

Determining Ethanol Content of Liquid Solutions Using Laser Feedback Interferometry with a Terahertz Quantum Cascade Laser

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Manuscript received June 22, 2018; revised July 12, 2018; accepted July 20, 2018. Date of publication July 24, 2018; date of current version August 1, 2018.

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 article, 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 favorably to THz time-domain spectroscopy techniques.

Index Terms—Electromagnetic wave sensors, laser feedback interferometry, terahertz (THz) sensing.

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 midinfrared wavelengths and those utilizing Raman spectroscopy [2]–[4], as well as recent technological developments that could be applied to the determination of ethanol content in liquid solutions, notably the use of nanoparticles to create localized 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 utilized 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]. There is also a potential for the use of THz metamaterials to facilitate the 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 utilizing laser feedback interferometry (LFI). Laser feedback interferometry is a useful tool for laser sensing and 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 characterization. This approach could be adapted to investigate other fluid mixtures at THz frequencies.

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Associate Editor: D. Uttamchandani.

Digital Object Identifier 10.1109/LENS.2018.2858927

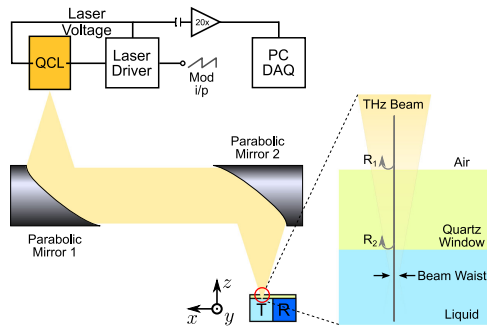


Fig. 1. Experimental setup of the system. (Inset) Compound nature of the target comprised of the cuvettes R (reference) and T (liquid under test).

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 of 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 digitized using a 16-b PC-DAQ with a 1 MS/s acquisition rate (National Instruments NI PCI-6251). Two 2-in parabolic mirrors ($f = 4$ in) 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 ($10 \times 10 \times 45$ mm³) 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: 1) the air-quartz and 2) quartz-liquid interfaces (see inset in 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

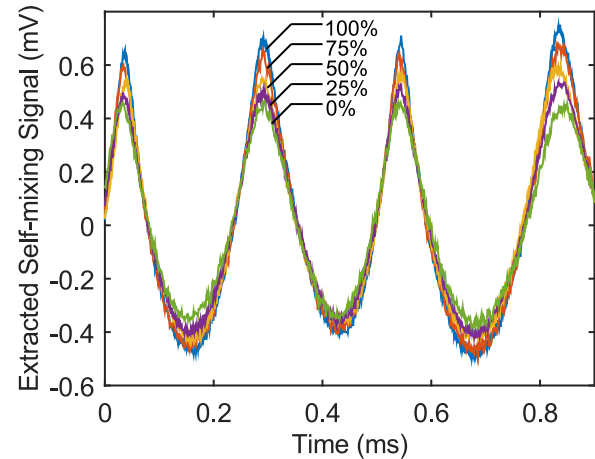


Fig. 2. Self-mixing signals corresponding to test water-ethanol solutions with ABW of 0% (green line), 25% (purple line), 45% (yellow line), 75% (orange line), and 100% (blue line).

standard model for self-mixing signals (via the excess phase equation [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 of 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, 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.

Fig. 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. Fig. 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 colored 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 Table 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

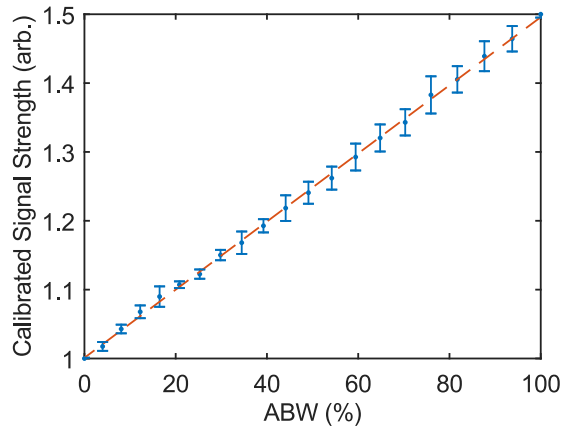


Fig. 3. Calibrated signal strength versus known ABW % water–ethanol solutions.

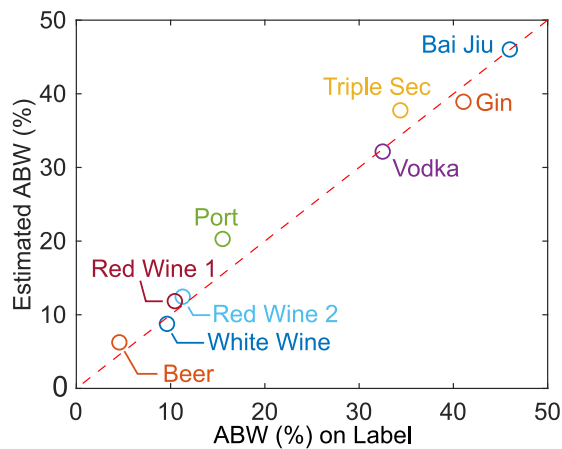


Fig. 4. ABW (%) (label) versus ABW (%) (estimate) for beverages under test.

TABLE 1. 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	15.6 (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)

evident here. Indeed, it is clear from Fig. 4 and Table I 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 operating frequency of the THz QCL used here (2.6 THz), this impact is much reduced when compared with 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 μm. 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 article, we proposed and demonstrated a system and a 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 with existing THz TDS ethanol-assaying techniques.

ACKNOWLEDGMENT

This work was supported in part by the Australian Research Council’s Discovery Projects funding scheme under Grant DP 160 103910; in part by the Queensland Government’s Advance Queensland programme; in part by the EPSRC, U.K., under Grant EP/P021859/1 and DTG Award; in part by the Royal Society (Wolfson Research Merit Awards WM110032 and WM150029); and in part by the European Cooperation in Science and Technology (COST) (Action BM1205).

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