State of the art Intracavity Optogalvanic Spectroscopy at Uppsala University

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Abstract

About five years ago, the first reports of a novel and ultrasensitive method for ro-vibrational spectroscopy of isotope ratios were published [1-3]. The method was called intracavity optogalvanic spectroscopy (ICOGS), and claimed a sensitivity and limit-of-detection (LOD) for detection of radiocarbon in the 10^{-15}range. Applied to measuring the isotopic composition of carbon samples, ICOGS utilizes the narrow linewidth ro-vibrational absorption lines of CO_2 in the long-wavelength IR spectrum, typically between 10 - 13 µm [4]. These absorption lines are strongly dependent on the isotopic composition of the CO_2 molecule, where a $^{14}CO_2$ line typically is separated by several hundred linewidths form the nearest $^{12}CO_2$ and $^{13}CO_2$ lines. In order to facilitate unambiguous detection of radiocarbon, which is typically 10^{10}-10^{12} times less abundant than the isotopes ^{12}C and ^{13}C, the sample is moved inside the laser cavity of a $^{14}CO_2$ laser. This intracavity approach has been claimed to increase the sensitivity of the detection by almost seven orders of magnitude as compared to traditional 'extracavity' optogalvanic spectroscopy [3]. However, despite the methodical and thorough efforts of at least five research groups worldwide, the exceptional claims regarding the sensitivity and LOD of ICOGS have not been possible to confirm.

As the first research group to properly repeat the original experiments, we recently reported [5] serious deficiencies in the reproducibility of the original results [1-3]. We found that ICOGS in its original embodiment suffers from considerable problems with the stability and reproducibility of the optogalvanic signal, and that these uncertainties, together with mix-ups and mistakes, likely are the explanation for the extraordinary sensitivity in the original reports. An example of the irreproducibility of the original results can be seen in Fig. 1 (a) where the shape of the P20 line of $^{14}C^{16}O_2$ with different ^{14}C concentrations is shown. As can be seen, the previously reported Voight profile-like line shape, indicating resonant absorption [3], was not found for ^{14}C concentrations in the 10^{-13} –10^{-11} range, but only for samples with much higher ^{14}C concentration. The problems with stability and reproducibility can be traced back to instabilities in the plasma source, in which the sample is partially ionized in order to extract the optogalvanic signal. The plasma sources currently used in ICOGS are based on 30 years old technology and suffer from problems with both electromagnetic interference and reproducibility in terms of the discharge conditions (pressure, temperature, etc.).

In order to overcome these problems, we aim to deploy a completely novel kind of plasma source, based on a stripline split-ring resonator (SSRR), for ICOGS, Fig. 1 (b). We have recently published a report on the applicability of such a plasma source for ordinary optogalvanic spectroscopy [6], and now intend to optimize it for ICOGS. Based on its intrinsic properties, an SSRR could not only improve the stability of the signal, but also reduce the non-resonant background in the spectrum, and facilitate analysis of smaller samples. The latter is due to its extremely small size, with an analyzed volume in the order of 10 µl, Fig. 1 (c). In this report, we summarize our criticism towards the original publications on ICOGS, and report on the latest development regarding our efforts in the deployment of the SSRR plasma source.

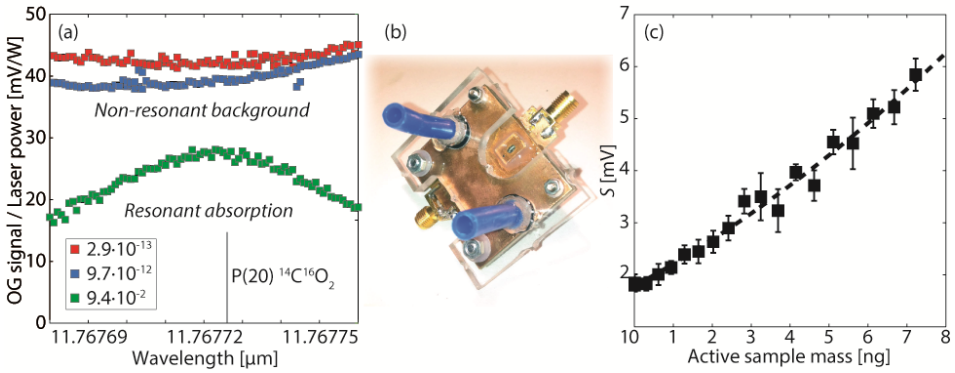

Figure 1.(a) *Scaled optogalvanic signal as a function of wavelength around the P20 line of $^{14}C^{16}O_2$ at ^{14}C concentrations between $2.9x10^{-13}$ and $9.4x10^{-2}$ and pressures between 40 and 470 Pa.* ***(b)*** *Photograph of a stripline split-ring resonator plasma source.* ***(c)*** *Optogalvanic signal as a function of the active sample mass, i.e., the mass of carbon in the plasma cell of the stripline split-ring resonator.*

References

1. Murnick, D., et al, *Nucl. Instrum. Meth. B*, 2010. 268(7–8): p. 708-711. **2.** Murnick, D., et al, *Nucl. Instrum. Meth. B*, 2007. 259(1): p. 786-789. **3.** Murnick, D., et al, *Anal. Chem.*, 2008. 80(13): p. 4820-4824. **4.** Bradley, L., et al, *IEEE J. Quantum Elect.*, 1986. 22(2): p. 234-267. **5.** Persson, A., et al, *Anal. Chem.*, 2013. 85(14): p. 6790-6798. **6.** Berglund, M., et al, *J. Appl. Phys.*, 2013. 114(3): p. 033302-11.