



# Rapid Quantification of Alcohol Content in Intact Bottles of Wine Using Scalar-Coupled Spectroscopy at Low Field

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## Abstract

Direct spectroscopic quantification of small molecules using low cost, low field ( $<0.1$  T) large bore portable magnets is not possible using conventional techniques due the presence of strong homonuclear coupling which results in complicated spectral patterns with resonances separated by much less than the achievable spectral linewidth. In contrast, a method using the signals from a Carr–Purcell–Meiboom–Gill (CPMG) train, in which the data are Fourier transformed in this indirect dimension, can produce so-called J-spectra in which several distinct spectral features can be distinguished. In this work, we evaluate this technique to quantify the amount of alcohol (ethanol) in intact bottles of wines or spirits.

## 1 Introduction

Low-field portable MRI has seen a recent renaissance [1–3] with the increased social awareness that clinical MRI scans are available as a diagnostic tool to less than 30% of the worldwide population [4–6]. Our group constructed a number of Halbach-based systems [7, 8] consisting of thousands of small permanent magnets [9, 10], and have even fabricated one on-site with colleagues in Mbarara in Uganda [11]. Other research groups have used or designed systems with two large permanent magnet poles connected by one or two yokes [12–14]. Such portable systems typically have  $B_0$  inhomogeneities of several hundreds or even thousands of parts

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per million (ppm) over the imaging field-of-view, but are still able to obtain, for example, *in vivo* images of the brain with spatial resolutions  $\sim 2$  mm.

Low-field portable and smaller benchtop systems also find extensive non-medical applications, as covered in a virtual special issue of the *Journal of Magnetic Resonance* [15, 16]. For example, small samples can be studied by high resolution NMR using systems such as the Magritek Spinsolve (operating at 60 or 80 MHz). However, the hundreds to thousands of ppm homogeneity mentioned previously would seem to preclude the use of spectroscopic techniques on much larger portable lower field systems. In addition, since such systems typically operate in the 1–3 MHz range, small molecules exhibit second order effects, i.e., strong homonuclear scalar coupling, which produces significantly more complicated spectral patterns than for weak coupling at higher frequencies.

The aim of this work is to investigate the possibility of quantifying the alcohol content of intact bottles of wine (or other products) using low field portable MR with rapid data acquisition. In the early 2000s, there were several studies of intact bottles of wine by Augustine et al. to estimate alcohol content and as well as the much lower concentrations of acetic acid associated with spoilage. These studies were performed using a superconducting 2 T magnet [17] or 4.7 T superconducting magnet [18]: these systems have the advantage of being able to study large (intact) samples, but the disadvantage of requiring large and expensive setups.

A number of different techniques have been presented for obtaining “high resolution” NMR spectra in inhomogeneous  $B_0$  fields. One of the early methods was proposed by Blümich et al. [19], and the topic was extensively reviewed in 2015 by Chen et al. [20]. Most of these techniques are inherently two-dimensional, in which spectral broadening in the second dimension (after Fourier transformation) is independent of, or weakly dependent on, the  $B_0$  homogeneity. The fact that the techniques are two-dimensional leads to significantly longer data acquisition times than for conventional one-dimensional spectroscopy. Here we extend our previous work [21, 22] on J-spectroscopy of strongly coupled spins at low field using a Carr–Purcell–Meiboom–Gill (CPMG) sequence [23–25] for quantitative estimation of alcohol content. Using this sequence signal evolution during the echo train decays as a function of  $T_2$  rather than  $T_2^*$ , and therefore the resolution in the indirect dimension is to first order independent of  $B_0$  homogeneity. Since the second dimension is encoded by a multi-echo readout, this sequence takes essentially an identical time to acquire as a conventional one-dimension experiment.

## 2 Methods

All experiments were performed on a portable custom-built MRI scanner operating at  $B_0 = 0.046$  T (Larmor frequency 1.96 MHz) with a 31 cm diameter bore, similar to the system described in detail previously [26], shown in Fig. 1. The  $B_0$  field is generated using a large number of permanent magnets arranged in a cylindrical dipolar Halbach array configuration and is directed transverse to the bore of the scanner [7]. Three orthogonal gradient coils [27] were used to perform first order shimming over the sample. A Magritek Kea 2 spectrometer was



**Fig. 1** (left) Photograph of the 46 mT portable Halbach-based MRI system. Electronics are located within the cabinet below the scanner. Shim trays are placed around the outside of the magnet. (right) Photograph of the segmented solenoid transmit/receive coil next to the wine bottle. Plastic supports ensure that the bottle is in the center of the magnet

used for data acquisition, with the supplied CPMG sequence modified [21] to allow a shorter echo time for the first echo than for subsequent echoes in order to maximize signal-to-noise (SNR). A custom-built 1 kW amplifier was used for RF transmission.

A solenoidal transmit/receive coil was especially designed to fit snugly around a wine bottle. It was constructed from Litz wire (1500 strands, 0.03 mm strand diameter, Eleckrisola) to achieve a high quality (Q)-factor. The length of the coil was 23 cm with a diameter of 11 cm, wound on an acrylic former with thickness 8 mm. Winding with an interturn gap of one wire diameter resulted in 65 turns and a total length of  $\sim 22$  m, corresponding to  $\sim$ one-sixth of a wavelength. The self-resonance frequency was measured as 5.9 MHz, indicating substantial inter-turn capacitance. Given a general rule-of-thumb that one should operate at least an order of magnitude below the self-resonance frequency, the coil was segmented by three equal capacitors of 101 pF (ATC Series E fixed non-magnetic capacitors). An L-shaped network was used for impedance matching to  $50\Omega$ , with a parallel 100 pF fixed plus 1–30 pF variable capacitor (Johannson), and a series 68 pF fixed capacitor. Placing the RF coil into the Faraday shield of the magnet increased the resonance frequency by  $\sim 70$  kHz. There was little effect on either resonance frequency or impedance matching introduced by the wine bottle.

Samples were prepared with different concentrations of ethanol in water, varying from 5 to 50% volume per volume (v/v), and placed in a wine bottle. The  $T_1$  values of pure water and pure ethanol were measured using a conventional inversion-recovery sequence in order to establish the required delay between co-added phase-cycled

scans in order to allow full magnetization recovery. Finally, data were acquired from a bottle of white wine with the alcohol content reported on the label as 11.5%.

For each sample a CPMG sequence was run with an initial echo time of 16 ms and subsequent echo times of 87.5 ms. As discussed in [22] the choice of echo time is a trade-off between higher SNR but reduced spectral separability at shorter values of this delay. For each echo 16 data points were acquired and 128 echoes were collected. Since the length of the solenoid is approximately twice its diameter, and the neck of the wine bottle sticks out of the front (Fig. 1), we expect there to be a significant  $B_1$  and  $B_0$  inhomogeneity over the entire bottle. Rather than using simple  $180^\circ$  pulses as in our previous studies a number of different composite refocusing pulses, with slightly different performance with respect to  $B_1$  and  $B_0$  offsets/imperfections [28] were evaluated. The pulse giving the best (in terms of SNR, particularly at the end of the CPMG echo train) was the TPG composite pulse of Tycko and Pines  $180^\circ_{256}180^\circ_{52}180^\circ_0180^\circ_{128}180^\circ_0180^\circ_{232}180^\circ_0180^\circ_{308}180^\circ_{104}$  [29]. Eight signal averages were acquired with an intersequence delay of 3 s, giving a total data acquisition time of approximately 25 s.

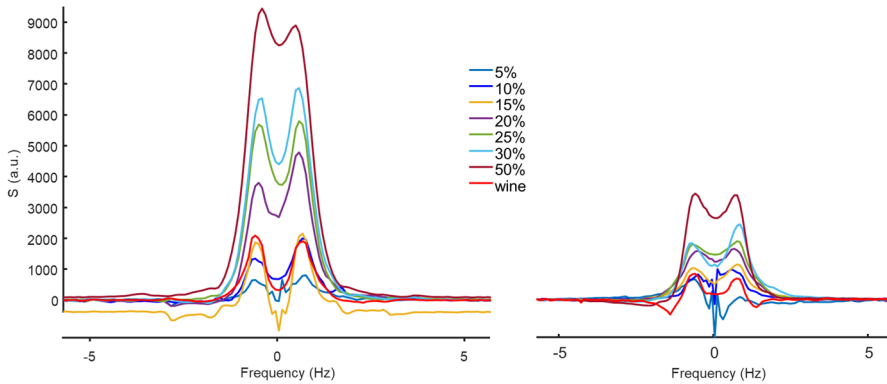
Data processing: as described in detail previously [21], each data set comprised a  $16 \times 128$  matrix, where  $N$  is the number of points acquired at each echo and  $M$  is the number of echoes. Data from both sides of the echo peak were combined according to  $S = S^+ + (S^-)^*$  where  $S^+$  represents the first 8 data points for each echo and  $N/2 + 1 \leq n \leq N$ , and  $S^-$  the second 8 data points with the order reversed:  $*$  represents the complex conjugate. The resulting data set was Fourier transformed along the time domain to yield 128 complex spectra. The spectral maxima were used as a single complex value for each echo, which was zero-filled to 256 data points. Fourier transformation along this dimension gave the unfiltered J-spectrum. Removal of the central peak, containing the peak from water and unresolved resonances was performed based on a Hankel singular value decomposition method (HSVD). Linear prediction single value decomposition (LPSVD) was used to estimate the intensities of the remaining peaks – the integrated intensities were used as an estimate of the ethanol concentration.

### 3 Results

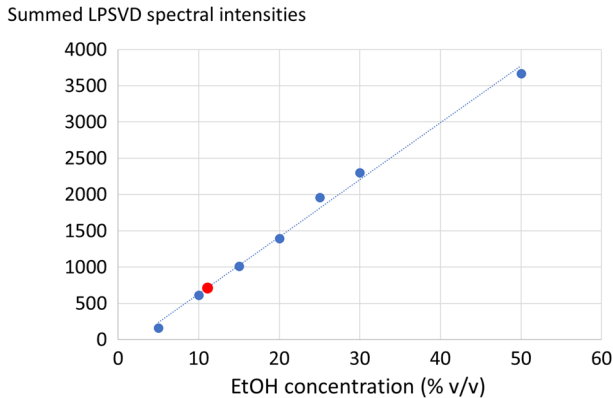
The Q-value of the solenoidal coil was estimated from the  $S_{11}$  plot on a network analyzer to be  $\sim 270$ , corresponding to a bandwidth of 14 kHz. The linewidth of the spectrum was estimated to be  $\sim 20$  Hz (the peak is distinctly non-Lorentzian). The  $T_1$  of pure water was measured to be  $2200 \pm 30$  ms, pure ethanol  $640 \pm 10$  ms and that of the wine sample  $990 \pm 8$  ms, all at room temperature.

Figure 2 shows spectra from each of the ethanol/water samples as well as from the intact wine bottle. The predominant feature are two peaks, symmetric about zero-frequency, separated by  $\sim 2$  Hz [22].

Figure 3 shows the sum of all the outputs of the LPSVD algorithm (after removal of the zero frequency term) vs. ethanol concentration. The graph is a straight line with an R value of 0.994. The value for the wine, 11.3%, is also shown, and compares well with the stated value of 11.5% on the label.



**Fig. 2** (left) Post-processed spectra from different v/v ratios of ethanol/water and the wine sample using a TPG composite  $180^\circ$  refocussing pulse, (right) corresponding spectra using a simple hard refocussing pulse. The receiver gain was the same for both sets of experiments



**Fig. 3** Plot of the sum of the LPSVD integrated intensities (corresponding primarily to the two peaks shown in Fig. 2) as a function of the ethanol concentration. Calibration experiments are shown in blue circles, with the results for the bottle of white wine by the red circle (color figure online)

## 4 Conclusion

This paper shows a simple method of estimating the alcohol content of intact bottles of spirits in a matter of seconds using a low-cost portable MR system based on the scalar coupling behavior during a CPMG sequence. The use of NMR to quantify ethanol was first shown by Augustine and co-workers in 2003 [17], who were also able to use high resolution NMR on a large bore superconducting magnet to estimate the quantities of acetic acid [18] in cases where the wine had undergone significant oxidation. Since the concentrations of the latter compound are hundreds of times less than those of ethanol, we unfortunately do not see a way of being able to reproduce these types of measurements at low field. Indeed, the use of high resolution

NMR for wine analysis is quite sophisticated and was extensively reviewed by Viskic et al. [30]. Analysis can be either “non-targeted or targeted”. Non-targeted refers to the use of techniques such as multivariate data analysis to find patterns for sample discrimination. Targeted analysis used a range of standard NMR sequences to determine the key components of a particular wine. Both types of technique require high resolution systems which can perform spectroscopic studies on small samples extracted from the bottle. Thus the sample preparation is rather time-consuming and laborious.

Possible extensions to this work would be to see if surface magnets [31–33] could be used in-situ without the need to disturb bottles which have been in place for a long time, incorporating methods used for obtaining CPMG trains in inhomogeneous  $B_0$  and  $B_1$  fields [34]. Alternative methods of estimating ethanol content using MR might include relaxation time measurements, as discussed at higher field strengths by various authors [35–37].

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**Availability of Data and Materials** Upon request from either author.

## Declarations

**Conflict of Interest** All authors declare that they have no conflict of interest.

**Ethical Approval** Not applicable.

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