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Concentration dependence and scale linearity of the carbon isotope ratio measurement systems based on CRDS

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Isotope ratio measurement systems based on optical spectrometers becomes widely used because of several important advantages. First is fundamental possibility to distinguish the isotopologues with the same molecular weight but different isotopic composition like $^{16}O^{13}C^{16}O$ and $^{16}O^{12}C^{17}O$. Second is fundamental possibility to perform calibration free absolute measurement of different isotopologues based on ab initio calculations of line intensities [1]. Third is experimental usability, field deployability and low cost of the optical instruments.

The disadvantage of the optical isotope ratio spectrometers available on the market compared to the isotope ratio mass spectrometers is still low accuracy associated not only with the capabilities of optical instruments as such, but also with the lack of high-precision measurement procedures. To improve the accuracy of the optical measurement system, the main factors affecting the measurement result should be investigated and eliminated.

In this study, we used CM-CRDS carbon isotope ratio measurement system consisted of Picarro G2131i analyzer, Picarro combustion module, Picarro Caddy Universal interface, homemade system of solenoid valves Camozzi. The calibration of the measurement system was made by combustion of certified reference materials from the International Atomic Energy Agency as recommended in [2]. The linearity of the delta scale was evaluated. Non-linearity of the delta scale leads to a bias if just one or two certified reference materials are used for calibration.

The measurement procedure of carbon isotope ratios in solid sample on CM-CRDS is as follows. A sample is broken down into elemental components in the combustion module. After the cleaning from interfering components, CO_2 is diluted with nitrogen and analyzed by CRDS instrument. The similar procedure is performed with reference material. The issue is that even if the mass of sample and reference material are the same, the concentration of CO_2 in the analyzed mixture is different. Mismatch of concentrations leads to bias in measured isotope ratios. The magnitude of concentration dependence is estimated in this study.

The obtained results are discussed and ways to eliminate the abovementioned issues are proposed.

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[2] Willi A. Brand et al. Assessment of international reference materials for isotope-ratio analysis (IUPAC Technical Report). Pure Appl. Chem., 2014, 86(3), Pages 425–467