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## Detection of multiple chemicals based on external cavity quantum cascade laser spectroscopy



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### ABSTRACT

A laser spectroscopy system based on a broadband tunable external cavity quantum cascade laser (ECQCL) and a mini quartz crystal tuning fork (QCTF) detector was developed for standoff detection of volatile organic compounds (VOCs). The self-established spectral analysis model based on multiple algorithms for quantitative and qualitative analysis of VOC components (i.e. ethanol and acetone) was detailedly investigated in both closed cell and open path configurations. A good agreement was obtained between the experimentally observed spectra and the standard reference spectra. For open path detection of VOCs, the sensor system was demonstrated at a distance of 30 m. The preliminary laboratory results show that standoff detection of VOCs at a distance of over 100 m is very promising.

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### 1. Introduction

Ethanol and acetone, as the most common type of volatile organic compounds (VOCs), are good organic solvents in plastic, rubber, paint and other industries, and also are commonly used as detergents in the laboratories [1]. However, continuous exposure to these VOCs can cause the senses of human body stimulated, many other discomfort symptoms and even the risk of cancer [2,3], and VOCs can react with oxidants easily in the atmosphere, which can cause ozone pollution and atmospheric acidification. Hence, study on real-time monitoring of VOCs is essential to optimize the living environment and protect human health [4].

To date, a variety of analytical techniques have been successfully developed for VOCs detection including gas chromatography-mass spectrometry (GC-MS) [5], cataluminescence (CLT)-based sensors [6] and calorimetric techniques [7]. In comparison to these conventional methods, the following methods based on laser absorption spectroscopy are capable of standoff measurements. Differential absorption spectroscopy (DOAS) has a good detective precision, but it is difficult to determinate many varieties of gases simultaneously using this method [8]. Cavity ring-down spectroscopy (CRDS) provides a powerful access to trace gas analysis with extremely high sensitivity and selectivity [9], however, this technique is not suitable for standoff detection. Besides,

there are some prominent techniques typically used for open-path detection of VOCs, such as Fourier transform infrared spectrometry (FTIR) [10], differential absorption lidar (DIAL) [11] and quantum cascade laser (QCLs) spectroscopy [12,13]. Among them, QCLs can provide continuous wavelength coverage over much of the mid-infrared (MIR) (typical  $>3\text{--}14\ \mu\text{m}$ ) with high power and excellent beam quality, and great progress has been made to increase the gain bandwidth from a single laser chip [14]. Recently, broad wavelength tuning is typically achieved by placing the QCL chip in an external cavity, which incorporates a dispersive element such as a diffraction grating, namely, the external-cavity QCL (ECQCL) technology [15,16]. By rotating the grating or mirror within the cavity, a single ECQCL module covering a wavenumber interval up to  $760\ \text{cm}^{-1}$  has been demonstrated [17]. Because of the wide wavelength tunability characteristic, the ECQCLs are well-suited to military and defense-related applications on trace explosive, chemical warfare agent, and toxic industrial chemical detection and atmospheric trace gas analysis [18–20].

In present study, an ECQCL based sensing system has been developed for simultaneous detection of multi-component VOCs. Experimentally, we have demonstrated for both ethanol and acetone measurements in both absorption cell method and standoff detection scheme. Instead of using an expensive infrared mercury cadmium telluride (MCT) detector, a cheap and miniaturized quartz crystal tuning fork (QCTF) as a light detector was successfully used for laser signal detection. A homemade cubic spline interpolation algorithm and multiple linear regression algorithm combing with the Pacific Northwest National

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Laboratory (PNNL) database [21] are used for signal processing. A preliminary evaluation of the sensor performance in laboratory conditions is demonstrated.

## 2. Signal Processing Algorithm

Generally, the theory of laser absorption spectroscopy can be described by the Beer-Lambert Law [22]. For small molecule, the data analysis was commonly performed by combing a line-shape function and a nonlinear least-squares fitting procedure, which uses the Levenberg-Marquardt algorithm to retrieve gas concentration information. The line-shape function is integrated with some related spectroscopic parameters, which can be directly taken from the main atmospheric database HITRAN [23]. However, this method is infeasible for large VOC molecules, since their absorption spectra show very wide band absorption features, and their spectroscopic parameters is not completely available. In this work, a multiple linear regression algorithm was developed to realize composition identification and concentration retrieve of VOCs measurements. In this algorithm, both experimental data and reference signal must have same spectral resolution or sampling points.

### 2.1. Cubic Spline Interpolation Algorithm

In this work, the standard reference spectrum is taken from the PNNL database, which is measured using FTIR method. Due to different experimental scheme, the spectral resolution of the experimental spectra recorded in this study cannot be recorded consistently with that of the reference spectra. To resolve this issue, a cubic spline interpolation algorithm (CSIA) was used to resolve the difference in sampling points. The CSIA algorithm is well known for signal processing, so it will not be described in detail. Only some terminology and the key points considered in this work will be discussed.

Assuming a cubic spline  $S(x)$  interpolating on the partition  $x_0 < x_1 < \dots < x_n$  is a function for which  $S(x_i) = y_i$ . It consists of  $n$  piecewise polynomial function  $S_i$ , which is joined at  $x_i$ , for  $i = 0, 1, \dots, n$ , so that the first and second derivatives of  $y'_i = S'(x_i)$  and  $y''_i = S''(x_i)$  are continuous. For the  $i$ th polynomial curve  $S_i$  defined over the fixed interval  $[x_i, x_{i+1}]$  has the cubic expression

$$S(x_i) = a_i(x-x_i)^3 + b_i(x-x_i)^2 + c_i(x-x_i) + d_i \quad (1)$$

where the cubic polynomial coefficients  $a_i$ ,  $b_i$ ,  $c_i$ , and  $d_i$  are given as

$$a_i = \frac{1}{\Delta x_i^2} \left( -2 \frac{\Delta y_i}{\Delta x_i} + y'_i + y'_{i+1} \right) \quad (2)$$

$$b_i = \frac{1}{\Delta x_i} \left( 3 \frac{\Delta y_i}{\Delta x_i} - 2y'_i - y'_{i+1} \right) \quad (3)$$

$$c_i = y'_i \quad (4)$$

$$d_i = y_i \quad (5)$$

As can see, these expressions for the cubic polynomial coefficients are given in terms of position data and derivatives. In actual calculation, the cubic curve can be rewritten in the Hermite expression as a linear function. More details of this algorithm can be found in literatures [24–26].

### 2.2. Multiple Linear Regression Algorithm

The multiple linear regression algorithm (MLRA) has been successfully for atmospheric multi-species detection in our previous work [27], which shows significant advantages on the simple peak ratio method (namely by referring the absorption peak of the experimental

spectrum to that of the standard reference spectrum. The main procedure can be summarized below.

The MLRA algorithm [28,29] which is the relationship between input variables ( $x_1, x_2, \dots, x_t$ ) and an output variable ( $Y$ ) is investigated and formulated as follows:

$$Y = \alpha + \beta_1 X_1 + \dots + \beta_t X_t + \varepsilon \quad (6)$$

where  $\alpha, \beta_1, \dots, \beta_t$  are the parameters to be determined,  $\varepsilon$  is the random error term. It is generally assumed that  $\varepsilon$  is subject to a normal distribution,  $\varepsilon \sim N[0, \sigma^2]$ . Let assume  $\{(Y_i, X_{i1}, \dots, X_{it}), i = 1, \dots, t\}$  be the observed value, regression analysis of the primary task is to use them to estimate  $\alpha, \beta_1, \dots, \beta_t$  and  $\sigma$ . The least squares estimates are denoted by  $a, b_1, \dots, b_t, \hat{\sigma}$ , and the estimated value of  $b_1, \dots, b_t$  can be calculated by the following linear equations:

$$\begin{cases} L_{11}b_1 + \dots + L_{1t}b_t = L_{1Y} \\ L_{21}b_1 + \dots + L_{2t}b_t = L_{2Y} \\ \dots \\ L_{t1}b_1 + \dots + L_{tt}b_t = L_{tY} \end{cases} \quad (7)$$

where

$$\begin{cases} X_j = \frac{1}{n} \sum_{k=1}^n X_{k,j}, j = 1, \dots, t \\ Y = \frac{1}{n} \sum_{k=1}^n Y_k \\ L_{ij} = \sum_{k=1}^n (X_{ki} - \bar{X}_i)(X_{kj} - \bar{X}_j), i, j = 1, \dots, t \\ L_{iY} = \sum_{k=1}^n (X_{ki} - \bar{X}_i)(Y_k - \bar{Y}), i = 1, \dots, t \end{cases} \quad (8)$$

According to Eqs. (7) and (8), the proportionality of each component  $b_1, \dots, b_t$  can be obtained when the known experimental spectrum  $Y$  and the standard reference spectrum  $X$  are available. Therefore, the MLRA algorithm takes full advantage of the whole absorption spectrum, instead of the only absorption peak used in the common peak ratio method, it can significantly reduce measurement errors.

## 3. Experimental Details

A detailed description of the experimental system has already been discussed in our previous papers [30]. Here, we focus on recent advances and improvements that make the system suitable for both measurement modes. A schematic of the experimental arrangement used in this work is shown in Fig. 1. The laser source is a commercial ECQCL purchased from Block Engineering (Marlborough, MA, USA) with an average output power of 0.5–20 mW, which provides a widely wavelength tuning range between 1150 and 1430  $\text{cm}^{-1}$  and has a physical dimension of  $6.25 \times 5 \times 4.9$  in. (L  $\times$  W  $\times$  H). The laser can be programmed to emit pulses from 20 to 300 ns with pulse repetition rate up to 3 MHz while maintaining a duty cycle up to ~15% in standard cooling configuration with internal fans. A visible diode laser was co-aligned with the ECQCL beam to facilitate the beam alignment. The out-coming beam from the ECQCL was directly divided into two parts by a beam splitter. The main beam was collimated by a beam expander (BE06R, Thorlabs) to reduce the emission angle and used for stand-off detection. The collimated light is reflected by a gold-coated round plane mirror (with a mean reflectivity >96% in the spectral band 0.8–20  $\mu\text{m}$ ) placed within a known distance from the sensor detection setup. The reflected light is collected and focused onto the tine of the QCTF via a telescope system with a focal length of 30 cm. The second beam was directly coupled into a single-pass glass gas cell (with two  $\text{CaF}_2$  windows, diameter 25 mm) with a path length of 29.6 cm for absorption spectral measurements. A collimating lens ( $\text{CaF}_2$ , diameter 36 mm,  $f = 60$  mm) behind the absorption cell focused the transmitted laser light onto the tine of the second

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