

Natural abundant ^{17}O NMR in a 1.5-T Halbach magnet

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We present mobile, low-field ^{17}O NMR as a means for monitoring oxygen in liquids. Whereas oxygen is one of the most important elements, oxygen NMR is limited by a poor sensitivity related to low natural abundance and gyro-magnetic ratio of the NMR active ^{17}O isotope. Here, we demonstrate ^{17}O NMR detection at a Larmor frequency of 8.74 MHz in a 1.5-T Halbach neodymium magnet with a home-built digital NMR instrument suitable for large-scale production and in-line monitoring applications. The proposed ^{17}O NMR sensor may be applied for direct, noninvasive measurements of water content in, for example, oil, manure, or food in automated quality or process control. Copyright © 2015 John Wiley & Sons, Ltd.

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Introduction

Recently, we proposed a high-sensitive mobile ^{27}Al NMR sensor for onboard ship monitoring of low concentrations of aluminosilicate zeolites in marine heavy fuel oil.^[1] Exploiting a large sample volume, fast experiment recycling, wideband excitation, and effective detection, this sensor enables ^{27}Al solid-state NMR detection of aluminum in parts per million (ppm) level concentrations using a 1.5-T permanent magnet of the Halbach type. Obviously, the developments associated with the ^{27}Al NMR sensor also offer possibilities for other applications of high-sensitive mobile NMR. In this communication, we describe a similar NMR sensor for oxygen detection based on the ^{17}O isotope. Although oxygen is one of the chemically most important elements, oxygen NMR is not widely applied because of intrinsic low NMR sensitivity. The only occurring NMR active oxygen isotope is ^{17}O , which possesses a nuclear spin of 5/2, usually strong quadrupolar coupling interactions, a low gyro-magnetic ratio, and is found in a natural abundance of only 0.037%.^[2] This leads to a natural abundant ^{17}O sensitivity, which is five orders of magnitude lower than the more frequently encountered sensitivity of ^1H .^[3] Although isotope enrichment may provide dramatic sensitivity enhancements, it is costly and impractical for most applications. A general oxygen sensor needs to rely on unlabeled samples. In such a setup, cost-efficient ^{17}O NMR may have a large variety of applications including monitoring of the water content in, for example oil, manure, or food, as an alternative to ^1H NMR methods based on relaxation-resolved quantification, which can be challenging in cases of variable and similar relaxation rates of water and other sample components.

Methods

The proposed ^{17}O NMR sensor is based on the home-built digital NMR instrument previously presented for low-concentration ^{27}Al detection^[1] and which is suitable for large-scale production. The various parts of the instrument are summarized as follows (for visualization of the hardware, we refer to Ref. [1]): (i) a permanent

magnet constructed as a dipolar Halbach cylinder array^[4,5] with a static magnetic field of 1.5 T (220-mm length, 25-mm inner diameter, and 150-mm outer diameter) and composed of eight neodymium blocks. The inhomogeneity of the magnetic field over the sample (*vide infra*) volume is about 2500 ppm given as full width at half maximum; (ii) an RF probe including low-noise preamplifiers and a solenoid RF coil (100-mm length and 10-mm inner diameter) in a shielded probe body. The probe bore is 9.2 mm and suitable for connection to a pipe system with the sample media flowing continuously through the probe. For demonstration purposes, however, we apply here a Teflon sample tube with 8-mm inner diameter and an effective sample volume of about 5 ml. The probe was tuned for 8.74 MHz with a quality factor of 55 and carefully optimized to minimize acoustic and spurious ringing according to recommendations of Buess and Petersen^[6] and Fukushima and Roeder,^[7] (iii) a digital RF console containing a field-programmable gate array unit operating with a sampling frequency of 50 MHz; (iv) a home-built 400-W power amplifier; and (v) a PC connected to a touch screen and the Internet for direct or remote user interaction. The instrumentation is assembled in a temperature-regulated cabinet ensuring a magnet temperature of 32 ± 0.1 °C. It is noted that this temperature stability is sufficient for the present application considering the 2500-ppm inhomogeneity of the neodymium magnet array with a field variation of -1200 ppm per $+1$ °C.

To optimize the sensitivity in the inhomogeneous magnetic field of the non-shimmed Halbach magnet, several spin echoes were acquired in each experiment using the Quadrupolar Carr–Purcell–Meiboom–Gill pulse sequence,^[8] and fast experiment recycling with recycle delays of 15–30 ms was applied.

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The performance of the oxygen sensor was evaluated through analysis of seven samples. One water, one ethanol, one acetone sample, and four samples prepared as homogenized mixtures of water and melted Vaseline (20% lubricant base oil) with different water contents of 0%, 0.5%, 2%, and 5%.

Results and discussion

Figure 1 shows ^{17}O echo trains of water, ethanol, and acetone acquired at 8.74 MHz with 24 echoes (300- μs echo separation) and accumulated over an experiment time of 13 h. The decays of the echo trains may be described by relaxation constants of 9.7 ms for water, 2.4 ms for ethanol, and 9.8 ms for acetone, based on fits to single-exponential decays and in agreement with the signal intensities obtained for three different recycle delays of 15, 25, and 30 ms. The fast relaxation rates may likely be ascribed quadrupolar relaxation associated with the asymmetrical electronic environment around the ^{17}O nuclei.

Figure 2 shows the intensities obtained from ^{17}O NMR evaluation of water (100%, 5%, 2%, 0.5%, and 0%), ethanol, and acetone, correlated to the calculated oxygen contents of these samples. Each sample was analyzed by the Quadrupolar Carr–Purcell–Meiboom–Gill pulse scheme exploiting 24 echoes and a recycle delay of 25 ms.

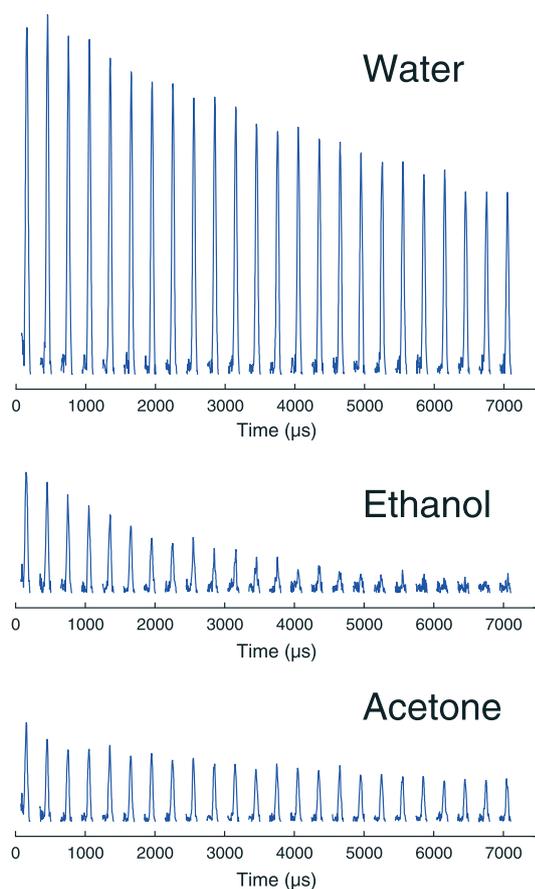


Figure 1. ^{17}O spin echoes obtained from water, ethanol, and acetone at 8.74 MHz. Each echo train shows 24 echoes acquired with an echo separation of 300 μs and accumulated over 656 600 scans with a recycle delay of 15 ms, 469 000 scans with a recycle delay of 25 ms, and 422 100 scans with a recycle delay of 30 ms to yield a total of 1 547 700 scans over an experiment time of 13 h. The pulse lengths were 25 μs for both $\pi/2$ and π pulses, and the shown FIDs are filtered to a 0.96- μs dwell time between data points (corresponding to 1.04-MHz spectral width).

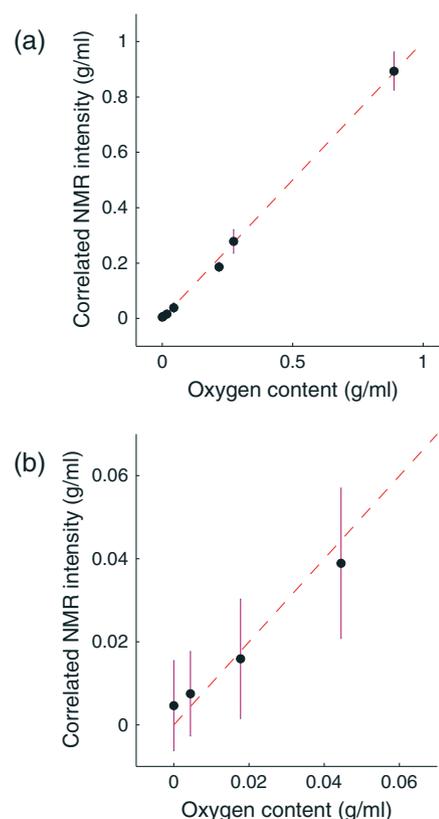


Figure 2. Calibrated ^{17}O NMR intensities obtained for samples of water (100%, 5%, 2%, 0.5%, and 0%), ethanol, and acetone to known oxygen contents. The correlation data are shown as mean values with error bars showing the standard deviations on 15-min measurements for each sample (a) representing all seven samples and (b) a close-up of the four samples with 0–5% water. Each 15-min NMR measurement was acquired at 8.74 MHz using the QCPMG pulse sequence with 24 echoes (300- μs separation), 28 000 scans, and a recycle delay of 25 ms and repeated 16 times for each sample to evaluate the deviation of the measurements.

Data were accumulated over 15 min and repeated 16 times for each sample. The obtained intensities show good agreement with the calculated oxygen contents of the samples (based on density and molecular weight), and the standard deviation on the individual correlated 15-min measurements as follows: 0.01 g/ml for the 0% and 0.5% water samples and up to 0.07 g/ml for the 100% water sample, whereas the mean standard deviation for all samples is 0.026 g/ml. This demonstrates the possible application of cost-efficient ^{17}O NMR as a tool for real-time monitoring of water content, which may be of particular interest for in-line quality or process control related to science, agriculture, or the food and oil industry.

Conclusion

We have presented a mobile ^{17}O NMR sensor based on a home-built digital field-programmable gate array spectrometer with a 1.5-T Halbach magnet. We have shown a good performance of the sensor with focus on monitoring of water content.

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