Frontiers of Isotope Ratio Measurements and the First Analyzers Fully Based on QC Technology

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Abstract: Recent advances in mid-IR laser and detector technologies increasingly allow for both ultra-compact and robust, field deployable analyzer developments. Highlights for unique real-world applications and novel instrumental developments are presented.
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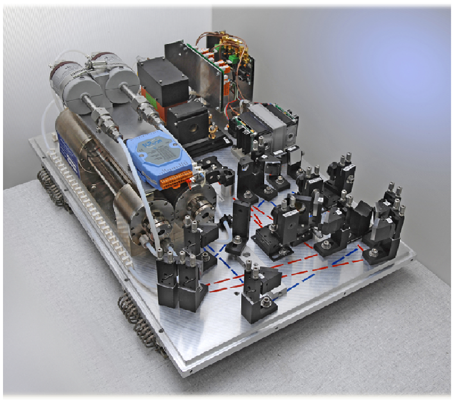
Isotope ratios of atmospheric trace gases contain highly valuable information about their sources, sinks and transport processes from the local to the global scale. The ongoing instrumental developments based on quantum cascade laser spectroscopy have led to high-precision analyzers, suitable for environmental studies based on isotopic ratio measurements for many relevant trace gases. It is rapidly gaining importance, because, unlike the isotope ratio mass spectrometry (IRMS), it can deliver real-time data with unprecedented temporal resolution at moderate cost and instrument size. Furthermore, laser spectroscopy is inherently specific to structural isomers having the same mass, and opposed to IRMS, it is capable to perform site-specific isotopomer measurements [1].

For quantitative detection of isotopic signatures of molecular species in ambient air, it is often necessary to reach a precision of 0.1 ‰. While addressing these requirements is still highly demanding, we illustrate the potential of QCL based gas analysis by highlighting some representative results from our *in situ*, continuous and high precision isotope ratio measurements of CO_2 in the free troposphere at 3850 m elevation [2,3]. For the first time, the three main CO_2 isotopologue mixing ratios ($^{12}C^{16}O_2$, $^{13}C^{16}O_2$ and $^{12}C^{18}O^{16}O$) have simultaneously been measured at one second time resolution over four years (from August 2008 to present). The instrument is based on differential absorption technique in the 4.3 µm spectral range (Fig 1a) . Being a fully cryogen-free setup, it is well suited for unattended field applications, delivering both $\delta^{13}C$ and $\delta^{18}O$ of CO_2 at atmospheric abundance with a precision of 0.02 ‰ for both $\delta^{13}C$ and $\delta^{18}O$-CO_2 at 10 minutes integration time [4]. We discuss methodologies for data analysis, present the current instrumental set-up, its performance and show the advantages of measuring with high temporal resolution isotopic signatures of CO_2 in the atmosphere.


a)

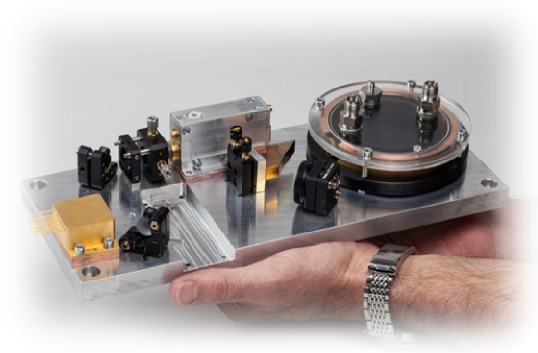

b)

Fig. 1. Optical layout of the a) high precision and b) ultra-compact spectrometer. Both are capable of measuring the CO_2 isotopologues at ambient air mixing ratios (~400 ppm).

Beside the complex, autonomous analyzer suitable for a large variety of field applications, there is an increasing need for compact, table-top and easy-to-operate analyzers in medical applications, especially for breath analysis. With the advent of quantum cascade technology, it is possible to conceive instrumentation exclusively based on III-V semiconductor materials.

We report on the development of an ultra-compact laser absorption spectrometer employing a cw quantum cascade laser (QCL) packaged in an HHL housing emitting at 2310 cm^{-1}, and a quantum cascade detector (QCD) optimized for this spectral range [6]. In this configuration, the concentrations of the four most abundant, stable CO_2 isotopes can be simultaneously analyzed. To obtain a small footprint of the optical set up (30×13 cm^2), we designed and developed a novel multipass cell consisting of a diamond turned, copper cylinder with a toroidal surface carved into the plane of the recirculating light beam [6]. This surface assures a minimal aberration of the laser beam. The cell geometry allows for a small detection volume of 40 ml, combined with a robust and easy optical alignment. Furthermore, the optical path in the cell can be adjusted from 16 cm to more than 4 m. A precision below 0.1 ‰ for $\delta^{13}C$ and $\delta^{18}O$ measurements have been demonstrated.

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