A BUTANOL POLARIZED PROTON TARGET

S. Mango^{†)}, Ö. Runólfsson and M. Borghini

CERN, Geneva, Switzerland.

SUMMARY

Dynamic proton polarizations around 40% have been reproducibly obtained in 5 cm³ samples made of 95% 1-butanol and 5% water mixtures, saturated with the free radical porphyrin, at temperatures close to 1°K in a magnetic field of 25 kOe.

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^{†)} Present address: DESY, Hamburg, Germany.

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1. INTRODUCTION

In the course of a systematic study of dynamic proton polarization in hydrogen-rich organic substances doped with free radicals, we have given special attention to alcohols $\text{CH}_3(\text{CH}_2)_n\text{OH}$ doped with porphyrexide^{*)}.

Ethanol was studied first, and it was found that the polarization could be considerably increased by mixing a small amount of water, with a maximum polarization of 35% obtained in the eutectic ethanol-water mixture¹⁾. However, such a value was found difficult to reproduce²⁾. Extending this investigation to other alcohols, we have found a similar behaviour of the polarization as a function of water addition. We shall report here on 1-butanol-water mixtures, and particularly on one mixture in which polarization as high as 44% has been produced, describing a technique that may be used to make polarized targets out of it and stressing the reproducibility of the results.

Even if this polarization is smaller than the 70% one that is currently produced in the now standard LMN targets (LMN=lanthanum magnesium nitrate, $\text{La}_2\text{Mg}_3(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$), alcohol targets should compare very favourably with them in many respects. Such a comparison of LMN and alcohols as target material is summarized in Table 1. It is seen that the hydrogen density is twice as high as in LMN and that the

^{†)} Present address: DESY, Hamburg, Germany.

^{*)} Fulka A.G., Buchs, Switzerland.

contamination by complex nuclei is much smaller: for instance, the ratio of the number of bound protons contained in such nuclei to the number of hydrogen nuclei is about 5 times smaller; the radiation length is some 4 times larger. The time needed to change the polarization sign, is about 20 times shorter in alcohol than in LMN; this should prove helpful, in particular for dealing with changes in monitor sensitivities. Another advantage is the higher resistivity against radiation due to the beam that can be expected from alcohol targets. For LMN, it is known that the proton polarization is reduced by a factor of 2 after accumulating some 2×10^{12} minimum ionizing particles/cm² ³⁾. In ethanol-water targets, this quantity has been found to be about 5×10^{14} particles/cm² ⁴⁾. It is expected to be of the same order of magnitude for butanol-water targets. This property is essential where high intensity beams are needed; for example, for experiments on processes with small cross-sections, in particular around electron accelerators.

2. EXPERIMENTAL APPARATUS

The samples to be polarized were put into a copper cavity and cooled down to temperatures around 1°K, by using a cryostat with continuous liquid helium flow, of the type used in standard CERN polarized targets⁵⁾. They were located in an electromagnet producing a magnetic field of 25 kOe, with an homogeneity of 10^{-4} over a volume of about 5 cm³. The proton dynamic polarization was then obtained by feeding the cavity with continuous power at 70,000 MHz usually less than 2 W, supplied by a carcinotron^{*)}. The proton polarization P_n was measured by comparing the absorptive part of the thermal equilibrium and of the enhanced proton NMR signals, detected by a fast sweep, frequency modulated, 107 MHz Q-meter⁶⁾; when necessary, non-linearity corrections were made according to the procedure described in Ref. 6. The relative accuracy of the measurement, $\Delta P_n / P_n$ is estimated to be 5%.

*) CO-40B, C.S.F., Courbevoie, France.

3. COMPOSITION OF THE SAMPLES

The 1-butanol-water mixtures were prepared from 99.8% pure 1-butanol $\text{CH}_3(\text{CH}_2)_2\text{CH}_2\text{OH}$ and double distilled water. A saturated solution of porphyrexide was prepared by adding 2 to 3% by weight of the radical to the alcohol-water mixture. All mixture ratios in this paper are given by weight. In most of the samples the unsolved radical was separated from the saturated solution as discussed below. The solvent mixture was prepared separately for each sample. As such solutions normally contain dissolved molecular oxygen, which is paramagnetic, and can influence the spin dynamics, desoxygenized samples were studied too. These were prepared by bubbling 99.99% pure, dry nitrogen gas through the alcohol and water for about 15 min. before mixing. With this procedure, the oxygen concentration in these liquids was reduced by a factor of ~ 10 , as measured with a Fieldlab Oxygen Analyser (supplied by Beckman Instrument Co., Fullerton, California). Then care was taken to contaminate the liquids as little as possible with oxygen during further manipulations.

Because the porphyrexide has an anisotropic g-tensor^{*)}, with values close to

$$g_1 = 2.000, \quad g_2 = 2.005 \quad \text{and} \quad g_3 = 2.010 ,$$

and because it exhibits anisotropic hyperfine structure due to one nitrogen nucleus, with values

$$A_1 \approx 27 \text{ Oe} \quad A_2 + A_3 \approx 0 ,$$

the corresponding resonance line at 25 kOe in such samples, with randomly-oriented fixed molecules, is rather broad (Fig. 1); in particular, the line width is not at all small compared to the proton resonance frequency. In these conditions, dynamic polarization is expected to occur because of electron-nucleus dipolar coupling through the combined action of the

*) g and A were crudely estimated from EPR measurements at 3.2 and 25 kOe, at room temperature, 77°K, and 1.05°K.

"solid state effect" ⁷⁾ and of the "DONKEY effects" ⁸⁾. It is not our intention to analyse here the particular way by which the protons are polarized, but rather to give experimental results and to describe sample preparations; because of the importance that what we expected to be minor details seem to have on the reproducibility of our results, we shall describe these preparations at some length.

4. SAMPLES OF SMALL SIZE; INFLUENCE OF WATER

The results reported in this section refer to porphyrin saturated solutions prepared by adding an excess of radical to the alcohol-water mixtures, and by shaking them at room temperature for about 10 minutes. These solutions, with excess porphyrin particles in suspension, were then poured into a 0.4 cm³ container, consisting of a section of standard 8 mm silver-plated copper rectangular waveguide, closed at its ends, with a slot on one of its narrow sides to allow the passage of the microwaves, and with a built-in coil for NMR measurements (Fig. 2). A 0.1 mm thick teflon sheet was then pressed against the slot by a system of gold-plated brass bars and screws, to make the container vacuum tight. Normally two such containers were put into the copper cavity, 21 mm in diameter and 50 mm long, which was then closed by soldering a cover onto it. The cooling of the continuous flow cryostat was then started from room temperature, and the unsolved radical particles had time to settle down at the bottom of the container before the freezing of the solution which occurred about 45 min later.

Results: Figure 3 shows polarization obtained in 1-butanol water mixtures as a function of the water concentration, both for normal oxygen content and for desoxygenized samples. Each curve exhibits a maximum for about 5% water, a sharp one for samples with oxygen, a much broader one for samples without oxygen. Figure 4 shows the corresponding relaxation rates obtained by observing the decrease of the NMR signal after switching off the microwave power. As one could expect, desoxygenized samples have smaller relaxation rates, but the maximum polarization mixtures seem to have the same rate, independent of the oxygen content. For samples containing more than 10% water, the signal consists of two parts, with distinctly different relaxation rates,

which are both shown in Fig. 4. By preparing samples with heavy water, we have observed that the slow part of the signal is much narrower than the fast one, and this can be taken as an indication that the sample contains two different phases, with different water (and probably different radical) concentrations.

5. SAMPLES OF A LARGE SIZE

Considering the results described in the previous section, we have tried to make an operational target out of desoxygenized 95% n-butanol, 5% water mixtures saturated with porphyrin. Such a choice was determined mainly by the consideration that the corresponding polarization is less sensitive to small variations in the actual water concentration. Other mixtures containing absorbed molecular oxygen from the air are more critical to mix and less reproducible, as the water and the oxygen contents in the alcohol change during the use of the bottles in which they are kept.

A successful way to prepare the solutions was to shake the mixture, desoxygenized as described in Section 3, with an excess of porphyrin, during about 15 min, at room temperature, then to leave it at rest for about 20 min, to separate the solution from the unsolved radical residue, to warm it up to some 40°C for 5 min, and finally to let the remaining unsolved radical particles settle down at room temperature for about 20 min more. The liquid was then separated from the solid residue again, and used to prepare the sample. This method will be referred to as method A.

An alternative way of preparation, which gave somewhat lower polarizations, was to warm up the mixture to 40°C and to shake it for about 15 min, then to centrifuge it for 5 to 10 min to separate the unsolved radical part. This will be referred to as method B.

In any case, we found it was of primary importance to get rid of any unsolved radical particles in the solutions, in order to avoid heating of the samples by the microwave absorption of these particles. Table 2 gives a comparison of the polarizations obtained with and without fulfilling this requirement.

The samples were frozen in liquid nitrogen as tiny spheres (types 1 and 2 in Table 2) or as a single block (type 4), that was sometimes milled before use (type 5). The spheres were prepared by letting drops of solution fall from a hypodermic needle onto a meniscus of liquid nitrogen. In order to speed up the preparation of samples of a large size a battery of 10 to 20 glass tubes, 10 mm in diameter, was placed vertically in the nitrogen dewar, making it possible to freeze many spheres simultaneously. The time needed to prepare a 5 cm³ sample was about 20 min. The size of the drops could be varied by using needles of various diameter. As no definite influence of the sphere size on the polarization could be ascertained, we chose to use spheres of 1.5 mm diameter, which offer a large cooling surface. The samples were then placed in the pre-cooled cavity together with the NMR-detection coil. The filling factor of the spheres was about 0.7 as found empirically. The size of the samples was limited by the homogeneous region of the magnetic field.

Results: As an example, Figs. 5 and 6 show the polarization and the relaxation rate $1/T_n$, where T_n is the proton spin-lattice relaxation time, as a function of the temperature, measured in such a sample made of small spheres, prepared according to method A. One can easily see the importance of working at temperatures as low as possible, as the polarization drops from 44% to 30% when the temperature is increased from 0.98°K to 1.3°K (Fig. 5).

Figures 7 and 8 show the polarization and the polarization build-up time of the same sample as a function of microwave power. Absolute power measurements are inaccurate, but we can estimate that the 20 db point corresponds to about 500 mW from the helium flow measurements; from previous estimations of the Q-value of microwave cavities, similar to the ones used in the present work, this corresponds to a maximum microwave rotating field of the order of 50 mOe.

Figure 9 shows the polarization as a function of the steady magnetic field value at fixed microwave frequency and power. The maximum positive and negative polarizations are separated by a magnetic field that corresponds to about four times the proton resonance frequency, as expected from the width of the porphyraxide resonance line.

Finally, Table 3 shows the results of measurements made on a set of samples prepared according to methods A and B, in order to test the reliability of these preparations. It is seen that a reproducibility good enough for making operational polarized targets has been attained.

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Table 1

Comparison of lanthanum magnesium nitrate and butanol
as target materials

	LMN	Butanol
Max. polarization	~70%	~40%
Hydrogen density (g/cm ³)	0.06	0.12 *)
Total density (g/cm ³)	2.0	0.9 *)
<u>Bound protons</u> Free protons	15	3.2
Radiation length (cm)	~10	~40
Acceptable number of min. ionizing beam particles/cm ²	~2 × 10 ¹² **)	~5 × 10 ¹⁴ ***)
Polarization build-up time (sec)	300	15

*) Liquid at the freezing point.

**) See Ref. 3.

***) Measured for ethanol-water targets, Refs. 2 and 4.

Table 2

Proton polarization at 1.05°K in 5 cm³ samples according to
sample preparation

Sample type	Solution preparation	Sample shape	Polarization
(1)	Method A	1.5 mm spheres	40%
(2)	Method B	1.5 mm spheres	37%
(3)	Unsolved porphyrexide not removed		25%
(4)	Method A	Single block	30%
(5)	Method A	Type (4) sample milled	39%

Table 3

Test of reproducibility of the sample preparation by
the methods A and B (5 cm³ sample made of 1.5 mm spheres)

Method	Sample No.	Polarization (%)	Relaxation time T _n (sec)
A	1	38	146
A	2	44	145
A	3	40	180
A	4	39.5	180
A	5	40	230
Average polarization: 40.3%			
B	6	37	100
B	7	36.5	100
B	8	37	120
B	9	39.5	150
B	10	36	110
Average polarization: 37.2%			

Figure captions

- Fig. 1 : A first derivative of the paramagnetic resonance line of porphyrexide dissolved in alcohol at 1.06°K in a magnetic field of 25 kOe.
- Fig. 2 : A container used for small samples.
- Fig. 3 : Proton polarization versus water content in 1-butanol, saturated with porphyrexide, at 1.05°K .
- Fig. 4 : Proton relaxation rate versus water content in 1-butanol, saturated with porphyrexide, at 1.05°K .
- Fig. 5 : Proton polarization versus temperature in sample No. 2 (Table 3).
- Fig. 6 : Proton relaxation rate versus temperature in sample No. 2.
- Fig. 7 : Proton polarization versus microwave power in sample No. 2, at 1.05°K . The 20 db point corresponds to about 500 mW in the cavity.
- Fig. 8 : Polarization rate versus microwave power in sample No. 2, at 1.05°K .
- Fig. 9 : Proton polarization versus magnetic field in sample No. 2, at 1.05°K .

FIG.1

FIG. 2

FIG. 3

FIG.4

FIG. 5

FIG. 6

FIG.7

FIG. 8

FIG.9