

DETECTION AND CLASSIFICATION OF LIQUID EXPLOSIVES USING NMR

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ABSTRACT

In this work, we present a novel method for non-invasive identification of liquids, for instance to allow for the detection of liquid explosives at airports or border controls. The approach is based on a nuclear magnetic resonance technique with an inhomogeneous magnetic field, forming estimates of the liquid's spin-spin relaxation time, T_2 , and diffusion constant, D , thereby allowing for a unique classification of the liquid. The proposed detectors are evaluated using both simulated and measured data sets.

Index Terms— detection of liquid explosives, classification, nuclear magnetic resonance

1. INTRODUCTION

On August 10, 2006, the British authorities announced that they had foiled an attempted terrorist attack aimed at blowing up airplanes using liquid explosives. The use of liquid explosives immediately caused worldwide restrictions on the allowed amount of liquids in carry-on luggage. Airport security can detect several forms of solid explosives, for instance using X-rays, metal detectors, and chemical sensors (see, e.g., [1] for a review on the topic). However, liquid explosives can be both odourless and clear, closely resembling water, making them exceedingly difficult to separate from typically allowed fluids, such as water or alcohol. Furthermore, liquid explosives can be so-called binary, or two-part, explosives, resulting from the reaction of two non-explosive substances that are easier to transport and/or harder to detect. An example of such a binary explosive is ANNM, formed by the mixing of nitromethane (easily acquired in the local drugstore) and ammonium nitrate. The resulting explosive was, for example, used in the Oklahoma City bombing in 1995. The current travel restrictions are insufficient for these forms of explosives; one terrorist may bring the nitromethane, a second the ammonium nitrate, mixing them after passing security or onboard the airplane. Even restricted to the allowed

amounts, the resulting explosive could cause severe fatal consequences. This work aims at developing a novel approach to classify liquids, thus allowing for a reliable detection of liquid explosives or liquids that can be used to form such explosives.¹ We exploit a non-invasive nuclear magnetic resonance (NMR) technique with an inhomogeneous magnetic field, forming the exciting radio frequency (RF) pulses into a Carr-Purcell-Meiboom-Gill (CPMG) sequence [2, 3]. This technique has previously been successfully applied both for the detection of liquid explosives [4] and in related problems such as oil well logging and drilling [5]. Typically, in the detection of hazardous substances, the signals resulting from the CPMG sequences were used to form estimates of the spin-lattice relaxation time, T_1 , and the spin-spin relaxation time, T_2 , using these time constants, in combination with other sensors, to classify the liquid [4]. Herein, different from the work in [4], we will instead use the resulting signals to form estimates of the spin-spin relaxation time, T_2 , and the diffusion constant, D . To the best of the authors' knowledge, a liquid's (T_2, D)-pair allows for a unique identification of the substance, thereby enabling the differentiation between, e.g., ordinary bottled water and nitromethane. In comparison with the approach used by Dr. Burnett and co-workers, the proposed technique allows for a faster classification since only T_2 , and not T_1 , is measured. In earlier works, such as [4], the effect of diffusion on the relaxation is assumed sufficiently small to be neglected. This assumption might not hold if the strength of the natural magnetic field is suddenly increased, e.g., if the sample contains metal. The technique proposed herein estimates the diffusion effect and makes use of it in the classification, thereby allowing for a more reliable classification.

2. DATA MODEL

The signal resulting from the exciting CPMG sequence can be well modelled as the real-valued sequence [4, 6]:

$$y(n) = I_0 \exp\{n\beta(\tau, G)\} + w(n), \quad n = 1, \dots, N, \quad (1)$$

where $w(n)$ denotes an additive noise sequence,

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¹Often, one is primarily interested in determining if the substance is either hazardous or benign. In general, such a classification is easier than the more general problem examined here.

$$\beta(\tau, G) = -\left(2\tau T_2^{-1} + \frac{2}{3}\gamma_H^2 G^2 D\tau^3\right), \quad (2)$$

$G = G_a + G_m$, with I_0 denoting the magnetisation of the spin system without any relaxation or diffusion effect, τ the time between the RF pulses, G_a the applied magnetisation, G_m the natural magnetic field, and γ_H the gyromagnetic ratio of hydrogen. Of these, $\gamma_H = 26.75 \times 10^7$, whereas τ and G_a are user parameters. The natural magnetic field, G_m , is also unknown as it may vary substantially between different experiments if the setup is changed or, for example, the sample contains traces of metal. Furthermore, I_0 will typically vary between experiments and should be treated as unknown². The problem of interest is thus: given $y(n)$, with G_a , τ and γ_H known, estimate T_2 and D . For sufficiently high signal-to-noise ratio (SNR), the additive noise in (1) can be neglected, allowing for the estimation of I_0 using the expression

$$\ln I_0 = \ln y(n) - \beta(\tau, G)n, \quad (3)$$

suggesting the estimate

$$\begin{aligned} \ln \hat{I}_0 &= \frac{1}{N} \sum_{n=1}^N [\ln y(n) - \beta(\tau, G)n] \\ &= \tilde{y} - \beta(\tau, G) \frac{N+1}{2}, \end{aligned} \quad (4)$$

where $\tilde{y} \triangleq \frac{1}{N} \sum_{n=1}^N \ln y(n)$. By incorporating the modelling errors in the noise process $\tilde{w}(n)$, and by expanding (1), using the estimate in (4), we obtain

$$\begin{aligned} \ln y(n) &= n\beta(\tau, G) \ln I_0 + \tilde{w}(n) \\ &= \tilde{y} + \left[n - \frac{N+1}{2}\right] \beta(\tau, G) + \tilde{w}(n), \end{aligned} \quad (5)$$

which, expressed in vector form, suggests the least squares (LS) estimate of $\beta(\tau, G)$:

$$\hat{\beta}(\tau, G) = \frac{12}{N(N+1)(N-1)} \sum_{n=1}^N \left(n - \frac{N+1}{2}\right) \ln y(n). \quad (6)$$

Using the obtained $\hat{\beta}(\tau, G)$ estimate, we now proceed to examine ways to estimate the spin-spin relaxation time, T_2 , and the diffusion constant, D .

2.1. The Rooting Algorithm (RA)

Assume that three measurements series are available, obtained by varying both G_a and τ pairwise. Denote the decay of these data series

²We note that in an ideal experiment, even for different τ values, I_0 can be expected to be constant. However, even small temperature variations and/or magnetic field drifts over time will cause it to be different with different τ values. Furthermore, for different G_a , I_0 can be significantly different due to temperature effect related to current heating in the gradient coils.

$$\beta_{ij} = -2\tau_i T_2^{-1} - \frac{2}{3}\gamma_H^2 D G_j^2 \tau_i^3 \quad ; \quad i, j = 1, 2 \quad (7)$$

$$G_j = G_{a,j} + G_m. \quad (8)$$

To find T_2 , we use the two data series that have the same G_a but different τ . First rewrite (7) as

$$-\frac{2}{3}\gamma_H^2 D G_j^2 = (\beta_{ij} + 2\tau_i T_2^{-1}) / \tau_i^3. \quad (9)$$

For data series with equal G_a , we have

$$\frac{\beta_{11} + 2\tau_1 T_2^{-1}}{\tau_1^3} = \frac{\beta_{21} + 2\tau_2 T_2^{-1}}{\tau_2^3}, \quad (10)$$

so that an estimate of T_2 can be obtained as

$$\hat{T}_2 = \left[\frac{\beta_{11}\tau_2^3 - \beta_{21}\tau_1^3}{2(\tau_1^3\tau_2 - \tau_1\tau_2^3)} \right]^{-1}. \quad (11)$$

For the estimation of D , we use the two data series that have equal τ but different G_a . Let

$$\begin{aligned} \tilde{\beta} = \beta_{i1} - \beta_{i2} &= -\frac{2}{3}\gamma_H^2 D \tau_i^3 (G_1^2 - G_2^2) \\ &= -\frac{2}{3}\gamma_H^2 D \tau_i^3 \tilde{G}_a (\bar{G}_a + G_m), \end{aligned} \quad (12)$$

where

$$\tilde{G}_a = G_{a,1} - G_{a,2} \quad (13)$$

$$\bar{G}_a = G_{a,1} + G_{a,2}. \quad (14)$$

Solving (12) for G_m yields

$$G_m = -\frac{1}{2} \left(\frac{\tilde{\beta}}{\frac{2}{3}\gamma_H^2 D \tau_i^3 \tilde{G}_a} + \bar{G}_a \right). \quad (15)$$

Inserting (15) in (7), we obtain $c_2 D^2 + c_1 D + c_0 = 0$, where

$$c_2 \triangleq \left(G_{a,j}^2 - G_{a,j} \bar{G}_a + \frac{1}{4} \bar{G}_a^2 \right) \frac{2}{3} \gamma_H^2 \tau_i^3 \quad (16)$$

$$c_1 \triangleq 2\tau_i T_2^{-1} - \beta_{ij} + \frac{\tilde{\beta} (\frac{1}{2} \bar{G}_a - G_{a,j})}{\tilde{G}_a} \quad (17)$$

$$c_0 \triangleq \frac{\tilde{\beta}^2}{4 \frac{2}{3} \gamma_H^2 \tau_i^3 \tilde{G}_a^2}. \quad (18)$$

Solving this second order equation yields two different roots; to decide which of the roots to use, we compare the Euclidian distance of the resulting (\hat{T}_2, \hat{D}) -pair, using \hat{T}_2 from (11) and \hat{D} from each root, with the known (T_2, D) -pairs of the substances of interest. The estimate of D is selected as the root minimizing this distance.

2.2. The Weighted Searching Algorithm (wSA)

As an alternative, we also consider an algorithm that estimates the unknown parameters using a nonlinear search. Let $\theta = [T_2^{-1}, D, G_m]$ denote the unknown parameters. These

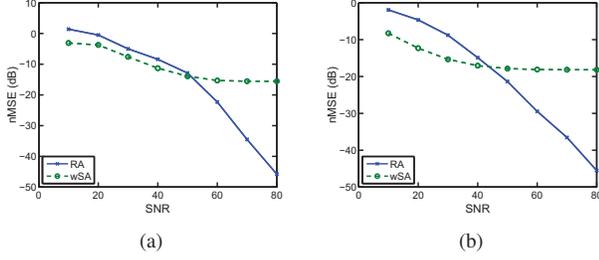


Fig. 1. Normalized MSE of the estimation of (a) T_2 , and (b) D when the user parameters are drawn from a uniform random distribution.

are then estimated using a weighted least-squares (WLS) approach:

$$\hat{\theta} = \arg \min_{\theta} \sum_{k=1}^K \left[\hat{\beta}_k - \beta_k \right]^2 w_k, \quad (19)$$

with $\hat{\beta}_k$ obtained from (6) and β_k defined as in (2). An intuitive way of determining the weights, w_k , is to use the inverse of the Cramér-Rao Lower Bound³ (CRLB) of the β_k estimate. Doing so, larger credit will be given to $\hat{\beta}_k$'s obtained by setting the user parameters τ and G_a such that the estimate gets lower variance. To formulate the CRLB, we will here assume that $\tilde{w}(n)$ can be modelled as a zero mean white Gaussian process with variance σ^2 . As shown in Section 4, the resulting weights are then formed as

$$w_k = [CRLB(\beta_k)]^{-1} = \frac{I_0^2 r^2 P(r)}{(1-r^N)(1-r)^3}, \quad (20)$$

where $P(r) = 1 - N^2 r^{N-1} + 2(N^2 - 1)r^N - N^2 r^{N+1} + r^{2N}$ and $r \triangleq e^{2\beta_k}$.⁴

3. NUMERICAL EXAMPLES

We examined the performance of the proposed classifiers, generating simulated nitromethane data according to the model (1) with $T_2 = 3.35$ s and $D = 2.62 \times 10^{-9} \text{m}^2 \text{s}^{-1}$. The user parameters τ and G_a were distributed uniformly in the intervals⁵ $[1, 20]$ ms and $\pm[1, 5]$ A, respectively. The sign of G_a was also chosen randomly. The natural magnetic field, G_m , and the initial magnetization, I_0 , were set to 11×10^{-4} T/m and 800, respectively. The data was corrupted with zero-mean white Gaussian noise with power σ_w^2 . The SNR was defined as $\text{SNR} = \sigma_s^2 \sigma_w^{-2}$, where σ_s^2 denotes the power of the noise-free signal. A total number of 10^5 Monte-Carlo simulations

³The CRLB is a theoretical lower limit for the variance of an unbiased estimator. See, e.g., [7, 8] for further details.

⁴We note that the noise variance has been removed from the weight since a pure scaling will not change the result.

⁵The transformation from A to T/m of G_a is done by multiplication with 47.15×10^{-4} T/(Am).

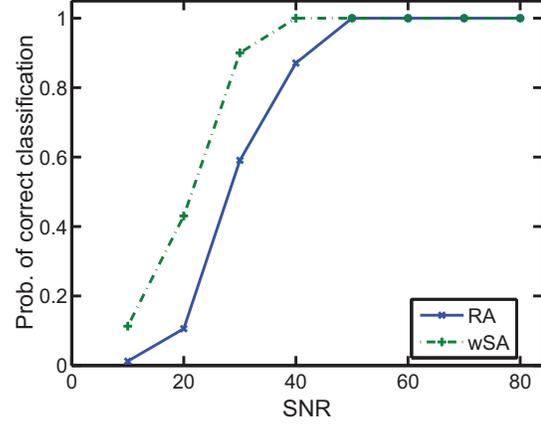


Fig. 2. Probability of correct classification versus SNR for nitromethane.

were performed. From each simulation, the estimates of D and T_2 were computed and compared with the true values using the normalized mean squared error:

$$\text{nMSE} = \frac{1}{N} \sum_{n=1}^N \left(\frac{x - \hat{x}_n}{x} \right)^2, \quad (21)$$

where x is the true parameter, \hat{x}_n is an estimate thereof from the n th simulation, and N is the number of simulations. Furthermore, if $|G_{a,i} - G_{a,j}| < \epsilon_{G_a}$, $i, j = 1, 2, 3$, $i \neq j$, where $\epsilon_{G_a} = 0.001$, the parameters were redrawn. Similarly for τ with $\epsilon_\tau = 0.001$ and for β with $\epsilon_\beta = 0.001$. This since β 's that are too similar in the three measurement series will cause failure of the estimation algorithms. For wSA, the lower limits of the search region for T_2 , D and G_m were set to 0.1 s, $1 \times 10^{-9} \text{m}^2 \text{s}^{-1}$, and 1×10^{-4} T/m, respectively, whereas the upper limits were 6 s, $5 \times 10^{-9} \text{m}^2 \text{s}^{-1}$, and 20×10^{-4} T/m, respectively. As initial values of the search we used 0.5 s, $2 \times 10^{-9} \text{m}^2 \text{s}^{-1}$, and 10×10^{-4} T/m, respectively. The values were chosen so that the T_2 - and D -values (see Tab. 1) of the substances of interest, together with the likely values of G_m , were comprised in the search region. The results of the simulations are shown in Fig. 1(a) and Fig. 1(b). As can be seen in Fig. 1(a), wSA outperforms RA for lower SNR, whereas RA works best for larger SNR.

We proceed to compare the algorithms in terms of probability of correct classification. Again, we generated simulated nitromethane data and added noise, but the user parameters were fixed and set to $\tau_1 = \tau_3 = 16$ ms, $\tau_2 = 10$ ms, $G_{a,1} = G_{a,2} = 1.6$ A and $G_{a,3} = 2.0$ A for RA; for wSA we set $\tau_1 = 16$ ms, $\tau_2 = 14$ ms, $\tau_3 = 10$ ms, $G_{a,1} = 1.6$ A, $G_{a,2} = 2.0$ A, and $G_{a,3} = -1.6$ A. The same boundaries and initial values as in the MSE study were used. The algorithms were evaluated using 5000 Monte-Carlo simulations. The results can be seen in Fig. 2 and we see that wSA was

Table 1. (T_2, D) -pairs for different substances

Nbr	Liquid	T_2 (s)	D ($10^{-9} \text{m}^2 \text{s}^{-1}$)
1	Oxygen free water [◊]	3.60	2.30
2	Ethanol [◊]	3.5	1.08
3	Acetone	3.00	4.25
4	Methanol [◊]	8.0	2.42
5	Benzene [◊]	19	2.21
6	Acetic acid [◊]	3.8	1.08
7	Cyclohexane [◊]	6.5	1.42
8	Toluene [◊]	12.5	2.27
9	Tap water (London)	2.24	2.37
10	Semi-skimmed milk	0.17	2.16
11	Liquid soap	1.70	1.96
12	Nitromethane	3.35	2.62

[◊]The values of T_2 and D for these substances have not been verified in our experiments and have to be considered approximative.

able to give correct classification in 100% of the trials for an SNR of 40dB and higher, whereas RA does this for an SNR of 50dB and higher. For low SNR the probability of giving correct classification is poor for both algorithms, even though the chance is higher for wSA.

Finally, we evaluate the algorithms on data measured in the laboratory using tap water, obtained with $\tau = 10, 12, 18, 20$ ms for $G_a = 1.6, -1.6, 2.0$ A, a total of 12 series. Taking three different series out of these 12, permuted such that the requirements of RA were fulfilled, we performed 72 trials. The results can be see in Fig. 3, were the performance of wSA on the same series is displayed. Interestingly, we note that RA is able to correctly classify 98.6% of the trials whereas wSA only does it in 40.3% of the trials, exhibiting an apparent bias. The reasons for this is a topic of further study.

4. DERIVATION OF THE WEIGHTING COEFFICIENTS

Let $\mu \triangleq I_0 e^{n\beta}$ and $\theta \triangleq [I_0, \beta]$. Using the Slepian-Bang formula (see, e.g., [7]), we can express the Fisher information matrix (FIM) as:

$$\text{FIM} = \frac{1}{\sigma^2} \sum_{n=1}^N \left(\frac{\partial \mu}{\partial \theta} \right)^T \left(\frac{\partial \mu}{\partial \theta} \right) \quad (22)$$

The CRLB is then given by the diagonal elements of the inverse of the FIM. We thus have that $\text{CRLB}(\beta) = [\text{FIM}^{-1}]_{22}$, where

$$\text{FIM} = \frac{1}{\sigma^2} \sum_{n=1}^N [e^{n\beta} n I_0 e^{n\beta}]^T [e^{n\beta} n I_0 e^{n\beta}]. \quad (23)$$

Using geometric progression on the inverse of (23), the expression in (20) is obtained.

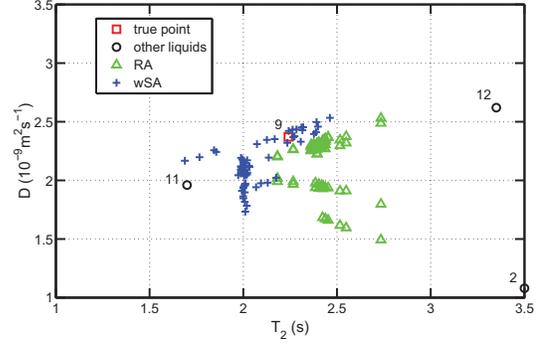


Fig. 3. The algorithms applied on measured tap water data. The numbers correspond to the ones in Tab. 1.

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