

# NMR - based liquid explosive detector

Anton Gradišek  
Jožef Stefan Institute  
Jamova 39, 1000 Ljubljana, Slovenia

Tomaž Apih  
Jožef Stefan Institute  
Jamova 39, 1000 Ljubljana, Slovenia

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## **Abstract**

Liquid explosives pose a threat to security on airplanes and other public places, since they can easily be concealed as benign liquids. A detector, able to quickly identify liquids, would increase the possibility to detect such threats and speed up security checks.

As a step towards a long term goal to develop a liquid explosive detector, we have constructed an experimental setup, based on a low cost 1.1 T permanent magnet with huge static magnetic field gradient 4.8 T/m which allows us to measure proton relaxation times  $T_1$  and  $T_2$  and the self-diffusion coefficient  $D$  in liquid samples in a thin slice excited by RF pulses. We have developed a simple model in order to explain non-exponential magnetization decay in inversion recovery  $T_1$  experiment in this setup. Measuring a wide variety of liquid samples, we have demonstrated that it is possible to discriminate between the liquids solely based on these parameters. We discuss further improvements to the detection method, among those the choice of magnetic field, based on fast field-cycling measurements.

# 1 Introduction

Liquid explosives pose a security threat, since it is possible to conceal them as beverages, cosmetic products etc. In 2006, a coordinated terrorist plot to detonate liquid explosives on several aircrafts traveling from the United Kingdom to the United States and Canada was discovered and foiled by the police. The incident raised security measures, limiting the amounts of liquids passengers are allowed to bring onto commercial aircraft in their hand luggage. A need for a new type of a detector arose, a detector that would be capable of fast discrimination or identification of liquids. Such detector would increase chances of discovering potential threats and would speed up security checks. Apart from explosives themselves, the detector would also identify components required for preparation of explosives, such as peroxide or acetone.

Nuclear magnetic resonance is a powerful analytical tool and can provide much information for detection and discrimination of liquid samples [3]. While high resolution NMR spectroscopy can be used to analyze chemical composition of the sample, this method is not appropriate for fast screenings as expensive superconducting magnets with high field homogeneity are required, besides, sample preparation and mounting is time-consuming. However, several NMR parameters can be measured without a high and homogeneous field. Measuring proton relaxation, one can obtain spin-lattice relaxation time  $T_1$  and spin-spin relaxation time  $T_2$ . If one uses magnetic field gradient, the self-diffusion coefficient  $D$  can be extracted as well. Additionally, the amplitude of the NMR signal carries information about the proton density in the sample.

Relatively few groups have investigated possibilities of using NMR techniques to construct a liquid explosives detector. A prototype "bottle scanner" has been built by Quantum magnetic, a device that scans the bar code of the bottle, measures  $T_1$  and  $T_2$  of the content and compares the values with values from its database [8]. The NMR system used an split-coil electromagnet with enough space to insert a bottle of diameter 11.4 cm, magnetic field corresponded to proton frequency 3 MHz. A further development of the detector was made by the Aachen group, where a permanent Halbach magnet and a surface coil were used instead [10]. A theoretical analysis of signal processing of CPMG decays to extract  $(T_2, D)$  pair for liquid discrimination was explored in [7].

In our approach, we have constructed a detector based on a permanent

magnet that enables us to measure  $T_1$ ,  $T_2$  and  $D$  in the same configuration without applying additional gradients - the inhomogeneity of the magnetic field suffices. This way, the detector becomes simpler and cheaper, since no pulse-gradient coils are needed. In the paper, we present the detector and an analysis of several liquid samples. We describe an additional effect in  $T_1$  measurements, introduced by diffusion in a static gradient, and we discuss further aspects of detection methods.

## 2 Experimental setup

We have constructed a portable system to measure  $T_1$ ,  $T_2$  and  $D$ . The system consists of a permanent magnet (by AMT&C, Russia [1]), a probe, RF transmitter and a spectrometer. The magnet is a Halbach-type cylindrical magnet of approximate outer dimensions 20 cm  $\times$  20 cm with Larmor frequency 50.2 MHz (corresponding magnetic field 1.1 T) in the lateral direction inside the bore of diameter 40 mm. In order to measure diffusion, the sample was positioned 13 mm off the center of the magnet where the magnetic field gradient is 4.8 T/m and Larmor frequency is 48.7 MHz. NMR probe was designed to take 10 mm sample tubes, samples typically had volume of 1 cm<sup>3</sup>. Due to small dimensions, the device could only be used to test small samples and to demonstrate the concept of the detection. To measure  $T_1$ , a standard inversion recovery (IR) sequence was used. Data was analyzed as described later in the paper.  $T_2$  and  $D$  were both determined by using a series of Carr-Purcell-Meiboom-Gill (CPMG) sequences [11].

## 3 Theoretical background

### 3.1 Diffusion and spin-spin relaxation

In a homogenous field, a CPMG echo train decays exponentially with decay time  $T_2$ . However, if magnetic field gradient  $g$  is present, the decay of echo amplitude is affected by self-diffusion as well. In this case, the amplitude of the  $n$ -th echo can be expressed as [12]

$$M(n2\tau) = M_0 \exp\left(-\frac{1}{3}(\gamma g)^2 D(n2\tau)\tau^2\right) \exp\left(-\frac{n2\tau}{T_2}\right), \quad (1)$$

where  $\tau$  is the spacing between pulses. Since  $n2\tau = t$ , this equation can be simplified as

$$M(t) = M_0 \exp\left(-\frac{1}{3}(\gamma^2 g^2 D \tau^2) + \frac{1}{T_2}\right) t. \quad (2)$$

Magnetization therefore decays with a characteristic time  $T'_2$ , where

$$\frac{1}{T'_2}(\tau) = \frac{1}{T_2} + \frac{1}{3}D(\gamma\tau g)^2. \quad (3)$$

If we plot a graph  $1/T'_2(\tau^2)$ , the slope of the line will be proportional to  $D$  while the intersection with  $y$ -axis will correspond to  $1/T_2$  (Figure 2). A problem can appear in the samples with a very slow diffusion, where magnetization decays mostly due to  $T_2$  and the diffusion contribution is negligible. In such cases, the solution is to use the stimulated echo (SE) sequence [6], which enables us to measure diffusion coefficients several orders of magnitude lower. However, measurements using SE take considerably longer time than using CPMG and are therefore inappropriate for fast screenings.

## 3.2 Spin-lattice relaxation

Inversion recovery sequence consists of an inverting  $\pi$  pulse, relaxation delay  $t$ , and a reading  $\frac{\pi}{2}$  pulse, in our case followed by another  $\pi$  pulse to produce the Hahn echo that we detect. In a homogenous magnetic field or if only a weak field gradient is present, the magnetization decays exponentially as

$$M(t) = M_0 - 2M_0 e^{-\frac{t}{T_1}}. \quad (4)$$

In the presence of a very strong magnetic field gradient and relatively slow spin-lattice relaxation, an additional effect occurs which makes the decay (Eq. 4) faster and even nonexponential. This effect is caused by a fact that due to strong gradient and large spread of resonating frequencies, the magnetization is inverted only in a thin slice of the sample and spins diffusing in and out of this slice change the magnetization decay observed. In the following we devise a simple model to quantify this effect.

Let us assume that the inverting pulse reverses the magnetization of all protons ( $N$ ) in the slice of width  $2a$ , where  $2a$  is defined by the gradient  $g$  and the length of the pulse  $t_\pi$  as  $2a \approx b/t_\pi g \gamma$ , where  $b$  is a numerical factor of order of magnitude 1. After time  $t$ , the magnetization is given as Eq. 4. However, in the time  $t$ ,  $\Delta N(t)$  protons will diffuse out of the slice and

will not contribute to the signal after the second pulse. In the same time,  $\Delta N(t)$  protons will diffuse into the slice. Those protons were not affected by the inverting pulse and carry the original magnetization  $M'_0$  each. Total magnetization after the second pulse can then be expressed as

$$M(t) = (N - \Delta N)(M'_0 - 2M'_0 e^{-\frac{t}{T_1}}) + \Delta N M'_0 = N M'_0 - (N - \Delta N) 2M'_0 e^{-\frac{t}{T_1}}. \quad (5)$$

To estimate  $\Delta N(t)$ , we analyze the time evolution of a box-like distribution on an interval  $[-a, a]$  with a height  $T_0$ , driven by the diffusion equation

$$\frac{\partial T}{\partial t} = D \frac{\partial^2 T}{\partial x^2}. \quad (6)$$

The well-known solution to this equation is

$$T(x, t) = \frac{T_0}{2} \left( \Phi \left( \frac{x+a}{\sqrt{2Dt}} \right) - \Phi \left( \frac{x-a}{\sqrt{2Dt}} \right) \right), \quad (7)$$

where  $\Phi(\xi)$  is the error function,

$$\Phi(\xi) = \frac{2}{\sqrt{\pi}} \int_0^\xi e^{-\frac{z^2}{2}} dz. \quad (8)$$

Approximating  $\Delta N(t) \approx N - 2a \cdot T(0, t)$  and taking into account that  $\Phi(\xi)$  is an odd function, the Eq. 5 simplifies to

$$M(t) = M_0 \left( 1 - \Phi \left( \frac{a}{\sqrt{2Dt}} \right) e^{-\frac{t}{T_1}} \right). \quad (9)$$

This model can serve us as to determine the range of parameters where the diffusion effects have to be taken into account for  $T_1$  determination. Since the diffusion coefficient  $D$  has been measured using the CPMG sequence and the slice width  $2a$  is determined by the pulse length and the field gradient, the value of  $T_1$  can be estimated. For a more detailed analysis, the excitation profile of the slice and shape of the pulses should be taken into account, acknowledging that the magnetization is fully inverted only at the center of the slice. A similar approach can be applied to analyze the magnetization decay measured by other pulse sequences, such as the saturation recovery.

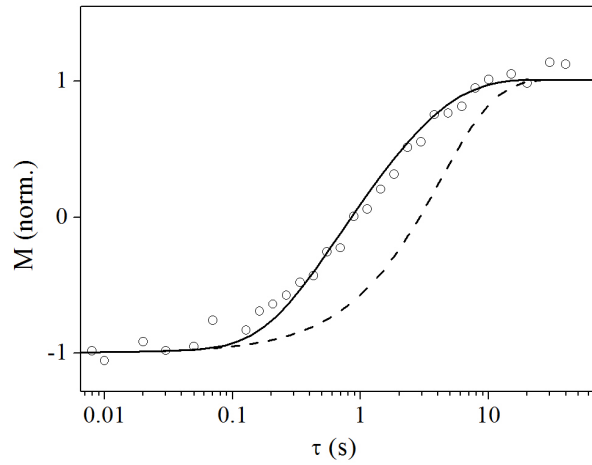


Figure 1: Magnetization decay in acetone in a huge magnetic field gradient, measured by inversion recovery sequence (circles). Solid line represents the model given by the Eq. 9 which takes in consideration the effect of diffusion in and out of the excited slice. Dashed line represents the magnetization decay given by the Eq. 4 using the same  $T_1$  as the solid line, corresponding to a decay in a homogenous field.

No	Sample	T <sub>1</sub> (s)	T <sub>2</sub> (s)	D (10 <sup>-9</sup> m <sup>2</sup> /s)
1	Acetone *	4.2	0.13	3.9
2	Peroxide *	3	0.08	2.7
3	Milk	0.84	0.44	2.4
4	Toluene *	3.4	0.16	2.25
5	Methanol *	2.7	long	2.2
6	Coca Cola *	2	long	1.9
7	White wine	1.1	0.18	1.55
8	Tetrahydrofuran *	2.8	0.78	1.36
9	Hexane	1.6	1.3	0.92
10	Ethanol	1.58	0.3	0.85
11	Whiskey	1.3	0.24	0.83
12	Banana	0.5	0.05	0.61
13	Isopropanol	1.35	0.24	0.59
14	Acetonitrile	1.7	1	0.57
15	Irish cream	0.47	0.09	0.3

Table 1: T<sub>1</sub>, T<sub>2</sub> and D for different samples, measured at Larmor frequency 48.7 MHz and static magnetic field gradient 4.8 T/m. T<sub>1</sub> was measured using inversion recovery sequence while T<sub>2</sub> and D were obtained using CPMG sequence. "\*" indicates samples for which T<sub>1</sub> had to be determined using Eq. 9. "Long" indicates T<sub>2</sub> values too long to measure precisely, as discussed in the paper.

## 4 Experimental results and discussion

The results of our measurements are presented in Table 1. All the samples were measured at the room temperature.

Diffusion coefficients measured match the values from [7] within the experimental error. In our experimental setup (huge field gradient), for samples with longer  $T_2$  (a couple of seconds), diffusion becomes the prevailing mechanism of echo amplitude decay even for the shortest possible values of  $\tau$ . Therefore, the  $T_2$  value calculated by the method described has a big experimental error and is therefore unreliable. In such cases, the detector would simply assign those samples "long  $T_2$ " and use the other two parameters for identification. Alternatively,  $T_2$  can be precisely determined by measuring a single CPMG sequence in a homogenous field. This could be implemented by using another coil, positioned in the center of the magnet, where the field is homogenous. Since the sample is big enough to stretch over both coils, both measurements could in principle be performed without moving the sample.

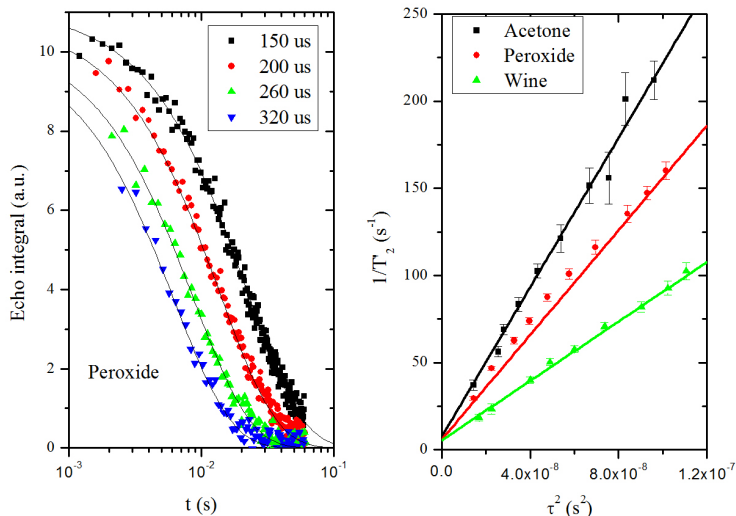


Figure 2: **Left:** CPMG echo amplitude decay curves in peroxide for different pulse spacings, together with the corresponding exponential fits. **Right:**  $1/T_2$  as a function of  $\tau^2$ . The slope of the line is proportional to  $D$  while the intersection with the  $y$ -axis corresponds to  $1/T_2$ .



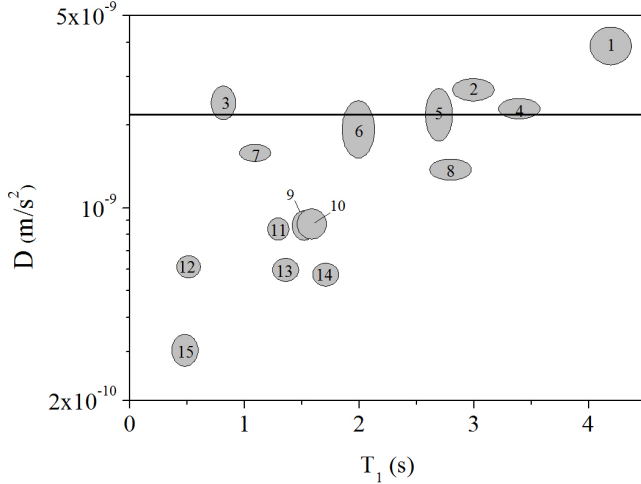


Figure 3:  $D$  vs.  $T_1$  plot for various samples, the horizontal and vertical symbol dimensions correspond to the experimental error. Legend to the numbers is given in the Table 1.

While  $T_2$  and  $D$  measurements are fast (using appropriate numerical methods two scans with different  $\tau$  are effectively sufficient [7]),  $T_1$  measurements are more time-consuming. Using the IR sequence, one needs to wait several  $T_1$ -times for each partial measurement. Applying advanced sequences, such as fast inversion recovery (FIR) [5] or superfast inversion recovery (SUFIR) [4], the time required for a measurement can in principle be significantly reduced, provided that the sequences are adapted for high gradients.

It is important to notice that in some liquids, such as syrups or creams,  $T_1$  and  $T_2$  can be multiexponential [10]. This effect presents a significant complication because a more detailed measurement of  $T_1$  is required in order to identify separate components with sufficient accuracy. On the other hand, a detailed analysis provides additional information about the sample.

Another important aspect is the amplitude of NMR signal. As discussed in [8], the amplitude depends of the sample volume - in order to compare amplitudes for different samples, one either needs to know the exact volume of the sample scanned. In our setup, the scanned volume is well-determined by magnetic field gradient and pulse lengths, therefore the volume is always

the same.

In our experimental setup, we were able to measure all three parameters  $T_1$ ,  $T_2$  and  $D$  under the same conditions (high static field gradient) with sufficient accuracy to make the discrimination possible. Although either  $T_1$  or  $D$  values of some of our samples overlap within the experimental error, they are mostly well-separated on a two dimensional  $D$  vs.  $T_1$  plot, as indicated on the Figure 3. For additional dimensions, we can use  $T_2$  or signal amplitude. A two-dimensional discriminating algorithm was discussed by [7] and can be expanded to include additional parameters.

Since  $T_1$  can be strongly dependent on the Larmor frequency, a question arises, whether different value of the field would be advantageous to better separate overlapping values of  $T_1$ . Higher magnetic fields (such as in our case) are preferred in respect to higher S/N ratios and higher field gradients for diffusion measurements and spatial resolution. On the other hand,  $T_1$  values of different samples span over a wider range at lower fields. Additionally, planar configurations that presumably have better geometry for a detector, are also connected with lower fields. We measured the dependence of  $T_1$  on the Larmor frequency between 10 kHz and 20 MHz using a fast field-cycling (FFC) relaxometer. Figure 4 shows typical field dependencies for various samples. We see that the relaxation times of pure substances, such as ethanol or peroxide, do not vary significantly in the measured range, therefore a choice of field does not significantly affect the resolution of the detection. On the other hand, the "mixtures" and high-viscosity samples such as milk, jam or honey, show significant field dependency. While the comparison between low and high field  $T_1$  is an informative parameter, the relaxation times in static low fields are difficult to measure because of the low S/N ratio. A FFC relaxometer uses pre-polarization of the sample to bypass this problem, but this solution is hard to implement in a portable detector.

While cylindrical configuration of the magnet is efficient in generating both homogenous and inhomogeneous magnetic field, other configurations have been explored. A lot of progress has been made with planar configurations of permanent magnets, combined with a surface sensor, such as NMR-MOUSE [2] and NMR-MOLE [9]. Such configurations are probably even more appropriate for the final version of the detector since the dimension of the sample is not limited by the borehole. Because magnetic field gradient enables spatial resolution, the system can in principle be used to scan separate parts of a bigger object.

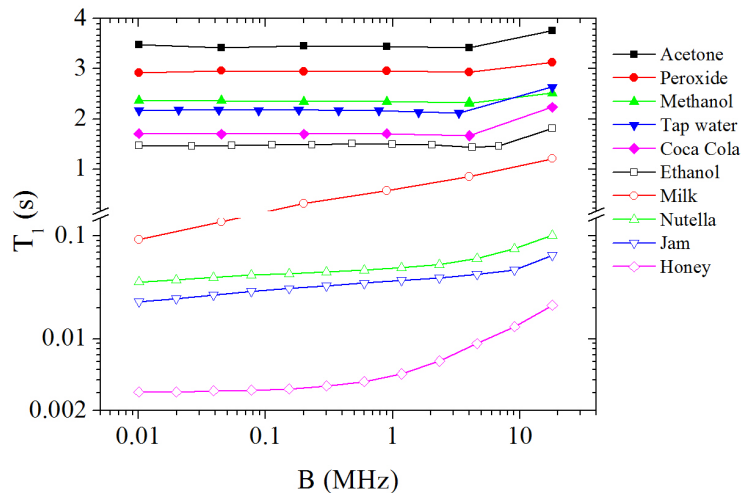


Figure 4:  $T_1$  as a function of magnetic field for various samples, measured with a FFC relaxometer. Nutella, jam and honey have slow diffusion coefficients and were not measured by CPMG sequence.

## 5 Conclusions

We tested whether it is possible to discriminate between various liquids using nuclear magnetic resonance in a small and inexpensive permanent magnet. We have constructed a portable detector that enables us to measure spin relaxation times  $T_1$  and  $T_2$  and self-diffusion coefficient  $D$  in the field of a permanent magnet without the need of gradient coils.

Our measurements suggest that a combination of two of the above parameters can serve as the basis for identification of the liquid and liquid-like samples, provided that we have a database of  $T_1$ ,  $T_2$  and  $D$  values for possible samples in advance. Using all three parameters or including the information about signal intensity can add to a more accurate identification.

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