

ABSTRACT

Researchers from Switzerland, the Netherlands, Germany, and the UK have developed a quantum cascade laser absorption spectrometer (QCLAS) coupled with a trace gas extractor (TREX) for high precision measurements of methane isotopologues in ambient air. With a compact and field-deployable instrument, real-time analysis of the three main and most abundant methane isotopologues can be performed simultaneously. The TREX-QCLAS achieves analytical precision on pre-concentrated methane of 0.1 and 0.5‰ for $\delta^{13}\text{C}$ - and $\delta\text{D-CH}_4$, respectively, and has the repeatability of 0.19 and 1.9‰ for $\delta^{13}\text{C}$ - and $\delta\text{D-CH}_4$, respectively. When compared to popular techniques of isotope mass-ratio spectrometry and other laser spectroscopy, the TREX-QCLAS has similar results with less labor-intensive features and automated real-time analysis for in situ measurements to better identify different emission sources.

METHANE ISOTOPOLOGUES

As one of the most important human emitted greenhouse gases, methane (CH_4) must be carefully monitored in the atmosphere from multiple sources due to the high heat absorption properties.¹ Natural gas, although the cleanest fossil fuel, contains methane, which if released into the atmosphere before being consumed by burning, can bring damaging effects to the environment. Careful considerations need to be made to limit the amount of methane released into the air from human activities. To increase accountability for companies producing methane emissions, various sources of methane emissions could be identified from ambient air analysis.

A potential method to distinguish individual sources of methane emission is to measure the ratios of isotopologues in that environment compared to standard compositions. Different sources will release different ratios of heavy and light isotopologues of methane. Isotopic composition is commonly reported in delta (δ) notation which compares the ratio of heavy vs. light isotopes in a sample to the ratio of an international standard measurement. **Equation 1** shows an example δ -notation of ^{13}C (Carbon with an extra neutron).

$$\delta^{13}\text{C} (\text{‰}) = \frac{(^{13}\text{C}/^{12}\text{C})_{\text{Sample}}}{(^{13}\text{C}/^{12}\text{C})_{\text{Standard}}} - 1 \quad (1)$$

Here the international isotopic standards used are Vienna Pee Dee Belemnite (VPDB) for $\delta^{13}\text{C}$ and Vienna Standard Mean Ocean Water (VSMOW) for δD . A negative delta value would indicate that the sample contains more of the heavy isotope than the standard ratio, while a positive delta

value indicates more of the light isotope than the standard ratio. **Figure 1** shows an emission and isotopic map of London based on 2013 National Atmospheric Emissions Inventory (NAEI) methane inventories. Most of the higher emission areas are associated with ^{13}C -depleted areas. This level of identification of methane isotopologues will distinguish emissions by sources or origin.

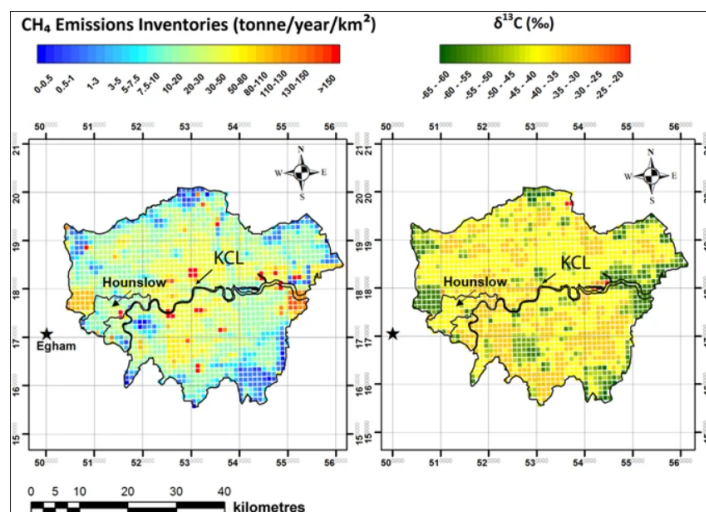


Figure 1. Emission (a) and isotopic (b) map for London based on 2013 NAEI methane inventories. Most of the hotspots are associated with ^{13}C -depleted areas. The large area affected by high emissions on the east side of the London region include biogenic methane sources, such as landfill sited and waste-water treatment plants.²

ISOTOPOLOGUE ISSUES

Measuring and analyzing isotopologues is challenging as the abundance of the isotopes can be very low. For example, methane ($^{12}\text{CH}_4$) without any additional neutrons has the overwhelming majority of naturally occurring abundance of greater than 98%. All other isotopologues combine for the remaining abundance. Although the heavier isotopologues make up a very small amount of methane in the air, the ratios of heavy to light isotopologues can still differentiate the source of the methane emission.

It is also difficult to measure multiple isotope ratios simultaneously. Not only does this require high-precision measurement methods, but it can also require two separate instruments with separate sample preparation. This process is time consuming and labor intensive when analyzing multiple isotopes. Automated preparation and analysis would save time and increase accuracy.

Another important parameter for effective analysis of methane sources is to minimize the amount of time between obtaining the sample and the analysis results. For real-time analysis, the instrument needs to be compact, enabling field-deployable measurements. Laboratory-based instrument use flask sampling and require constant calibration. Flask sampling requires accurate and consistent collection at the source then transport for analysis.¹ Automated real-time analysis requires compact instruments enabling field-deployable measurements.

SOLUTION & METHOD

Researchers from Switzerland, the Netherlands, Germany, and the UK have developed a real-time analysis of methane isotopologues in ambient air using Quantum Cascade Laser Absorption Spectroscopy (QCLAS). By utilizing a trace gas extractor (TRES) coupled to the spectrometer, CH_4 mole fractions can be enhanced well above ambient levels and can separate other interfering trace gases (N_2O and CO_2).

The use of mid-infrared (MIR) quantum cascade lasers (QCL) generates high precision, high spectral purity, and high optical power in continuous wave operation at room temperature.¹ This enables a compact design with potential parts-per-trillion measurements while eliminating the need for flask sampling.

Because the system is simultaneously measuring $^{12}\text{CH}_4$, $^{13}\text{CH}_4$, and CH_3D , the separate development of the TRES enables trace gas measurement of CH_4 which has a mole fraction in ambient air on the order of 1.8 ppm. Another barrier that the instrument overcomes is the very low natural abundance of CH_3D . By using the TRES, the CH_4 can be extracted from the ambient air and placed into a separate absorption cell for laser spectroscopy. **Figure 2** shows a schematic of the TRES unit.

The TRES unit enables preconcentration of the methane gas by removing the majority of the bulk gases (N_2 , O_2 , and Ar) in the gathered sample. This is achieved by temperature swing adsorption on a cold trap, filled with specific adsorbent material to capture the methane.¹ The adsorbing

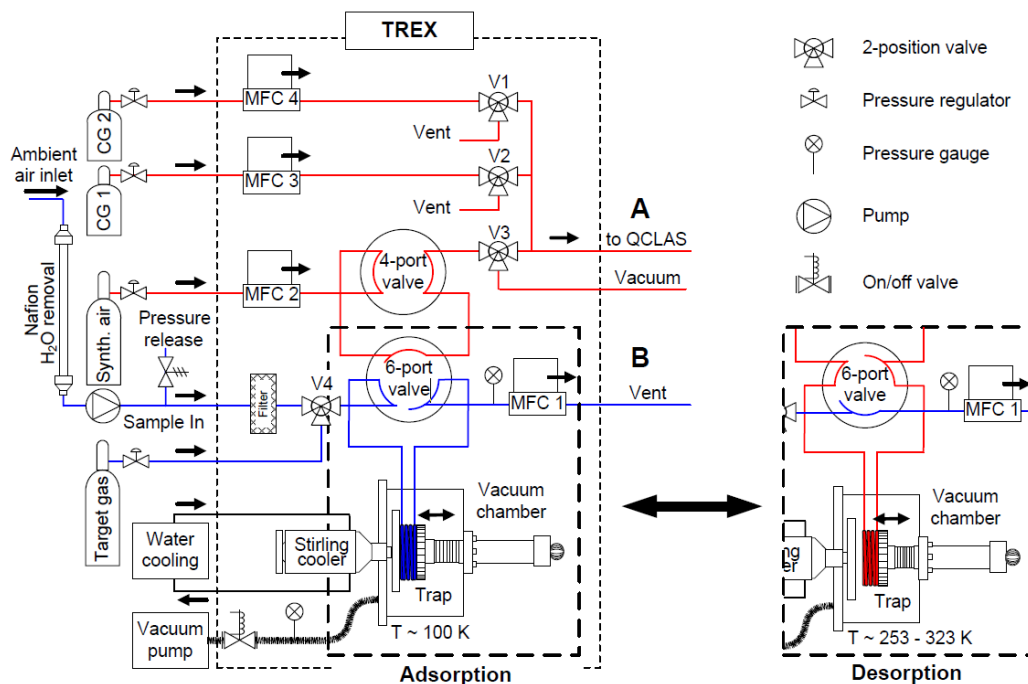


Figure 2. Schematics of the preconcentration unit (TRES). The blue lines indicate the flow of sample air and TG, i.e., ambient air CH_4 -mole fractions, while red lines represent the flow of calibration gas and desorbed air, i.e., high CH_4 -mole fraction. MFC 1-4 and V 1-4 stand for mass flow controllers and 2-position valves, respectively.¹

material is porous polymers that separate light gases from ambient air. To increase the methane adsorption capacity, the trap's temperature is maintained at ~100 K. When coupled with the QCLAS, the TREX has three main phases for preconcentration (**Figure 3**).

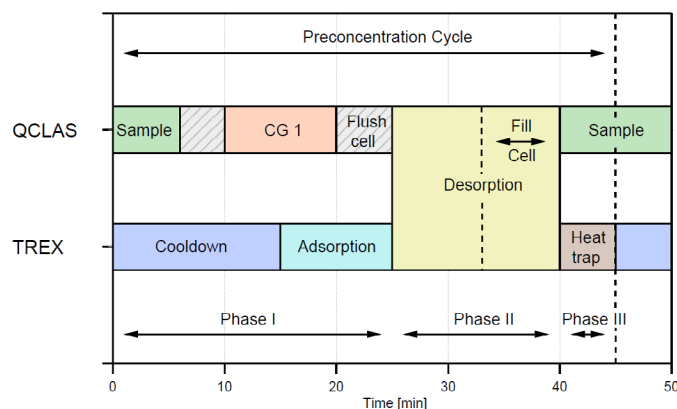


Figure 3. Workflow of QCLAS (top) and TREX (bottom) during a complete measurement cycle consisting of three phases: CH₄-adsorption (phase I), CH₄-desorption (phase II) and trap conditioning (phase III).¹

In Phase 1, the trap is cooled to ~100 K and the methane gas from the ambient air sample is adsorbed. For a 7.5 L sample gas volume, the adsorption takes around 500 seconds. In Phase 2, the trap is heated to 175 K which initiates the desorption of mainly volatile bulk gases (N₂, O₂, and Ar), while the CH₄ desorption is initiated when the trap's temperature is increased to 258 K. The other gases can be vented away from the CH₄ before it is desorbed from the trap. When the trap is purged with high-purity synthetic air (20.5% O₂ in N₂, purity 99.999%), a two-way solenoid valve encloses the desorbed and now isolated methane in the QCLAS absorption cell. Phase 3 involves heating the trap to 323 K and purging it with more synthetic air for 5 minutes to remove any residual gas compounds. The flow of ambient air and preconcentration in the TREX unit can be seen in **Figure 2**.

The QCLAS is operated when the preconcentrated sample (or calibration gas) fills the multipass cell. The multipass cell has an optical path length of 76 m and a volume of 0.5 L. To measure both $\delta^{13}\text{C}$ - and δD -CH₄ simultaneously, the QCLAS requires a dual-laser configuration, each with its wavenumber selected for one of the isotopologues. The distributed feedback (DFB) QCLs had wavenumbers of 1295.7 and 1307.0 cm⁻¹ for $\delta^{13}\text{C}$ - and δD -CH₄ respectively. These wavenumbers are chosen for maximum sensitivity for the low abundant isotopologues. This experiment demands high-precision measurements and equipment, laser control and temperature control being among the most important. Low noise and stable current are critical to the success of the spectroscopy measurements, and tight control of the temperature of the laser ensures long-term performance.

RESULTS

The TREX-QCLAS is compared to other gas analysis techniques, mainly commercial laser spectroscopic techniques and techniques using flask or bag sampling. The comparison experiment was performed over two weeks with over 250 measurement cycles from the TREX-QCLAS. The two commercial laser spectroscopy techniques include cavity ring-down spectroscopy (CRDS) and an off-axis integrated cavity output spectrometer (OA-ICOS), as well as the flask and bag methods which use an isotope-ratio mass spectrometer (IRMS). The latter method requires more intensive labor for collecting the samples into bags and flask for measurements.

The new TREX-QCLAS instrument showed analytical precision of 0.1 and 0.5‰ for $\delta^{13}\text{C}$ - and δD -CH₄ respectively for the preconcentrated methane (10 minutes averaging time). The repeatability is 0.19 and 1.9‰ for $\delta^{13}\text{C}$ - and δD -CH₄, respectively, which is similar to the IRMS techniques used. **Figure 4** shows the measured isotopologue ratios of different methane sources. These measurements show agreement between the various methods of methane analysis in ambient air. The CRDS involves extensive calibration (causing breaks in measurements), and the IRMS requires the extra work of flask or bag sample collection.

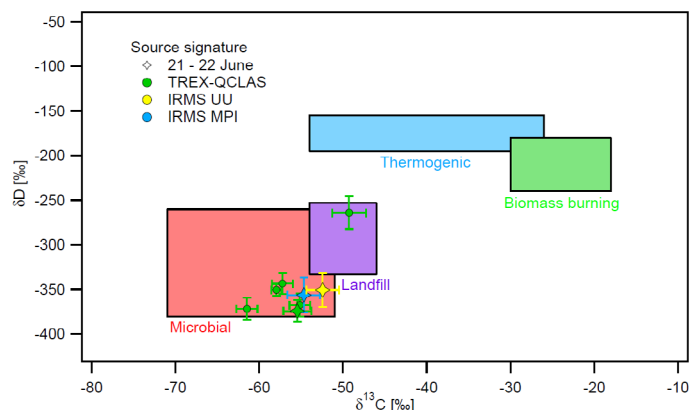


Figure 4. δD -CH₄ vs. $\delta^{13}\text{C}$ -CH₄ of different CH₄ sources. The symbols indicate CH₄ source signatures derived from Keeling plots. The error bars are uncertainties derived from the linear regression. The star-symbols are source signatures from 21 June noon till 22 June noon derived from different techniques. The shadings indicate typical values for different source categories from the literature.¹

A linear dependence was discovered of $\delta^{13}\text{C}$ - and δD -CH₄ on the temperature of the laser heatsink. To account for this difference in temperature when measuring the ambient air, the laser heatsink temperature was controlled to a precision

of ~1 mK and was recorded. This temperature data allowed application of a drift correction to the data post-processing for more accurate results.

This experiment showed that the TREX-QCLAS system is a suitable alternative to techniques previously used in laboratories relying on flask sampling. Because the TREX-QCLAS makes measurements in real-time, temporal changes in ambient CH₄ isotopic composition can be observed. Not only can this method and spectrometer analyze the three main CH₄ isotopologues simultaneously, it also has the potential to be applied for the analysis of isotopic compositions of trace gases such as N₂O and other volatile organic compounds. The compact nature of the instrument and ability for simultaneous measurements allow for field experiments with precision and repeatability for identifying regional source processes.¹

This design can better enable regulation of methane emissions with identification of the source using ambient air measurements. There can be more accountability for pollution in the world with high-precision gas analysis.

WAVELENGTH'S ROLE

Due to the high precision demands of the spectrometer, researchers upgraded the electronic equipment to utilize the high performance capabilities of Wavelength Electronics' QCL drivers and temperature controllers. These critical components enable the sensitive measurements and analysis of methane isotopologues.

For the researchers,¹ "laser operation stability is of utmost importance" highlighting the need for ultra-low noise laser drivers. Wavelength Electronics' QCL1000 OEM driver limit noise produced to as low as 0.5 μA RMS up to 100 kHz and an average current noise density of 1.5 nA/√Hz. These drivers minimized laser intensity variations and frequency jitter in the laser spectrometer for the precise methane measurements.¹ **Figure 5** shows the QCL1000 OEM with output current of up to 1 A and compliance voltage of 20 V.



Figure 5. QCL1000 OEM QCL Driver

Not only does the current of the lasers need to be controlled, but the temperature of the lasers needs to remain stable for best results:

- Repeatable experiments and tests
- Narrow linewidth and stable wavelength
- Improve long-term performance
- Accurate results due to the linear dependence of δ¹³C- and δD-CH₄ on laser heatsink temperature

The laser temperature was controlled to ~1 mK precision and recorded at high resolution for drift correction. "The long-term performance was improved by tighter and more precise control of the laser heat-sink temperature by deploying high-precision controllers."¹ By using Wavelength Electronics' PTC5K-CH temperature controllers, researchers were able to maintain narrow linewidth, stable wavelength, and the longevity of the lasers and spectrometer. The PTC5K-CH controller drives up to ±5 A of current to a thermoelectric or a resistive heater with temperature stability as low as 0.0012°C over one hour.

Figure 6 shows the PTC5K-CH.



Figure 6. PTC5K-CH Temperature Controller

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2. Zazzeri, G., Lowry, D., Fisher, R.E. et al. Evaluating methane inventories by isotopic analysis in the London region. *Sci Rep* 7, 4854 (2017). <https://doi.org/10.1038/s41598-017-04802-6>

USEFUL LINKS

- QCL1000 OEM [Product Page](#)
- PTC5K-CH [Product Page](#)

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No changes were made to the images. They are presented here in their original form.

The captions for Figures 1 & 3 have been modified from their original form.

PRODUCTS USED

QCL1000 OEM, PTC5K-CH

KEYWORDS

Spectroscopy, methane, greenhouse gas, isotope, isotopologue, quantum cascade laser, trace gas, preconcentration, real-time, in situ, field-deployable, ambient air, laser driver, temperature controller

REVISION HISTORY

Document Number: CS-LDTC08

REVISION	DATE	NOTES
A	March 2021	Initial Release