. 2.

Growth of the magnetization M in time.

If the time interval $t_3 - t_1$ (i.e. the free growth time) is sufficiently long $t_3 - t_1 \geqslant 5T_1$ the height of the recorded line is proportional to the completely desaturated value of the nuclear magnetization $M_\infty$. The momentary values of magnetization vector M during its growth can be obtained by choosing a shorter time interval $t_3 - t_1$. We evaluated that the best accuracy can be obtained if $0{,}6\ T_1 > t_3 - t_1 > 1{,}5\ T_1$. The most practical way is to make one $M_\infty$ record, immediately three or four M records and then one $M_\infty$ record again. The equality of both $M_\infty$ indicates that the amplification factor did not change during the whole measurement.

The measurement of the $t_3 - t_1$ time can be done by means of the stop clock if this is a long one. In the case of short time intervals the measurement can be done using the time marks (A on fig. 1). Then the mirror oscillograph must have three separate mirror devices: for the output record (C), for the time marks (A) and for the $t_1$ moment record (B). This last mirror device is connected with the 50 c.p.s. modulation circuit.

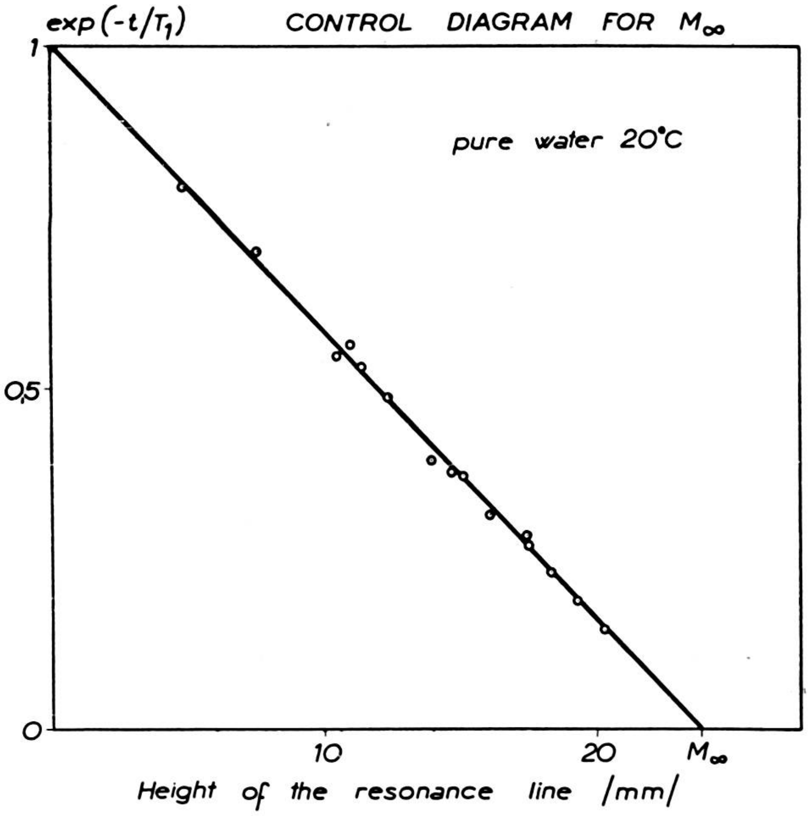


Fig. 3.
Control diagram for $M_\infty$.

The evaluation of $T_1$ from the data obtained in this manner is done by means of a plot $-\ ln\ (1 - M/M_\infty)$ versus $t_3 - t_1$ (fig. 2).

It is also very useful to make a control diagram of exp $(- t/T_1)$ versus M putting for $T_1$ the obtained value (fig. 3). If the measurement is correct all points should lie on a straight line (of course if the sample obeyed the single exponential increase law) which intersects the vertical axis in point 1 and the horizontal axis in point $M_\infty$. Even a small error in $M_\infty$ can be found this way.

*Discussion.*

Using the described method it is possible to observe the nuclear relaxation process phenomenon with lower than in other methods perturbations introduced by the nuclear resonance apparatus. This comes from the fact that using the other methods it is necessary to fulfil several conditions which practically are difficult or even not possible to satisfy simultaneously.

Using the described method it is necessary to fulfil only tree conditions which do not cause technical difficulties. These conditions are:

The time of passage $\tau \ll T_1$ where $\tau \approx \frac{H_1}{H_m \omega_m}$

$$H_m = \text{const.}$$

$$\omega_m = \text{const.}$$

The described method in comparison with Giulotto's does not require the fulfilment of the adiabatic passage condition and the condition which connects $T_1$ with $\omega_\infty$.

Our method was successfully used in Cracow Laboratory for measurements of spin-lattice relaxation times in liquids over the range 0,5 — 100 sec. The accurancy of measurement of $T_1$ for pure water in 20° C is estimated as less than 3 per cent.

REFERENCE

1. Chiarotti, G., G. Christiani, L. Giulotto, G. Lanzi, *Nuovo Cimento, 12,* 519 (1954).