Intracavity optogalvanic spectroscopy: Is there any evidence of a radiocarbon signal?

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In 2008, the first report of an ultrasensitive method for ro-vibrational spectrometry of radiocarbon dioxide was published. The method, called intracavity optogalvanic spectroscopy (ICOGS), claimed a sensitivity and limit-of-detection comparable to accelerator mass spectroscopy. ICOGS was claimed to utilize the isotope-dependent ro-vibrational absorption lines of carbon dioxide in the infrared spectrum. In order to facilitate unambiguous detection of radiocarbon, the sample was placed inside the cavity of a radiocarbon dioxide laser. This intracavity approach was claimed to increase the sensitivity by seven orders of magnitude compared with traditional optogalvanic methods. However, despite the methodical and thorough efforts of several research groups worldwide, these claims have not been possible to reproduce. Instead, we have previously reported serious deviations from the original results, where we found that ICOGS suffers from considerable problems with the stability and reproducibility of the optogalvanic signal, and that misinterpretations of these uncertainties likely are the explanation for the claimed sensitivity in the first reports. Having identified the stability and reproducibility of the detection as major concerns, we decided to improve the setup by with state-of-the-art plasma source technology. Deploying a custom-made stripline split-ring resonator optogalvanic detector, we have now investigated the applicability of

ICOGS to radiocarbon detection even further. Measurements have been made with a wide range of parameters including different gas mixtures at various pressures and wavelengths. We have also conducted measurements with gas flowing through the sample cell to investigate the effect of plasma induced decomposition of the sample. Still, we have seen no indications of a significant radiocarbon signal in a concentration range between 0.29 Modern and 9.7 Modern, i.e., the range of interest to the radiocarbon community. Hence, our conclusions after four years of working in this field, is that ICOGS is not a viable method for radiocarbon detection.

Introduction

Six years ago, the first reports of a new, ultrasensitive radiocarbon detection method, utilizing ro-vibrational spectroscopy, were published by Murnick *et al* [1, 2]. The method was called intracavity optogalvanic spectroscopy (ICOGS), and claimed a limit-of-detection (LOD) in the 10^{-15} range ($^{14}C/^{12}C$), for detection of radiocarbon in carbon dioxide samples. In this application, ICOGS utilized the narrow linewidth ro-vibrational absorption lines of CO_2 in the long-wavelength IR spectrum, typically between 10 - 13 μm [3].

Apart from being less complicated and expensive than competing technologies, ICOGS could supposedly facilitate analysis of smaller samples [1]. The latter would, in turn, facilitate new applications where the total sample amount is inherently limited. An example of such an application is the project The Human Regenerative Map, where the turnover of cells in the human body is studied by radiocarbon dating of cell DNA, using the so called bomb-peak method [4]. Here, ICOGS could be beneficial, since the most interesting cell types are not abundantly available, e.g., cells from specific areas of the brain.

To facilitate unambiguous detection of ^{14}C, which is typically 10^{10} and 10^{12} times less abundant than ^{13}C and ^{12}C, the sample is moved inside a $^{14}CO_2$ laser cavity. This “intracavity”

approach has been claimed to increase the sensitivity by almost 7 orders of magnitude, compared to extracavity optogalvanic (OG) spectroscopy [1, 2]. However, despite the methodical and thorough efforts of at least five research groups worldwide - one of them being the Division of Ion Physics at Uppsala University - the exceptional claims regarding the sensitivity and LOD of ICOGS have not been possible to confirm. Instead, after two years of extensive work, we realized that the fundamental validity of the claims made by Murnick *et al* had to be questioned.

The first publications on ICOGS contained two compelling arguments for the methods capability to unambiguously detect ^{14}C [1]: 1.) Strong Voight-like absorption peaks in the P-band of $^{14}C^{16}O_2$ for ^{14}C concentrations in the 10 Modern range. 2.) A linear dependence between the amplitude of the OG signal and the ^{14}C concentration for concentrations between 0.1 and 10 Modern.

We have previously attempted to reproduce both these results, however, unsuccessfully [5, 6]. Although we could not exclude the possibility of an electrical intracavity enhancement of the OG signal, no signs of resonance were found in the P-band of $^{14}C^{16}O_2$ for the relevant ^{14}C concentrations, only non-resonant background. Moreover, no significant dependence between the OG signal and the ^{14}C concentration could be found.

In our in-depth investigation of the published conclusions, we found several possible explanations for the irreproducibility of the results [6]: 1.) Undefined stability of the pressure and flow in the sample cell during a measurement. Both these parameters strongly affect the OG effect, and small variations can easily be misinterpreted as a radiocarbon signal. 2.) Impact of different discharge conditions on the stability and reproducibility of the OG signal. Our investigation showed that it is extremely difficult to reproduce the exact discharge conditions in successive measurements. 3.) Mix-up of data. Several indications suggest that

the Voigt profile in Ref. [1] actually show the signal from the reference cell, i.e., from a sample with a ^{14}C concentration of 10^9 Modern rather than the reported 10 Modern. 4.) Misinterpretation of the concept of LOD. Even if the results presented in Ref. [1] would be correct, the LOD is still overestimated by at least two orders of magnitude based on the published data [7].

In addition, we repeated the experiments with varying initial conditions to make sure that the results were consistent [6]. A total of 12 experiments with varying pressure (15 Pa, 50 Pa and 100 Pa), laser transition (P20 and P22), gas composition (pure CO_2 and 2.5% CO_2 in N_2) and ^{14}C concentration (0.29 Modern, 3.3 Modern and 9.7 Modern), all showed the same result, where no significant dependence of the OG signal on the concentration of ^{14}C could be found [6]. A summary of these results, together with those of Ref. [1] can be found in figure 1.

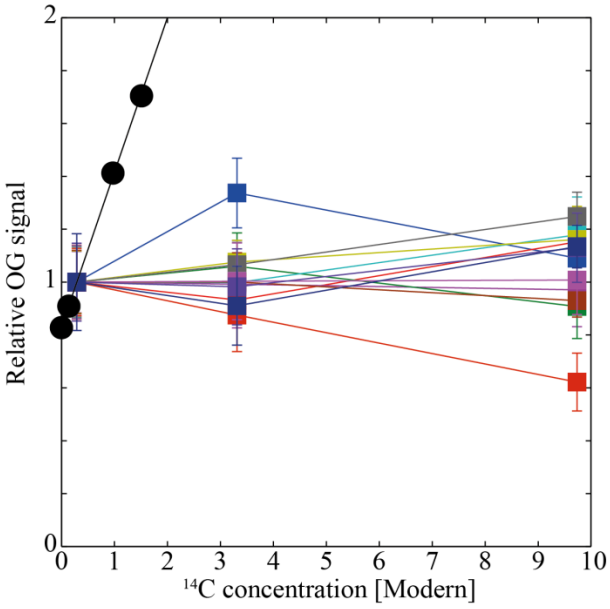

Figure 1. OG signal as a function of 14C concentration for the experiments of Ref. [6] (squares) and Ref. [1] (circles). The results were normalized to the OG signal at a 14C concentration of 0.29 Modern.

Many of the problems found while trying to reproduce the experiments of Murnick *et al* could be traced back to the, above mentioned, irreproducibility of the discharge conditions in the sample cell, since measurements with identical initial conditions rendered significantly

different results. This was partly due to the excitation and detection scheme of the original ICOGS setup, which was based on a 30 year old technology [8], sensitive to, e.g., thermal and electromagnetic interference, making it unsuitable for sensitive spectroscopic applications [6].

To try to counter these problems, we have developed a new plasma source for ICOGS, which is based on a stripline split-ring resonator (SSRR). This novel concept has been shown to exhibit good electromagnetic compatibility [9], facilitat colder plasma (excitation at 2.7 GHz instead of 38 MHz), and enabled separation of the plasma generation circuitry from the OG signal detection, which helpes to improve the signal-to-noise ratio (SNR) [10, 11]. Most importantly, the SSRR improved the reproducibility of the detection by one order of magnitude [11] compared with the measurement scheme used in previous ICOGS studies, which is promising with regards to our previous findings [5, 6]. The SSRR concept has now been developed further, to enable integration inside the laser cavity of a $^{14}CO_2$ laser. Moreover, the system described in Ref. [6], has been updated, not only with the new SSRR sample cell, but also with a mass flow controller to enable measurements in flow mode.

In this report, the results of our continued investigations into the question if ICOGS can be used for unambiguous radiocarbon detection are presented. The OG signal from different gas mixtures at several laser lines, pressures, and flows has been recorded. The results are discussed with respect to the new detection scheme, but also with a broader scope, trying to assess the general potential of ICOGS as an analytical method for radiocarbon measurements.

Methods

The SSRR used in this study was based on that described in Ref. [11]. However, the hole through the gap of the resonator was made wider, more precisely 5 mm wide, which was about the same diameter as the waist of the intracavity beam of the $^{14}CO_2$ laser. The resulting ring structure had an inner and outer diameter of 5.01 mm and 6.64 mm, respectively.

Moreover, the cell was sealed with antireflection coated, ½″ ZnSe windows (WG70530-F, Thorlabs Inc., Newton, NJ, USA) instead of the previously used Ge windows, in order to minimize intracavity losses. Initially, Brewster angle window mountings were considered, however, mounting the windows parallel to the beam turned out to be more suitable, since it was much less mechanically complicated and only had a limited effect on the circulated laser power. Figure 2 show the basics of the SSRR, with the relevant electrical and fluidic connections highlighted.

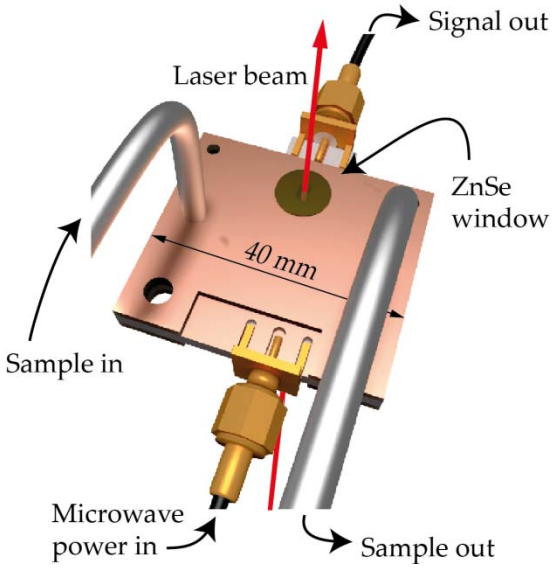

Figure 2. Configuration of the SSRR used in this study.

The electronics for igniting and maintaining the plasma, and detecting the OG signal, closely resembled that of Ref. [11] , where a custom made power supply delivered microwave power to the resonator with an variable amplitude controlled by a digital attenuator. The OG signal was detected by two bond-wire Langmuir probes extended into the plasma, and recorded by a data acquisition (DAQ) unit. However, the detection was somewhat different from the setup described in Ref. [11] in that one of the Langmuir probes was connected to the DAQ via a source meter (Model 2400, Keithley Instruments Inc., OH, USA), which made it possible to apply a constant voltage bias to probe. Such biasing of the plasma was found to improve both

the amplitude and stability of the OG signal [12]. A bias voltage of 30 V was used throughout this study.

The new SSRR was integrated with the optical system described in Ref. [6], where the gap through the SSRR was centered on the intracavity beam of a $^{14}CO_2$ laser. Hence, the gap effectively served as an intracavity diaphragm, reducing the output power of the laser by roughly 85%. Optical losses in the ZnSe windows of the SSRR cell removed another 15%, leaving a typical output power of 0.5-1 W, depending on which laser line that was studied. The output of the laser was investigated in a reference cell, based on the same technology as used in the original ICOGS reports [1, 2, 6, 8], together with two power meters – one thermopile for average power measurements and one pyroelectric for fast time resolved detection of laser pulses [6]. The wavelength of the laser was also measured in an IR spectrum analyzer. The only difference between the optical system of Ref. [6] and that used in this study was the laser tube which had been exchanged due to degrading performance. However, the gas composition of the new tube was identical to the old one.

The fluidic system of the old setup was thoroughly redesigned, where a mass flow controller (pMFC PFC-50, MKS Instruments Inc., MA, USA) was installed on the inlet to the SSRR. Two pressure gauges – a TPR 265 compact pirani gauge (Pfieffer Vacuum, Asslar, Germany) and an MKS Type 622 capacitance manometer (MKS Instruments Inc., MA, USA) – measured the pressure upstream the mass flow controller and downstream the SSRR, respectively. The system could be injected with samples from five different gas sources, Table 1. Of these, four were pure CO_2 samples with varying ^{14}C concentration, and one was pure N_2. The samples were stored in different types of canisters, where the N_2 and the CO_2 with low ^{14}C concentration were kept in ordinary gas cylinders, whereas the CO_2 samples with higher activity were kept in small test tubes. These test tubes only contained around 2 mg C, which was too little gas for flow experiments. Instead, the samples with high ^{14}C

concentration were only used in experiments without flow. A schematic diagram of the electronics, optics and fluidics of the system is shown in figure 3.

A total of eight different parameters were recorded in each experiment namely: the OG signals from the SSRR and reference cells, the laser power from the two power meters, the mean voltage between the Langmuir probes, the piezoelectric voltage applied to the wavelength tuning of the laser, the microwave power reflected from the resonator, and the flow though the mass flow controller. Much of these data were mostly used to monitor the setup; however, the two OG signals and the mean probe voltage were post processed to calculate the OG response of the sample. The post processing was conducted with the algorithm described in the supplementary information of Ref. [11], and the OG signal of the SSRR was finally scaled by both the signal from the pyroelectric power meter, and the mean voltage.

Table 1. Isotopic composition and storage of the different samples used in the study.

Gas	$\Delta^{13}C$ [per mil]	^{14}C conc. [Modern]	Container
CO_2	0.13	0.29	Gas cylinder
CO_2	-23.7	1.03	Gas cylinder
CO_2	-26.1	3.3	Test tube
CO_2	-25.1	9.7	Test tube
N_2	-	-	Gas cylinder

Table 2. Variation of different parameters in the study.

Parameter	Investigated interval	Presented interval
Laser line	P10-P28, R12-R20	P20
Pressure	5-200 Pa	50 Pa & 100 Pa
Flow	0-5 sccm	0 sccm & 0.8 sccm
Gas	Pure CO_2, 2.5% or 5% CO_2 in N_2	Pure CO_2 & 2.5% CO_2 in N_2

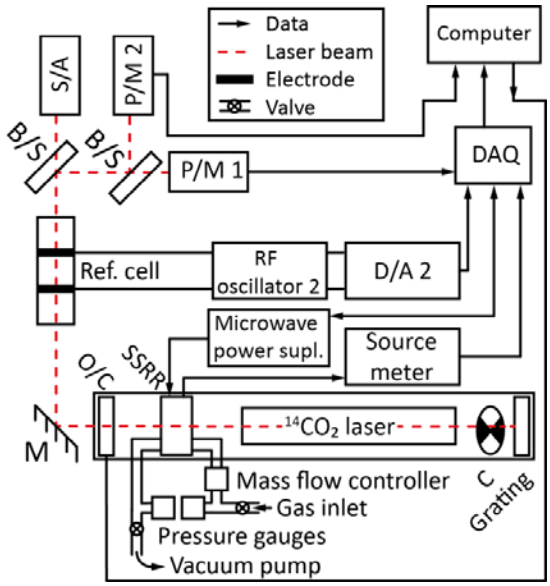

Figure 3. Schematic description of the system, including optics, fluidics and electronics. Here, S/A represents spectrum analyzer, P/M power meter, B/S beam splitter, DAQ data acquisition, D/A differential amplifier, O/C output coupler, C chopper, and M mirror.

The foundation of the study presented here, was more than 170 experiments with different gas mixtures at different laser lines, pressures, and flows. The particular intervals of these variations are summarized in Table 2. The presented experiments were chosen to informatively illustrate the basis of the conclusions, which, still, was consistent with all the results.

Results & Discussion

Similar to earlier studies, both the spectral distribution of the OG signal, recorded by scanning the wavelength of the laser across a certain laser transition, and its average, recorded by keeping the wavelength constant at the center of a transition, were investigated. Figure 4 show four OG spectra of samples of 5% CO_2 in N_2 with varying ^{14}C concentration. Here, the laser was scanned twice across the P20 transition (λ=11.77 μm), even though the x-axis is scaled in Volts, correlating to the potential applied to the piezoelectric actuator that was used to vary the length of the laser cavity, and, hence, the resonant lasing frequency. In our laser 1 V corresponded approximately to 0.9 MHz. The laser power measured by the pyroelectric power meter is also shown as a reference.

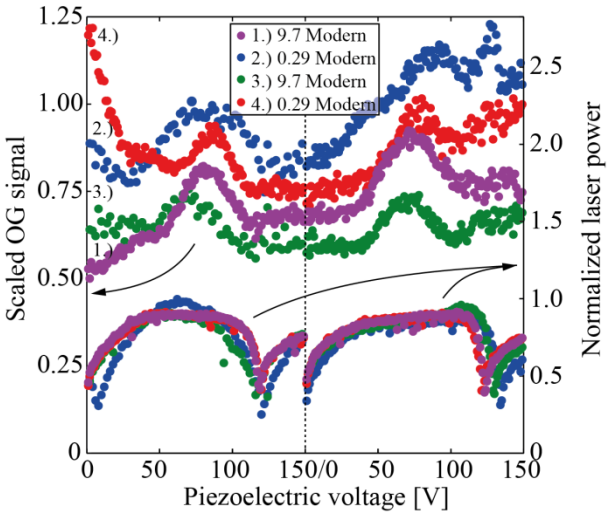

Figure 4. OG signal (left y axis) scaled by laser power and floating potential in four separate and consecutive experiments with 5% CO2 in N2 at 100 Pa. The laser was centered at the P20 transition, and the CO2 had a 14C concentration of either 0.29 Modern or 9.7 Modern. The corresponding normalized laser power, measured by the pyroelectric power meter, is also shown (right y axis).

Interestingly, the scaled OG spectra showed peaks roughly centered on the laser transition. This kind of response was significantly different from what had been observed in the old setup (Ref. [6]), where only spectra indicating non-resonant background were found [5, 6]. Hence, the peaks were initially interpreted as promising signs of resonant absorption from ^{14}C. Similar peaks were also observed at other laser transitions, in both the R and P bands, and with samples of both pure CO_2 and CO_2 diluted in N_2. Still, a clear correlation between the peak amplitude and the concentration of ^{14}C in the sample could not be found in any of these measurement conditions.

Figure 5 shows the collected results of 38 experiments, entailing both pure CO_2 and CO_2 in N_2 with three different ^{14}C concentrations, recorded at the P20 transition. As can be seen, no significant dependence between the OG signal and the ^{14}C concentration could be found. Instead, the OG signal appeared to be essentially independent of the ^{14}C concentration, still suffering from the problems with reproducibility between measurements with identical initial conditions. These results were more or less representative of all the conducted experiments

(see table 2), and the particular parameters P20 and 100 Pa were presented mostly for comparison with earlier studies [1, 2, 5, 6].

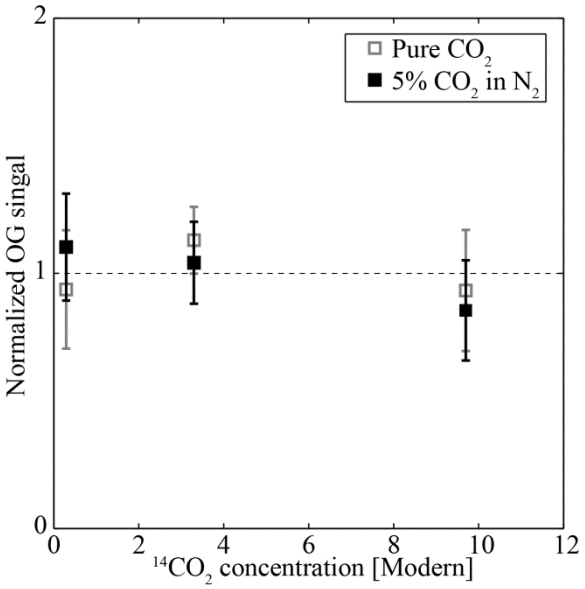

Figure 5. Normalized OG signal at the P20 transition as a function of 14C concentration in two different gas compositions, both at a pressure of 100 Pa. Each concentration shows the average and standard deviation of up to six separate experiments with identical initial conditions, normalized to the total average for the respective gas composition. The error bars corresponds to 1σ.

In a previous study [5], chemical reactions in the plasma causing dissociation of CO_2, were identified as one possible cause of instabilities in the measurements. In order to counter such effects, measurements were also made while flowing CO_2 through the SSRR at a constant rate, using the mass flow controller, since the continuous supply of fresh sample gas should help reducing chemically induced concentration variations. However, such measurements consumed a lot of gas, wherefore only CO_2 from the two gas tubes, table 1, could be used in the flow experiments.

Figure 6 show the results of a total of seven experiments with pure CO_2 at two different ^{14}C concentrations, flown through the SSRR at a constant rate of 0.8 sccm and a pressure of 50 Pa. As can be seen, the flow helped to improve the reproducibility, as indicated by the greatly reduced uncertainty at each concentration, compared with figure 5. This reduced uncertainty

helped to highlight the lack of a significant dependency between the OG signal and the ^{14}C concentration even further. However, it should be noted that only pure CO_2 was investigated in the flow experiments, since the option of mixing large volumes of CO_2-N_2 was not available in the present setup.

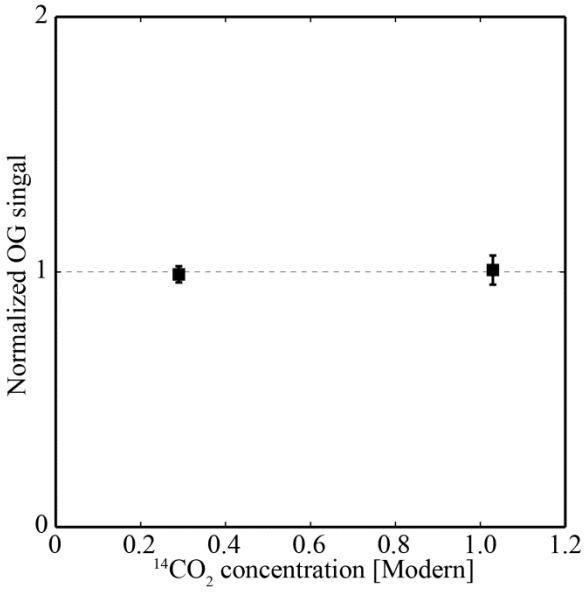

Figure 6. Normalized OG signal as a function of ^{14}C concentration for pure CO_2 at a flow of 0.8 sccm and a pressure of 50 Pa. Each concentration shows the average and standard deviation of up to four separate experiments with identical initial conditions. The error bars corresponds to 1σ.

Although the experiments conclusively showed a lack of correlation between the OG signal and the ^{14}C concentration, the question regarding origin of the peaks observed in the OG spectra, figure 4, remained. The fact that the peaks seemed to be independent of the ^{14}C concentration, but still appeared at several different laser transitions, suggested that they either were generated by a highly unstable process, or not spectroscopic in origin at all. If they were caused by, e.g., higher order $^{12}CO_2$ or $^{13}CO_2$ peaks overlapping the P20 transition of $^{14}CO_2$, it is unlikely that they should appear at other transitions, and, given the difference in $\Delta^{13}C$ between the samples, table 1, they should still have varied in amplitude. Instead of being spectroscopic in origin, we speculate that the peaks may also be caused by non-linear thermal effects in the SSRR, caused by heating of the device from the laser beam. Such effects have

been observed to affect the OG signal, especially in microwave OG systems that utilize Langmuir probes for signal detection [10, 13]. The fact that the hole through the SSRR served as a diaphragm for the laser beam, could make it vulnerable to such effects. If that is the case, it should be possible to remove the heating by adding a second diaphragm to the cavity, with a slightly smaller diameter than the hole. However, this was not possible to verify in the present system, since the laser became unstable if the beam waist was reduced even a little below 5 mm. Such verification could still be made with an SSRR with a wider hole or with a more reliable laser. Finally, despite the lack of a ^{14}C signal, the experiments clearly showed that it was possible to integrate an SSRR inside an optical cavity without major optical losses, even without the use of, e.g., Brewster angle windows. These results may prove interesting to other cavity-enhanced methods for IR spectroscopy.

Conclusion

Since the start of the project in 2010, we have not been able to reproduce the results of Murnick *et al* [1, 2]. Despite more than one year of additional experiments since our last report [6], and several iterations of the setup, including replacing the plasma excitation source, and the OG detection scheme with a custom-made SSRR sample cell, we have found no indications that ICOGS is capable of unambiguous ^{14}C detection in the 0.2 to 10 Modern range.

No other research group has, to our knowledge, been able to demonstrate ICOGS as a radiocarbon measurement method for the isotopic ratio span routinely accessible to AMS. On the contrary, we know from personal communications [14] that results that support our conclusions soon will be published.

Hence, in summary, we want to notify anyone who is planning to begin work in this field that reproducibility is a major concern. In other words, we do not envisage ICOGS in the

embodiment described by Murnick et al [1, 2] as a potential analytical method for the radiocarbon community.

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