

Determining ethanol content of liquid solutions using laser feedback interferometry with a terahertz quantum cascade laser

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Abstract—Over the last decade, terahertz (THz) time domain spectroscopy has been investigated as a technique for assaying the ethanol content of liquid solutions — indeed, operating at THz frequencies addresses some of the challenges that traditional optical refraction measurements face, such as delineation between sugar–ethanol content, fluorescence, and problems arising from carbonation or other dissolved gasses. In this work, we propose an alternative system and method for assaying ethanol content of liquid solutions at THz frequencies which employs a laser feedback interferometer built around a 2.6 THz quantum cascade laser. The system is tested against a series of controlled water–ethanol solutions as well as a series of commercially-available beverages. The accuracy of the estimated ethanol content compares favourably to THz time domain spectroscopy techniques.

Index Terms—Terahertz Sensing, Laser Feedback Interferometry

I. INTRODUCTION

Measurement of ethanol content of various liquid solutions (including alcoholic beverages) is of significant interest, notably from a process control viewpoint during manufacture as well as to ensure final products meet regulatory guidelines. Traditional optical refraction-based measurements of alcohol (ethanol) content are affected by the difficulty in distinguishing changes in signal arising from alcohol content and sugar content [1]; typically an additional density measurement (using a hydrometer) is also required to assay the final alcohol content. More sophisticated optical techniques exist, including those operating at near- and mid-infrared wavelengths, and those utilising Raman spectroscopy [2]–[4], as well as recent technological developments which could be applied to the determination of ethanol content in liquid solutions, notably the use of nanoparticles to create localised surface plasmon resonance detectors [5], [6]. However, even these suffer from interference due to fluorescence, challenges arising from carbonation (requiring liquids to be degassed prior to measurement), and difficulty separating sugar and ethanol contributions from observed spectral signatures [2].

Terahertz (THz) time domain spectroscopy (TDS) has been utilised in the literature to measure various normal alcohols (such as methanol, ethanol, n-propanol) [7]–[9], alcohol–water mixtures [10]–[14], alcohol–fuel mixtures [15], as well as determining ethanol content in commercially-available alcoholic beverages [10], [16].

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There is also potential for the use of THz metamaterials to facilitate detection of ethanol content in liquid solutions in a similar way to nanoparticles [17]. However, at the lower end of the THz spectrum (< 2 THz) the separation of signal contributions sugar and ethanol remains a challenge, and can affect the accuracy of measured ethanol content [10]. Fortunately, since the contributions to the signal from sugar in solution decrease faster with increasing THz frequency than those attributed to ethanol (see [10]), using a higher frequency THz source such as a THz quantum cascade laser (QCL) would mitigate this effect.

In this article we propose a simple system for assaying ethanol–water mixtures based on a THz QCL utilising laser feedback interferometry (LFI). Laser feedback interferometry is a useful tool for laser sensing, utilizing the so called self-mixing effect [18], [19]. Due to the possibility of extracting the LFI signal from across the laser terminals without the need for an external or separate detector, LFI is particularly applicable in the THz frequency range, which suffers from a lack of convenient, fast and sensitive detector technologies [20], [21]. Previously, we have developed a method for material characterization [22], [23] utilizing this effect. However, several complicated and time consuming calibration, sample preparation, and signal processing techniques were required to produce accurate results. The method proposed here is substantially simpler, and once calibrated, the system only requires a small sample of the liquid for characterisation. This approach could be adapted to investigate other fluid mixtures at THz frequencies.

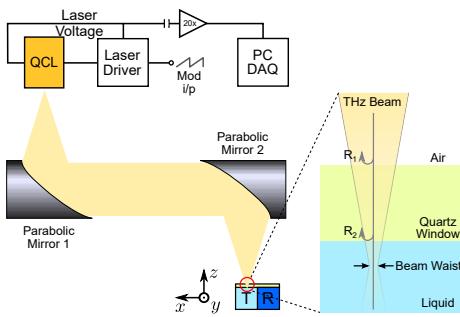


Fig. 1. Experimental setup of the system. Inset shows the compound nature of the target comprised of the cuvettes R (reference) and T (liquid under test).

II. EXPERIMENTAL SETUP AND MODELING

The experimental setup (see Fig. 1) used a 2.59 THz QCL mounted in a free flow cryostat operating at a temperature of 15 K. The THz QCL consisted of a 11.6- μm -thick GaAs/AlGaAs bound-to-continuum active-region [24] that was processed into a semi-insulating surface-plasmon ridge waveguide with dimensions 1.78 mm \times 140 μm . The laser was biased by a laser driver (Thorlabs LDC500C) with a DC current 0.42 A, superimposed with a 1 kHz sawtooth wave modulation with an amplitude of 75 mA (producing a 900 MHz frequency sweep). The signal was monitored by measuring the voltage across the THz QCL's terminals after passing through an AC coupled 20 \times amplifier (SRS SR560). This amplified signal was then digitised using a 16-bit PC-DAQ with a 1 MS/s acquisition rate (National Instruments NI PCI-6251). Two 2-inch parabolic mirrors ($f = 4$ -inch) were used to collect, collimate, and focus the emitted beam onto a target area. The signal was processed by negating the current-induced power ramp leaving only the interferometric self-mixing fringes (which we refer to as the self-mixing signal) [25].

Two 4.5 ml ($10 \times 10 \times 45 \text{ mm}^3$) cuvettes were used to hold the fluids under test. The two identical cuvettes were modified so that they shared a common 3 mm thick z -cut quartz window and were mounted on a three-axis ($x - y - z$) motorized stage. One cuvette was filled with deionized water as a reference material, with the other containing the liquid being assayed. Measurements of both the water reference and the liquid under test were taken in rapid succession, with a motorized stage shifting the two cuvettes (x -axis) between the measurement point.

It is well known that the amplitude of the self-mixing fringes (β) is directly proportional to the reflectivity of the external target [26], [27]. In this setup, the external target is a compound target consisting of a quartz window and the liquid under test. Due to the long focal length of the mirrors used and the large resulting depth of field, the effective reflectivity of the compound target depends on the reflectivity of two interfaces: the air-quartz and quartz-liquid interfaces (see inset Fig. 1). The reflectivity at the quartz-liquid interface will change with the liquid under test, leading to a corresponding change in β . We exploit this relationship to create a calibrated system for assaying ethanol content.

In order to calibrate the system, we extract β for both the water reference ($\beta_{\text{water ref.}}$) and a series of liquids under test with known water-ethanol solutions ($\beta_{x\% \text{ ethanol}}$). This is achieved by fitting the standard model for self-mixing signals (via the excess phase equation

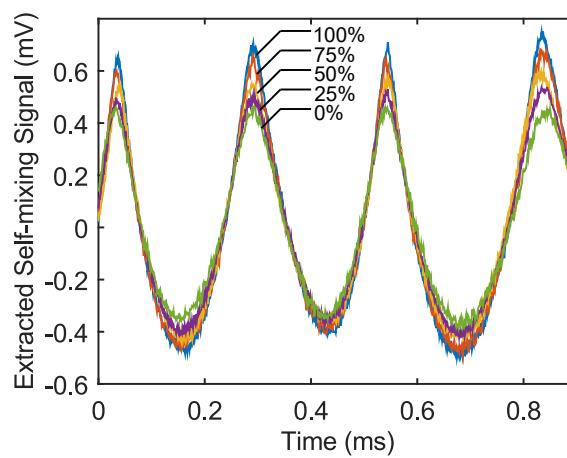


Fig. 2. Self-mixing signals corresponding to test water-ethanol solutions with ABW of 0% (green line), 25% (purple line), 45% (yellow line), 75% (orange line), and 100% (blue line).

[28]) to the measured self-mixing signals. The longitudinal (z -axis) position of the target was set to be that at which the difference between the β of the reference water and a 100 % ethanol solution, ($\beta_{\text{water ref.}} - \beta_{100\% \text{ ethanol}}$) was maximal. For this longitudinal position the beam waist is located just beyond the quartz-liquid interface.

At this position, the system was calibrated by mapping the ratio of $\beta_{0\% \text{ ethanol}}/\beta_{\text{water ref.}}$ to 1.0, and the $\beta_{100\% \text{ ethanol}}/\beta_{\text{water ref.}}$ to the (arbitrary) value 1.5. This normalization to $\beta_{\text{water ref.}}$ mitigates against temporal changes in the self-mixing signal amplitude resulting from small changes in the external cavity path (such as atmospheric changes like humidity, and temperature, and minor mechanical changes).

III. RESULTS AND DISCUSSION

Two experiments were performed, with the first using a series of ethanol-water mixtures ranging from 0 to 100 % ethanol content [in alcohol by weight (ABW)] to produce a known test-curve for the system. The second was a test of samples of various alcoholic drinks whose ethanol content was estimated using the calibrated system.

Figure 2 shows the typical self-mixing signals obtained for several ethanol concentrations. It can be clearly seen that the amplitude (and thus ultimately β) of the signals changes significantly with different water-ethanol mixtures. Four separate measurements of water-ethanol mixtures ranging from 0 to 100 % were performed. Figure 3 shows the calibrated signal strength for the known test solutions (blue dots show mean and error bars show ± 1 standard deviation, from the four measurements), demonstrating a linear relationship (red line) with ABW.

To test the calibrated system, we estimated the ABW % of nine different alcoholic beverages (shown as the coloured circles in Fig. 4). The estimated ABW [and alcohol by volume (ABV)] together with the label ABW (and ABV) and of the beverages under test is shown in Tab. 1.

The Triple Sec, port, and beer samples contain significantly more sugar (in solution) than the other beverages under test. Despite the low sensitivity of THz radiation to sugar content, its impact is still evident here. Indeed, it is clear from Fig. 4 and Tab. 1 that the estimated ABW is slightly larger than that stated by the manufacturer on the label for these beverages. Nevertheless, due to the relatively high

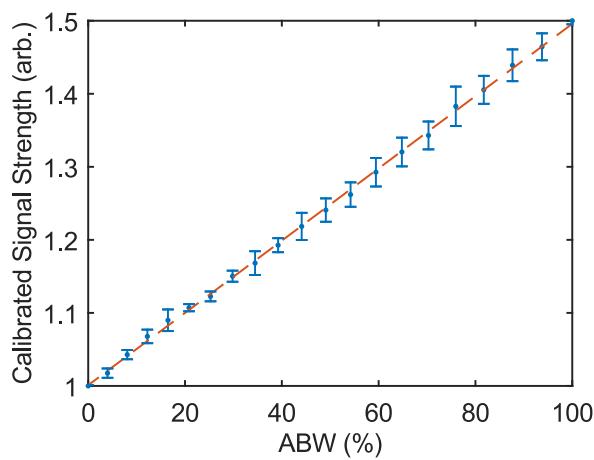


Fig. 3. Calibrated signal strength vs. known ABW % water–ethanol solutions.

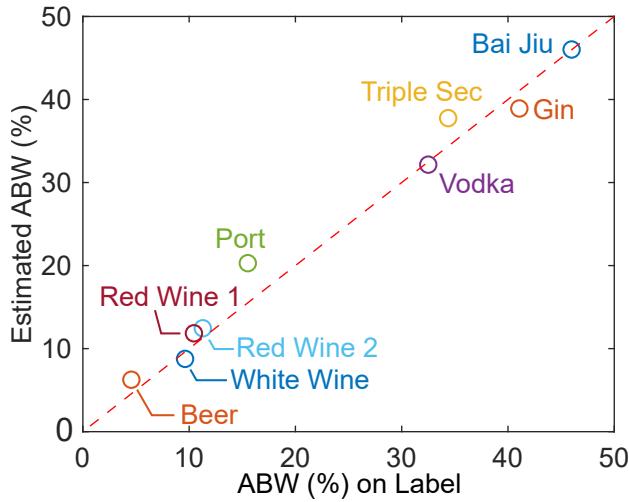


Fig. 4. ABW (%) (label) vs. ABW (%) (estimate) for beverages under test.

TABLE 1. The ABW (%) [ABV (%)] on the label of the beverages under test, compared with the ABW (%) [ABV (%)] estimated from the calibrated system.

Beverage Name	ABW (ABV) on Label (%)	Estimated ABW (ABV) (%)
Beer	4.8 (6.0)	7.1 (8.4)
White Wine	9.7 (12)	8.6 (10.7)
Red Wine 1	10.5 (13)	11.7 (14.4)
Red Wine 2	11.4 (14)	12.3 (15.1)
Port	15.61 (19)	20.1 (24.2)
Vodka	32.6 (38)	32.03 (37.4)
Triple Sec	34.5 (40)	37.63 (43.3)
Gin	41.2 (47)	38.8 (44.6)
Bai Jiu	46.1 (50)	45.8 (51.8)

operating frequency of the THz QCL used here (2.6 THz), this impact is much reduced when compared to THz TDS measurements which operate over a lower frequency range [10]. For the remaining beverages under test, estimated ABW aligns well with the expected

linear relationship — deviations are on the same order as for THz TDS measurements.

For all these measurements, only a small volume of liquid was used for testing (~ 1 mL). However, the minimum volume of liquid required is much less. This is a consequence of the high attenuation of the THz signal for both ethanol and water at the measurement frequency (2.6 THz) — the longitudinal depth of either liquid required to act as a half-space for THz waves is < 500 μ m. As such, with only minor changes to the geometry of the external optical components, the same system could be implemented using a quartz window on which a single drop of liquid under test is placed for measurement.

IV. CONCLUSION

In this work we proposed and demonstrated a system and method of assaying the ethanol content of liquid solutions. The system is built around a THz QCL operating at 2.6 THz as a laser feedback interferometer, employs a reference to mitigate environmental effects during measurement, and only requires a small volume of liquid for testing. The method compares well to existing THz TDS ethanol assaying techniques.

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REFERENCES

- [1] J. J. Palmer, *How to Brew: Everything you need to know to brew beer right the first time*, 3rd ed. Brewers Publications, 2006.
- [2] A. Nordon, A. Mills, R. T. Burn, F. M. Cusick, and D. Littlejohn, "Comparison of non-invasive nir and raman spectrometries for determination of alcohol content of spirits," *Anal. Chim. Acta*, vol. 548, no. 1, pp. 148–158, 2005.
- [3] P. C. Ashok, B. B. Praveen, and K. Dholakia, "Near infrared spectroscopic analysis of single malt scotch whisky on an optofluidic chip," *Opt. Express*, vol. 19, no. 23, pp. 22 982–22 992, Nov 2011.
- [4] M. Friedel, C.-D. Patz, and H. Dietrich, "Comparison of different measurement techniques and variable selection methods for ft-mir in wine analysis," *Food Chem.*, vol. 141, no. 4, pp. 4200–4207, 2013.
- [5] L. La Spada and L. Vigni, "Electromagnetic nanoparticles for sensing and medical diagnostic applications," *Materials*, vol. 11, no. 4, p. 603, 2018.
- [6] R. Iovine, L. La Spada, and L. Vigni, "Nanoplasmonic sensor for chemical measurements," in *Optical Sensors 2013*, vol. 8774. International Society for Optics and Photonics, 2013, p. 877411.
- [7] J. Kindt and C. Schmuttenmaer, "Far-infrared dielectric properties of polar liquids probed by femtosecond terahertz pulse spectroscopy," *J. Phys. Chem.*, vol. 100, no. 24, pp. 10 373–10 379, 1996.
- [8] Y. Yomogida, Y. Sato, R. Nozaki, T. Mishina, and J. Nakahara, "Dielectric study of normal alcohols with thz time-domain spectroscopy," *J. Mol. Liq.*, vol. 154, no. 1, pp. 31–35, 2010.
- [9] L. Liu, R. Pathak, L.-J. Cheng, and T. Wang, "Real-time frequency-domain terahertz sensing and imaging of isopropyl alcohol–water mixtures on a microfluidic chip," *Sens. Actuator B-Chem.*, vol. 184, pp. 228–234, 2013.
- [10] P. U. Jepsen, U. Møller, and H. Merbold, "Investigation of aqueous alcohol and sugar solutions with reflection terahertz time-domain spectroscopy," *Opt. Express*, vol. 15, no. 22, pp. 14 717–14 737, 2007.
- [11] P. U. Jepsen, J. K. Jensen, and U. Møller, "Characterization of aqueous alcohol solutions in bottles with thz reflection spectroscopy," *Opt. Express*, vol. 16, no. 13, pp. 9318–9331, 2008.
- [12] R. Li, C. D'SAgostino, J. McGregor, M. D. Mantle, J. A. Zeitler, and L. F. Gladden, "Mesoscopic structuring and dynamics of alcohol/water solutions probed by terahertz time-domain spectroscopy and pulsed field gradient nuclear magnetic resonance," *J. Phys. Chem. B*, vol. 118, no. 34, pp. 10 156–10 166, 2014.

- [13] D. Jahn, A. Soltani, J. C. Balzer, W. Withayachumnankul, and M. Koch, "Fabry-pérot interferometer for sensing polar liquids at terahertz frequencies," *J. Appl. Phys.*, vol. 121, no. 20, p. 204502, 2017.
- [14] J. Sultana, M. S. Islam, K. Ahmed, A. Dinovitser, B. W.-H. Ng, and D. Abbott, "Terahertz detection of alcohol using a photonic crystal fiber sensor," *Appl. Opt.*, vol. 57, no. 10, pp. 2426–2433, Apr 2018.
- [15] E. Arik, H. Altan, and O. Esenturk, "Dielectric properties of ethanol and gasoline mixtures by terahertz spectroscopy and an effective method for determination of ethanol content of gasoline," *J. Phys. Chem. A*, vol. 118, no. 17, pp. 3081–3089, 2014.
- [16] C. Guo, J. Liu, and Z. Hong, "Determination of alcohol degree in chinese spirit with terahertz time-domain transmission spectroscopy," *Proc. SPIE*, vol. 8195, pp. 81950Z-1 – 81950Z-7, 2011.
- [17] N. I. Zheludev and Y. S. Kivshar, "From metamaterials to metadevices," *Nature materials*, vol. 11, no. 11, p. 917, 2012.
- [18] S. Donati, "Developing self-mixing interferometry for instrumentation and measurements," *Laser Photon. Rev.*, vol. 6, no. 3, pp. 393–417, 2012.
- [19] T. Taimre, M. Nikolić, K. Bertling, Y. L. Lim, T. Bosch, and A. D. Rakić, "Laser feedback interferometry: tutorial on the self-mixing effect for coherent sensing," *Adv. Opt. Photon.*, vol. 7, no. 3, pp. 570–631, Sep 2015.
- [20] F. Mezzapesa, M. Petruzzella, M. Dabbicco, H. Beere, D. Ritchie, M. Vitiello, and G. Scamarcio, "Continuous-wave reflection imaging using optical feedback interferometry in terahertz and mid-infrared quantum cascade lasers," *IEEE Trans. Terahertz Sci. Tech.*, vol. 4, no. 5, pp. 631–633, Sept 2014.
- [21] P. Dean, A. Valavanis, J. Keeley, K. Bertling, Y. L. Lim, R. Alhathloul, A. Burnett, L. Li, S. Khanna, D. Indjin, T. Taimre, A. D. Rakic, E. Linfield, and A. G. Davis, "Terahertz imaging using quantum cascade lasers – a review of systems and applications," *J. Phys. D: Appl. Phys.*, vol. 47, no. 37, p. 374008, 2014.
- [22] A. D. Rakić, T. Taimre, K. Bertling, Y. L. Lim, P. Dean, D. Indjin, Z. Ikonić, P. Harrison, A. Valavanis, S. P. Khanna, M. Lachab, S. J. Wilson, E. H. Linfield, and A. G. Davies, "Swept-frequency feedback interferometry using terahertz frequency QCLs: A method for imaging and materials analysis," *Opt. Express*, vol. 21, no. 19, pp. 22 194–22 205, 2013.
- [23] S. Han, K. Bertling, P. Dean, J. Keeley, A. D. Burnett, Y. L. Lim, S. P. Khanna, A. Valavanis, D. Indjin, E. H. Linfield, A. G. Davies, T. Taimre, , and A. D. Rakic, "Laser feedback interferometry as a tool for analysis of compound mixtures at terahertz frequencies: towards imaging and identification of plastic explosives," *Sensors*, vol. 16, no. 352, pp. 352–1–9, 2016.
- [24] S. Barbieri, J. Alton, H. E. Beere, J. Fowler, E. H. Linfield, and D. A. Ritchie, "2.9 THz quantum cascade lasers operating up to 70 K in continuous wave," *Appl. Phys. Lett.*, vol. 85, p. 1674, 2004.
- [25] K. Bertling, T. Taimre, G. Agnew, Y. L. Lim, P. Dean, D. Indjin, S. Hoeffling, R. Weih, M. Kamp, M. von Edlinger *et al.*, "Simple electrical modulation scheme for laser feedback imaging," *IEEE J. Sensors*, vol. 16, no. 7, pp. 1937–1942, 2016.
- [26] J. A. Roumy, J. Perchoux, Y. L. Lim, T. Taimre, A. D. Rakic, and T. Bosch, "Effect of injection current and temperature on signal strength in a laser diode optical feedback interferometer," *Appl. Opt.*, vol. 54, no. 2, pp. 312–318, 2015.
- [27] R. Kliese and A. D. Rakić, "Spectral broadening caused by dynamic speckle in self-mixing velocimetry sensors," *Opt. Express*, vol. 20, no. 17, pp. 18 757–18 771, Aug 2012. [Online]. Available: <http://www.opticsexpress.org/abstract.cfm?URL=oe-20-17-18757>
- [28] R. Kliese, T. Taimre, A. Bakar, Y. L. Lim, K. Bertling, M. Nikolić, J. Perchoux, T. Bosch, and A. D. Rakić, "Solving self-mixing equations for arbitrary feedback levels: a concise algorithm," *Appl. Opt.*, vol. 53, no. 17, pp. 3723–3736, 2014.