

Optical isotope ratio spectroscopy – complementing isotope ratio mass spectrometry

Jelka Braden-Behrens¹, Heleen Meuzelaar², Joachim Mohn³, Javis A. Nwaboh¹, Stefan Persijn², Francesca Rolle⁴,
Michela Sega⁴, Pharahilda M. Steur⁵, Lars Wacker⁶, Kerstin Zeyer³, Olav Werhahn¹, Volker Ebert¹

¹Physikalisch-Technische Bundesanstalt (PTB), Bundesallee 100, 38116 Braunschweig, Germany

jelka.braden-behrens@ptb.de, olav.werhahn@ptb.de

²VSL, Thijssseweg 11, Delft, the Netherlands

³Empa, Überlandstrasse 129, 8600 Dübendorf, Switzerland

⁴Istituto Nazionale di Ricerca Metrologica (INRIM), Strada delle Cacce 91, 10135 Torino, Italy

⁵Centre for Isotope Research, University of Groningen, Nijenborgh 6, 9747 AG Groningen, The Netherlands

⁶Danish Fundamental Metrology (DFM), Kogle Allé 5, 2970, Denmark

Abstract: Isotope ratio measurements and scale definitions are typically related to mass spectroscopy. This work discusses the challenges of optical isotope ratio spectroscopy and its prospects to significantly complement isotope ratio mass spectrometry. © 2021 The Author(s)

1. Introduction

Isotope ratios of carbon dioxide, nitrous oxide and methane are widely measured to get insight into the global cycle, as well as sources and sinks of these atmospheric species. The scientific community measuring isotope ratios of atmospheric gas species is referring to *delta* scales when reporting isotope signatures. These *delta* scales are defining isotope ratios relative to some “artefact” serving as the primary reference material, e.g. the VPDB-carbonate for ¹³C/¹²C in CO₂. Referring to artefacts, the *delta* value is the only exception from SI-traceability of quantities in gas metrology. Therefore, the metrology community has set out in recent years to improve SI-traceability for stable isotope research. This is documented by the projects SIRS and STELLAR, conducted under the European Metrology Programme for Innovation and Research (EMPIR). Parts of both projects are devoted to advancing optical methods for measuring isotope ratios in CO₂, N₂O, and CH₄ in air. With new optical technology and a steadily growing set of portable OIRS instruments, the optical isotope ratio approach has significantly matured and is widely used in most of the atmospheric monitoring efforts worldwide, e.g. the GAW or the ICOS network [1]. On the other hand, when it comes to accuracy and scale defining activities, IRMS technologies are still the highest reference. STELLAR aims to further develop and validate solutions for the challenges OIRS is facing in order to close-up to isotope ratio mass spectrometry even for very demanding accuracies. This paper discusses the aspects of measurement and calibration strategy, uncertainty and OIRS inherent advantages.

2. OIRS measurement and calibration strategy

OIRS instruments measure the absorption of infrared light, that is related to the amount fraction of a specific isotopologue. These measurements yield isotopologue amount fractions, that can be used to calculate absolute isotope ratios. With further improvements of spectral fitting procedures and the quality of the spectral reference data of the isotopologues, instruments that require less frequent or less complex calibration, or even optical gas standards (OGS)[1] that do not need calibration with gas standards, can be realized. Furthermore, OIRS enables a variety of calibration approaches: measuring isotopologue amount fractions, OIRS instruments can be calibrated with material that differs in a) amount fraction and b) isotopic composition. Thus, amount fraction is an additional parameter that can be modified during calibration. This yields an enhanced flexibility of calibration opportunities modifying either amount fraction, isotopic composition, or both. This flexibility of calibration approaches can help to become less dependent or even independent from a materialized specific set of primary reference artefacts such as VPDB.

3. OIRS uncertainty assessment

Sources of uncertainty were quantified for different optical CO₂ isotope analyzers in the projects SIRS and STELLAR. The uncertainties of two different laser-based analyzers used in the SIRS project (DFG-LAS and QCLAS) are dominated by the reproducibility and the calibration material (Table 1). For the mid spectral resolution (1 cm⁻¹, range 800-4000 cm⁻¹) FTIR analyzer used in SIRS, precision and regression-related uncertainties dominate (Table 1). Potential improvements of the uncertainty of the various OIRS approaches are related to the calibration, data processing (e.g. spectral line parameters), instrumentation and gas sampling conditions (e.g. gas temperature, ad-/desorption).

Table 1: Uncertainty estimates for different OIRS devices [4].

Source, all for $k = 1$	$\delta^{13}\text{C} / \delta^{18}\text{O}$ in ‰ DFG-LAS (PTB)	$\delta^{13}\text{C} / \delta^{18}\text{O}$ in ‰ QCLAS (RUG)	$\delta^{13}\text{C}$ in ‰ FTIR (INRIM)
Instrument Reproducibility, u_{repr}	0.03 / 0.04	0.02 / 0.03	0.02 ^a
Calibration material, u_{cm}	0.03/ 0.06	0.03 / 0.06 ^b	n/a
Amount fraction dependency, $u_{\text{amount frac}}$	0.001/0.001	0.005/0.006	n/a
Gas matrix mismatch, u_{matrix}	0.001/0.001	<i>not yet specified</i>	n/a
CLS regression of MALT ^c ; u_{malt}	n/a	n/a	0.16
Spectral line parameters; $u_{\text{line data}}$	n/a	n/a	0.25
Combined standard uncertainty	0.05 / 0.07	0.04 / 0.07 ^b	0.30

^a In case of the FTIR analyzer, Allan deviation is given as a measure of precision instead of the reproducibility over several days.
^b Based on more recent work [5]
^c see [3] for details

3. OIRS-inherent advantages

As based on a different physical property than IRMS (amount fraction-dependent photon absorption instead of mass), OIRS provides a complementary method. A major advantage of OIRS techniques is that the photon absorption is sensitive to the isotopologue-specific molecular structure and not the total mass. Hence molecules of the same total mass but different structure and mass distribution, such as $^{17}\text{O}^{12}\text{C}^{16}\text{O}$ and $^{16}\text{O}^{13}\text{C}^{16}\text{O}$ for CO_2 , $^{15}\text{N}^{14}\text{N}^{16}\text{O}$ and $^{14}\text{N}^{15}\text{N}^{16}\text{O}$ for N_2O , or $^{13}\text{C}^1\text{H}_4$ and $^{12}\text{C}^1\text{H}_3$ for CH_4 can be distinguished. Further, due to smaller, more mobile and robust instruments with much faster response times and the possibility for continuous measurements, OIRS techniques enable direct field measurements at much higher temporal resolution. Due to reduced instrument costs, sample preparation and complexity, multiple instruments can be deployed which can increase, e.g., also spatial resolution. Furthermore, uncertainties related to storage and transport of samples are eliminated by applying in-field measurements. In cases, where simultaneous analysis of amount fractions and isotopic compositions are of interest, such as for Keeling mixing models [2], OIRS techniques can provide those simultaneous measurement in the same air parcel by the same instrument. This eliminates efforts and uncertainties related to independent measurements of amount fractions and isotope ratios by different analyzers.

5. Conclusions

Besides technological challenges, we conclude that OIRS techniques provide considerable advantages and complement IRMS in many ways. OIRS techniques enable measurements at remote sites with high spatio-temporal resolution. Providing a measurement of a complementary quantity, OIRS techniques can drastically expand isotope ratio measurements into field, multi-point or high temporal resolution scenarios. With further developments in both, spectrometer design and gaseous reference materials with known absolute ratios, OIRS will provide one further step towards SI traceability of isotope ratios.

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