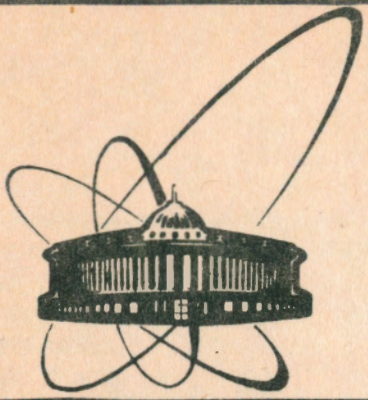

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PENTANOL-BASED TARGET MATERIAL WITH POLARIZED PROTONS

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Рабочее вещество для мишени с поляризованными протонами на основе пентанола

1-Пентанол — перспективный материал для мишени с поляризованными протонами, благодаря его высокой стойкости к радиационным повреждениям. С целью создания вещества мишени были исследованы растворы как 1-пентанола, так и 2-пентанола с комплексами пятивалентного хрома. В качестве вещества мишени предложен материал, представляющий собой раствор комплекса EHBA-Cr(V) в стеклообразной матрице на основе 1-пентанола, 3-пентанола и 1,2-пропандиола. Вещество мишени исследовано методами электронного парамагнитного резонанса и дифференциальной сканирующей калориметрии.

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Pentanol-Based Target Material with Polarized Protons

1-Pentanol is a promising material for a target with polarized protons owing to its high resistance to radiation damage. To develop the target,the solutions of 1-pentanol or 2-pentanol with complexes of pentavalent chromium were investigated. The material based EHBA-Cr(V) solution in a glass-like matrix, consisting of 1-pentanol, 3-pentanol and 1,2-propanediol,was proposed as a target material. It was investigated by the electron paramagnetic resonance and differential scanning calorimetry methods.

The investigation has been performed at the Laboratory of Nuclear Problems, JINR.

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Experimental studies of spin effects, especially in reactions with small cross sections, require not only polarized targets but also particle beams of high intensity, over 10^8 particles/cm^{2}s. Intense irradiation largely breaks nuclear spin polarization in the target material[1-4]. Experience shows that one can consider this breaking to be proportional to the radiation damage of the target material itself[2]. Usually, radiation damages show up as accumulation of coloured centres in the material. In ref.[3,5] a relative unit of colouring capability (RCC) was proposed. As RCC unit is the relative time necessary for colouring in a fixed beam. RCC values for alcohols most often used in polarized targets are listed in Table 1.

A decrease in polarization due to irradiation is usually estimated by the formula[1-4] $P_{finite} = P_o \cdot e^{-\Phi/\Phi_o}$, where P_{finite} is polarization after irradiation with an accelerated particle flux Φ per cm^2. P_o is the original polarization (before irradiation). Φ_o is the particle flux per cm^2 decreasing polarization of nuclei by a factor of e from the original value. The absolute value of Φ_o is also called characteristic dose of depolarization. The values of Φ_o for alcohol according to ref.[2] are listed in Table 1. Complex compounds of pentavalent chromium (Cr(V)) in propanediol and ethanediol, where maximum polarization of protons and deuterons is obtained[7-9], have $\Phi_o = (1.8\text{–}2.5)\times 10^{14}$ particles/cm^2. If these materials are used in target with beams of intensity $1 \cdot 10^{10}$ particles/s, the target material must be frequently annealed and replaced every 1–2 days because there are damages that are not recovered by annealing. So, the problem is to find a material of higher resistance against ionizing radiation and capable of providing high polarization.

Table 1 clearly shows that pentanol is a promising material for a target with polarized protons.

First experiments with 1-pentanol as a target material were described in ref.[10], then in ref.[3,11-14]. The paramagnetic admixture, which is necessary for proton polarization, was the stable free radical porphyrexide and then the stable complex compound of Cr(V) with **2-ethyl-2-hydroxybutyric** acid-EHBA-Cr(V)[16]. The authors of ref.[15] and later papers[1,3,10,11] noticed that a small amount of water increased polarization of protons in alcohol solutions, that the best dynamic nuclear polarization results are likely to be obtained in mixtures near eutectic composition. However, the "eutectic effect" was not explained. To understand the role of water, viscosimetric study of binary pentanol-water or pentanol-pinacol solutions was carried out at temperatures[17] from -50°C to - **100°C.** It was found that water and pinacol admixtures

increase viscosity of the solution, especially near the melting temperature, i.e. these admixtures are favourable for vitrification. In this case thermal motion decreases in the material, and it hinders regrouping of molecules, which is necessary for crystallization of either the solvent or the admixtures. Vitrification is quite a complicated process accompanied by changes in physical properties of solutions, such as volume, density, dielectric properties, etc. Yet, a primitive explanation of the "eutectic effect" can probably be the fact that in the region of eutectic compositions the vitrifying

Table 1

Material	Chemical formula	RCC	Φ_o, $1 \cdot 10^{14}$ part./cm^2
Ethanediol	$C_2H_4(OH)_2$	8	2.5
1,2–Propanediol	$C_3H_6(OH)_2$	< 8	1.8
1–Butanol	C_4H_9OH	24	4.5
1–Pentanol	$C_5H_{11}OH$	500	

capability of solutions grows stronger. In ref.[18] they experimentally proved the relationship between glass formation and polarization of protons in hydrogen rich glasses based on amines, borohydrides and ammonia. Though glassiness of solutions was determined by eye, it was shown that "de-vitrification" of materials lead to sharp decrease in proton polarization. In ref.[19] they studied the phase state of a target material based on ammonium boranes and amines using differential scanning calorimetry. Two conclusions are indicated: maximum polarization occurs at or near the eutectic point reminiscent of alcohol-water mixture[15] and the polarization rises more rapidly than the glass fraction. So it became clear that one should try to find glass-like matrices when making target materials. In the paper[20], which was done at CERN many years after the papers[15,17], there is the most complete differential scanning calorimetry investigation of different target materials based on ordinary and deuterated alcohols, which are actually glass-like matrices.

But must water always play the role of a vitrifying admixture? Water itself is known not to form glass at a reasonable cooling rate. Adding water to the target material increases viscosity of a solution in the region of eutectic compositions and thus favours vitrification, but mainly it favours solving the paramagnetic admixture, e.g. EHBA-Cr(V). Also, the presence of water reduced resistance of the target material to radiation[2].

1-pentanol-based target material

The aim of our work, which we began in 1985, was to try and make a target material based on pentanol without water, which could change into good "glass" when cooled. As a paramagnetic admixture, we used a complex compound of Cr(V) synthesized in propanediol [Cr(V)-PD] with the concentration of paramagnetic centres $2.5 \cdot 10^{20}$ cm^{-3}. The proportion of the complex in the pentanol solution was 18.5% by weight. This admixture increases viscosity and density of the target material and favours vitrification. Adding the [Cr(V)-PD] complex to pentanol at room temperature makes the solution turbid. However, at a temperature below -50°C it is possible to avoid turbidity and immediately freeze the solution in liquid nitrogen. No signs of crystallization were observed. The solid solution was transparent. This solution was investigated by the electron paramagnetic resonance (EPR) method. The EPR spectrum of the [Cr(V)-PD] complex in pentanol is a symmetric singlet $g = 1.980 \pm 0.01$. The spectral line width is $\Delta H = 14 \cdot 10^{-4}$T in the solid solution and $\Delta H = 2.6 \cdot 10^{-4}$T in the liquid solution. The Cr(V) concentration in the solution was $\sim 3 \cdot 10^{19}$ cm^{-3}. The proton polarization obtained in this sample in the only experiment was 44% *) at T = 0.3 K in the magnetic field 2.6 T [21] (figs. 1, 2). The working material was a set of fragments $\sim$ 2 mm in size, obtained by crushing the frozen solution.

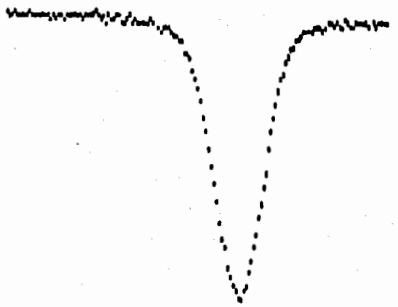


Fig. 1. NMR signal from protons in 1-pentanol at T = 0.8 K in the magnetic field B = 2.7 T.

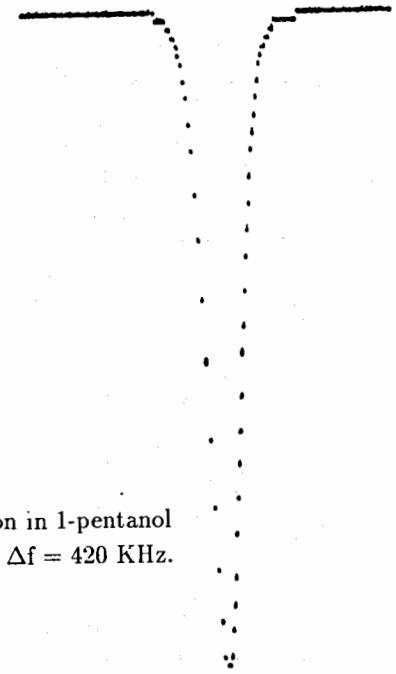


Fig. 2. NMR signal from proton in 1-pentanol at 44% polarization of protons, Δf = 420 KHz.

*)Measurement was performed by Yu.F. Kiselev and A.F. Prutkoglyad at the Institute of High Energy Physics (Serpukhov)

Thus, we managed to get a water-free target material based on the solution of [Cr(V)-PD] in pentanol. The solid solution was transparent, which allows us to state that the material was in a glass–like state. The material contains $C_H = 13\%$ of hydrogen, the free–to–bound proton ratio is n = 3.34, the liquid state density is d = 0.86 g/cm^3. For comparison, the corresponding characteristics of pure 1-pentanol are $C_H = 13.6\%$, n = 3.16, d = 0.81 g/cm^3, the melting point is -78.5°C. The disadvantages of this target material are a rather complicated procedure for making a transparent solution and the fact that it is difficult to make frozen balls suitable for the target in an ordinary way.

Recently, however, foreign laboratories have sometimes been using targets in the form of a block[21,22], the target resonator being filled with a liquid material and frozen. The advantage of these targets over frozen ball targets is that the material fills the resonator full while balls fill it only 65% full. Besides, in some experiments ^{3}He and ^{4}He in the beam are undesirable.

The material proposed can be used in these targets.

Target material based on EHBA-Cr(V) solution in glass–like matrix

It is known that admixtures providing a glass-like state are necessary for a target material to have an amorphous structure during polarization[1,3,10,17–20]. The most often used admixture is water[1,3,10,15,17]. However, among pentanol isomers there are 2-pentanol and 3-pentanol, which do not have the melting point and form good glass.

To check if the structure is amorphous or crystalline, we measured heat capacity and thermal relaxation in 2-pentanol and 1-pentanol. Alcohol samples were cooled from 292 K to 1.5 K at a rate of 1 K/min. Energy relaxation measurement at low temperatures showed that 1-pentanol is a crystalline substance. 2-pentanol has larger heat capacity than 1-pentanol and reveals properties typical of an amorphous substance[23].

Amyl alcohols, including 1-pentanol, 2-pentanol and 3-pentanol, are difficulty soluble. For the first experiments we chose 2-pentanol, which, for example, better dissolves in water than 1-pentanol and 3-pentanol. Following the recommendations of ref.[11–14,17], we took the stable complex of pentavalent chromium EHBA-Cr(V) as a paramagnetic admixture[16]. At room temperature the complex poorly dissolves in pentanol. Its solubility considerably increases with temperature. Heating the solution in a boiling water bath we obtained a 0.1 M solution of the complex in 2-pentanol. We noticed that the solution changes its colour if heated to more than 60°C. It is quite possible that oxidation of reagents takes place. The EPR spectrum of the solution is a line typical of targets based on Cr(V) complexes with $\Delta H = (2.5–3)\cdot 10^{-4}$T. The concentration of Cr(V) in the solution was less than $3.5 \cdot 10^{19}$cm^{-3}. When the solution is cooled the dissolved substance partly precipitates from it. To increase

the stability of the EHBA-Cr(V) solution in 2-pentanol, we added to some samples EHBA to have[24] pH = 3–4. The acid dissolves in 2-pentanol well, but does not practically improve solubility of the EHBA-Cr(V) complex. The 0.1 M EHBA-Cr(V) solution in 2-pentanol was diluted with 1-pentanol to the concentration $1 \cdot 10^{-3}$ M. The EPR spectrum of this solution slightly differs from the spectrum of the solution before dilution. Probably, the exchange of complex and solution ligands takes place.

We thus failed to prepare an EHBA-Cr(V) solution in 2-pentanol with the concentration required for target materials.

Secondary alcohols are more susceptible to oxidation, so for 2-pentanol the probability to oxidize is higher than for 1-pentanol. We had no information on resistance of pentanol isomers to radiation, which might be lower than that of 1-pentanol. Amorphous substances are usually less resistant to radiation damage. The foregoing made us return to experiments with 1-pentanol as the basic matrix for a target material and look for a method to get solution with a sufficient concentration of the paramagnetic admixture and with glass-forming properties.

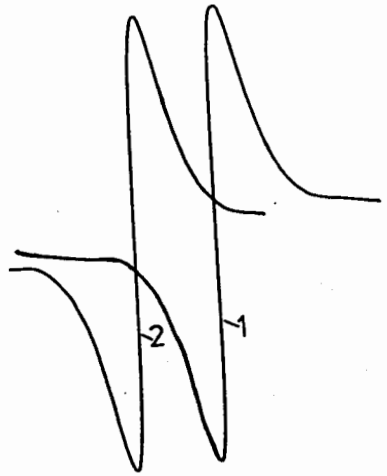
It is known that solubility of a polar substance can be improved by adding a solvent with a large dielectric constant. Sometimes water with $\varepsilon_{H_2O} = 80.4$ was added to target materials. We decided to use 1,2-propanediol with $\varepsilon_{C_3H_6(OH)_2} = 32$, which, as we found, agrees with 1-pentanol rather well, increases viscosity and density of solution, forms glass if rapidly cooled. The paramagnetic admixture was EHBA-Cr(V) complex. Besides, we added one more glass-forming admixture 3-pentanol, which has a more symmetric structure than 2-pentanol and might improve solubility of EHBA-Cr(V) on the principle "similar in similar".

A sample was prepared in the following way: propanediol was mixed with 3-pentanol. Then EHBA-Cr(V) was added to the solution, so that to have the concentration of paramagnetic centres $5 \cdot 10^{19}$cm^3. The solution immediately coloured, the complex partially dissolved. Then 1-pentanol (83%) was added, and the solution was intensively stirred until the complex dissolved completely.

For comparison, we made a sample as described in ref.[12–14], which consisted of EHBA-Cr(V) solution in 1-pentanol with 5% of water added. Both solutions were studied by the EPR method. The EPR line width was the same for the two samples (fig. 3). The samples were also analysed using differential scanning calorimetry (fig. 4). The heating rate was 8 degrees/min. The curve of the water sample shows the melting peak at $T_m = 194$ K. The target material that we propose is glass. Its vitrification temperature is $T_g = 130$ K. The results obtained are in agreement with ref.[20].

Thus, we managed to obtain solution of the EHBA-Cr(V) complex in 1-pentanol, which is glass. The final conclusion regarding suitability of this material can be drawn from the study of proton polarization and other characteristics after exposing a target to a particle beam of high intensity.

Fig. 3. EPR spectra of EHBA-Cr(V) solutions (concentration $5 \cdot 10^{19}$ cm^{-3} at T = 295 K.
1 – solvent: 1–pentanol (83%), 3–pentanol, 1,2–propanediol.
2 – solvent: 1–pentanol (95%), water (5%).



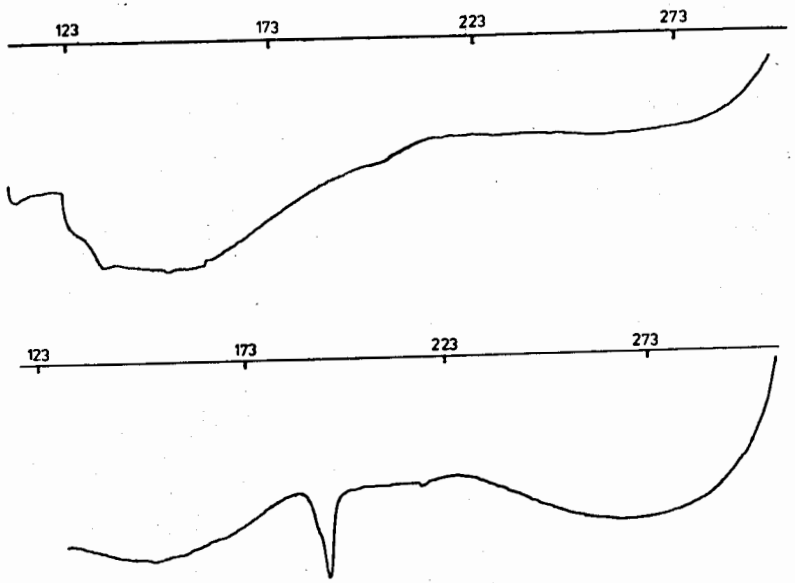


Fig. 4. Differential calorimeter scans of EHBA-Cr(V) solution (concentration $5 \cdot 10^{19}$ cm^{-3})
1 – solvent: 1–pentanol (83%), 3–pentanol, 1,2–propanediol.
2 – solvent: 1–pentanol (95%), water (5%).

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